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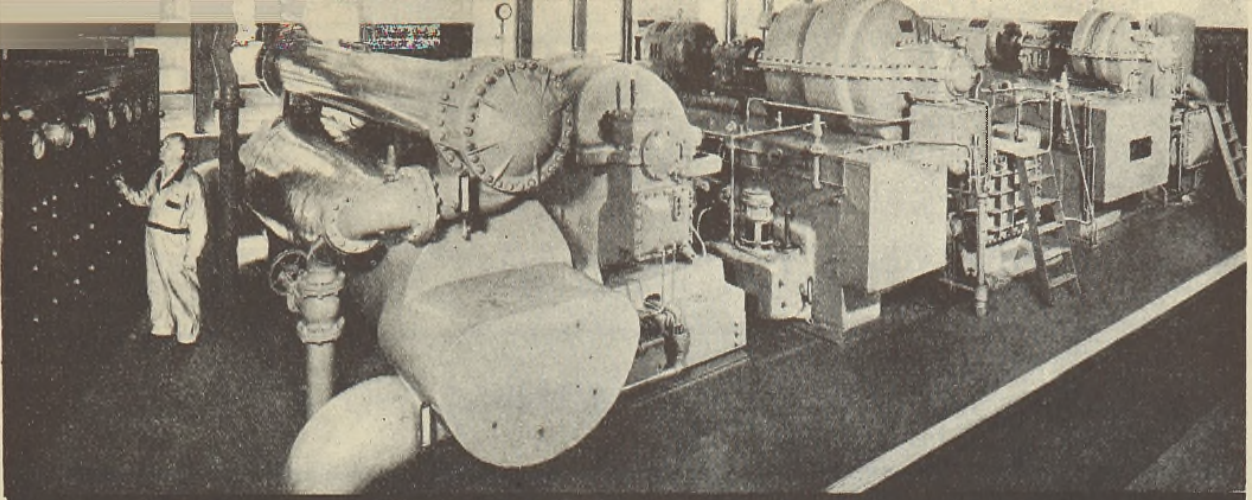

Shown above are three centrifugal refrigerating compressors in a brewery, which provide 800 tons of cooling, equal to melting an acre of ice 7 inches thick, every day; however, they occupy only half of a 50 X 50 foot room. (Courtesy of Brewing Corporation of America)

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INDUSTRIAL AND ENGINEERING CHEMISTRY

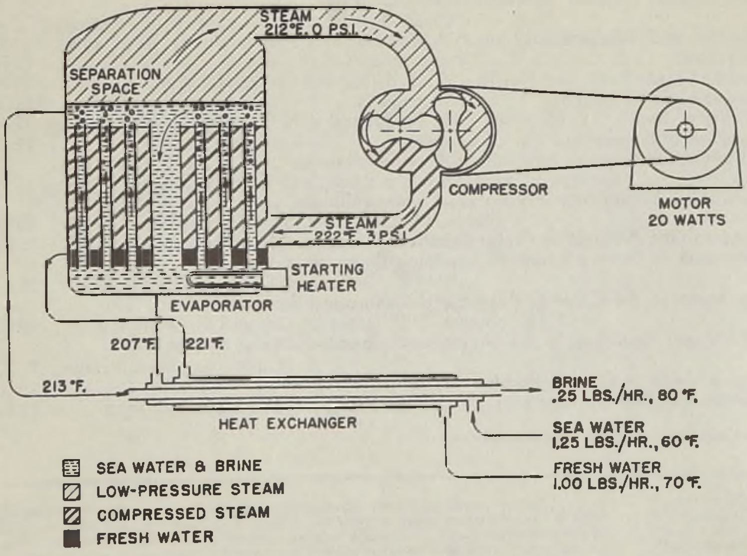
REPORTS ON THE CHEMICAL WORLD TODAY

Engineering

Compression Distillation. Modern engineering is perfecting for efficient use many mechanisms which were conceived years ago but which failed upon construction. The needs and research of war have speeded this trend. The gas turbine is perhaps the outstanding example of an old idea made practical through the successful application of new materials and techniques. Another such adaptation, recently announced, is compressive distillation, an idea patented as early as 1856. Even now, in its comparative newness, compressive distillation has features which indicate extensive application in future evaporation technology. The illustration diagrams the essential operating scheme. As the operation was developed largely for the Navy, with a view to distilling sea water for drinking, the illustration places emphasis on this feature. The work was carried on before the war by Arthur D. Little, Inc., under the leadership of R. V. Kleinschmidt, now a Commodore in the Navy but soon to return to the Little organization. The first description of the apparatus was given by Allen Latham at the American Society of Mechanical Engineers meeting in New York on November 27. In operation, sea water enters the boiler by way of a triple-passage heat exchanger. Heat is transferred from the distilled water and the waste brine. The feed, heated by this exchange to about 207° F., enters the evaporator where it mixes with the large amount of brine present, then rises by convection past vertical heat exchanger tubes. The vapors coming from the surface of the brine solution are carried through an entrainment separator to a compressor where, by mere compression of the steam, the temperature is raised to 222° F. This increase in temperature is obtained simply by raising the pressure of the steam 3 pounds per square inch. The liquid brine boils at about 213° F. so that there is a temperature differential of about 9° F., which permits heat exchange between the vapors and the brine. This interchange takes place in the vertical tubes, around which the brine is constantly circulating. As the amount of heat transferred is enough to keep the brine boiling, the evolution of steam, therefore the process, is continuous. No cooling water is necessary, since the heat exchange between the steam, the condensate, and the brine is almost complete.

According to the authors, the unit can produce a pound per hour of distillate with an energy expenditure of only 20 watts. In a single-effect evaporator, the energy used would be about 300 watts; therefore the sea water unit is equivalent to approximately fifteen evaporator effects. On a unit capable of producing 1000 gallons of distillate per day, the heat loss is about 55 B.t.u., so that the total energy raised per pound of distillate is about 70 B.t.u. In practice, not all of this heat is put in at the compressor; about half is supplied by heaters.

In the all-electric models the formation of scale is of little consequence, as the heater does less work and the compression load is stepped up. In the gas engine drive, however, the heaters are (*Continued on page 8*)



An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries

run on waste heat from the engine; an increased load on the compressor, caused by scale formation, means more waste heat and, thereby, lower efficiency. One of the foreseeable problems in the adaptation of these units to the evaporation field is the size of compressor, but the promoters feel that this too can be solved by modern improvements.

Jets, Turbines, and Fuels. *"Tomorrow to fresh woods, and pastures new"* (Milton).

The oft advertised race between the motor makers and the fuel fanciers, as to which was farthest along the road to perfection and waiting for the other to catch up, has had other recent entrants; and now the two former main attractions are not sure that they are racing each other after all. The new entrants are the gas turbine and jet propulsion, and both bring with them problems which may in time alter our old conception of power plants and the fuel necessary to run them. The new motors are possibly the forerunners of a revolution in gasoline technology and motor manufacture. Only time will tell, and at present the preponderance of opinion is that it will take plenty of time for the telling. Nevertheless the technology of the new power plants is important to the chemical industry.

The most recent development which seems important to the commercial field in the forseeable future is the combination gas turbine–jet propulsion motor—the Jetprop of General Electric Company and the geared-turbine propeller drive of Westinghouse Electric Corporation.

This new power plant combines the gas turbine and jet propulsion, the turbine driving a propeller and the jet, through its rearward thrust, giving an extra boost to the plane. There are specific advantages to this motor which indicate its use in airplanes. It is lighter than the most highly developed reciprocating gasoline engine, which had gone below 1 pound of engine weight per horsepower developed. It is simple in construction, and as the power demands increase, construction actually becomes simpler. This is exactly the reverse of the case of reciprocating engines which are becoming more complex as time goes on. Engine vibration is zero; it is more efficient to obtain full power continuously from the turbine; the turbine can and does burn any kind of fuel; its streamlining is a decided advantage when compared to the huge wind resistance of the usual piston engine. All this adds up to change in the airplane field, and "soon" may be the password.

The gas turbine which, because of its recent development to a state of usefulness, has made this revolution possible is not new. It goes back to Hero who, in 130 B. C., made a gadget that turned figures on an altar. Da Vinci made a turbine that fitted into a chimney and supplied power to turn the roasting spit, but the first patent was taken out in 1791. Therefore the idea is free and not subject to basic infringement. The real development was metallurgical, for during the war alloys were brought out which made it possible to build gas turbines that ran efficiently. The motor runs at about

(Continued on page 10)

1300° F. and gas temperatures reach 1500° F. At these temperatures steel is glowing. At present the alloy composition is supposed to be secret. In operation the turbine sucks or has air rammed into the front ducts of the motor. The air is compressed by an axial flow unit, which is a many-vaned fanlike arrangement on a tapered cone, the air being forced by the blades and the rotation of the cone shaft to pass into a smaller and smaller area. When the air has reached the final compression area, it passes into the combustion chamber where it supplies the oxygen to burn injected liquid fuel.

The mixture of gases, at high temperature and velocity, passes to the turbine, giving it a rotation of 10,000 r.p.m.

The turbine through reduction gears drives the propeller, and the energy remaining in the gases is expended as a jet. Most of the energy is expended in driving the propeller and compressor, but about one fifth is thought to be available as jet power. The gas turbine, operating on four to eight times the quantity of air used by piston engines of comparable power, has a huge amount of air to serve as a jet stream. At sea level the gas turbine can be 28% efficient on a fuel basis; at 15,000 feet, as a result of temperature differences, the efficiency goes up to 32%.

As an interesting side light, horsepower in the conventional sense means nothing in rating turbine engines, as the force is expressed as thrust. Speed must be given, and at 375 miles per hour 1 pound of thrust is equivalent to 1 horsepower. Engineers, in calculating the applicability of these new power plants to airplanes, think that installation weights of equal power for the three would be: piston engine, 20,800 pounds; turbine, 15,200 pounds; jet, 8000 pounds. Assuming equal load at takeoff, the most economical performances would be: for the conventional, 250 m.p.h., 0.120 mile per pound of fuel, and a range of 4800 miles; for the turbine propeller, 280 m.p.h., 0.145 mile per pound of fuel, and a range of 5700 miles. The jet would cruise at 35,000 feet, as compared to 20,000 for the others, with a velocity of 460 m.p.h., obtain 0.066 mile per pound of fuel, and have a range of 3500 miles. In takeoff run, maximum rate of climb, maximum speed, best cruising speed, range, and cargo capacity, the turbine propeller is calculated to be superior to the piston airplane. The gas-turbine propeller-drive engine has not actually been used in flight yet, though it is expected to be announced momentarily.

FUEL CONSIDERATIONS. At present cooperative research is being conducted with petroleum companies to determine the best fuel for use in turbine type motors. The development is taking two directions, depending on the type of airplane for which it is developed. Some planes must accommodate the highest B.t.u. per pound of fuel (fighters) because the volume for storage is not available. Others, in cases where pay load is important but where ample space is available, want to develop a fuel of high B.t.u. per gallon. Gasoline per pound has a high B.t.u. content; kerosene per gallon has a high B.t.u content. For the military at present,

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high-octane gasoline is the experimental fuel because of the necessity of meeting the requirements of the two types of motors. Gasoline with tetraethyllead is on the way out for these motors because of its corrosive action and deposition of lead salts. Antiknock fuel is not necessary for the motor anyway. The turbine is an open motor, exposed to the atmosphere; and moisture from the atmosphere, combining with deposited lead salts, would cause corrosive trouble.

For military use, gasoline has another advantage over kerosene as a fuel. The explosive range for gasoline is smaller, and should bullets penetrate the self-sealing gas tank, the chance of explosion if gasoline is the fuel is less than if kerosene is present. Much of the development work is still going on as far as the motor is concerned. Despite the theoretical predictions already stated, the motor has a higher fuel rate than the piston motor, and many of the bugs have to be worked out. But this will be the motor of the future for the airplane; for its use the development of leaded high-octane antiknock fuels will probably cease, and the creation of high B.t.u. fuels will occupy research teams. However, the automobile is still an important consumer at the gas pumps, and though it has no use for triptane or 100 octane at present, reciprocating engines may be improved in the future. At present fuel is far ahead of the automobile motor.

So, unless the gas turbine invades the automotive field, refiners' investments are safe for a while anyway; one of the engineers of a company intimately engaged in developing the turbine sees the application of small units to the automotive field in the future. True, it is far off and will require a complete change of drive mechanism, but it appears to be on the way.

The chemical industry has gone far along the road to perfecting highly branched compounds and mixtures of incomparable antiknock value. It now appears that the mechanical engineers have thrown the search in reverse and are going to be content with cruder fuels.

H. P. Ain't What She Used to Be. Colonel Donald Putt, of Wright Field, spoke before the American Petroleum Institute recently on the Army and petroleum research. He made many significant points, but one, especially, brought home the importance of high-octane fuel in the reciprocating engine.

The Liberty engine used during the first World War had a displacement of 1650 cubic inches. It produced about 420 horsepower on a fuel estimated to have had an octane number of 55. Near the end of World War II our version of the Rolls-Royce Merlin engine also had a displacement of 1650 cubic inches, but the horsepower developed was 2000, not 420. Although part of this improvement is attributed to mechanical refinements (the two are strikingly similar; both are twelve-cylinder, liquid-cooled, V-type engines) the chief reason for the phenomenal improvement is a fuel which has an octane rating estimated at 115 to 145.

(Continued on page 14)

Aerosol for Civilians. From a small steel container, inappropriately called a "bomb", came a lethal spray during the war which aided greatly in controlling the Army's worst enemy in the South Pacific—disease-carrying flies and mosquitoes. The aerosol, about approximating a highball glass in size, was conceived and developed by two brilliant government scientists, Dr. Lyle D. Goodhue and Capt. W. N. Sullivan, of the Agriculture Department's Bureau of Entomology and Plant Quarantine, Beltsville, Md.

Acres of print paper have been devoted to scientific advances and inventive gadgets far less important than the aerosol. Its prewar introduction and trial were not accompanied by bass drum thumping, red fire, or shouted announcements. Still it was singularly successful—so much so that approximately 40,000,000, each one deadly effective against insects, were made for the armed forces.

But would the aerosol have any value to civilians? Many felt that its cost was too high, and that it was wasteful of material. The war is now over and the answer is at hand. Some 25 manufacturing companies are making, or planning to make the bomb for civilians, among them the Westinghouse Electric Corporation, The Bridgeport Brass Co.; and the more recently formed Airosol, Inc. Over one million aerosol bombs have been sold to civilians since V-J Day, but in view of some very significant improvements it could be safely assumed that these constituted what merchandising experts allude to as market sampling.

The pressure in aerosol bombs for civilians may be lower (85 pounds in the present); some types have discarded the screw valve on top of the bomb for a more easily manipulated button on the container's side. Most interesting probably is the 4-ounce refillable aerosol being developed by a large food manufacturer. In this device, the insecticide under pressure is sold to the consumer in a tin can, which is sealed in the usual manner and inserted into the aerosol's steel jacket. This development may be the answer to the objection that the aerosol is costly. In the past it has been a workmanlike assembly of steel and alloy metal parts which had to be discarded after its contents and pressure were spent. The tin can replacement will be light and low in cost, but will differ slightly from the conventional tin. It should further lower the prices for aerosols to civilians. They already have dropped from an introductory cost of $4 to under $2.50. During the coming year we are promised aerosols appreciably below $2.

On one score alone the aerosol merits the approval of all engaged in the manufacture and sale of insecticides. It contains the proper proportions of DDT and other ingredients, leaving nothing to be guessed at by experimental buyers. The DDT content ranges from 1 to 3%, and the maximum has been accorded safe by Federal authorities. The civilian formula, in fact, may not vary greatly from the Army's. This called for 3% DDT, 2% of a 20% pyrethrum concentrate, 5% cyclohexanone, 5% lubricating oil, and 85% Freon gas as propellant.

Commercial air transport companies were probably the first to extend large-scale industrial use to

(Continued on page 22)

the aerosol idea. This is logical considering the possibility of the airplane becoming a carrier of insects from one section to the other. The aerosol, originally adopted by the Army for controlling insects in airplanes, was soon found to be highly effective in tents, huts, and barracks.

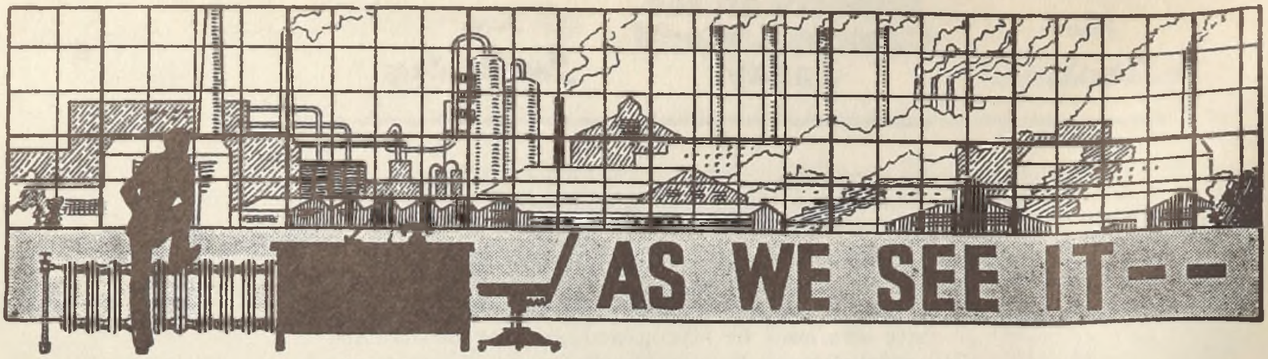
For agriculture, aerosols weighing as much as 90 pounds have been made for experimental use. Dr. Goodhue and co-workers report that good results against the aphid have been obtained on a 100-acre patch of peas. An even more interesting outgrowth of all this work is the aerosol fly-spraying of dairy barns through piping installations connected with a pressure tank containing the insecticides and propellant. A button actuates the valve and dairymen are thereby enabled to clear flies from a barn in a simple operation.

Here is the idea which some feared might not prove practical outside of the Army. Here are the fruitful results from patient research conducted in a government laboratory which, as a privately sponsored venture, would have yielded handsome financial returns. The aerosol bomb, however, was assigned to the U. S. Department of Agriculture as a public service patent, and for use of its essential idea no payment of royalties is required.

Some manufacturing features of the aerosol may be patented or patentable and one mentioned in this connection is the capillary method of charging the bomb. For his work in developing this revolutionary insecticide dispersal method, Dr. Goodhue has been notified that he is to be the 1945 recipient of the $1000 John Scott Award.

Much Ado about Nothing. At a recent symposium on nuclear chemistry held by the Chicago Section of the AMERICAN CHEMICAL SOCIETY, Glenn T. Seaborg announced the production of isotopes of elements 95 and 96. At the end of his epoch-making paper he included an anecdote about the atomic bomb process and General Leslie R. Groves, who was in charge of the entire project. While the plants to produce plutonium were being designed (the decision to spend enormous amounts of money had already been reached, based only upon the assertion of the nuclear scientists that such a process was possible), the first bit of the new element, plutonium, was made in the Chicago Metallurgical Laboratories. So small was the sample that, when the General was shown the whole amount, he remarked with justification, "I don't see anything".

Yet these infinitesimal bits were all our chemists had to work on in determining the separation procedures for plutonium. In the original Army release on the Hanford Engineer Works, which was the country's plutonium production center, it was mentioned that only a microgram (0.000001 gram) was made. The accuracy for the chemical techniques had to be within 3% of a microgram. A human breath weighs 750,000 micrograms and a dime, 2,500,000 micrograms. Yet these incomprehensibly small amounts were the solid foundation on which was built the mighty Hanford works.



Styrene Catalyst. Early in the rubber program a dehydrogenator for ethylbenzene was needed to make the much needed copolymer of GR-S, styrene. The first chemical to fill this gap was a desiccated Alabama bauxite, which served well and long until it was replaced by a material supplied by Rubber Reserve Corporation. Wood and Capell of the Floridin Company report now on research on other bauxites for this same purpose; their conclusions are that, on an all-round basis, Alabama bauxite is the superior dehydrogenator because it maintains its activity for a much longer period than the best imported material which had a higher conversion rate.

Time, Temperature, Pressure, Charge. Petroleum cracking has much mystery yet to be explained away, and Sung, Brown, and White add immeasurably to our knowledge of this operation in their current contribution concerning the thermal cracking of petroleum. Variation of the important conditions of time, temperature, pressure, and composition of charge lead these authors to conclude that increases in temperature and pressure make for less coke and high polymers, and to obtain the most from partially cracked stock, high temperature and pressure are indicated along with low conversion. For a virgin fraction, however, high pressure, combined with a moderate temperature and conversion, seems best. In the many data and charts worked up by the authors, you will find reaction and polymerization rates neatly calculated.

Design for Distilling. Evidence accumulated during the review of the paper, "System of Distillation Equations", by W. D. Harbert of the Lion Oil Company, indicates great originality and major importance to designers of distillation equipment. A simplified algebraic method of calculating liquid composition and plate number, the new method eliminates much tedium in arriving at necessary design ends. Harbert, in a practical manner, shows the applicability of the mathematics to four examples, chosen for their gradation from the simplest to the most complex case capable of solution. Though the full evaluation of this new system is in the future, it is felt that the science of column design and distillation theory has received a huge lift.

Essay on Bacon. Smith, Brady, and Comstock, of the North Carolina Agricultural Experiment Station, sought ways to prevent what little bacon we had from spoiling. Their determinations of the effect of antioxidants on the prevention of rancidity in bacon make a conclusive report. Several antioxidants were tested, and all were effective. Nordihydroguaiaretic acid, about which we had an I. & E. C. Report not long ago (August, 1945, advertising section, page 12), was particularly effective, as was gossypol, a by-product of cottonseed. Treatments described should more than double the keeping time of bacon according to the authors' interpretation of their work.

MVK Production. Methyl vinyl ketone is a chemical building block of some interest to the elastomer and plastics industries, and its preparation in an economical way is always important news. Four authors from Iowa State College report on the production of MVK from methylvinylcarbinol. Through the use of two catalysts, a zinc oxide–cupric oxide mixture, and the zinc in combination with the cuprous form, the authors were able to obtain yields of about 63% of theoretical. With better equipment to control the reaction temperature rise, even better yields are expected. Though the results were approximately the same with both catalysts, the cupric oxide is preferred because of its higher oxidation state and because of the necessity of treating the cuprous catalyst with nitrogen before use.

Skinless Varnishes. The thin skin of dried paint which forms over the surface of new paint is more of a nuisance to the manufacturer than to the painter, who probably gives the matter no second thought. But to the research chemist in the paint industry, it is a problem which ought to be solved, and so the power of chemical knowledge is brought to bear. Johnson, of Commercial Solvents Corporation, writes of an extensive study he has made of the use of nitroparaffins as skinning preventives. He has tabulated and summarized the results. The amino compounds, he concludes, seem to be more effective than the nitro types.

In Praise of Phase. The application of phase studies is one of the most interesting kinds of practical chemistry, and it fascinates scientists on each demonstration. Now Morgen and Walker, of the University of Florida, working on the very practical application of separating sodium acetate from solutions of sodium hydroxide, add more lore to an already well-documented study of the applicability of phase theory. This time it has to do with the naval stores industry. In the destructive distillation of pine stumps, a small amount of acetic acid is left in aqueous solution. It is too dilute to recover unless it is passed through an ion exchange resin and later washed out by sodium hydroxide. Crystallization of the acetate from the hydroxide is the problem, and this exhaustive paper reports the answer.

Saddle-Point Azeotrope. Absolutely new is an invariant azeotrope found by Ewell and Welch in the ternary system methanol-acetone-chloroform. In their article "Rectification in Ternary Systems Containing Binary Azeotropes", the authors discover a mixture of approximately 23% methanol, 30% acetone, and 47% chloroform which has an intermediate boiling point between the lowest and the highest point. This phenomenon shows a low point in the rectification diagram which is not according to Hoyle. It opens up a new and strange field in the science of rectification.

With the Departments. Murdock this month again discusses a major method of waste disposal—lagoons. Lagoons, which can be neatly divided into three types, are useful, but as pointed out, trouble often results if certain limitations are exceeded. Von Pechmann maintains that keen insight and careful evaluation are necessary to keep within bounds the cost and number of tests on raw material used in making chemical products. Munch writes this month on spectrochemical instruments and the latest improvements in this field. Brown's subject is the pulley, and he portrays its development through the years to its present state of efficiency.

INDUSTRIAL AND ENGINEERING CHEMISTRY
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Editorials
WALTER J. MURPHY, EDITOR

Is the United States Really the Land of Plenty?

A FEW weeks ago your Editor viewed for the first time the breath-taking expanse of the Mesabi Range in Minnesota. Aside from the unusual display of color and the evidence of great engineering skill, one is most impressed by the size of what is no longer there. Perhaps this is an awkward description. Possibly it would be more convincing to report that the high-grade iron ores in the Mesabi deposit made it possible for the United States to fight and win World War I and World War II, but should we be called upon to fight a third world war, we will be forced to do so without cheap high-grade ore that can be used directly in the blast furnace.

How much longer will the supply of high-grade ore last? Your Editor's guide, who has devoted the best part of a lifetime supervising mining operations, simply shrugged his shoulders when asked this question and replied by posing the query, "At what annual rate will we use the rapidly diminishing supply of high-grade ore in the years ahead?"

At the prewar rate of extraction it is authoritatively estimated that the remaining tonnage will be exhausted in 22 years. It is most unlikely that future demand will follow the volume trend of depression years. Probably the cream of our iron ore resources therefore will be depleted by 1950—certainly by 1955.

Steel is the most basic of all the commodities required to maintain the industrial life of a nation in peace or war and while the situation regarding adequate resources of high-grade iron ore plainly is most serious, it is by no means the only natural raw material about which we should be concerned.

In recent weeks two distinguished public servants have called the Nation's attention to the grave danger of continuing a "do-nothing" policy. Testifying at the hearings in Washington on science mobilization legislation, elder statesman Bernard M. Baruch strongly urged not only that a national inventory of our resources be made without delay, but that immediate steps be taken to develop processes for tapping our resources of low-grade ores. With characteristic bluntness Harold L. Ickes, in an article in the *American Magazine*, listed America with the "have-not" nations and warned us that the United States has now "less than a 35-year peacetime supply of 21 minerals".

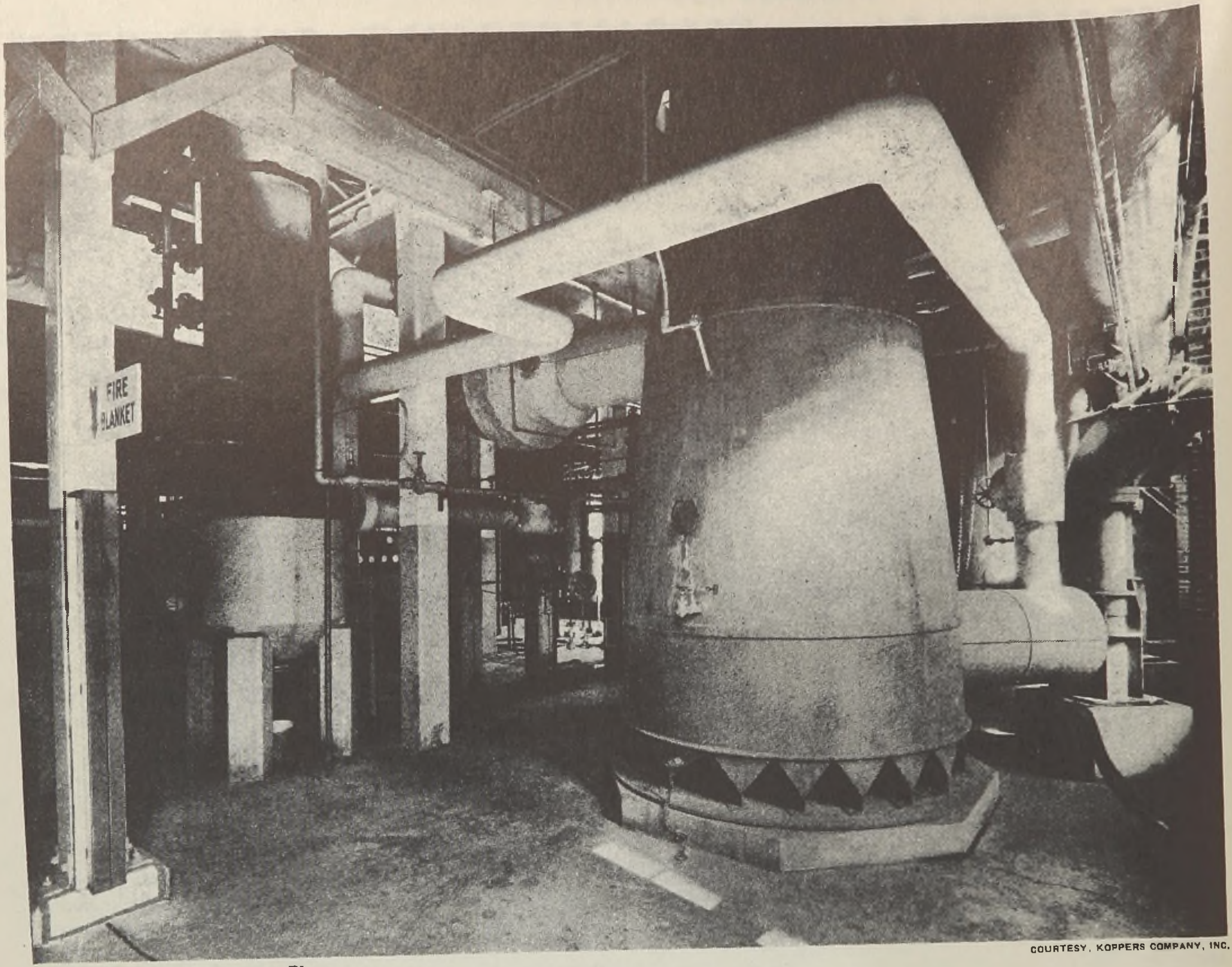
In Mr. Ickes' opinion this country no longer deserves to be listed with the British Empire and Russia—nations with adequate supplies of essential minerals. It is most unfortunate but true, as Mr. Ickes points out, that the prodigal harvest of minerals that we have reaped to win World War II has bankrupted some of our most vital mineral resources. We do not possess an inexhaustible supply, and tragically the American public does not realize the full significance of what this means to the future welfare and position of this country. The fact that we provided the large bulk of the natural raw materials poured into the production of the machines and munitions required to fight World War II is now nothing more than past history—water over the dam. We cannot hope to survive on past history alone. If we are to maintain the dominant industrial power and military might of this country, we must preserve and conserve what we have left of high-grade mineral resources and develop processes for efficiently utilizing low-grade materials.

The Secretary of the Interior has made a number of constructive suggestions designed to increase our known mineral resources: (1) to stockpile minerals; (2) to explore our country more extensively than ever before; (3) to hunt for better methods of recovering metals from scrap; (4) to have access, in common with other peacefully disposed nations, to minerals in the lands that have been conquered in the recent war.

Stockpiling implies the purchase of raw materials from other countries. At the moment we are in the process of negotiating loans to a number of foreign countries, including Great Britain and Russia, both "have" nations in the matter of important minerals. Let us ask, then, that repayment of these loans be made in natural raw materials, especially since we contributed so heavily of our resources to the common war effort. For example, we furnished approximately 60 per cent of the total petroleum used, although we now possess but 36 per cent of the world's known oil reserves.

Our greatest hope in preventing future shortages of the 21 minerals mentioned by Mr. Ickes is our scientific brainpower. Given sufficient backing, our chemists and chemical and metallurgical engineers will develop processes for the efficient utilization of what are today submarginal reserves. We should not wait, however, for another critical period in world history before a comprehensive research program is initiated. While research has been started in certain fields by both Government and private industry, we must be assured that the problem is being attacked on all fronts. The proposed National Science Foundation would be the logical body to assume responsibility, provided its make-up is truly scientific, not political.

We are at a serious stage in our history. Unless we continue to have almost unlimited supplies of a wide variety of natural raw materials, our present standard of living will be materially lowered and we will have to accept a relatively minor position in world affairs. Americans will resent any such limitations when they know that they can be averted by intelligent planning and immediate action on long-range programs of preservation, conservation, and research, particularly the latter.



COURTESY, KOPPERS COMPANY, INC.

Reactor in a Styrene Cracking Plant

BAUXITE . . . Dehydrogenation Catalyst for Styrene Production

W. H. WOOD AND R. G. CAPELL
Floridin Company, Warren, Pa.

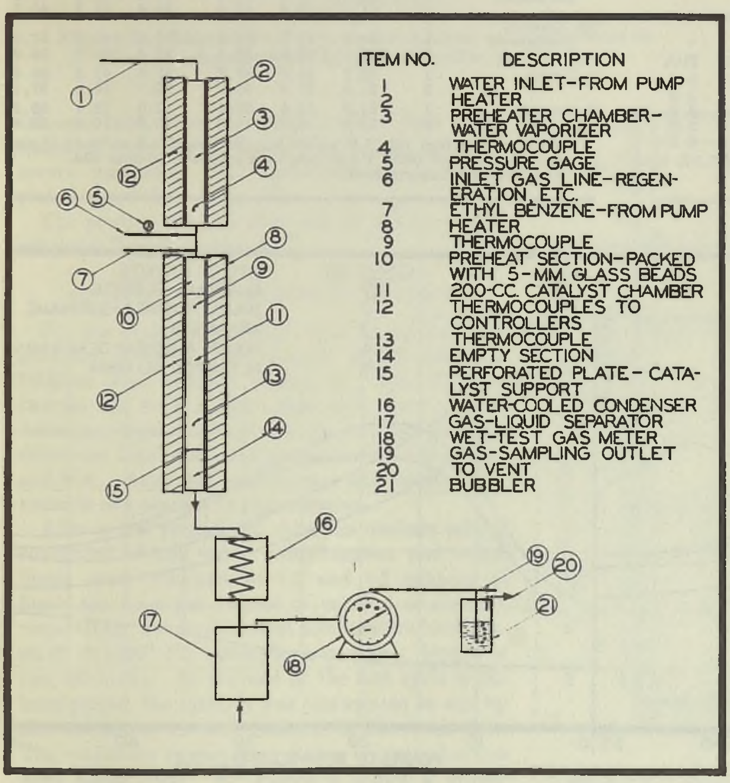
SHORTLY after the outbreak of World War II, the country's dire need for synthetic rubber necessitated large-scale production of styrene for GR-S type rubber. In the early part of this program Florite (*1*, *2*), desiccant grade Alabama bauxite, was employed as the catalyst for the dehydrogenation of ethylbenzene to styrene. This naturally occurring bauxite was later replaced by a catalyst manufactured under the auspices of the Rubber Reserve Corporation.

This company's research division has investigated various typical bauxites for their catalytic activity in the dehydrogenation reaction, and the results are reported here. Alabama, Arkansas, Demerara, and Suriname bauxites (the last two from South America) were tested. Activated alumina was also included in the program.

Test runs were made in the 200-cc. laboratory test unit shown in Figure 1. The unit consists, primarily, of a preheater section for the vaporization of water to steam, the catalyst or reactor chamber, product condenser, liquid-gas separator, and gas meter. Both distilled water and ethylbenzene were fed continuously from one-liter calibrated glass burets by means of a dual proportioning pump. The preheater was made from extra strong $^3/_4$-inch iron pipe filled with $^6/_{16}$-mesh cracked porcelain. The catalys chamber was made from 1-inch, standard stainless steel pipe Both preheater and catalyst ovens were electrically heated by means of aluminum-bronze cylinders wrapped with chromel A wire, the temperature of each being regulated by a suitable temperature controller. The gas-liquid separator consisted of a one liter glass separatory funnel, fitted with a two-hole stopper accommodating the condenser outlet line and a gas exit line to th meter.

Four naturally occurring bauxites (Alabama, Arkansas, Demerara, and Suriname) and activated alumina were tested for their activity as dehydrogenation catalysts for the production of styrene from ethylbenzene. At a constant temperature level of 1200° F. for 50 hours of continuous operation, Suriname bauxite gave an over-all yield of 40% styrene (a 3 to 5% advantage over the others). With operation, simulating commercial practice, at a constant 40% yield, Alabama bauxite was superior since it maintained its activity 25% longer than Suriname bauxite. Arkansas and Demerara bauxites, as well as activated alumina, appear to show excessively long induction periods for the best commercial operation.

An Aerial View of a Plant of the Floridin Company, Quincy, Fla. Here Bauxite, Which Early in the War Was an Important Dehydrogenation Catalyst, Is Milled and Processed



ITEM NO.	DESCRIPTION
1	WATER INLET-FROM PUMP
2	HEATER
3	PREHEATER CHAMBER-WATER VAPORIZER
4	THERMOCOUPLE
5	PRESSURE GAGE
6	INLET GAS LINE-REGENERATION, ETC.
7	ETHYL BENZENE-FROM PUMP
8	HEATER
9	THERMOCOUPLE
10	PREHEAT SECTION-PACKED WITH 5-MM. GLASS BEADS
11	200-CC. CATALYST CHAMBER
12	THERMOCOUPLES TO CONTROLLERS
13	THERMOCOUPLE
14	EMPTY SECTION
15	PERFORATED PLATE-CATALYST SUPPORT
16	WATER-COOLED CONDENSER
17	GAS-LIQUID SEPARATOR
18	WET-TEST GAS METER
19	GAS-SAMPLING OUTLET
20	TO VENT
21	BUBBLER

Figure 1. Diagram of 200-Cc. Dehydrogenation Unit

• • •

OPERATION

For comparative results, a uniform testing procedure was adopted which became standard for this laboratory. Ethylbenzene and water were fed at rates of 200 and 300 ml. per hour (i.e., 1.0 and 1.5 liquid space velocity, respectively); this gave a mole ratio of steam to ethylbenzene of 10.2 or a partial pressure of ethylbenzene of about 65 mm. of mercury since atmospheric pressure was employed throughout. Constant-temperature runs were made at 1200° F. for 50 hours before regeneration. During constant conversion runs, the temperature was varied to maintain the amount of styrene in the hydrocarbon product at approximately 42% by weight (i.e., about 40% yield on the feed). At constant conversion levels, the runs were terminated when the 42% level could no longer be maintained at 1250° F. in the case of Suriname bauxite and 1300° F. in the case of Alabama bauxite.

Water was pumped from a graduated one-liter buret to the preheater, where it was vaporized to steam at 900° F. Ethyl-benzene was pumped from its buret into the steam stream at a point just ahead of the reactor section where the steam helped

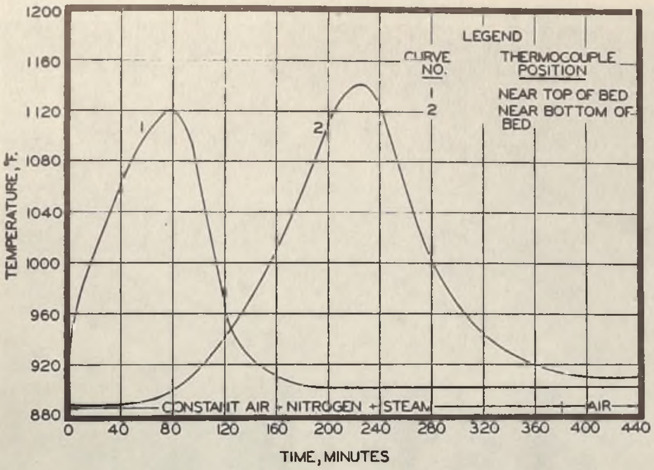


Figure 2. Typical Regeneration Curve (Alabama Bauxite)

vaporize it. The mixture passed into the reactor, over an 8-inch section of glass balls for further preheating, then through the catalyst bed and condenser, and finally collected in the gas-liquid separator. The liquid was drawn off hourly and weighed, the water layer discarded, and the hydrocarbon layer weighed and analyzed for styrene. The product gas was led from the gas-liquid separator through a wet-test gas meter from which it was vented, or periodic samples were taken for analysis.

Feed rates were kept unusually constant, the maximum deviation rarely exceeding 0.5%. Temperature control was of the order of ±2° F. with the temperature gradient throughout the catalyst bed 10° to 15° F. On those runs where sufficient data were available, material balances were excellent for such a small unit, varying between 99.3 and 100.2%.

ANALYSES

The ethylbenzene was obtained from the Dow Chemical Company. The values of all physical characteristics agreed closely with those reported in the literature (5) for pure ethylbenzene. Fractional distillation in a packed glass laboratory column, capable of accurately evaluating synthetic mixtures of benzene, toluene, and ethylbenzene in the ratio of 2:2:96, indicated the ethylbenzene to be 99.6% pure.

The hourly product samples were separated from their water layers, dried, and analyzed by means of a refractometer which had been calibrated against synthetic mixtures of ethylbenzene and styrene. During the first runs the styrene was also evaluated by bromine number determinations (3) and fractional distillation of the product. All three values agreed within 1%, so the refractive index method was employed thereafter. This is the same conclusion reached by Mavity *et al.* (4) after an extensive study of the validity of the method. Because of the similarity of the refractive indices of benzene, toluene, and ethylbenzene, the error in the amount of styrene measured would be only 0.5% in the presence of 5% benzene and negligible in the case of 5%

Table I. Weight Per Cent Analysis of Bauxites (Volatile-Free Basis)

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2
Alabama[a]	65.5	10.1	19.9	2.9
Suriname	82.3	2.5	12.4	2.8
Arkansas	84.3	9.3	2.1	4.3
Demerara	91.0	2.3	3.5	3.2
Activated alumina	99.6	0.3	0.1	0.0

[a] Alabama bauxite also analyzes 0.3% CaO, 0.1% MgO, and 1.2% not accounted for.

Table II. Styrene Conversion with Various Bauxites as Catalysts at 1200° F.[a]

	Cycle No.	Wt. % Styrene in Hydrocarbon Recovered			Wt. % Styrene Yield[b]		
		1–12 hr.	1–25 hr.	1–50 hr.	1–12 hr.	1–25 hr.	1–50 hr.
Alabama (Florite)	1	60.4	46.5	35.6	57.2	44.8	34.8
	2	59.8	48.4	37.3	56.5	46.5	36.4
So. America (Suriname)	1	62.3	51.2	40.4	58.8	48.9	39.8
	2	61.4	53.2	42.1	58.4	51.2	40.5
So. America (Demerara)	1	34.1	41.7	38.0	32.8	40.2	37.2
	2	28.1	36.9	36.1	27.4	34.8	35.3
Arkansas	1	38.2	43.0	37.7	37.6	41.3	36.3
	2	31.9	41.3	38.9	30.7	39.4	37.4
Activated alumina	1	12.5	18.4	30.4	12.3	18.1	30.2
	2	10.3	10.7	13.5	10.0	10.6	13.4

[a] Ethylbenzene feed rate 1.0 v./hr./v.; H_2O rate, 1.5 v./hr./v.; constant temperature of 1200° F.; atmospheric pressure, 50-hour run.
[b] Based on ethylbenzene feed.

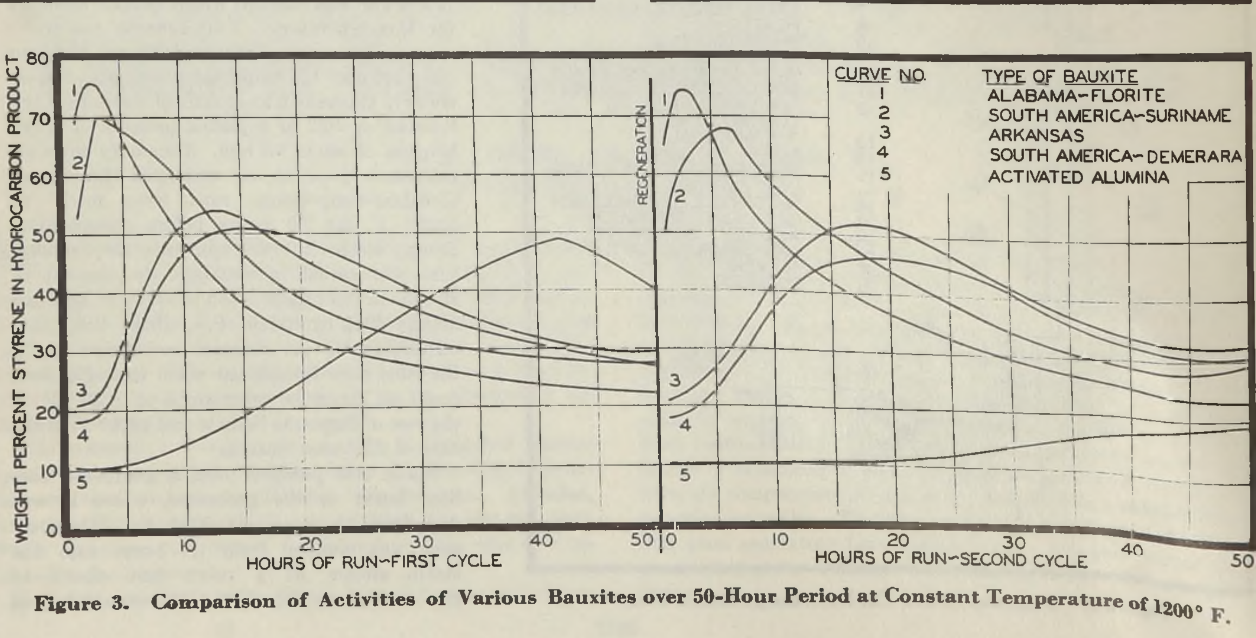


Figure 3. Comparison of Activities of Various Bauxites over 50-Hour Period at Constant Temperature of 1200° F.

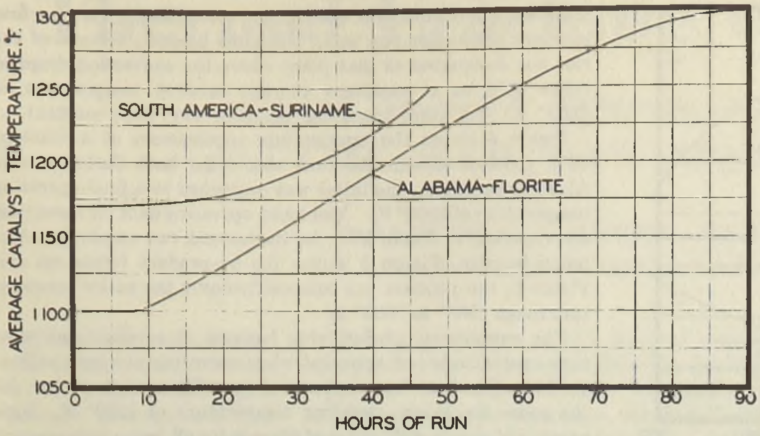


Figure 4. Temperature Requirement to Maintain Constant Styrene Yield of 40%

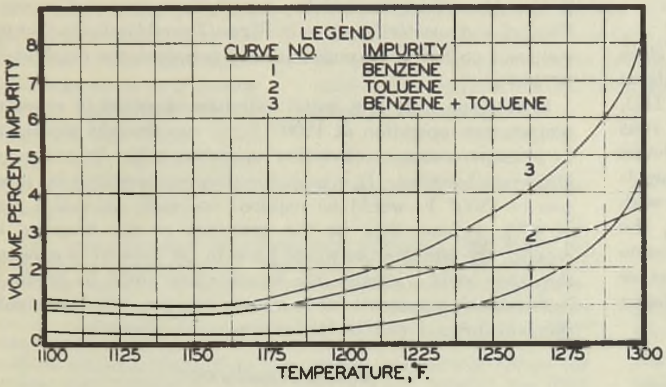


Figure 5. Liquid By-Product Formation as a Function of Temperature, with Alabama Bauxite as Catalyst

toluene, both amounts being greater than those indicated from the curves in Figure 5 at the most severe conditions. The reproducibility of styrene yields is not closer than 1%.

The product gas was analyzed by the use of conventional Burrell equipment.

CONSTANT-TEMPERATURE EVALUATION

For the evaluation of their activity as dehydrogenation catalysts, four typical, readily available bauxites were selected (Table I). The Alabama bauxite has both a high silica and iron content; Arkansas, high silica but low iron; Suriname, low silica and high iron; and Demerara, both low silica and iron. Activated alumina was also tested as an example of a practically pure alumina.

After a few preliminary runs the uniform testing conditions chosen were: ethylbenzene and water liquid space velocities of 1.0 and 1.5 volumes of liquid per hour per volume of catalyst (v./hr./v.), respectively, average catalyst temperature held constant at 1200° F.; atmospheric pressure; length of run, 50 hours. At the end of the first cycle or 50-hour period, the catalyst was regenerated *in situ* by the addition of air and nitrogen to the steam flow. The maximum temperature during regeneration was kept below 1200° F. Figure 2 shows a typical regeneration curve. The system was then adequately purged, and the cycle repeated to determine the regenerative characteristics of the catalyst.

Results of the tests are given in Figure 3 and Table II. Alabama and Suriname bauxites show a high initial activity (75 and 70% conversion, respectively) with a rapid decline after the first few hours. The high initial activity can probably be attributed to the high iron content of the bauxites (20 and 12%) since the low-iron bauxites did not exhibit this characteristic. Arkansas and Demerara bauxites have a low initial activity, rapidly increasing to a maximum of a little over 50% conversion some 12–15 hours later. This maximum was not attained until after 42 hours of operation in the case of activated alumina. The results indicate that within the limits tested, silica has little or no effect on the activity of the bauxite.

The induction period is defined as the time required for the hydrocarbon product to attain 40% by weight styrene. This definition becomes apparent in the section devoted to operation at a constant conversion level. Both before and after regeneration, the induction periods of the Alabama and Suriname bauxites were zero, and their catalytic activities did not suffer during the first cycle or their subsequent regenerations. Arkansas and Demerara bauxites showed induction periods of 7 and 8 hours, respectively, during the first cycle, which were increased, after regeneration, to 10 and 12 hours for the second cycle. For industrial applications, activated alumina, as such, is of little value since it has a 32-hour induction period for the first cycle. Its activity was so seriously impaired during the first cycle and/or its regeneration that an induction period for the second cycle can be recorded only as greater than 50 hours.

The data for these runs (Table II) give the yields for

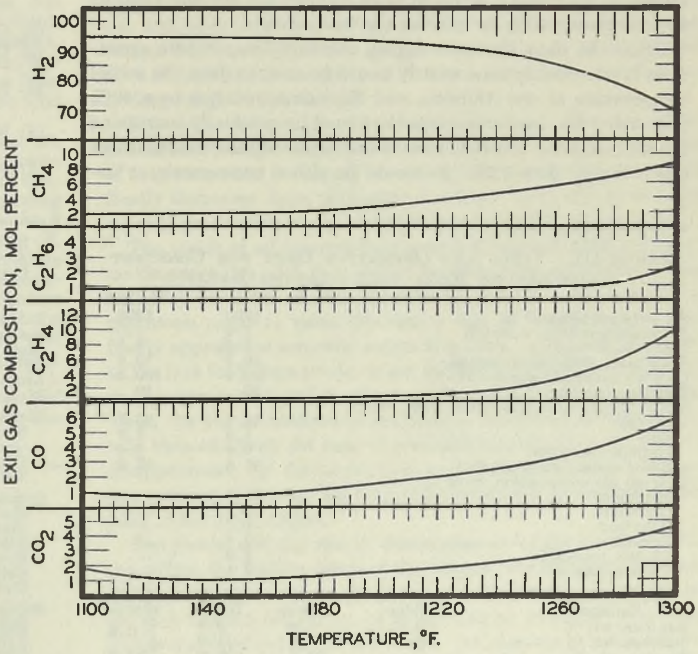


Figure 6. Exit Gas Composition as a Function of Temperature with Alabama Bauxite as Catalyst

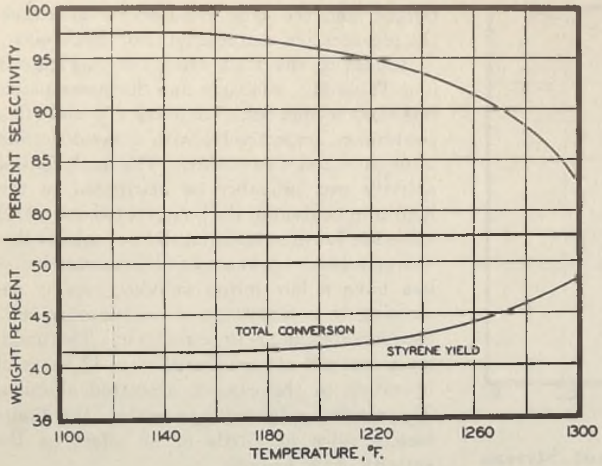


Figure 7. Yield-Conversion-Selectivity Variation with Temperature, Using Alabama Bauxite at Constant Yield of 40 Weight % Styrene

12, 25, and 50 hours, based on the ethylbenzene feed. Data for material balances, gas analyses, and product compositions are available only for the run using Alabama bauxite (Table III), but it is believed that the material balances for the other runs are equally good. The results show that for the first 12 hours Alabama and Suriname bauxites give styrene yields of approximately 60%, or about twice as great as those obtained with Arkansas and Demerara bauxites. On the other hand, the over-all yields at 50 hours have become fairly uniform, Suriname perhaps enjoying a 3 to 5% advantage in yield over the other bauxites. Carbon deposition for both Suriname and Alabama bauxites was 0.4%.

OPERATION AT A CONSTANT CONVERSION LEVEL

Because of the considerable variation in styrene yields obtained during constant temperature conditions, this type of operation was believed unsuitable for plant practice. It was decided, therefore, to make a series of runs holding the styrene yield at approximately 40% by varying the temperature.

From the data obtained during constant-temperature operation, it was readily seen that it would be easy to drop the initial temperature of the Alabama and Suriname bauxites to a 40% conversion level and maintain that level by gradually increasing the temperature. At that time it was believed that temperatures much higher than 1250° F. would be either uneconomic or impractical for commercial operation. Accordingly, for the first constant conversion run using Suriname bauxite, the end of the run was designated as that point where the conversion dropped below 40% at a maximum average catalyst temperature of 1250° F. All other operating variables were kept constant.

Figure 4 shows the temperature requirement at a constant 40% yield of styrene for runs employing both Suriname and Alabama bauxites; the latter was continued to a final operating temperature of 1300° F. Yield and operating data for these runs are reported in Table IV. In the second run employing Alabama bauxite, Figure 5 shows the by-product formation and Figure 6, the product gas composition over the entire temperature range 1100° to 1300° F.

The superiority of Suriname bauxite at constant temperature operation is not apparent when operating at constant conversion. The time-temperature curves in Figure 4 show that, for the same maximum operating temperature of 1250° F., Suriname will give a 40% yield of styrene for 48 hours as compared to 59 hours for Alabama bauxite. Other things being equal, this represents a considerable saving in time between regenerations for large-scale manufacture. If an ultimate styrene yield of 90% is chosen for commercial operation, the by-product curves in Figure 5 and selectivity curve in Figure 7 would indicate that this yield can no longer be maintained at temperatures much above 1275° F.

Because of their low initial activities observed in constant-temperature operation at 1200° F., it was thought inadvisable to attempt constant-conversion operation with Arkansas and Demerara bauxites. It is probable that temperatures far in excess of 1200° F. would be required to reach an initial yield of 40% styrene; then as the activities of the bauxites increased, the temperature would have to be lowered to maintain the same yield. Finally, the temperature would be gradually increased to compensate for the loss in activity. Such manipulation was deemed inadvisable for commercial operation.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of R. C. Amero and W. T. Granquist in the preparation of this paper.

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TABLE III. YIELD AND OPERATING DATA FOR CONSTANT-TEMPERATURE RUNS WITH ALABAMA BAUXITE

	Cycle 1	Cycle 2
Av. catalyst temp., ° F.	1200	1200
Ethylbenzene rate, v./hr./v.	1.0	1.0
H_2O rate, v./hr./v.	1.5	1.5
Mole ratio, H_2O/ethylbenzene	10.2	10.2
Over-all material balance, wt. %	99.9	100.2
Length of run, hr.	50	50
Yields (based on ethylbenzene feed), wt. %		
Styrene	34.6	36.4
Gas	1.9	1.9
Carbon deposition	0.4	0.4
Total hydrocarbon product	97.6	97.8
Over-all gas composition, mole %		
Hydrogen	91.7	...
Methane	2.9	...
Ethylene	1.0	...
Ethane	0.4	...
Carbon monoxide	1.6	...
Carbon dioxide	2.4	...

HYDROCARBON PRODUCT	ETHYLBENZENE FEED	1-10 HOURS	21-30 HOURS	41-50 HOURS
Benzene, wt. %	0.1	1.4	0.3	0.6
Toluene, wt. %	0.1	2.6	1.0	
Styrene, wt. %	....	63.7	29.0	23.6
Ethyldenzene, wt. %	99.8+	32.3	69.7	75.8

TABLE IV. YIELD AND OPERATING DATA FOR CONSTANT-CONVERSION RUNS WITH ALABAMA AND SURINAME BAUXITES

	Alabama	Alabama	Suriname
Ethylbenzene rate, v./hr./v.	1.0	1.0	1.0
H_2O rate, v./hr./v.	1.5	1.5	1.5
Mole ratio, H_2O/ethylbenzene	10.2	10.2	10.2
Over-all material balance, wt. %	99.5	99.3	99.3
Length of run, hr.	90	59	48
Max. temp., ° F.	1300	1250	1250
Yields (based on ethylbenzene feed), wt. %			
Styrene	40.3	40.0	40.7
Gas	2.5	1.7	2.0
Carbon deposition	0.1	..	...
Total hydrocarbon product	96.8	97.2	97.0
Over-all gas composition, mole %			
Hydrogen	86.9	92.5	...
Methane	4.2	2.5	...
Ethylene	3.1	1.1	...
Ethane	1.1	1.0	...
Carbon monoxide	2.4	1.4	...
Carbon dioxide	2.3	1.5	...
Hydrocarbon product composition, wt. %			
Benzene	1.4	0.4	...
Toluene	1.9	1.2	...
Styrene	41.6	41.2	...
Ethylbenzene	55.1	57.2	...

Thermal Cracking of Petroleum

EFFECT OF TIME, TEMPERATURE, PRESSURE, AND TYPE OF CHARGING STOCK ON PRODUCTS

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Experimental data on the thermal cracking of industrial combined-feed and virgin close-cut fractions have been obtained. The effect of time, temperature, pressure, and type of charging stock on the distribution and type of product and on the rates of the reactions involved has been evaluated from these results. Specific rates of reaction for the decomposition of the close-cut fractions for the production of gas and light distillate oils of various end points have been calculated. The specific polymerization rates of gas and gasoline have been determined, as well as qualitative information on the rate of formation of coke. The application of these data to commercial operations is indicated.

THE important variables in the thermal cracking of petroleum are time, temperature, pressure, and type of charging stock. The effect of these variables on the distribution and type of product obtained by the decomposition of close-cut fractions into gas, gasoline, coke, and other fractions is important in establishing the type of decomposition and polymerization reactions that occur. The design and efficient operation of thermal cracking units are based upon the rates at which these reactions proceed.

The apparatus and procedure were described previously (*5*) and shown to give results which are well within the range of accuracy required for the design and operation of thermal cracking units. The apparatus consisted of two bombs fitted with the necessary transfer lines, valves, and fittings. The bombs were immersed in a molten salt bath (50% potassium nitrate and 50% sodium nitrate), brought to the desired temperature before the charge was introduced. At the start of a run, bomb 1 was filled with molten solder and bomb 2 with nitrogen. The oil was charged to bomb 1. The pressure in bomb 1 was controlled by releasing solder from bomb 1 to bomb 2 through a manually controlled throttle valve. The increase in volume in the cracking zone of bomb 1 was followed by measuring the nitrogen displaced from bomb 1. At the end of a run, all of the products were displaced from bomb 1 by solder, expanded to low pressure, and cooled to about 60° F. The uncondensed vapors were metered and passed over activated charcoal in order to recover light gasoline fractions. The coke was scraped from the bomb and weighed.

The physical properties of the three charging stocks used are shown in Table I. Charging stock 1 was a Pennsylvania combined feed, obtained from a commercial cracking plant and containing about 75% of recycled material. This was the charging stock used by Huntington and Brown (*5*). Charging stocks 3 and 4 were close-cut fractions from a virgin mid-continent crude oil.

The results are summarized in Table II. The effective time at the cracking temperature was calculated from the actual time-temperature curves on the basis that the cracking rate doubles for each 18° F. temperature increase. It was found later that the cracking rate for the formation of gas, coke, and gasoline and coke actually doubled for a 19–22° F. increase for charging stock 1 and for a 20.7–24.3° increase for charging stocks 3 and 4. Since the actual cracking temperature fluctuated both above and below the indicated reaction temperature during the run, the equivalent times reported in Table II are within the experimental accuracy, and no second correction was applied to the data.

TABLE I. PHYSICAL PROPERTIES OF CHARGING STOCKS

Charging Stock No.	1	3	4
Gravity at 60° F., °A.P.I.	24.8	35.3	31.5
Column distillation, ° F.			
Initial b.p.	180	421	444
10% over	400	525	609
30%	452	540	634
50%	507	551	635
70%	574	567	665
90%	673	593	700

The term "gasoline" in Table II refers to the products boiling below 390° F. in a column distillation plus the light gasoline fractions recovered by charcoal from the uncondensed vapor products. This "gasoline" corresponds to a raw refinery gasoline having an A.S.T.M. end point of 390° F.

The apparent loss due to retention of material in the lines and to handling was prorated among all of the products recovered on a weight basis.

EFFECT OF TIME AND TEMPERATURE

The effect of time and temperature on the yields of various products is shown in Figures 1, 2, and 3. Where numerals only are used to represent the experimental points, the points are at the center of the numerals. When both letters and numerals are used, the points are at the center of the letters. The slopes of these curves are proportional to the rates of production of the various products.

The material collected after each run may be classified into three groups: (*a*) the ultimate products of the cracking reactions, gas and coke; (*b*) the intermediate products which boil in the ranges between the boiling range of the ultimate products and that of the original charge; and (*c*) the material boiling within the boiling range of the charge.

The yields of gas and coke increase with time. The rate of gas production is high initially and decreases with time. The rate of coke formation is initially zero, increases slowly with time, and finally decreases upon prolonged heating. Both the yields and rates of production of gas and coke increase with temperature.

The yields of all intermediate products increase from zero to a maximum value and then decrease with increasing time. The rate of production of the intermediate products decreases to a maximum negative value (maximum rate of disappearance) and finally approaches zero with increasing time. This is attributable to the fact that these products are themselves cracked to gas and, to a lesser extent, polymerized or condensed to light residues. Thus, the yields decrease as cracking is continued beyond a certain time at which the rate of production is equal to the rate of disappearance by decomposition and polymerization. Higher temperatures increase the rate of all reactions, giving a sharper peak in the yield curves.

The yields, and the rate of disappearance of the fractions boiling within the boiling range of the original charge, decrease with increasing time as the result of an increasing resistance to cracking and, to a limited extent, of production by secondary reactions of new material in this boiling range. An increase in temperature increases the rate of disappearance of these fractions.

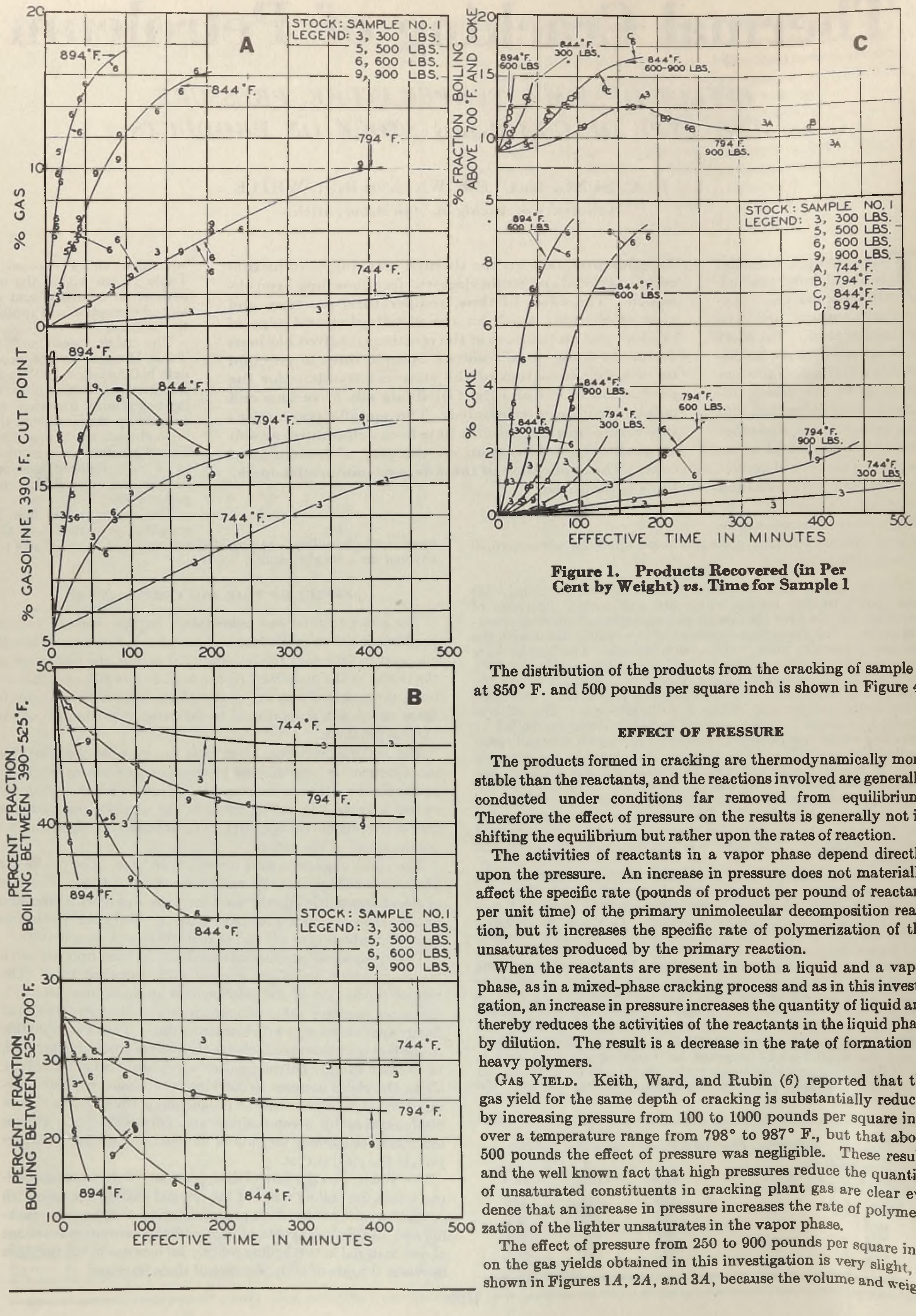

Figure 1. Products Recovered (in Per Cent by Weight) vs. Time for Sample 1

The distribution of the products from the cracking of sample 3 at 850° F. and 500 pounds per square inch is shown in Figure 4.

EFFECT OF PRESSURE

The products formed in cracking are thermodynamically more stable than the reactants, and the reactions involved are generally conducted under conditions far removed from equilibrium. Therefore the effect of pressure on the results is generally not in shifting the equilibrium but rather upon the rates of reaction.

The activities of reactants in a vapor phase depend directly upon the pressure. An increase in pressure does not materially affect the specific rate (pounds of product per pound of reactant per unit time) of the primary unimolecular decomposition reaction, but it increases the specific rate of polymerization of the unsaturates produced by the primary reaction.

When the reactants are present in both a liquid and a vapor phase, as in a mixed-phase cracking process and as in this investigation, an increase in pressure increases the quantity of liquid and thereby reduces the activities of the reactants in the liquid phase by dilution. The result is a decrease in the rate of formation of heavy polymers.

Gas Yield. Keith, Ward, and Rubin (6) reported that the gas yield for the same depth of cracking is substantially reduced by increasing pressure from 100 to 1000 pounds per square inch over a temperature range from 798° to 987° F., but that above 500 pounds the effect of pressure was negligible. These results and the well known fact that high pressures reduce the quantity of unsaturated constituents in cracking plant gas are clear evidence that an increase in pressure increases the rate of polymerization of the lighter unsaturates in the vapor phase.

The effect of pressure from 250 to 900 pounds per square inch on the gas yields obtained in this investigation is very slight, as shown in Figures 1*A*, 2*A*, and 3*A*, because the volume and weight

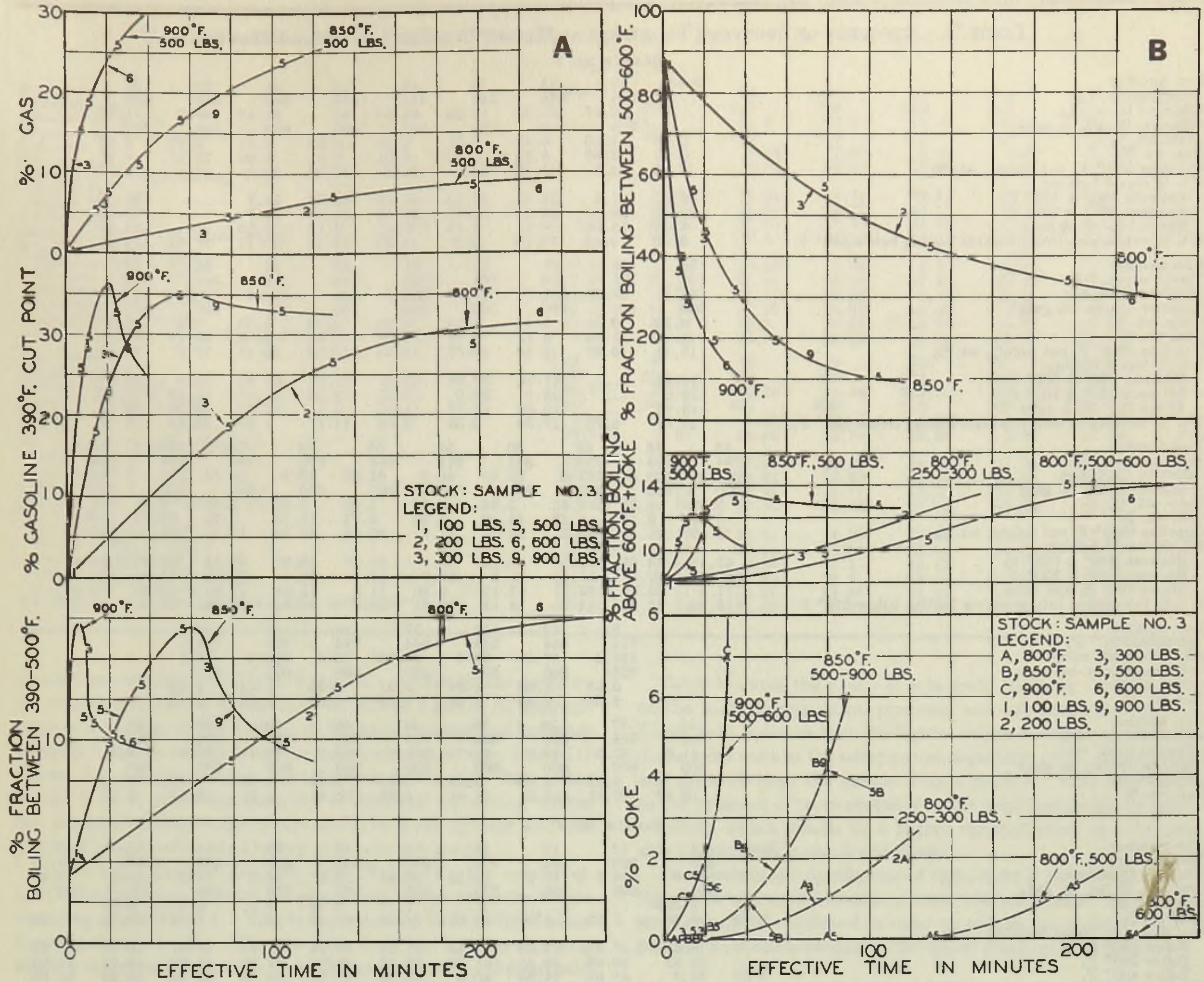

Figure 2. Products Recovered (in Per Cent by Weight) vs. Time for Sample 3

of the vapor relative to that of the liquid is small at pressures above 250 pounds. Keith, Ward, and Rubin reached this condition at higher pressures (above 500 pounds) because they operated at higher temperatures.

Gasoline Yield. The polymerization of the higher-boiling gasoline fractions probably occurs in the liquid phase, and an increase in pressure increases gasoline yield because it decreases gas yield and the polymerization of unsaturates in the gasoline boiling range.

High-Boiling Residue Yield. The effect of pressure on the yields of heavy polymers and coke boiling above the range of the charging stock may be observed by examining the curves for 844° F. in Figure 1*C*, for 800° in Figure 2*B*, and for 800° in Figure 3*B*. In all cases an increase in pressure decreases the yield of the heavy polymer product for the same time and temperature.

Coke Yield. The influence of pressure on coke yields is the same as on heavy polymer yield, as shown by the curves for 794° and 844° F. in Figure 1*C*, for 800° in Figure 2*B*, and for 800° and 850° in Figure 3*B*. The fact that the formation of coke is affected by pressure in the same manner as the formation of heavy polymers is consistent with the concept that coke formation is the final stage of successive polymerization and recracking, at least in a liquid- or mixed-phase cracking process for the production of gasoline.

CONVERSION

Reaction time, temperature, pressure, and the character of the charging stock are generally recognized as the independent variables which affect cracking. In commercial processes time and temperature are the major factors determining the extent to which the reactions are allowed to proceed before gas, gasoline, and residuum are separated from the cracking stock. For this reason the conversion (also called "depth of cracking") is used frequently to express the combined effect of time and temperature. The conversion is computed as the weight per cent yield of material boiling below the boiling range of the original charge. The conversion, as defined above, does not include the material boiling above the boiling range of the original charge formed by secondary reactions; but since the amount of this material is usually small, the conversion does indicate the extent of decomposition which has occurred.

An increase in temperature at constant pressure for the same conversion increases the proportion of lighter materials in the cracked products, and decreases the yield of heavy polymers and coke because the temperature coefficients for the cracking reactions which produce the lighter materials are greater than those for the polymerization reactions which produce the heavy polymers. Thus, increasing the temperature at constant pressure for the same conversion increases the amount of gas, and may or

Table II. Recovery of Products, Expressed as Weight Per Cent of Total Recovery

Sample No. 1

Run number	Stock	12	15	16	18	19	21	22	23
Temperature, ° F.	....	844	844	844	844	844	844	844	844
Effective time, min.	....	16.37	39.33	15.06	41.27	40	88.47	186.2	35.77
Pressure, lb./sq. in. gage	....	300	500	300	600	600	600	600	600
Coke, wt. %	0.00	1.10	0.49	0.39	0.94	0.95	2.21	8.82	0.88
Gas, wt. %	0.00	2.30	5.25	1.70	6.94	5.91	5.50	16.27	4.97
Gasoline (390° F. cut point), wt. %	5.73	12.9	14.28	12.1	16.8	17.64	20.0	14.5	12.78
Wt. % liquid boiling:									
Between 390° & 525° F.	49.17	47.4	31.47	46.13	45.35	35.66	41.7	....	40.52
Between 525° & 700° F.	36.17	26.85	30.53	30.78	24.15	31.25	21.7	....	28.05
Above 700° F. & coke	8.93	10.36	8.21	9.16	6.41	9.18	10.56	....	13.46
Wt. % conversion into products boiling below 390° F.	0.00	9.66	14.06	8.2	18.36	18.18	20.31	27.81	12.24

Run number	25	26	27	29	31	32	33	42	43
Temperature, ° F.	794	794	794	794	744	744	744	844	844
Effective time, min.	78.5	68.17	241.7	82.73	338.2	422	180.2	138.9	167.7
Pressure, lb./sq. in. gage	600	600	600	300	300	300	300	600	600
Coke, wt. %	0.79	0.23	1.24	1.69	0.24	0.59	0.33	9.0	8.6
Gas, wt. %	4.96	0.73	6.13	2.45	0.98	1.97	0.94	13.71	14.88
Gasoline (390° F. cut point), wt. %	13.11	10.67	16.59	12.67	12.94	15.15	10.11	17.0	16.77
Wt. % liquid boiling:									
Between 390° & 525° F.	39.94	....	41.36	39.98	45.01	45.41	42.84	34.8	34.38
Between 525° & 700° F.	28.0	....	24.9	32.0	29.25	28.26	32.65	14.15	13.95
Above 700° F. & coke	13.76	....	10.62	12.71	11.07	9.1	13.43	18.34	17.83
Wt. % conversion into products boiling below 390° F.	12.57	5.70	17.39	9.58	8.94	11.5	5.35	26.98	28.11

Run number	45	46	48	50	51	53	54	55	56	58
Temperature, ° F.	794	794	794	844	844	844	894	894	794	894
Effective time, min.	205.8	102.6	167.8	92.05	40.5	61.03	15.5	15.14	392.5	9.6
Pressure, lb./sq. in. gage	900	900	900	900	900	900	600	600	900	600
Coke, wt. %	0.69	0.36	0.46	3.32	0.50	1.08	3.17	2.62	1.68	1.09
Gas, wt. %	5.96	3.18	4.58	12.19	6.85	9.71	11.15	9.73	10.33	5.8
Gasoline (390° F. cut point), wt. %	15.29	14.43	15.3	16.31	17.9	20.83	16.89	17.3	18.73	21.76
Wt. % liquid boiling:										
Between 390° & 525° F.	43.46	43.67	41.55	36.52	40.7	39.37	38.91	39.85	39.93	40.89
Between 525° & 700° F.	25.35	27.8	25.85	21.2	24.9	17.8	20.0	20.52	19.34	25.55
Above 700° F. and coke	11.6	10.79	12.51	13.12	9.36	11.8	12.04	11.66	11.09	5.54
Wt. % conversion into products boiling below 390° F.	13.86	12.01	14.36	23.43	19.31	25.3	23.32	22.24	23.91	22.29

Run number	9	13	14	17	24	28	30
Temperature, ° F.	794	844	844	844	794	794	794
Effective time, min.	137.4	17.8	39.5	25.38	55.2	205.1	82.7
Pressure, lb./sq. in. gage	300	300	300	500	300	600	300
Coke, wt. %	0.93	1.09	1.56	0.37	0.30	1.83	1.62
Gas, wt. %	2.36	2.52	5.46	1.70	1.40	3.42	2.12

Run number	35	37	38	39	44	49	59	60	61
Temperature, ° F.	894	894	894	894	794	844	894	894	894
Effective time, min.	51.0	87.0	42.2	41.7	204.9	89.0	13.1	30.8	18.8
Pressure, lb./sq. in. gage	600	600	600	600	600	900	600	600	600
Coke, wt. %	7.75	8.22	7.19	6.68	2.66	3.63	1.63	4.89	3.58
Gas, wt. %	15.47	16.41	12.31	14.41	4.35	10.56	6.25	13.49	9.20

Sample No. 3

Run number	Stock	11	12	13	14	15	16	33	34	35	36
Temperature, ° F.	...	800	800	850	900	900	850	850	850	850	850
Effective time, min.	...	67.9	229.3	19.8	10.12	30.27	72.3	35.2	21.3	104.3	55.4
Pressure, lb./sq. in. gage	...	300	600	300	300	600	900	500	500	500	500
Coke, wt. %	...	1.303	....	....	....	7.12	4.31	2.31	0.31	3.6	....
Gas, wt. %	0.00	2.58	7.97	6.21	10.98	21.62	17.48	11.3	7.78	23.88	16.98
Wt. % gas + liquid boiling:											
Below 200° F.	...	8.45	17.21	13.67	19.83	31.91	29.34	21.92	15.57	36.19	29.91
Below 300° F.	...	15.53	30.40	23.63	31.52	39.12	43.09	33.86	24.58	48.21	42.03
Below 400° F.	0.00	25.2	41.55	34.63	40.4	50.55	51.54	43.58	31.48	58.22	53.06
Gasoline (390° F. cut point), wt. %	...	21.68	32.82	27.54	28.56	28.14	33.63	31.31	22.95	33.0	35.04
Wt. % liquid boiling:											
Between 390° & 500° F.	3.35	13.67	16.52	9.93	14.63	9.87	10.85	12.69	10.28	9.86	15.58
Between 500° & 600° F.	88.5	52.49	29.6	44.12	40.52	13.4	16.13	31.63	46.44	10.5	19.2
Between 600° & 700° F.	8.15	3.88	5.3	6.27	2.62	3.85	4.27	4.95	4.35	5.48	8.15
Above 600° F. & coke	8.15	9.57	13.09	12.2	5.31	26.97	21.91	13.07	12.55	12.76	13.22
Above 700° F. & coke	...	5.69	7.79	5.93	2.69	23.12	17.64	8.12	7.2	7.28	5.07
Wt. % conversion into products boiling below 390° F.	0.00	24.26	40.79	33.75	39.54	49.76	51.11	42.61	30.73	56.88	52.0

Run number	37	38	39	40	41	42	43	44	45	46
Temperature, ° F.	800	800	800	800	800	925	900	900	900	850
Effective time, min.	129.6	78.5	197.3	3.36	116.7	25.43	25.7	7.85	11.35	14.4
Pressure, lb./sq. in. gage	500	500	500	100	250	500	500	500	500	500
Coke, wt. %	....	....	1.22	....	1.94	6.87	1.28	1.04	1.61	....
Gas, wt. %	7.35	5.04	8.85	0.44	5.39	33.84	26.04	15.34	19.09	5.46
Wt. % gas + liquid boiling:										
Below 200° F.	14.93	11.43	17.8	0.56	12.01	42.69	37.29	23.19	27.86	10.71
Below 300° F.	23.68	17.72	27.44	0.66	19.2	52.19	50.06	34.63	39.45	18.68
Below 400° F.	35.04	24.3	39.31	0.86	27.23	59.55	59.69	43.01	50.02	24.3
Gasoline (390° F. cut point), wt. %	26.66	18.59	28.77	0.37	20.03	25.11	32.75	26.14	29.95	18.02
Wt. % liquid boiling:										
Between 390° & 500° F.	12.59	8.95	13.4	4.45	11.1	7.12	9.97	11.15	10.85	11.51
Between 500° & 600° F.	42.75	57.49	34.95	87.03	51.23	18.16	20.0	36.68	28.28	56.23
Between 600° & 700° F.	5.9	4.75	6.75	1.74	6.45	3.37	4.25	3.65	4.46	6.96
Above 600° F. & coke	10.65	9.93	14.03	7.71	12.25	15.77	11.24	10.64	11.83	8.78
Above 700° F. & coke	4.75	5.18	7.28	5.97	5.8	12.4	6.99	7.04	7.37	1.82
Wt. % conversion into products boiling below 390° F.	34.01	23.63	37.62	0.81	25.42	58.95	58.79	41.48	49.04	23.48

(*Continued on page 1157*)

may not increase the amount of gasoline produced, depending primarily upon the initial boiling point of the original charge. If the initial boiling point of the charge is well above the boiling range of the gasoline, an increase in temperature may increase the gasoline production; if the initial boiling point of the charge is within or near the gasoline boiling range, the gasoline production may be decreased because of the increased gas production. Thus with specified limits of coke and residuum production, it is possible to increase the conversion at constant pressure by increasing the temperature of the operation.

TYPE OF CHARGING STOCK

Typical data showing the yields of gas, gasoline, coke, and heavy polymers for the same time, temperature, and pressure are summarized in Table III to show the difference between the

Table II. Recovery of Products, Expressed as Weight Per Cent of Total Recovery (*Continued*)

Sample No. 4

Run number	Stock	19	20	21	22	24	25	30
Temperature, ° F.	...	800	800	850	900	800	900	850
Effective time, min.	...	114.9	97.9	23.2	14.43	241.2	25.24	36.47
Pressure, lb./sq. in. gage	...	300	300	300	300	900	900	300
Coke, wt. %	...	....	1.72	2.07	2.59	3.45	10.36	1.42
Gas, wt. %	...	7.48	5.73	8.68	17.61	14.89	23.99	10.49
Wt. % gas + liquid boiling:								
Below 200° F.	...	13.81	14.91	15.01	28.18	22.29	34.6	20.15
Below 300° F.	...	22.67	18.55	24.77	40.51	33.53	46.12	31.22
Below 400° F.	0.00	32.89	26.25	32.93	49.67	43.74	54.07	40.37
Gasoline (390° F. cut point), wt. %	...	24.3	20.01	23.35	31.14	27.84	29.47	28.93
Wt. % liquid boiling:								
Between 390° & 500° F.	0.15	11.24	10.99	12.04	9.3	14.16	8.73	12.62
Between 390° & 600° F.	6.08	21.15	22.16	24.99	17.47	24.96	15.34	23.2
Between 500° & 600° F.	5.93	9.91	11.17	12.95	8.17	10.8	6.61	10.58
Between 600° & 700° F.	83.92	24.04	26.90	26.91	19.01	16.8	9.54	22.62
Above 700° F. & coke	10.0	23.03	25.2	16.07	14.77	15.51	21.66	14.76
Wt. % conversion into products boiling below 390° F.	0.00	31.78	25.74	32.03	48.75	42.73	53.46	39.42

Run number	31	47	48	49	50	51	52	53
Temperature, ° F.	900	850	850	900	800	800	900	850
Effective time, min.	34.4	20.5	52.23	11.86	212.9	126.8	36.03	11.46
Pressure, lb./sq. in. gage	600	500	500	500	500	500	500	250
Coke, wt. %	9.22	....	1.52	4.75	1.96	....	7.15	....
Gas, wt. %	26.17	6.67	18.49	16.74	12.98	8.63	31.28	5.84
Wt. % gas + liquid boiling:								
Below 200° F.	38.44	14.94	27.89	25.55	20.86	14.33	39.2	8.89
Below 300° F.	50.7	23.47	39.92	35.26	31.46	24.66	49.52	14.94
Below 400° F.	57.25	33.52	50.93	44.71	43.89	35.48	57.57	21.31
Gasoline (390° F. cut point), wt. %	30.48	24.05	31.57	27.06	29.99	25.28	25.72	14.71
Wt. % liquid boiling:								
Between 390° & 500° F.	8.66	10.47	10.74	11.74	13.86	12.48	7.04	9.14
Between 390° & 600° F.	14.52	24.13	20.12	18.84	26.61	21.28	13.48	18.05
Between 500° & 600° F.	5.86	13.48	9.38	7.1	12.75	8.78	6.43	8.91
Between 600° & 700° F.	11.0	20.65	17.45	23.8	18.55	32.45	14.23	52.42
Above 700° F. & coke	15.83	22.81	12.37	13.56	11.87	12.38	15.3	8.98
Wt. % conversion into products boiling below 390° F.	56.65	32.72	50.06	43.8	42.97	33.91	57.0	20.55

yields from charging stocks 1, 3, and 4. Although the pressure for charging stock 1 is higher than for stocks 3 and 4, an approximate comparison of the yields can be made because the behavior of stock 1 differs widely from that of stocks 3 and 4. Table III shows that charging stock 1 cracks at a lower rate than either stocks 3 or 4, since the quantity of material remaining within the original boiling range of the stock is much greater and the yields of gas, gasoline, and heavy polymers are lower.

At the same gas plus gasoline yield (Table IV), the combined-feed charging stock 1 gives a higher yield of gas than the virgin charging stocks 3 and 4. This is confirmed by the results of other investigations (*1*, *13*). The gas yield from the heavier charging stock 4 is greater than that from charging stock 3. Apparently at equal yields of gas plus gasoline, the heavier virgin material is more completely decomposed than the lighter virgin material. This is substantiated by the fact that less material remains within the original boiling range for charging stock 4 than for charging stock 3. From the point of view of maximum gasoline production with minimum gas production, light virgin charging stocks are the most suitable.

The coke yield from the partially cracked charging stock 1 is much larger than for either stock 3 or 4. Similar data have been obtained by others (*1*, *7*, *13*). This may be attributed to the unsaturated character of the cracked charging stock which results in greater polymerization in the liquid phase.

Table III. Yields of Products from Cracking at Constant Time, Temperature, and Pressure

Sample No.	1		3		4	
Temperature, ° F.	844		850		850	
Pressure, lb./sq. in. abs.	600		300		300	
Boiling range of charging stock, ° F.	390–700		500–600		600–700	
Time, minutes	30	60	30	60	30	60
Yields, % by wt.						
Material in original boiling range	70.8	61.3	35.9	18.2	22.3	15.7
Gas	4.5	8.8	10.2	17.4	11.4	19.8
Gasoline	15.8	20.2	29.0	35.0	27.4	32.4
Gas and gasoline	20.3	29.0	39.2	52.4	38.8	52.2
Heavy polymers and coke	9.8	11.0	13.5	13.0	19.2	11.1
Coke	0.57	1.96	0.51	2.01	0.34	1.94
Coke ÷ gasoline	0.0357	0.0973	0.0178	0.0575	0.0125	0.0598

Table V shows the yields of coke from charging stocks 3 and 4 at the same temperature, pressure, and gas-plus-gasoline yield. These data indicate that the lighter virgin charging stock 3 produces more coke at the same gas-plus-gasoline yield, temperature, and pressure than the heavier virgin stock 4. This may be due to the presence of more material in the vapor phase of the lighter material, which results in a higher concentration of polymerizable unsaturates in the liquid phase.

The commercial significance of these data is that if light charging stocks are used because of their low gas yields, higher pressures should be employed in order to reduce the concentration of polymerizable unsaturates in the liquid phase to a minimum.

SPECIFIC REACTION RATES

Decomposition. Previous investigators (*2*, *5*, *6*, *7*) correlated cracking rates by the unimolecular rate equation:

$$k = \frac{1}{t} \ln \frac{A_o}{A_o - X} \tag{1}$$

where k = specific reaction velocity constant, reciprocal sec.
t = time, sec.
A_o = original charging stock, lb.
X = charging stock decomposed at time t, lb.

The activation energies were computed from the Arrhenius equation:

$$\frac{d \ln k}{dT} = \frac{Q}{RT^2} \tag{2}$$

where k = reaction velocity constant
Q = activation energy
T = absolute temperature
R = gas constant

The values of k calculated from experimental data decrease with increasing conversion and, therefore, must be extrapolated to 0% conversion in order to obtain the true reaction velocity constant. Previous work evaluated the reaction velocity constants for the production of gas and gasoline. The results from charging stocks 3 and 4 of this investigation have been used to determine the reaction velocity constants for the production of gas and light distillates of various end points.

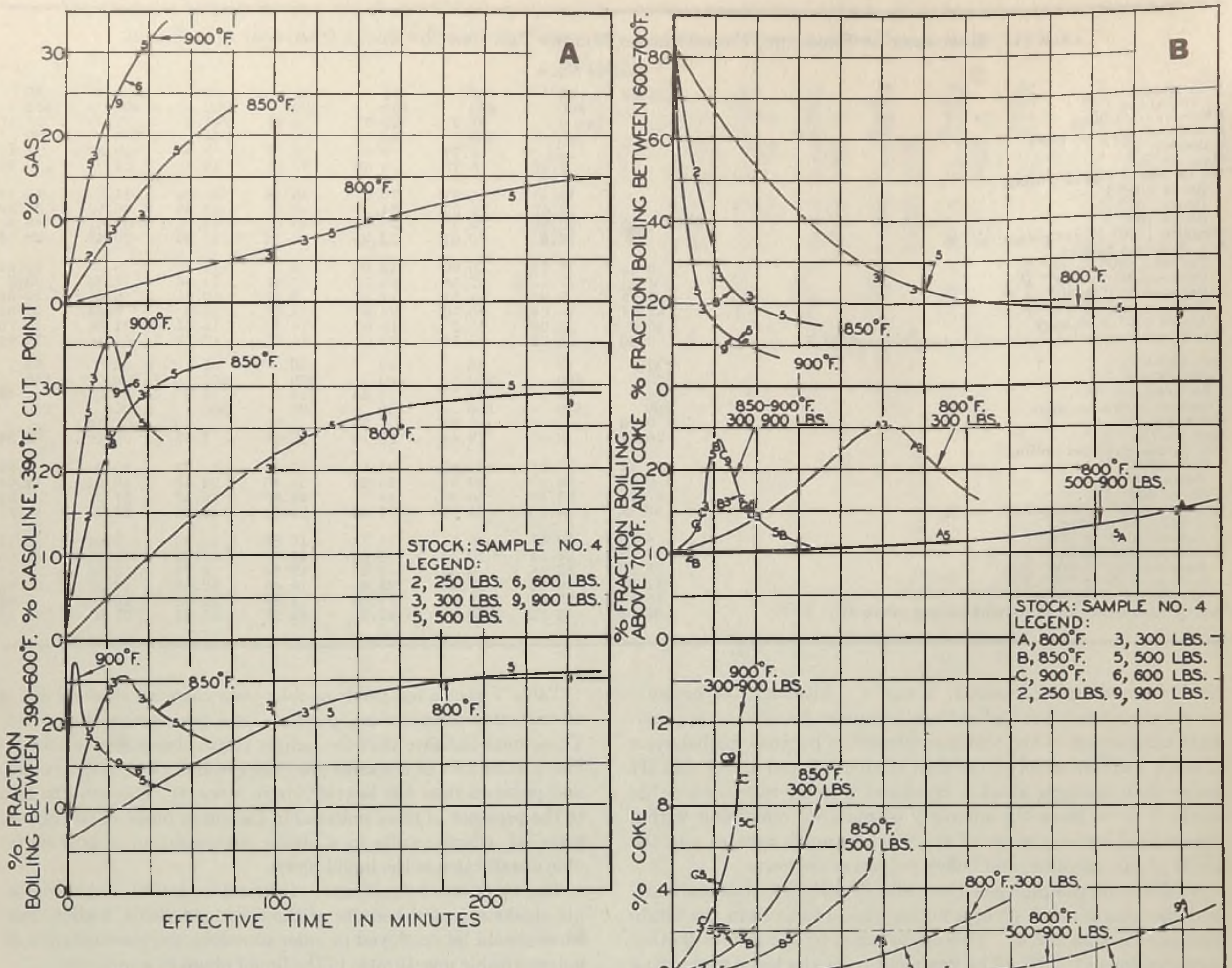

Figure 3. Products Recovered (in Per Cent by Weight) *vs.* Time for Sample 4

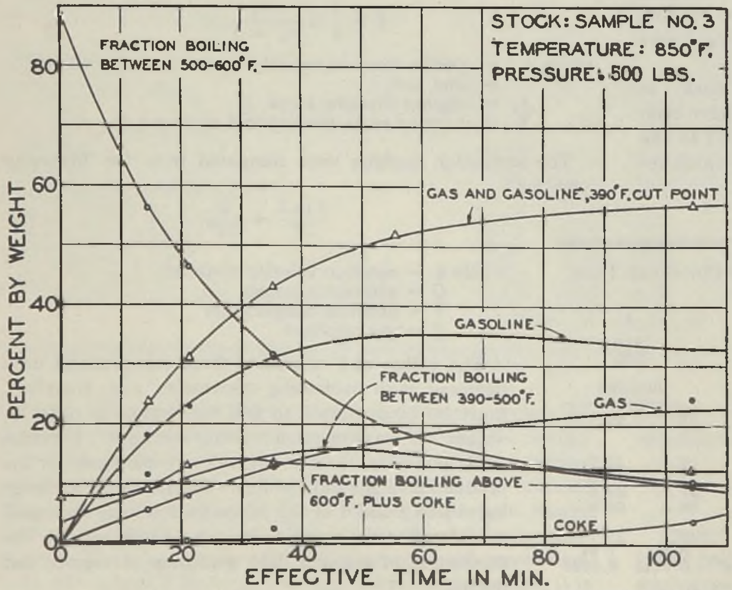

Figure 4. Effect of Time on Amount of Products

Figure 5 shows the calculated values of k as a function of per cent conversion to gas and distillates of specified end points and the extrapolation of these curves to 0% conversion. The reaction velocity constants for primary decomposition obtained from Figure 5 are plotted as a function of the reciprocal of absolute temperature in Figure 6. Figure 6 shows that the reaction velocity constant increases with the end point of the gas and distillate considered as a product.

Figure 7 compares the reaction velocity constant from this investigation for the production of gas and gasoline with the results of other investigators. All the velocity constants determined from liquid-phase cracking show identical slopes when plotted against reciprocal temperature, whereas those from vapor-phase cracking have a lower slope. This indicates that liquid-phase decomposition requires a greater energy of activation than vapor-phase decomposition.

Table VI shows the activation energy for primary decomposition into gas and distillate of various end points for charging stocks

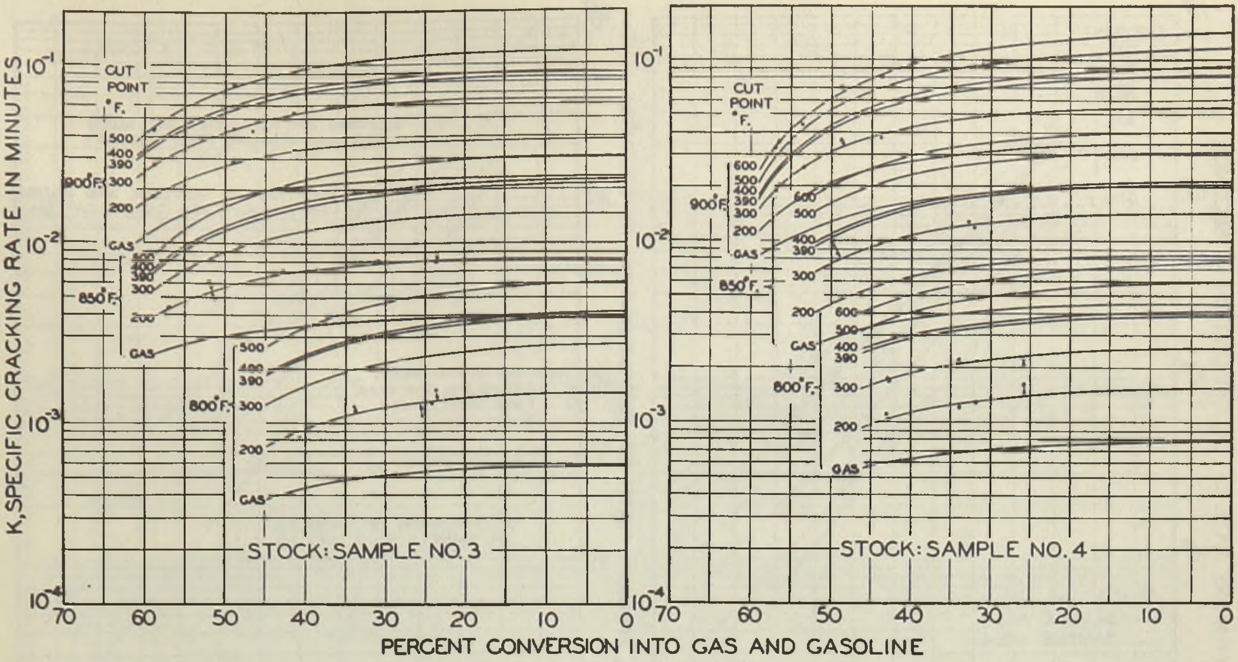

Figure 5. Variation in Specific Cracking Rate with Conversion

Table IV. Yields of Products from Cracking at Constant Temperature, Pressure, and Gas-Plus-Gasoline Yield

Temperature, ° F.	844	850		850	
Pressure, lb./sq. in. abs.	600	500		500	
Charging stock No.	1	3		4	
Yields, % by wt.					
Gas + gasoline	20	20	40	20	40
Gas	7.1	4.8	10.2	5.3	12.2
Gasoline	12.9	15.2	29.8	14.7	27.8
Gas ÷ gasoline	0.382	0.316	0.342	0.360	0.439
Coke	1.6	0	1.1	0	....
Coke ÷ gasoline	0.086	0	0.037	0	....

Table V. Yields of Coke and Gasoline from Charging Stocks 3 and 4 at 800° F.

	Stock 3			Stock 4		
Pressure, lb./sq. in.	300	500	500	300	500	500
Yields, % by wt.						
Gas + gasoline	20	30	40	20	30	40
Gasoline	15.8	23.6	30.8	15.6	23.0	28.9
Coke	0.45	0.50	1.60	0	0	1.5
Coke ÷ gasoline	0.0285	0.0212	0.0520	0	0	0.0519

3 and 4. The values indicate that higher activation energies are required for the production of lighter products. The activation energy for the destruction of a carbon-hydrogen linkage has been determined as 92,000 calories and that for a carbon-carbon linkage as 72,000 calories (*9*). Thus, higher activation energies for lighter products indicate either that a higher proportion of carbon-hydrogen rupture takes place in gas production, or that the formation of a smaller molecule requires a greater number of carbon-carbon ruptures. The activation energies for the production of gas and gasoline is 58,130 calories for charging stock 3 and 58,700 for charging stock 4. Other investigators obtained 57,100 calories (*6*) for the production of gas and gasoline, 59,200 calories (*5*) for gas, gasoline, and coke, and 53,400 calories (*2*) for gas, gasoline, and tar from vapor-phase cracking.

The relatively small difference between the activation energies from charging stocks 3 and 4 indicates that the activation energies for the decomposition of all close-cut fractions from the same virgin crude oil are approximately equal.

Specific Polymerization Rates of Gas and Gasoline. The decomposition and polymerization reactions that proceed during cracking may be represented diagrammatically as in Figure 8. It is apparent that the cracking process is not simple and that a rigorous treatment of the nine reactions shown is extremely difficult, if not impossible. Average polymerization reaction velocity constants for gas and gasoline may be evaluated by defining $G = L + V$ and by integrating Equation 3:

$$\frac{dG}{dt} = (K_1 + K_2)A_G - K_G G^2 \tag{3}$$

where G = weight % of gas + gasoline at time t

K_G = polymerization reaction velocity constant for gas + gasoline, (lb. sec.)$^{-1}$

A_G = weight % of material producing gas + gasoline at time t

The weight per cent of material producing gas and gasoline, A_G, may be evaluated if it is assumed: (1) The products heavier than gasoline, excluding those produced by polymerization of gas or gasoline, have the same decomposition velocity constants as the original charging stock; i.e., the effect of reaction $A \xrightarrow{K_3} P$ is negligible. (2) The products heavier than gasoline produced by the polymerization of gas and gasoline do not recrack to gas and gasoline; i.e., the reactions $P \xrightarrow{K_5} V$ $P \xrightarrow{K_6} L$ are negligible. Thus,

$$\frac{-dA_G}{dt} = (K_1 + K_2)A_G \tag{4}$$

$$A_G = A_o e^{-(K_1 + K_2)t} \tag{5}$$

where A_o = weight % of original charge

Substituting the value of A_G given by Equation 5 in Equation 3 and writing in integral form:

$$G = (K_1 + K_2)\,A_o \int_0^t e^{-(K_1 + K_2)t}\,dt - K_G \int_0 G^2 dt \tag{6}$$

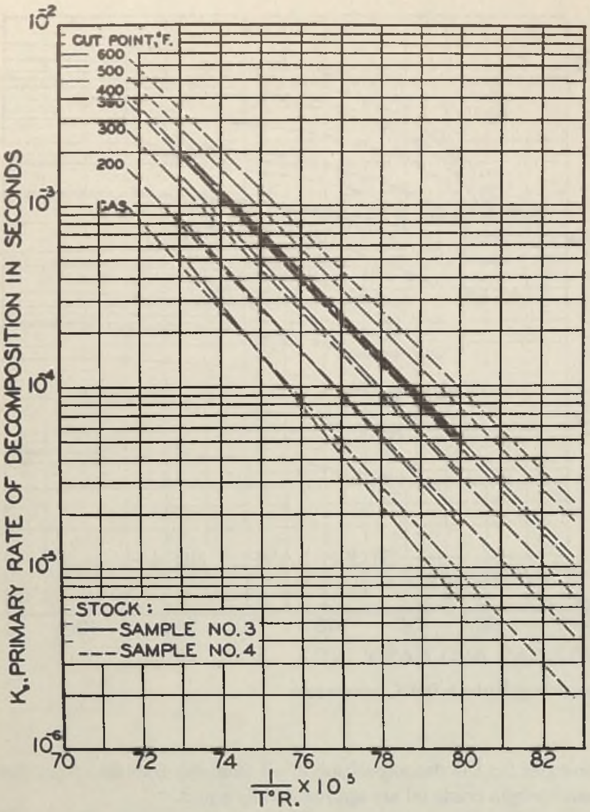

Figure 6. Primary Rate of Decomposition into Gas and Liquid Boiling below the Cut Point Indicated, as Affected by Temperature

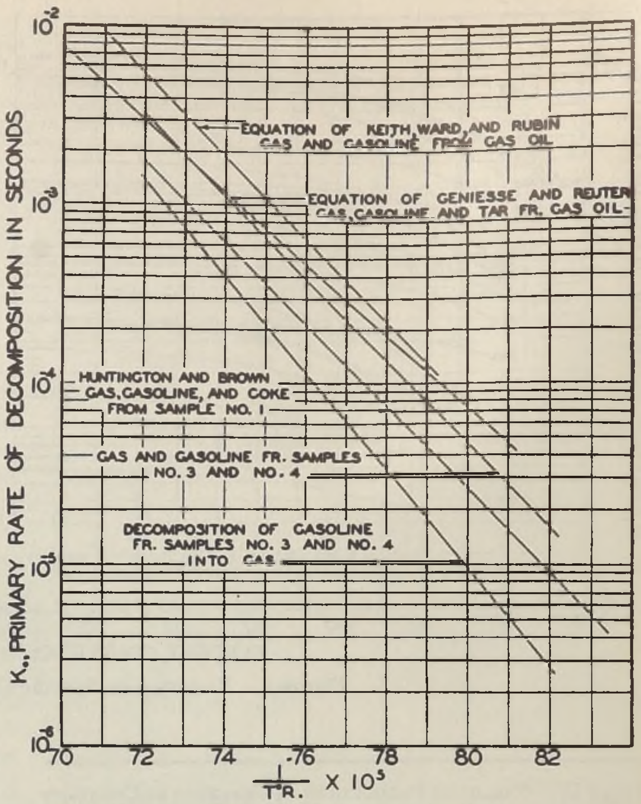

Figure 7. Primary Rate of Decomposition of Products Indicated, as Affected by Temperature

Table VI. Activation Energy for Primary Decomposition into Distillate Products

Charging Stock No.	Calories/Gram Mole at Cut Point of: Gas	200° F.	300° F.	390° F.	400° F.	500° F.	600° F.
3	70,500	61,700	59,900	58,130	58,300	55,850	...
4	61,500	59,100	58,900	58,700	58,720	55,850	55,850

Furthermore, since the rate of polymerization of gas into fractions heavier than gasoline is probably negligible, the rate of polymerization of gas and gasoline is equal to the rate of polymerization of gasoline alone:

$$K_G G^2 = K_L L^2 \tag{7}$$

$$K_L = K_G \left(\frac{G}{L}\right)^2 \tag{7A}$$

Values of K_L were calculated from the experimental data by Equations 6 and 7*A*, and are plotted as a function per cent conversion to gas and gasoline in Figure 9. These curves show that the specific rate of polymerization of gasoline is low at low percentage conversions, increasing to a maximum and then decreasing with increasing percentage conversion. The rate of polymerization increases with increasing temperature and with decreasing pressure.

Specific Decomposition Rate of Gasoline. The reaction velocity constant K_4 (Figure 8) for the decomposition of gasoline to gas may be evaluated by a similar procedure. As before,

$$\frac{dV}{dt} = K_1 A_V - K_{VL} V^2 \tag{8}$$

where A_V = weight % of material producing gas

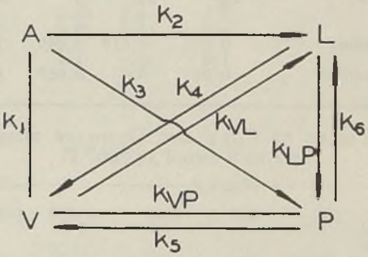

Figure 8. Diagram of Decomposition and Polymerization Reactions

A_0 = initial cracking stock, %
A = initial cracking stock remaining, %
L = gasoline, %
V = gas, %
P = polymerization and decomposition products boiling above end point of gasoline, %
$G = L + V$
$K_1, K_2, K_3, K_4, K_5, K_6$ = specific decomposition rates
K_{VL}, K_{VP}, K_{LP} = specific polymerization rates

The weight per cent of material producing gas, A_V, may be evaluated if it is assumed that the products, excluding those produced by gas polymerization, have the same decomposition velocity constants for gas production as the original charge, and that the products resulting from gas polymerization do not produce gas. Then,

$$A_V = A_0 e^{-K_1 t} \tag{9}$$

The rate of gas production is also given by the following equation:

$$\frac{dV}{dt} = K_1 A_G + K_4 L - K_{VL} V^2 \tag{10}$$

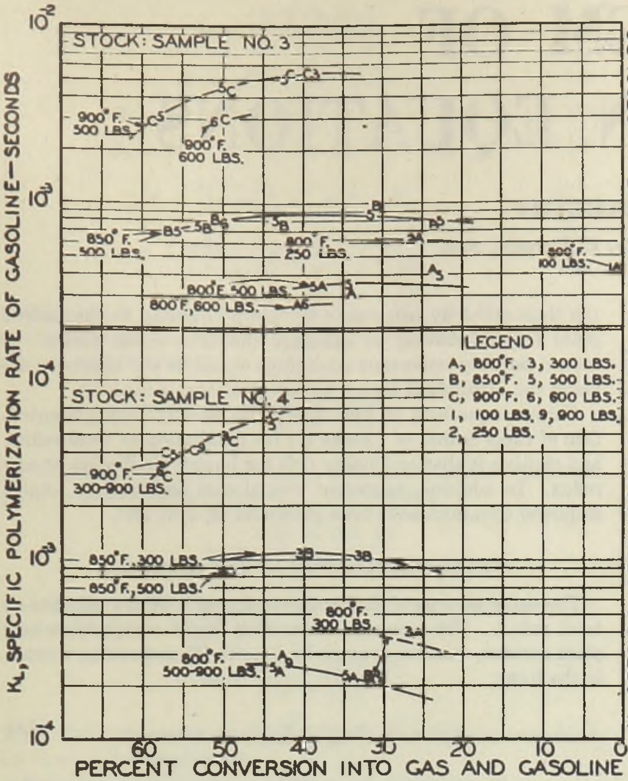

Figure 9. Variation in Specific Rate of Polymerization of Gasoline with Conversion

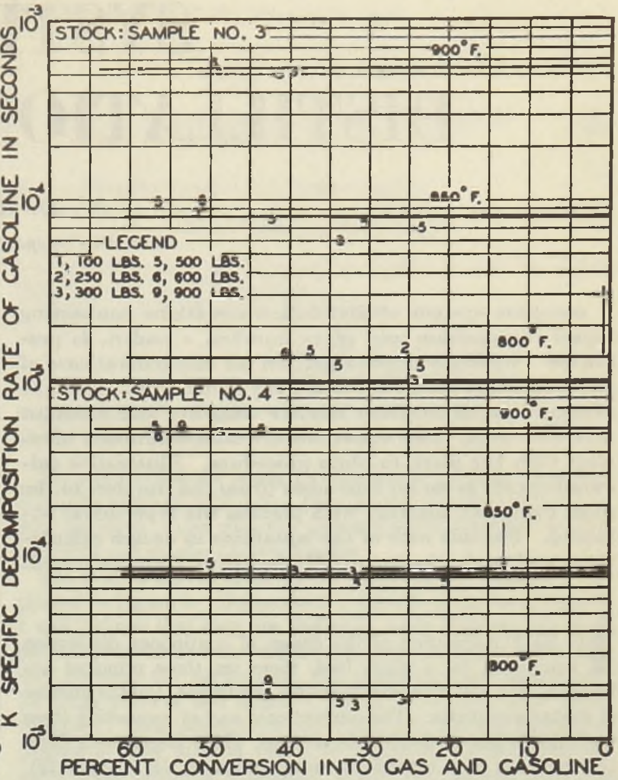

Figure 10. Specific Decomposition Rate of Gasoline *vs.* Conversion

which shows the rate of gas production as a function of the rate of decomposition of the material, A_G, heavier than gasoline and the gasoline, and the specific rate of polymerization of the gas.

Combining Equations 8, 9, and 10:

$$K_4 = K_1/LA_o[e^{-K_1t} - e^{-(K_1 + K_2)t}] \tag{11}$$

The values of K_4 evaluated from the experimental data by Equation 11 are plotted in Figure 10, which shows that the specific rate of decomposition of gasoline is virtually independent of conversion. The values for K_4 are included in Figure 7. The energy of activation for the decomposition of gasoline into gas from Equation 2 and Figure 10 is 72,100 calories, or approximately the value for the rupture of the carbon-carbon linkage obtained by Pease (*9*).

Specific Rate of Coke Formation. Owing to the scarcity of data obtained under varied conditions of time, temperature, and pressure for different stocks, and the attendant difficulty in evaluating the amount of materials polymerizable to coke, no attempt has been made to determine quantitatively the specific rate of coke formation. But from the discussion on the effect of time, temperature, and pressure, it may be predicted that the specific rate of coke formation will be increased either by an increase in temperature or by a decrease in pressure in mixed-phase processes as is the specific polymerization rate of gasoline. The specific rate of coke formation under a constant temperature and pressure will increase from a low value at a low percentage conversion into gas and gasoline to a higher value at higher percentage conversion. As the percentage conversion is further increased by prolonged heating, the specific rate of coke formation may decrease from a maximum. The fact that high-temperature and short-time operations give a low yield of coke indicates that the specific rate or coke formation may have a lower temperature coefficient than that for the specific cracking rate of gas and gasoline production.

CONCLUSIONS

1. An increase in temperature increases all the reaction rates involved. In general, an increase in temperature increases the ultimate yield of the volatile materials more than the yields of heavy polymers and coke.
2. An increase in pressure results in a decrease in the rate of polymerization and coke formation in mixed-phase processes. An increase in pressure materially reduces the ultimate yield of coke produced from polymerization at the same percentage conversion.
3. An increase in percentage conversion increases the proportion of gas and coke formed, but decreases the proportion of gasoline and other light liquid fractions produced.
4. The character of charging stock not only influences decomposition but also influences polymerization and coke formation. From the viewpoint of keeping low the ratios of both gas to gasoline and coke to gasoline, for the partially cracked stock of wide and low boiling range, high temperature under high pressure operation at low percentage conversion seems most desirable; for virgin close-cut fractions, high pressure coupled with moderate temperature and percentage conversion appears to be most favorable.

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SYSTEM OF DISTILLATION EQUATIONS

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A complete system of distillation equations connecting liquid composition and plate number, x and n, is presented. Included is the equation for the general case of any number of components and any reflux ratio. With the assumptions of constant relative volatility and constant internal reflux, these equations are mathematically identical with the plate-to-plate procedure. Illustrative calculations are given for four cases (from the simplest to the most complex), together with plots of the type curves obtained. Possible uses of the equations in design calculations and in developing distillation theory are indicated.

IN THE calculation of the design of continuous distillation equipment for a given feed, there are three principal unknowns: the end products, the reflux conditions, and the number of contacts or plates. The conventional way of connecting these variables is the plate-to-plate method, which began with Sorel (*11*) and has been extensively developed since (*5, 7, 8, 9, 12*). This method is based on the concept of the theoretical or equilibrium plate, which is considered to be a perfect contact so that the vapor and liquid streams leaving the plate are in equilibrium. The material relations for the plates of the section of tower above the feed plate can be written as follows:

The component material balance,

$$(Vy)_{n+1} = (Lx)_n + Dx_D \tag{1}$$

The vapor-liquid equilibrium,

$$y = Kx \tag{2}$$

where $\Sigma\, x = 1.0$ and $\Sigma\, y = 1.0$

The general plate-to-plate procedure for the section of tower above the feed plate consists of beginning with a known composition at the top of the column and calculating down the plates, from liquid to vapor to liquid, by the alternate use of Equations 1 and 2 until a desired composition for the feed plate is reached. The internal reflux conditions are determined by heat balances. The answers obtained are numbers of plates, and the method inherently demands that the reflux conditions and end products be set and that numbers of plates be the calculated unknowns.

In this type of calculation two important simplifying assumptions can frequently be made (*8, 9*). The first is that, while the volatilities of the components, measured as K values, change with temperature, the ratios of the volatilities do not. This is known as constant relative volatility. The second assumption is that the molal ratio of liquid to vapor, L/V, is constant for the plates of a section of tower. This is known as constant internal reflux. The error resulting from these assumptions is frequently quite small.

The repetitious plate-to-plate calculations are often long and tedious, and the resultant calculated numbers of plates are a series of points which are difficult to analyze mathematically. Because of these and other disadvantages, it would seem desirable to reduce the plate-to-plate procedure to algebraic equations with liquid compositions and plate numbers, x and n, as variables. One advantage that might result from such equations would be the time saved by being able to "jump" directly to the desired plate without having to calculate the intervening plates. A second possibly important advantage would be the ability to develop the distillation theory by direct algebraic analysis.

Certain equations of this type have already been presented. One of them is that of Fenske (*3*) for distillation at total reflux, and another is that of Smoker (*10*) for binary distillation at any reflux. In addition, numerous special case and semi or totally empirical equations have been presented (*2, 4, 6, 12*)[1].

BINARY DISTILLATION AT TOTAL REFLUX

The simplest type of distillation is that of a binary mixture at total reflux. The equation connecting liquid composition and plate number, x and n, is given by Fenske (*3*) and can be written in the form:

$$a_n = \frac{a_0}{a_0 + b_0\,\alpha^n} \tag{3A}$$

$$b_n = \frac{b_0\alpha^n}{a_0 + b_0\,\alpha^n} \tag{3B}$$

a represents the more volatile component and b, the less volatile; n is the plate number and α is the relative volatility; a_0 and b_0 are the known liquid composition on plate $n = 0$; and a_n and b_n are the unknown liquid composition on plate n. An x *vs.* n curve of the type given by Equation 3 is shown on Figure 1 for the conditions of $a_0 = 0.8$, $b_0 = 0.2$, and $\alpha = 1.5$. Curves for the components are symmetrical about the point for which $a = b = 0.5$, and approach 0 and 1 asymptotically for large values of n.

BINARY DISTILLATION AT ANY REFLUX

The next step is to obtain the equation of composition *vs.* plate number, x *vs.* n, for the distillation of a binary mixture at any reflux ratio. This equation, which corresponds to Equation 3 for total reflux, is

$$a_n = \frac{A_1a' + A_2b'\,\bar{\alpha}^n}{a' + b'\,\bar{\alpha}^n} \tag{4A}$$

$$b_n = \frac{B_1a' + B_2b'\bar{\alpha}^n}{a' + b'\,\bar{\alpha}^n} \tag{4B}$$

In order to evaluate the constants of this equation, the conditions of distillation for above the feed plate must be known. These required knowns are: the liquid composition on plate $n = 0$, a_0, and b_0; the overhead product composition, a_D and b_D; the reflux conditions, L/V and D/V; the relative volatility, $\alpha = K_a/K_b$. These known values are arranged algebraically as follows to give the constants of Equation 4:

$$u = \frac{1 + (D/V)(b_D)(\alpha - 1)}{(L/V)(\alpha - 1)} \tag{5}$$

$$v = \alpha/(\alpha - 1) \tag{6}$$

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[1] For a different treatment of the general subject of x *vs.* n equations, the reader is referred to a recent article by A. J. V. Underwood [*J. Inst. Petroleum*, 31, 111 (April, 1945)], which appeared after the submission of this paper for publication.

$$w = \frac{(D/V)(b_D)(\alpha)}{(L/V)(\alpha - 1)} \tag{7}$$

$$G = \sqrt{(v - u)^2 - 4w} \tag{8}$$

$$B_1 = (v - u - G)/2;\quad A_1 = 1 - B_1 \tag{9}$$

$$B_2 = (v - u + G)/2;\quad A_2 = 1 - B_2 \tag{10}$$

$$b' = \frac{b_0 - B_1}{B_2 - B_1};\quad a' = 1 - b' \tag{11}$$

$$\bar{\alpha} = \frac{\alpha A_1 + B_1}{\alpha A_2 + B_2} = \frac{u + v + G}{u + v - G} \tag{12}$$

Equation 4 can be proved to be identical with the plate-to-plate procedure as follows: With the above definitions and for plate $n = 0$, the following is an identity:

$$b_0 = \frac{B_1 a' + B_2 b' \bar{\alpha}^0}{a' + b' \bar{\alpha}^0}$$

If this algebraic expression for b_0 is put through the plate-to-plate procedure so as to obtain b_1, the result is:

$$b_1 = \frac{B_1 a' + B_2 b' \bar{\alpha}^1}{a' + b' \bar{\alpha}^1}$$

And if this plate-to-plate calculation is repeated so as to obtain b_2, the result is:

$$b_2 = \frac{B_1 a' + B_2 b' \bar{\alpha}^2}{a' + b' \bar{\alpha}^2}$$

Then if this process is repeated n times, the resultant expression for b_n vs. n is Equation 4B.

Equation 4B solved for n in terms of b_n becomes:

$$n \log \bar{\alpha} = \log \frac{a'(b_n - B_1)}{b'(B_2 - b_n)} \tag{13}$$

This is the form of the equation used for determining the numbers of plates.

Smoker (*10*) gives an equation for the same relation as Equation 4 but with a different arrangement of variables. The use of Equations 4 and 13 is illustrated in example I.

Example I. In a binary distillation the overhead vapors are totally condensed and the liquid reflux is returned to the tower at its boiling point. Then the overhead product and the liquid from the condenser have the same composition, and the condenser liquid can be considered to be the known liquid from plate $n = 0$. The composition of this condenser liquid is:

$$a_0 = a_D = 0.9 \text{ and } b_0 = b_D = 0.1$$

The reflux conditions for the distillation are $L/V = 0.8$ and $D/V = 0.2$. The relative volatility is $\alpha = K_a/K_b = 1.5$.

It is desired to determine the constants of Equation 4 and to solve for the liquid compositions on plate $n = 8$. It is also desired to know the number of plates required for a value of $b_n = 0.41$.

The terms defined by Equation 5 to 12 are obtained as follows:

$$u = \frac{1 + (0.2)(0.1)(0.5)}{(0.8)(0.5)} = 2.525 \tag{5}$$

Similarly,

$$v = 3.000 \tag{6}$$

$$w = 0.075 \tag{7}$$

$$G = 0.725 \tag{8}$$

$$B_1 = -0.125;\quad A_1 = 1.125 \tag{9}$$

$$B_2 = 0.600;\quad A_2 = 0.400 \tag{10}$$

$$b' = 0.310;\quad a' = 0.690 \tag{11}$$

$$\bar{\alpha} = 1.302 \tag{12}$$

With these constants Equation 4 becomes:

$$a_n = \frac{(1.125)(0.690) + (0.40)(0.310)(1.302)^n}{(0.690) + (0.310)(1.302)^n} \tag{4A}$$

$$b_n = \frac{(-0.125)(0.690) + (0.60)(0.310)(1.302)^n}{(0.690) + (0.310)(1.302)^n} \tag{4B}$$

If $n = 8$ is substituted in the above equation,

$$a_8 = 0.553, \text{ and } b_8 = 0.447$$

is obtained as the liquid composition on plate $n = 8$, the eighth plate from the top of the column.

With $b_n = 0.41$, Equation 13 becomes

$$n \log 1.302 = \log \frac{0.690\,[0.41 - (-0.125)]}{(0.310)(0.600 - 0.41)} \tag{13}$$

and this solved for n gives $n = 6.95$ as the number of plates required to reach a liquid composition of $b = 0.41$ and $a = 0.59$.

The substitution of $n = 8$ in the equations of example I is mathematically identical with going through the plate-to-plate procedure for eight plates with the assumptions of constant relative volatility and constant internal reflux.

The x vs. n curves given by the equations of example I are plotted on Figure 2. Comparison of the sets of curves of Figures 1 and 2 shows that they are similar in many respects. In both cases the curves are S-shaped, are symmetrical about a point midway between the asymptotes, and approach these asymptotes for large positive and negative values of n. For total reflux (Figure 1) these asymptotes are 0 and 1.0, and for any reflux (Figure 2) they are the values of A and B. A plate-to-plate calculation, beginning with either A_1 and B_1 or A_2 and B_2 for the liquid composition, gives the same composition for the succeeding plates. Such a section of tower where no change takes place in the stream compositions has been termed a "constant zone", and so the values of A and B can be termed "constant zone compositions". The terms a' and b' of Equation 4 give the location of the required known composition between the asymptotes and, therefore, by analogy with the a_0 and b_0 terms of Equation 3, can be termed a "pseudo known composition". Similarly $\bar{\alpha}$ of Equation 4 corresponds to α of Equation 3 and so can be termed a "pseudo relative volatility".

MULTICOMPONENT DISTILLATION AT TOTAL REFLUX

The x vs. n equation for this case, corresponding to Equations 3 and 4 for binary distillation, is:

$$a_n = \frac{a_0}{a_0 + b_0\alpha^n + c_0\beta^n + \dots e_0\delta^n} \tag{14A}$$

$$b_n = \frac{b_0\alpha^n}{a_0 + b_0\alpha^n + c_0\beta^n + \dots e_0\delta^n} \tag{14B}$$

$$c_n = \frac{c_0\beta^n}{a_0 + b_0\alpha^n + c_0\beta^n + \dots e_0\delta^n} \tag{14C}$$

. . . .

$$e_n = \frac{e_0\delta^n}{a_0 + b_0\alpha^n + c_0\beta^n + \dots e_0\delta^n} \tag{14E}$$

Here $a, b, c \dots e$ is the liquid composition with the components arranged in order of decreasing volatility; and $\alpha, \beta \dots \delta$ are the relative volatilities based on the most volatile component, a. Subscript 0 indicates plate $n = 0$ for which the composition is considered known, and subscript n indicates the general plate—i.e., any plate. This system of equations exactly satisfies the two requirements that

$$a + b + c + \dots e = 1 \tag{15}$$

$$(x/a)_n = (K_a/K_x)^n (x/a)_0 \tag{16}$$

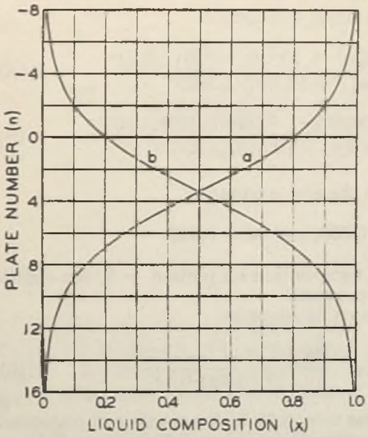

Figure 1. Plot of Equation 3 for Binary Distillation at Total Reflux for the Conditions of $a_0 = 0.8$, $b_0 = 0.2$, and $\alpha = 1.5$

where x represents any component. Equation 16 is one form of the Fenske equation (*3*) as applied to multicomponent distillation. Equation 14 can be compared with Equation 56 of Underwood (*12*), which is for a single plate. An example of substitution in Equation 14 is given by example II.

Example II. The distillation is for five components and at total reflux. The known composition on plate $n = 0$ is: $a_0 = 0.02$, $b_0 = 0.25$, $c_0 = 0.50$, $d_0 = 0.20$, $e_0 = 0.03$; and the relative volatilities are: $\alpha = 1.5$, $\beta = 2.0$, $\lambda = 2.5$, $\delta = 3.0$. It is desired to set up Equation 14 and solve for the liquid composition on plate $n = (-4)$. For these conditions Equation 14A becomes:

$$a_n = \frac{0.02}{(0.02)+(0.25)(1.5)^n + (0.50)(2.0)^n + (0.20)(2.5)^n + (0.03)(3.0)^n} \tag{14A}$$

and for plate $n = (-4)$, the plate which is four plates above the plate of known composition, this equation gives:

$$a_{(-4)} = 0.1883 \tag{14A}$$

Similarly, the corresponding equations for the other components give:

$$b_{(-4)} = 0.4654;\quad c_{(-4)} = 0.2945$$

$$d_{(-4)} = 0.0483;\quad e_{(-4)} = 0.0035$$

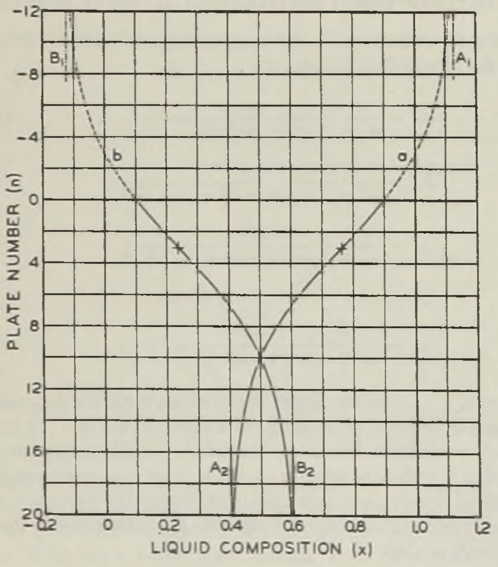

Figure 2. Plot of Equation 4 for Binary Distillation at Any Reflux for the Conditions of Example I

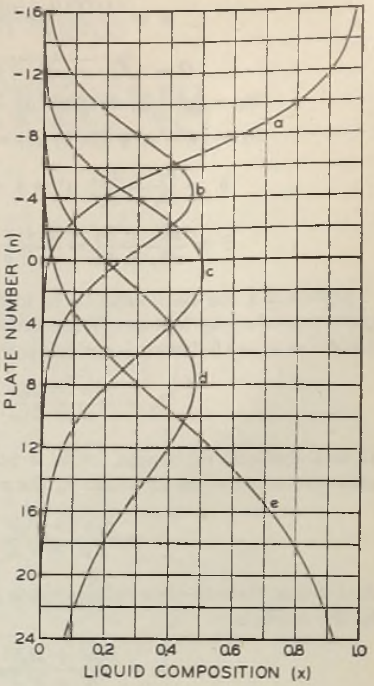

Figure 3. Plot of Equation 14 for Multicomponent Distillation at Total Reflux for the Conditions of Example II

The x *vs.* n curves for this example are given on Figure 3, and the points obtained above are plotted at $n = (-4)$.

MULTICOMPONENT DISTILLATION AT ANY REFLUX

The final case for which the equation of x *vs.* n is desired is the general one of any number of components and any reflux ratio. This equation, which corresponds to Equations 3, 4, and 14 for the special cases already given, is:

$$a_n = \frac{A_1a' + A_2b'\overline{\alpha}^n + A_3c'\overline{\beta}^n + \ldots A_5e'\overline{\delta}^n}{a' + b'\overline{\alpha}^n + c'\overline{\beta}^n + \ldots e'\overline{\delta}^n} \tag{17A}$$

$$b_n = \frac{B_1a' + B_2b'\overline{\alpha}^n + B_3c'\overline{\beta}^n + \ldots B_5e'\overline{\delta}^n}{a' + b'\overline{\alpha}^n + c'\overline{\beta}^n + \ldots e'\overline{\delta}^n} \tag{17B}$$

$$c_n = \frac{C_1a' + C_2b'\overline{\alpha}^n + C_3c'\overline{\beta}^n + \ldots C_5e'\overline{\delta}^n}{a' + b'\overline{\alpha}^n + c'\overline{\beta}^n + \ldots e'\overline{\delta}^n} \tag{17C}$$

…………………………………

$$e_n = \frac{E_1a' + E_2b'\overline{\alpha}^n + E_3c'\overline{\beta}^n + \ldots E_5e'\overline{\delta}^n}{a' + b'\overline{\alpha}^n + c'\overline{\beta}^n + \ldots e'\overline{\delta}^n} \tag{17E}$$

Comparison with Equation 4 for binary distillation shows that this equation has the same structure and the same type constants; it simply contains additional terms for the additional components present. To find the values of the constants in Equation 17, it is necessary that the complete conditions of the distillation be known. These required known conditions are: the liquid composition on plate $n = 0 - a_0, b_0, c_0 \ldots e_0$; the overhead product composition $-a_D, b_D, c_D \ldots e_D$; the reflux ratios, L/V and D/V; the relative volatilities $- \alpha, \beta, \ldots \delta$. The methods for finding the values of the constants of Equation 17 from these known conditions are given in the following paragraphs. These methods correspond to those for the binary case (Equation 4), but because of the greater complexity of the multicomponent case, less direct solutions are necessary.

The first constants of Equation 17 to be determined are the constant zone compositions, the capital letter terms $A, B, C \ldots E$. These constants are sets of solutions of the following equation, which is from Brown and Martin (*1*):

$$X = \sum \frac{(D/V)(x_D)}{K_x - (L/V)} = 1 \tag{18}$$

$$\text{or } A + B + C + \ldots E = \frac{(D/V)(a_D)}{K_a - (L/V)} + \frac{(D/V)(b_D)}{(K_a/\alpha) - (L/V)} + \frac{(D/V)(c_D)}{(K_a/\beta) - (L/V)} + \cdots \frac{(D/V)(e_D)}{(K_a/\delta) - (L/V)} = 1 \tag{18}$$

where $A = \frac{(D/V)(a_D)}{K_a - (L/V)}$; $B = \frac{(D/V)(b_D)}{(K_a/\alpha) - (L/V)}$; etc.

All the terms of this equation are known constants except K_a. The setting of a value of K_a sets each term of the equation and the sum. If this sum is 1, then the equation is satisfied and the resultant values of $A, B, C \dots E$ are a constant zone composition. As in binary distillation, these constant zone compositions have the property that a plate-to-plate calculation beginning with one gives the same composition for the succeeding plates.

The degree of K_a in Equation 18 is that of the number of terms in the equation, which is the same as the number of components. Then there are as many values of K_a that satisfy Equation 18 as there are components; consequently, there are as many constant zone compositions as there are components. The number of positive terms in these compositions change from 1 through 2 and 3 up to the total. This last composition in which all of the terms are positive is the constant zone approached as the plate-to-plate procedure is repeated for large numbers of plates, and is the constant zone commonly referred to in the literature. To distinguish between them, the constant zone compositions are subscripted with the number of positive terms they contain. Thus B_2 is the mole fraction of component b in the constant zone composition that has two positive terms.

The constants $a', b', c' \dots e'$ of Equation 17 are the pseudo known composition, and correspond to the terms a' and b' of Equation 4 and a_0, b_0, etc., of Equation 14. These constants express the required known composition of plate $n = 0$ in relation to the values of $A, B, C \dots E$. The system of equations for their determination follows:

$$a_0 = A_1a' + A_2b' + A_3c' + \dots A_5e' \quad (19A)$$
$$b_0 = B_1a' + B_2b' + B_3c' + \dots B_5e' \quad (19B)$$
$$c_0 = C_1a' + C_2b' + C_3c' + \dots C_5e' \quad (19C)$$
$$\dots\dots\dots$$
$$e_0 = E_1a' + E_2b' + E_3c' + \dots E_5e' \quad (19E)$$

In these equations the liquid composition on plate $n = 0$ and the constant zone compositions (as given by Equation 18) are known so that there are as many equations as unknowns, and a solution is possible. A dependent equation resulting from Equations 18 and 19 is:

$$a' + b' + c' + \dots e' = 1 \quad (20)$$

The barred Greek letters of Equation 17 ($\bar{\alpha}, \bar{\beta} \dots \bar{\delta}$), the pseudo relative volatilities, correspond to the relative volatilities of Equation 14 and to $\bar{\alpha}$ of Equation 4. They are defined by the following equations:

$$\bar{\alpha} = \frac{A_1 + (B_1/\alpha) + (C_1/\beta) + \dots (E_1/\delta)}{A_2 + (B_2/\alpha) + (C_2/\beta) + \dots (E_2/\delta)} \quad (21A)$$

$$\bar{\beta} = \frac{A_1 + (B_1/\alpha) + (C_1/\beta) + \dots (E_1/\delta)}{A_3 + (B_3/\alpha) + (C_3/\beta) + \dots (E_3/\delta)} \quad (21B)$$

$$\dots\dots\dots$$

$$\bar{\delta} = \frac{A_1 + (B_1/\alpha) + (C_1/\beta) + \dots (E_1/\delta)}{A_5 + (B_5/\alpha) + (C_5/\beta) + \dots (E_5/\delta)} \quad (21D)$$

The determination of the constants of Equation 17 for the distillation of a three-component mixture is illustrated in the calculations which follow,

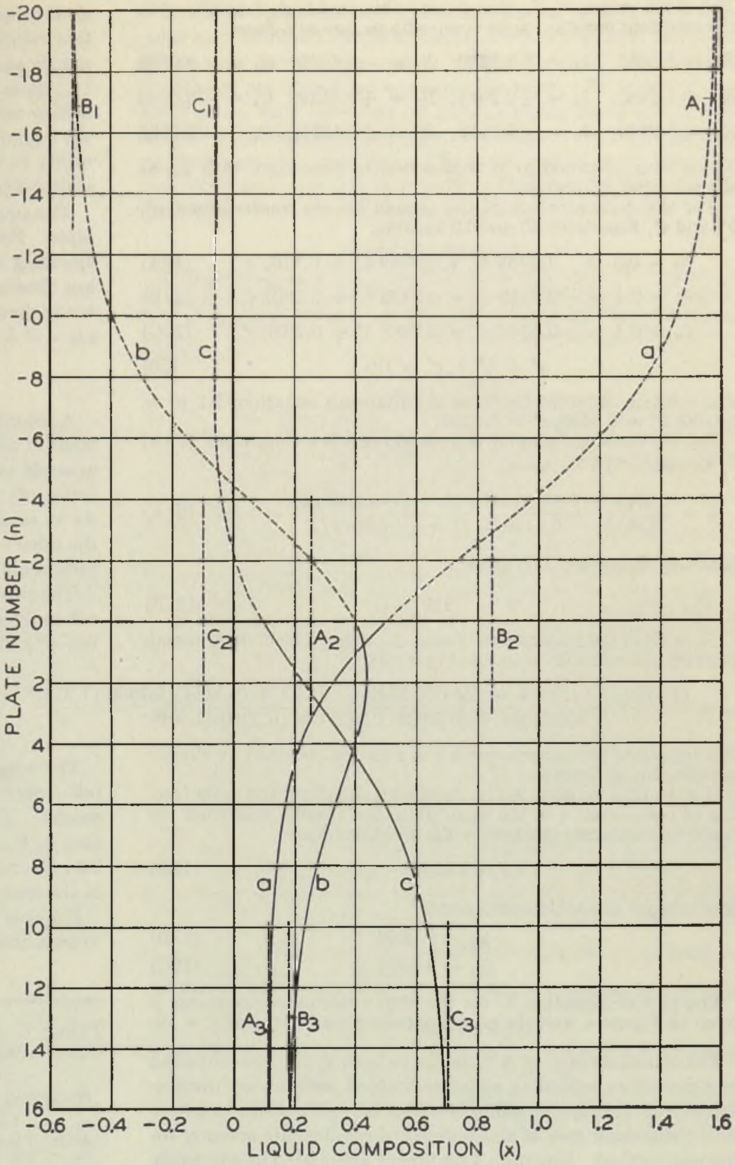

Figure 4. Plot of Equation 17 for Multicomponent Distillation at Any Reflux for the Conditions of Example III and Table I

EXAMPLE III. In a three-component distillation the overhead vapors are totally condensed, and the liquid reflux from the condenser is returned to the tower at its boiling point. Then the overhead product and the liquid reflux are the same, and this condenser liquid can be considered to be the known liquid from plate $n = 0$. The composition of this condenser liquid is: $a_0 = a_D = 0.50$; $b_0 = b_D = 0.40$; $c_0 = c_D = 0.10$. The reflux conditions for the distillation are $L/V = 0.8$ and $D/V = 0.2$. The relative volatilities are $\alpha = K_a/K_b = 4/3$ and $\beta = K_a/K_c = 2$. It is desired to determine the constants of Equation 17 for these distillation conditions and to solve for the liquid composition on plate $n = 12$.

The first constants to be determined are the constant zone compositions, A, B, and C. For the above conditions Equation 18 becomes

$$A + B + C = \frac{(0.2)(0.50)}{K_a - 0.8} + \frac{(0.2)(0.40)}{(K_a/4/3) - 0.8} + \frac{(0.2)(0.10)}{(K_a/2) - 0.8} = 1 \quad (18)$$

The three values of K_a that satisfy this equation, together with the resultant constant zone compositions, are as follows:

$K_a = 0.8633;\ A_1 = +1.5789;\ B_1 = -0.5246;\ C_1 = -0.0543$

$K_a = 1.1930;\ A_2 = +0.2544;\ B_2 = +0.8439;\ C_2 = -0.0983$

$K_a = 1.6569;\ A_3 = +0.1167;\ B_3 = +0.1807;\ C_3 = +0.7026$

These were obtained by a trial-and-error procedure with K_a as the principal unknown.

For the determination of the pseudo known compositions, a', b', and c', Equations 19 and 20 become:

$$a_0 = 0.5 = 1.5789\,a' + 0.2544\,b' + 0.1167\,c' \qquad (19A)$$

$$b_0 = 0.4 = -0.5246\,a' + 0.8439\,b' + 0.1807\,c' \qquad (19B)$$

$$c_0 = 0.1 = -0.0543\,a' - 0.0983\,b' + 0.7026\,c' \qquad (19C)$$

$$a' + b' + c' = 1.0 \qquad (20)$$

The solution obtained for these simultaneous equations is: $a' = 0.2100$, $b' = 0.5540$, $c' = 0.2360$.

For the determination of the pseudo relative volatilities, $\bar{\alpha}$ and $\bar{\beta}$, Equation 21A becomes:

$$\bar{\alpha} = \frac{1.5789 + (-0.5246/4/3) + (-0.0543/2)}{0.2544 + (0.8439/4/3) + (-0.0983/2)} = 1.382 \qquad (21A)$$

Similarly, Equation 21B gives:

$$\bar{\beta} = 1.919 \qquad (21B)$$

Then all of the constants of Equation 17 have been determined. For component a this equation becomes:

$$a_n = \frac{(1.5789)(0.2100) + (0.2544)(0.5540)\,(1.382)^n + (0.1167)(0.2360)(1.919)^n}{(0.2100) + (0.5540)(1.382)^n + (0.2360)(1.919)^n} \qquad (17A)$$

The equations for components b and c can be obtained by similar substitution in Equation 17.

If $n = 12$ is substituted in the above equation, the mole fraction of component a in the liquid from the twelfth tray from the overhead condenser (plate $n = 12$) is obtained as:

$$a_{12} = 0.1232 \qquad (17A)$$

Similarly for the other components

$$b_{12} = 0.2094 \qquad (17B)$$

$$c_{12} = 0.6674 \qquad (17C)$$

The plot of Equation 17 for the above calculated constants is given on Figure 4, and the points obtained are plotted at $n = 12$.

The equations of x vs. n which have been given were obtained by a procedure beginning with the simplest case, binary distillation at total reflux, and adding one distillation condition at a time until the general case of any number of components and any reflux was reached. Equation 4 for binary distillation at any reflux was proved to be identical with the plate-to-plate procedure; and Equation 14, for any number of components at total reflux, is easily proved. No corresponding conventional algebraic proof is given for the more complex general case, Equation 17. This equation is, however, mathematically exact. This is indicated by the values in Table I where plate compositions obtained with Equation 17 are compared with the corresponding compositions given by the plate-to-plate method. The two sets of values are obviously identical.

COLUMN DESIGN

The first and obvious use of the x vs. n equations is in the design of distillation equipment in place of the plate-to-plate procedure. For sections of tower of more than a few plates, the use of these equations permits considerable saving in time. Thus in example III the corresponding plate-to-plate calculation for twelve plates would have been much more time consuming. A requirement for the use of the equations in this way is that the assumptions of constant relative volatility and constant internal reflux do not lead to excessive error in the results. For certain systems, such as water and heavy water or normal and isohexanes, the errors because of these assumptions are quite small. If sufficient care is taken in the selection of average values for the relative volatilities and internal reflux, the method can be made sufficiently accurate for most calculations for the "regular" systems—i.e., those that do not contain abnormalities such as constant-boiling mixtures, etc. With systems such as ethanol and water the equations cannot be used. In general, the binary equations would be employed where there are large numbers of plates or very sharp separations so that graphical methods would be difficult.

The equations given are for the section of tower above the feed plate. For column design work, it is necessary to know the corresponding equations for the section below the feed plate. These are obtained by the following substitutions in the equations already given: $-W$ and x_W in place of D and x_D; L_s and V_s in place of L and V.

DISTILLATION THEORY

A second possible use for the x vs. n equations is in the development of distillation theory. These equations permit an algebraic analysis of the distillation process that is not possible with the series of points resulting from the plate-to-plate calculation. As an example, a study will be made of the qualitative effect of the other components present in a distillation system on the separations obtained between the cut components.

The two variables are (1) the separations obtained between the cut components, a and b, as defined by the following "separation ratios": for above the feed plate, b_D/a_D; for below the feed plate, a_W/b_W; overall, $(b_D/a_D)(a_W/b_W)$. (2) The amounts of other components of various volatilities present in the distillation system.

The other conditions of the distillation are considered to remain constant, and only the first of the above varies with the second. The constant conditions include the internal reflux ratios, L/V and L_s/V_s, the numbers of plates above and below the feed, the relative volatilities, and the ratio of the cut components in the feed.

For this analysis, a multicomponent distillation is considered to be a binary distillation in which the mole fractions of the cut

TABLE I. ACCURATE CALCULATION OF EQUATION 17 FOR THE CONDITIONS OF EXAMPLE III AND COMPARISON WITH PLATE-TO-PLATE METHOD

CONSTANTS OF EQUATION 17 (CALCULATED AS SHOWN IN EXAMPLE III)

A_1 =	+1.578,894,442	B_1 =	−0.524,595,643	C_1 =	−0.054,298,799
A_2 =	+0.254,410,160	B_2 =	+0.843,885,893	C_2 =	−0.098,296,053
A_3 =	+0.116,695,398	B_3 =	+0.180,709,749	C_3 =	+0.702,594,853
a' =	0.209,967,564	b' =	0.553,972,715	c' =	0.236,059,721

$\bar{\alpha}$ = 1.381,926,407 $\bar{\beta}$ = 1.919,221,322

COMPARISON OF PLATE LIQUID COMPOSITIONS AS GIVEN BY PLATE-TO-PLATE (UPPER VALUES) AND BY EQUATION 17 (LOWER VALUES)

Plate No. n	Liquid Compositions a	b	c
−20	+1.573,496,873 +1.573,496,871	−0.519,020,738 −0.519,020,737	−0.054,476,135 −0.054,476,134
−16	1.559,384,922 1.559,384,927	−0.504,464,380 −0.504,464,384	−0.054,920,542 −0.054,920,543
−12	1.509,977,236 1.509,977,242	−0.453,732,858 −0.453,732,864	−0.056,244,378 −0.056,244,378
−8	1.353,353,635 1.353,353,643	−0.295,647,058 −0.295,647,066	−0.057,706,577 −0.057,706,577
−4	0.981,352,787 0.981,352,795	+0.055,844,260 +0.055,844,248	−0.037,197,047 −0.037,197,043
0	0.50 0.50	0.40 0.40	+0.10 +0.10
4	0.224,414,908 0.224,414,897	0.400,063,035 0.400,063,010	0.375,522,057 0.375,522,093
8	0.142,595,837 0.142,595,834	0.273,562,037 0.273,562,023	0.583,842,126 0.583,842,143
12	0.123,194,782 0.123,194,782	0.209,370,272 0.209,370,267	0.667,434,946 0.667,434,951
16	0.118,400,196 0.118,400,196	0.188,718,455 0.188,718,454	0.692,881,349 0.692,881,350

components, a and b, total less than 1; i.e., other components are present. Two terms, are defined as follows:

P = sum of mole fractions of cut components, a and b, in liquid from plates. Q = sum of mole fractions of cut components, a and b, in vapor from plates

For binary distillation P and Q are equal to 1. It can be shown that with the above definitions Equations 5, 6, and 7 for binary distillation become:

$$u = \frac{Q + (D/V)(b_D)(\alpha - 1)}{(L/V)(\alpha - 1)} \tag{22}$$

$$v = P\alpha/(\alpha - 1) \tag{23}$$

$$w = \frac{P\alpha\ (D/V)(b_D)}{(L/V)(\alpha - 1)} \tag{24}$$

also $$a + b = A_1 + B_1 = A_2 + B_2 = P \tag{25}$$

The above equations make it possible to determine what effect changes in P and Q have on the constants of Equation 4 (the binary x *vs.* n equation) and on the resultant separations obtained between a and b. These effects can be summarized by the following three rules:

For $P = Q < 1$, the separation ratios obtained are exactly the same as for $P = Q = 1$. That is, when P is equal to Q, the separation obtained between a and b is exactly the same as it would be for a binary distillation with no other compounds present.

For the section of tower above the feed plate, if P is decreased more than Q, the separation becomes poorer (i.e., b_D/a_D increases), and if Q is decreased more than P, the separation becomes better (i.e., b_D/a_D decreases).

For the section of tower below the feed plate, these conditions are exactly reversed. If P is decreased more than Q, the separation becomes better (i.e., a_W/b_W decreases), and if Q is decreased more than P, the separation becomes poorer (i.e., a_W/b_W increases).

Then if the effect on P and Q of changes in the amounts of the other components is known, the qualitative changes in the separation ratios can be found with the above rules.

In the examples to follow, the binary distillation of the cut components is set up as a standard, and the effect of additional components on the separation ratios are determined. Five different cases are considered as follows:

If a component more volatile than the cut components is added to the feed to the column, it will concentrate more in the vapor than in the liquid, both above and below the feed plate. Then from the above rules: (1) Above the feed plate Q is decreased more than P and a better separation is obtained. (2) Below the feed plate Q is decreased more than P and a poorer separation is obtained. (3) The over-all separation is better.

If a component less volatile than the cut components is added to the column feed, it concentrates more in the liquid than in the vapor, both above and below the feed. Then from the rules given: (1) Above the feed plate P is decreased more than Q and a poorer separation is obtained. (2) Below the feed plate P is decreased more than Q and a better separation results. (3) The over-all separation is better.

If a component intermediate in volatility between the cut components is added to the tower feed, it concentrates in the liquid above the feed plate and in the vapor below the feed plate. Then from the rules given: (1) Above the feed plate P is decreased more than Q and a poorer separation results. (2) Below the feed plate Q is decreased more than P and a poorer separation is obtained. (3) The over-all separation is poorer.

If a component more volatile than the cut components is added to the bottom of a tower (such as steam to a petroleum column), this component will concentrate more in the vapor than in the liquid throughout the tower. Then from the rules given: (1) Above the feed plate Q is decreased more than P and a better separation is obtained. (2) Below the feed plate Q is decreased more than P and a poorer separation results. (3) The over-all separation is poorer.

If a component less volatile than the cut components, such as an absorbing fluid, is added to the top of a tower, it will concentrate more in the liquid than in the vapor throughout the tower. Then from the rules given: (1) Above the feed plate P is decreased more than Q and a poorer separation is obtained. (2) Below the feed plate P is decreased more than Q and a better separation results. (3) The over-all separation is poorer.

It should be emphasized again that the above discussion concerns only changes in separation ratios with changes in amounts of the other components present. All of the other conditions of distillation are considered to remain the same. By means of the rules given, such questions on column performance can be answered as the approximate effect of changes in the column feed on the separations obtained. The conditions of a multicomponent distillation can be estimated by comparison with the simpler distillation of the cut components as a binary mixture.

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NOMENCLATURE

$A, B, \ldots E$ = constant zone compositions as defined in text (constants of Equations 4 and 17); given mathematically by Equations 9 and 10 for binary distillation and Equation 18 for multicomponent distillation
D = overhead distillate withdrawn as product, moles per unit time
G = constant in Equations 9, 10, and 12; defined by Equation 8
K = Vapor-liquid equilibrium constant, $y = Kx$
L = liquid overflow from plate, moles per unit time
P = sum of mole fractions of cut components, a and b, in L, total liquid from plates; P = 1.0 for binary distillation
Q = sum of mole fractions of cut components, a and b, in V, total vapor from plates; Q = 1.0 for binary distillation
V = vapor rising from plate, moles per unit time
W = bottoms withdrawn as product, moles per unit time
X = constant zone composition for general component; corresponds to $A, B, C \ldots E$ for specific components
$a, b, c \ldots e$ = components arranged in order of decreasing volatility from a, the most volatile, to e, the least volatile: also the mole fraction of these components in the liquid (corresponds to x)
$a', b', c' \ldots e'$ = pseudo known composition (constants of Equations 4 and 17); defined by Equation 11 for binary distillation and by Equation 19 for multicomponent distillation
n = plate number measured from plate ($n = 0$) which is plate for which liquid composition is known; up is negative and down is positive
u, v, w = constants used to determine Equation 4; defined by Equations 5, 6, and 7
x = mole fraction of component in liquid; also general component
y = mole fraction of component in vapor
$\alpha, \beta \ldots \delta$ = relative volatilities based on most volatile component; a, $\alpha = K_a/K_b$, $\beta = K_a/K_c \ldots \delta = K_a/K_e$
$\bar{\alpha}, \bar{\beta} \ldots \bar{\delta}$ = pseudo relative volatilities (constants of Equations 4 and 17); defined by Equation 12 for binary distillation and by Equation 21 for multicomponent distillation

Subscripts

On $a, b, c \ldots e$ and x: 1, 2, 3 … n indicate plate number of composition; D indicates overhead product; W indicates bottoms product

On $A, B, C \ldots E$ and X: 1, 2, 3, etc., indicate number of constant zone as given by number of positive terms in constant zone composition

On K: $a, b, c \ldots e$, and x indicate components

On L and V: s indicates stripping section below feed plate; all other terms are for section above feed plate

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CATALYTIC CRACKING OF PURE HYDROCARBONS

Aromatics and Comparison of Hydrocarbon Classes

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The cracking of twenty-two aromatic hydrocarbons over a silica-zirconia-alumina catalyst is reported. A wide range of behavior is observed, from nearly inert compounds like toluene or biphenyl to highly reactive ones such as aromatics with substituent alkyl or cycloalkyl groups containing three or more carbon atoms, for which the removal of the whole substituent group is the chief cracking reaction. Results from catalytic cracking of the various hydrocarbon classes are reviewed. The stability of compounds of a given carbon number in processing over the cracking catalyst increases in the order: olefins, aromatics with C_4 or larger substituent groups, naphthenes, polymethyl aromatics, paraffins, and unsubstituted aromatics. This order differs substantially from that found in thermal cracking.

PREVIOUS papers of this series described the cracking of a number of paraffins, olefins, and naphthenes over a silica-zirconia-alumina catalyst under conditions similar to those employed in the commercial cracking of petroleum fractions (*4*, *5*, *6*). Results are given here from the cracking of various kinds of aromatics. As before, an effort is made to compare the catalytic with the thermal cracking of the same compounds. Thomas, Hoekstra, and Pinkston (*13*) studied the catalytic cracking of some alkylbenzenes, and reported results similar to ours.

The catalyst employed was described previously (*4*); it was obtained from Universal Oil Products Company, and was designated as UOP cracking catalyst, type B. The sample was found to contain 86.2% silica, 9.4% zirconia, and 4.3% alumina, by weight, and was in the form of 3 × 3 mm. cylindrical pellets. This catalyst gives results similar to those from the synthetic silica-alumina catalysts currently employed on a large industrial scale.

The experimental procedure, definitions, and terminology were given in an earlier paper (*4*). The preferred conditions of operation of the reaction system, which was arranged for flowing the hydrocarbon vapor over a fixed bed of catalyst, were: catalyst volume 50 cc. of pellets, atmospheric pressure, temperature 500° C., process period one hour, and flow rate about 13.7 moles of hydrocarbon per liter of catalyst per hour. The last three conditions were altered in many cases to attain suitable extents of reaction. The aromatics chosen covered a fairly wide range of structural types, and included compounds from C_7 to C_{15}. Properties and sources of materials follow, with compounds arranged in the order of increasing molecular weight:

Toluene was Baker's C.P. grade, further purified by treatment over a dehydrogenation catalyst and distillation. It had a boiling point of 110.7° C., d_4^{20} 0.8664, n_D^{20} 1.4964.

Ethylbenzene from Eastman Kodak Company had b.p. 136.3° C., d_4^{20} 0.8677, n_D^{20} 1.4958.

p-Xylene from Eastman had b.p. 138.0° C., d_4^{20} 0.8581, n_D^{20} 1.4950.

Indan (or hydrindene) from Eastman had b.p. 177.5° C., d_4^{20} 0.9499, n_D^{20} 1.5321, bromine number 4.3.

Mesitylene from Eastman had b.p. 165.0° C., d_4^{20} 0.8644, n_D^{20} 1.4982.

Isopropylbenzene from the Dow Chemical Company had a boiling range (5–95%) of 152–153° C., d_4^{20} 0.8621, n_D^{20} 1.4912.

n-Propylbenzene from Dow had a boiling range (5–95%) of 155–158° C., d_4^{20} 0.8617, n_D^{20} 1.4917.

Pseudocumene, Eastman technical grade, had a boiling range (5–95%) of 167–175° C., d_4^{20} 0.8871, n_D^{20} 1.5038, and probably did not contain over 50% pseudocumene. A second, purer sample from methylation of *p*-xylene had b.p. 168–169° C., d_4^{20} 0.8744, n_D^{20} 1.5047.

Tetralin from Eastman was purified by fractional distillation. The portion used had a boiling range of 205.9–206.8° C., n_D^{20} 1.5405–1.5435 (average 1.5419), d_4^{20} 0.9714, sulfur 0.0006% by weight.

n-Butylbenzene from Eastman had a boiling range of 181–182.5° C., d_4^{20} 0.8564, n_D^{20} 1.4882.

sec-Butylbenzene from Eastman had a boiling range of 173–174° C., d_4^{20} 0.8605, n_D^{20} 1.4901.

tert-Butylbenzene from Eastman had a boiling range of 168–169° C., d_4^{20} 0.8648, n_D^{20} 1.4930.

Methylnaphthalenes: Eastman practical grade α-methylnaphthalene was distilled in a 60-cm. Vigreux column, and the fraction 243–244° C. was used. Judging by the properties, it was a mixture of α- and β-methylnaphthalenes, along with impurities. The sulfur content was 0.98%, nitrogen about 0.25%. It had d_4^{20} 1.0188, n_D^{20} 1.6073.

Cyclopentylbenzene was prepared by condensation of cyclopentene with benzene in the presence of aluminum chloride. It had a boiling range of 210–215° C., d_4^{20} 0.9451, n_D^{20} 1.5269.

Pentamethylbenzene from Eastman had a melting range of 45–60° C., while the melting point of the pure compound is 54° C. Fractional distillation showed the presence of about 50% tetramethylbenzenes, probably durene (melting point 79.3° C.). The mixture as received was used for the cracking experiment.

Amylbenzenes, from Sharples Chemicals Inc., were said to contain at least 90% secondary amyl structures, with the rest tertiary. The sample had a boiling range of 185–195° C., d_4^{20} 0.8611, n_D^{20} 1.4885.

Biphenyl from Eastman melted at 68.9° C.

Cyclohexylbenzene, prepared by the condensation of cyclohexene with benzene in the presence of aluminum chloride, had a melting range of 5.0–5.8° C., boiling range of 230–233.5° C., d_4^{20} 0.9417, n_D^{20} 1.5252.

Triethylbenzenes from Dow were fractionated under vacuum and a middle fraction boiling from 158–161° C. at 200 mm. was taken, n_D^{20} 1.4960.

1,1-Diphenylethane from Dow had boiling range (5–95%) of 272.1–274.6° C., d_4^{20} 0.9882, n_D^{20} 1.5658.

tert-Butylnaphthalene was made by aluminum chloride alkylation of naphthalene with isobutene. The monobutylnaphthalene, probably largely beta-substituted, was recovered by fractionation, with d_4^{20} 0.9648, n_D^{20} 1.5757.

Amylnaphthalenes from Sharples were said to be 100% beta-substituted, and to contain at least 90% secondary amyl structures with the rest tertiary. They had a boiling range (initial, 95%) of 279–306° C., d_4^{20} 0.9645, n_D^{20} 1.5727.

INDIVIDUAL CRACKING BEHAVIOR

TOLUENE. Tests at 500° and 550° C. showed toluene to be very stable over the catalyst at these temperatures (Table I). Gas production was very small, and even at 550° there was only a trace of lower-boiling liquid. The total cracking in this run at 550° was estimated to be about 1.2% by weight of the charge. The recovered toluene had a refractive index of 1.4967, compared to 1.4964 for the charged toluene, and was therefore nearly free of condensation products. It was light yellow in color. The run at 500° C., low space velocity, and short process period, was perhaps as severe as that at 550°, but a careful balance of toluene showed that only 1.7% or less disappeared, confirming the high degree of stability. An experiment reported by Natanson and Kagan (*8*), however, showed about 25% disproportionation of toluene to benzene and xylenes in treatment over silica-alumina at 430° C. and the very low flow rate of 0.5 mole per liter per hour.

ETHYLBENZENE. Results from the cracking of ethylbenzene at 500° C. showed the main reaction was scission next to the ring to yield benzene and ethylene. About 1.5% of toluene was formed compared to 6% benzene, indicating a minor amount of cracking within the side chain. The refractive index of the remaining material above toluene showed a styrene content, if present, of less than 3%.

***n*-PROPYLBENZENE.** Cracked at 500° C., *n*-propylbenzene yielded almost exclusively propylene and benzene by scission next to the ring. The *n*-propylbenzene was 43% decomposed. Some of the propylene initially formed was saturated to propane.

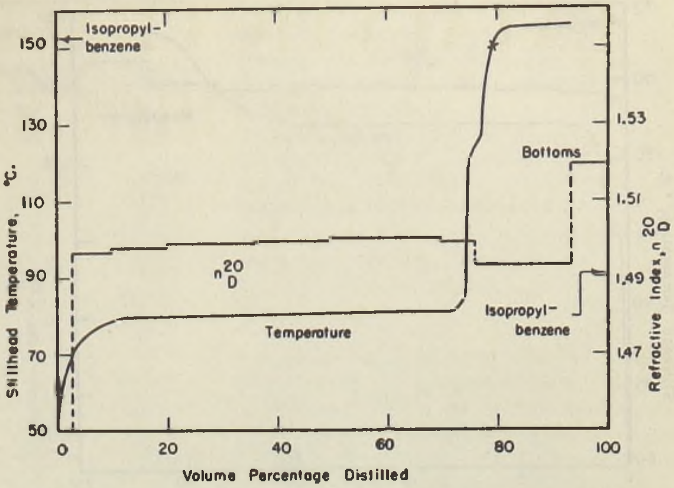

Figure 1. Distillation Curve for the Liquid Product from the Catalytic Cracking of Isopropylbenzene at 500° C.

ISOPROPYLBENZENE. Figure 1 is a distillation curve for the liquid product. The main reaction was scission next to the ring to yield benzene and propylene. This proceeded very extensively (about 80%) at 500° C. and a flow rate of 13.7 moles per liter per hour. The efficiency of benzene production, computed from the amount of feed cracked, was 90%. The mechanism is thus particularly well defined for a cracking reaction. Products other than propylene and benzene were present in much smaller amounts; there was no toluene, and C_8 aromatics were only about 3% of the charge. Isopropylbenzene decomposed nearly twice as extensively as *n*-propylbenzene.

BUTYLBENZENES. Three isomeric butylbenzenes (normal, secondary, and tertiary) were cracked under mild conditions—namely, 400° C. and 12.5 moles per liter per hour flow rate—to compare the relative stabilities. The results show that the structure of the alkyl group had a marked effect on the extent of cracking; *tert*-butylbenzene was 80.4% decomposed while *n*-butylbenzene was only 13.9% decomposed and *sec*-butylbenzene fell between with 49.2% decomposed. It is improbable that these marked differences in extents of cracking can be ascribed to differences in thermodynamic equilibria; rather, it is believed that they are mainly the result of rate differences caused by the several unique structures of the butyl group. Although free-energy limitations indicate that dealkylation cannot be 100% complete under the conditions used, an unlisted experiment with *n*-butylbenzene, at half the flow rate used for the run listed in Table I, gave nearly twice the dealkylation (about 24% decomposition compared to 13.9%), showing that equilibrium was not limiting the reaction in the latter run. With all three compounds the chief reaction was dealkylation to benzene and butenes. This was followed by a certain amount of secondary reaction of the butenes, which are known under these conditions to give lighter gas, isomerized butenes, butanes, and higher-boiling material. Distillation and spectrophotometric analysis of the cuts indicated that toluene was less than 1% of the liquid product in all the runs. Combined C_7, C_8, and C_9 aromatics were not over 4% by weight of the charge for any of the runs.

AMYLBENZENES. The amylbenzenes, a mixture of secondary and tertiary monoamylbenzenes, were cracked at 500° C. The extensive reaction, chiefly to give pentenes and benzene, was similar to those of the butyl- or propylbenzenes. A loss of 13% in the distillation of the liquid product made the distribution of the products somewhat uncertain, but it appeared that benzene recovery was 94% of the theoretical for the simple splitting to benzene and pentenes, based on the disappearance of amylbenzenes. The C_5 material actually recovered (50% of the theoretical amount based on disappearance of charge) contained 86% olefins. Distillation clearly showed that liquids other than

TABLE I. CATALYTIC CRACKING OF MONOALKYLBENZENES

Hydrocarbon	Toluene		Ethylbenzene	*n*-Propylbenzene	Isopropylbenzene	*n*-Butylbenzene	*sec*-Butylbenzene	*tert*-Butylbenzene	Amylbenzenes
Temperature, ° C.	500	550	500	500	500	400	400	400	500
LHSV[a]	0.53	1.44	1.69	1.93	1.91	1.95	1.91	2.05	2.38
Flow rate, moles/l./hr.	5.0	13.6	13.8	13.8	13.7	12.5	12.3	13.2	13 8
Process period, min.	15	60	60	60	60	45	45	45	60
Gaseous product									
Moles/mole charge	0.020	0.033	0.069	0.373	0.700	0.124	0.441	0.694	0.195
Vol. % H_2	31.8	45	24.6	5.6	2.5	12.7	4.4	0.6	17.1
CH_4	...	...	...	3.5	3.0	0.0	0.0	...	23.4
C_2H_4	...	...	32.5	2.0	0.6	1.8	0.3	0.2	6.7
C_2H_6	...	...	...	1.7	3.5	0.0	0.3	...	7.5
C_3H_6	...	...	...	76.2	86.2	13.7	5.4	3.5	19.0
C_3H_8	...	...	...	7.4	0.8	10.0	1.1	1.1[c]	3.4
Iso-C_4H_8	...	...	...	1.0	1.2	10.0	3.6	76.7	8.1
n-C_4H_8	...	...	...	1.0	2.1	11.8	73.4	7.3	7.1
C_4H_{10}	...	...	...	1.6	0.1	40.0	11.5	10.6	7.7
Total olefins	33.3	16	51.5	80.2	90.1	37.3	82.7	87.7	40.9
Total saturates	34.9	39	23.9	14.2	7.4	50.0	12.9	11.7	42.0
C No. of saturates[b]	2.0	2.2	2.5	...	...	...	...	...	...
Material balance, wt. % of charge									
Gas	0.9	0.5	1.7	12.1	23.3	4.3	17.5	28.7	4.0
Liquid below original b.p.	0.0	0.6	7.7	27.8	50.7	8.5	31.0	50.7	(78)
Remaining liquid	96.0	94.8	86.8	55.4	15.3	83.4	45.1	15.6	(12)
Carbon	0.6	4.1	1.3	1.5	3.9	1.1	0.7	1.0	3.0
Loss	2.5		2.5	3.2	6.8	2.7	5.7	4.0	3

[a] Liquid hourly space velocity. [b] Carbon No. = *n* in C_nH_m. [c] C_1, C_2, and C_3 saturates, carbon No. 2.5.

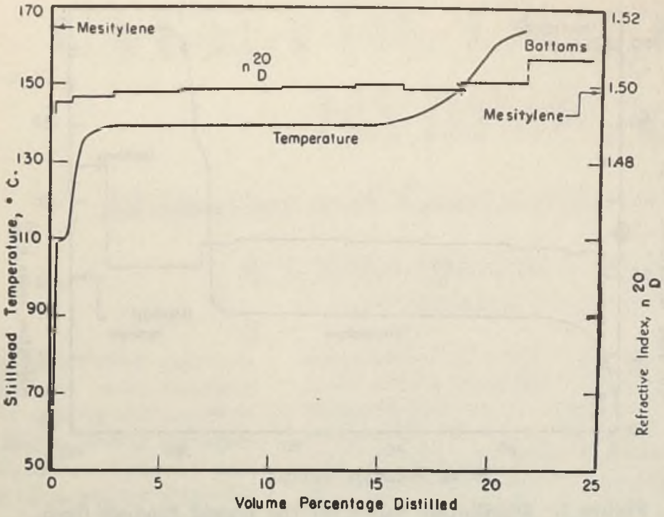

Figure 2. Distillation Curve for the Liquid Product from the Catalytic Cracking of Mesitylene at 500° C.

pentenes, benzene, and uncracked amylbenzenes were small in amount—about 5% from 40–75° C. and the same from 85–180° C.

p-Xylene. This compound was treated under more severe conditions than were normally employed—namely, at 550° C. and a flow rate of 4 moles per liter per hour (Table II). Decomposition was quite extensive, only 47.1% by weight of the charge being recovered as xylenes. Besides 23.8% of lower-boiling liquid, chiefly toluene, there was also formed 16.1% higher-boiling liquid, chiefly C_9 aromatics. A disproportionation or methyl-group transfer must therefore have taken place. Analysis of the remaining xylenes showed that isomerization to approximately an equilibrium mixture had occurred, as follows:

	% in Xylene Fraction	
Isomer	Exptl. from *p*-xylene	Theoretical at 550° C.(*10*)
Para	27.4	21
Meta	47.3	58
Ortho	25.3	21

The analysis of the xylene fraction was made by ultraviolet absorption.

Mesitylene (1,3,5-Trimethylbenzene). Mesitylene reacted to a moderate extent when passed over the catalyst at 500° C. The distillation curve in Figure 2 shows that the chief reaction was removal of one methyl group. No benzene was formed, only a trace of toluene, and considerable xylenes. A fair amount of condensation product was indicated by the elevated refractive index of the recovered mesitylene fraction (1.5073 compared to 1.4982 for mesitylene), and further distillation led to isolation of 6.3% by weight on the charge of bottoms above 185° C., with n_D^{20} 1.5305. Isomerization of mesitylene was not examined. The gas analysis showed appreciable amounts of C_2, C_3, and C_4 compounds, believed to have been formed by the combination of C_1 fragments initially removed from mesitylene.

Pseudocumene (1,2,4-Trimethylbenzene). Technical pseudocumene decomposed about as extensively as mesitylene when cracked at 500° C. The lower-boiling products were toluene and xylenes, in about equal amounts. The fact that the feed was a technical grade casts doubt on the results. In another run at 550° C. a pure pseudocumene from the methylation of *p*-xylene was charged. The high temperature coupled with the low flow rate of 3.2 moles per liter per hour caused the conversion of over 60% of the pseudocumene to other products. The gas was 5.5% by weight and was chiefly methane and hydrogen, although small amounts of C_2, C_3, and C_4 were also present, an indication of secondary recombination reactions. Toluene and xylenes amounted to 4 and 22% by weight of the charge, respectively. There was little or no benzene. Since the xylene product was an equilibrium mixture of the isomers, no conclusion can be reached as to which methyl group was most readily removed from the pseudocumene. About 13% of the pseudocumene charged appeared as higher-boiling material, over 80% of which distilled within 40° C. above the boiling point of the feed and was, therefore, presumably tetramethylbenzenes or other C_{10}–C_{11} aromatics. The bottoms above 209° C., amounting to 2.3% by weight of the charge, contained 42% of material boiling in the range 209–230° C., with n_D^{20} 1.5657.

Pentamethylbenzene. The trimethylbenzenes cracked much more readily than toluene. To ascertain the extent of this trend for benzenes with even more methyl groups, the behavior of pentamethylbenzene was studied. Unfortunately, the sample of pentamethylbenzene used was of poor quality, containing much tetramethylbenzene. The amount of cracking, which could be gaged only approximately, was of the order of the amounts for the trimethylbenzenes under equivalent conditions—namely, about 20% by weight of the feed. The cracked gas was chiefly methane, and the lower-boiling liquid, C_9 and C_{10} aromatics.

Triethylbenzenes. The cracking behavior of triethylbenzenes was between those of monoalkylbenzenes and poly-

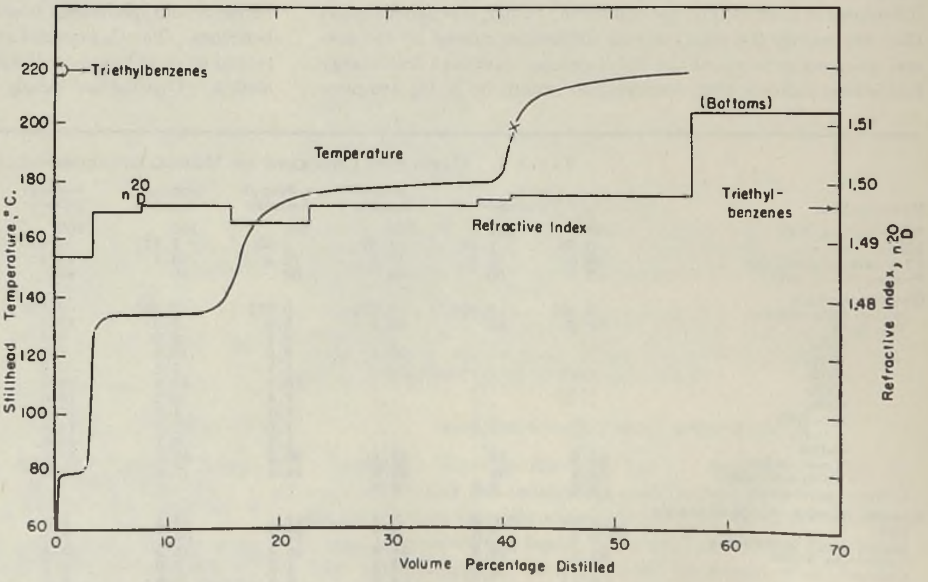

Figure 3. Distillation Curve for the Liquid Product (79% Yield by Weight) from the Catalytic Cracking of Triethylbenzenes at 500° C.

TABLE II. CATALYTIC CRACKING OF POLYALKYLBENZENES

(Process period 60 minutes)

Hydrocarbon	p-Xylene	Mesitylene	Pseudocumene[a]		Pentamethylbenzene	Triethylbenzenes
Temperature, ° C.	550	500	500[a]	550	500	500
LHSV	0.50	1.9	1.9	0.46	2.4[b]	2.6
Flow rate, moles/l./hr.	4.0	13.7	13.0	3.2	13.6	13.7
Gaseous product						
Moles/mole charge	0.508	0.084	0.140	0.460	0.170	0.606
Vol. % H_2	49.8	24.6	41.3	23.0	10.6	29.0
CH_4	40.2	58.9	...	71.6	...	5.1
C_2H_4	2.9	3.4	...	1.4	...	12.2
C_2H_6	3.2	3.0	...	1.7	...	7.3
C_3H_6	2.6	1.9	...	0.8	...	17.9
C_3H_8	0.3	4.7	...	0.9	...	4.6
Iso-C_4H_8	1.0	0.1	...	0.3	...	1.9
n-C_4H_8		0.5	...		...	14.5
C_4H_{10}		2.9	...	0.3	...	7.5
Total olefins	6.0	5.9	21.3	2.5	10.5	46.5
Total saturates	44.2	69.5	37.4	74.5	78.9	24.5
C No. of saturates	1.1	...	1.7	...	1.2	...
Material balance, wt. % of charge						
Gas	5.2	1.1	2.1	5.5	2.1	11.3
Liquid below original b.p.	23.8	17.6	14.6	30.0	(15)[c]	31.2
Remaining liquid	63.1	77.9	76.8	51.2	(75)[c]	48.0
Carbon	2.1	1.6	3.2	8.8	2.9	3.5
Loss	5.8	1.8	3.3	4.5	5.0	6.0

[a] Technical grade in run at 500° C.
[b] Based on liquid at 100° C.
[c] See text.

methylbenzenes. The removal of one or more side chains gave rise to a little benzene, considerable ethylbenzene, and even more diethylbenzene. The distillation curve in Figure 3 also shows that no toluene was formed. The presence of large amounts of C_3 and C_4 material in the gas suggests that C_2 fragments initially cracked off underwent further reaction, perhaps a combination on the catalyst surface.

METHYLNAPHTHALENES. Redistilled α-methylnaphthalene when treated at 500° C. was about 10% reacted, chiefly to lower-boiling materials and coke (Table III). Naphthalene isolated by distillation was 3% of the charge. The 1.2% of liquid distilling from 80° to 200° C. was nearly 100% mononuclear aromatics, of which the origin is somewhat obscure, especially since the feed contained some impurities—for example, 0.98% sulfur in combined form and about 0.25% nitrogen; it may have been the nitrogen or sulfur compounds that cracked rather than the hydrocarbon.

***tert*-BUTYLNAPHTHALENE.** This compound, like other aromatic compounds with large alkyl groups, cracked very extensively. Products were gas, containing much isobutene and butane, and a solid (freezing point 66° C.), which was doubtless impure naphthalene. The run was interrupted after 15 minutes because the reaction system became clogged with solid product, and therefore the material balance is only approximate. The high carbon formation is in part explained by the short duration of the run.

AMYLNAPHTHALENES. Cracking was very extensive. Products were a small amount of gas, liquid which was entirely C_5 hydrocarbons and contained 91.5% olefins, and a solid (impure naphthalene freezing at 70.5° C.). The complete cracking of amylnaphthalenes contrasts with the low reactivity of methylnaphthalene; the difference is analogous to that between amylbenzenes and toluene.

BIPHENYL. This compound underwent practically no reaction in treatment at 550° C. Gas formation was very small. The lack of reaction was substantiated by the melting point of the recovered biphenyl sample, which was only 0.7° C. below that of the charge; this indicated only 1.4 mole % of substances other than biphenyl in the solid product. Some material was formed which colored the products yellow-orange; the feed was nearly colorless.

Cracking in the presence of hydrogen was tried in an effort to cause splitting to benzene. An equimolal mixture of biphenyl and hydrogen was treated at 550° C., but there was insufficient reaction to lower the melting point of the biphenyl more than 0.5° C. in this test.

1,1-DIPHENYLETHANE. This compound was not chosen as a likely representative of any petroleum hydrocarbons, but rather because of the information to be gained by studying a substance of its particular structure. Decomposition in cracking at 500° C. was very extensive (about 75%) and proceeded almost exclusively to benzene and ethylbenzene with only a trace of toluene. The benzene yield was 90% of the theoretical, based on the feed decomposed; the ethylbenzene fraction was 75% of theoretical. In the ethylbenzene fraction there was only 2–6% olefin, probably styrene. Since a simple cracking reaction would produce benzene and styrene, there was evidently much saturation of styrene over the catalyst by hydrogen transfer. Carbon formation was quite high; this usually accompanies hydrogen transfer reactions between olefins.

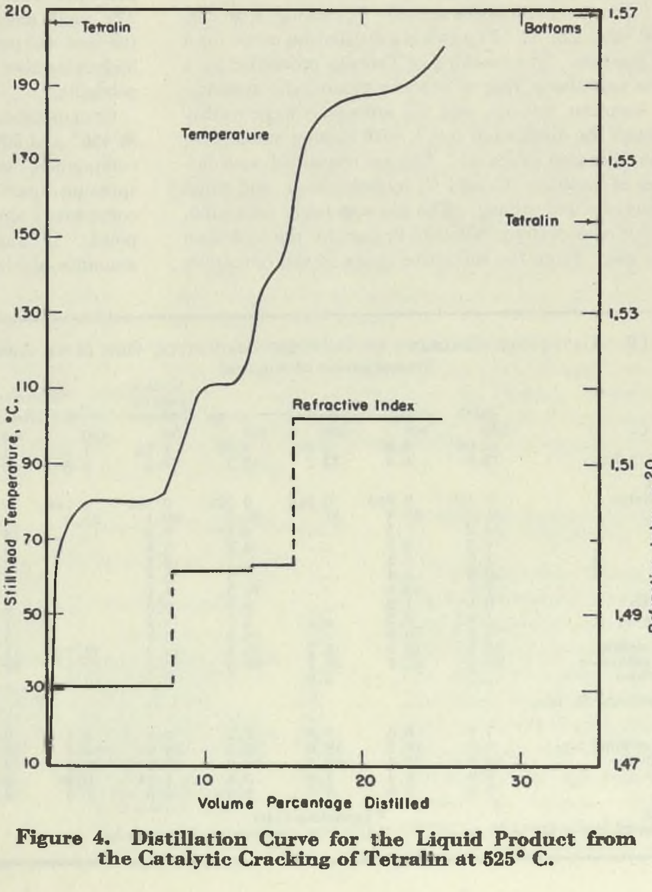

Figure 4. Distillation Curve for the Liquid Product from the Catalytic Cracking of Tetralin at 525° C.

TABLE III. CATALYTIC CRACKING OF BICYCLIC AROMATICS, BOTH RINGS AROMATIC

Hydrocarbon	Methylnaphthalenes	*tert*-Butylnaphthalene	Amylnaphthalenes	Biphenyl	1,1-Diphenylethane
Temperature, ° C.	500	500	500	550	500
LHSV	1.94	2.6	2.7	1.07[a]	1.26
Flow rate, moles/l./hr.	13.8	13.5	13.2	6.8	6.8
Process period, min.	60	15	60	60	60
Gaseous product					
Moles/mole charge	0.104	(0.51)	0.212	0.026	0.131
Vol. % H_2	58.9	15.0	26.5	...	28.7
Total olefins	10.3	48.6	33.1	...	31.8
Total saturates	30.8	36.4	40.4	...	39.5
C No. of saturates	1.5	4.2	2.0	...	1.9
Material balance, wt. % of charge					
Gas	0.9	(13)	3.0	...	1.7
Liquid below original b.p.	4.2	(71)[b]	18.8[c]	...	69.0
Remaining material	87.4		72.6[b]	...	13.9
Carbon	4.6	9.2	1.2	0.4[d]	4.6
Loss	2.9	6.8	4.4	...	10.8

[a] Based on liquid at 100° C.
[b] Solid
[c] Includes C_8 only.
[d] CO from regeneration not included.

INDAN (HYDRINDENE). When indan was cracked at 500° C. (Table IV), the amount of decomposition was rather small. The gas was 51.3% hydrogen. The lower-boiling liquid was almost wholly aromatic; it contained a little benzene, somewhat more toluene, and some C_9 aromatic material boiling below indan. This C_9 fraction contained no more than 10% olefins. The remaining liquid consisted chiefly of unchanged indan, but the bottoms from the distillation, which amounted to 26% of the charge to the run, had n_D^{20} of 1.5558 (indan 1.5383, indene 1.5768) and thus contained dehydrogenated or more highly condensed material. Carbon formation in the cracking of indan was fairly high (4.8% by weight of the charge).

TETRALIN (TETRAHYDRONAPHTHALENE). Cracking was carried out at 500° and 525° C. Figure 4 is a distillation curve for a typical liquid product. The cracking of Tetralin proceeded by a splitting of the naphthenic ring to produce monocyclic aromatic compounds. Benzene, toluene, and C_{10} aromatics were readily identified through the distillation curve, with smaller amounts of C_8 and C_9 aromatics also indicated. The gas contained considerable quantities of methane, C_3 and C_4 hydrocarbons, and small amounts of ethylene and ethane. The gas was fairly saturated. Dehydrogenation was evident, reflected in part by the hydrogen content of the gas. From the refractive index of the remaining liquid above 200° C. from the run at 525° C. (69% yield of such liquid, n_D^{20} 1.5694), it is apparent that naphthalene or condensation products of Tetralin must have been formed in the dehydrogenation reactions. Naphthalene (melting at 80.2° C.) was isolated from the product of this run in an amount equal to 16% of the charge. Transfer of hydrogen to the olefins produced also seems to have occurred, for although the monocyclic C_{10} aromatics from cracking Tetralin (which boil below Tetralin) should have unsaturated side chains, the C_{10} (175–195° C.) cut was found to contain only 2% olefins. It is also possible that some indan or methylindan was present in this cut. The low olefin content of the gas again points to saturation. Bloch and Thomas (*1*) gave more complete analyses of products from cracking Tetralin. Although obtained under somewhat different conditions, their results agree in a general way with ours.

CYCLOPENTYLBENZENE. Cyclopentylbenzene cracked rapidly over the catalyst; the chief reaction was scission at the link between the rings to give benzene and cyclopentene. The yield of benzene was practically quantitative at 1 mole per mole of feed cracked; but the yield of C_5 material was only about 0.35 mole per mole of feed cracked, so that it is necessary to postulate additional reactions, such as cracking off part of the cyclopentyl ring followed by dealkylation of the remainder to benzene, or secondary reaction of initially formed C_5 fragments. Yields of products were as follows:

Fraction, ° C.	Wt. % of Charge
25–57 (C_5)	11.9
57–85 (C_6)	46.8
85–208	9.5
208–218	8.5
Bottoms	9.5

The gas was rich in hydrogen. The C_5 fraction contained 64% olefins and was evidently a mixture of cyclopentene and cyclopentane. The C_6 fraction contained 90% benzene and 6% olefins. The small amount of material boiling above benzene but below the feed was probably alkylbenzenes. Distillaton bottoms with a high refractive index (n_D^{20} 1.5855) gave evidence of condensation products.

CYCLOHEXYLBENZENE (PHENYLCYCLOHEXANE). When cracked at 450° and 500° C., cyclohexylbenzene gave large yields of C_6 compounds, as Figure 5 shows. The principal reaction was splitting apart of the two rings; the C_6 fraction (66–82° C.) constituted almost the entire liquid product of lowered boiling point. It was made up of benzene, naphthenes, and small amounts of olefins and paraffins. Analysis of the C_6 fractions showed for the run at 450° C. (in per cent by weight): 6.5 olefins, 54.5 aromatics, 36 naphthenes, 3 paraffins; and for the run at 500° C.: 8 olefins, 48 aromatics, 41 naphthenes, and 3 paraffins. In conjunction with refractive index measurements, the flat portion of the distillation curve, rising gradually from 70° to 80° C., appears to indicate the presence of methylcyclopentane. Dehydrogenation appears again as an auxiliary but important reaction leading to hydrogen in the gas and highly aromatic substances in the distillation bottoms. The high degree of saturation of the gas, and especially of the C_6 fraction, is noteworthy; it indicates considerable hydrogen transfer to the initially formed olefinic products.

TABLE IV. CATALYTIC CRACKING OF BICYCLIC AROMATICS, ONE RING AROMATIC
(Process period 60 minutes)

Hydrocarbon	Indan	Tetralin			Cyclopentylbenzene	Cyclohexylbenzene		
Temperature, ° C.	500	500	500	525	500	450	500	500[a]
LHSV	1.68	0.87	1.87	1.86	1.12	1.16	1.11	0.24[b]
Flow rate, moles/l./hr.	13.5	6.4	13.7	13.7	7.2	6.8	6.5	1.43[b]
Gaseous product								
Moles/mole charge	0.149	0.310	0.516	0.322	0.302	0.144	0.358	0.116
Vol. % H_2	51.3	36.4	57	35.3	60.1	25.8	51.1	90.2
CH_4	14.2	7.5	...	4.7[c]	7.1	...	18.1	...
C_2H_4	4.2	2.7	...	3.2	5.4	...	5.7	...
C_2H_6	7.9	5.3	...	...	8.1	...	4.9	...
C_3H_6	10.6	9.4	...	17.3	6.8	...	7.9	...
C_3H_8	7.0	18.1	...	21.3	5.1	...	4.1	...
Iso-C_4H_8	0.5	1.5	...	0.6	0.6	...	0.4	...
n-C_4H_8	1.2	2.3	...	2.7	1.2	...	1.1	...
C_4H_{10}	3.1	16.8	...	14.9	5.6	...	6.7	...
Total olefins	16.5	15.9	16.3	23.8	14.0	16.7	15.1	6.3
Total saturates	32.2	47.7	26.7	40.9	25.9	57.5	33.8	3.5
C No. of saturates	...	...	2.9	...	...	2.9	...	3.1
Material balance, wt. % of charge								
Gas	2.2	6.6	7.8	7.2	3.3	3.3	3.7	0.5
Liquid below original b.p.	6.9	19.8	19.6	20.9	68.2	64.8	68.7	2.6
Remaining liquid	83.3	65.7	68.3	69.6	18.0	23.2	17.8	91.9
Carbon	4.8	1.9	1.0	0.8	1.5[d]	0.9[d]	1.4[d]	5.0
Loss	2.8	6.0	3.3	1.5	9.0	7.8	8.4	

[a] Thermal run.
[b] Based on heated free space of 70 cc.
[c] Including C_2H_6.
[d] CO from regeneration not included.

Temperature increase from 450° to 500° C. caused a little more cracking and greater hydrogen production. The gasoline fractions formed at the two temperatures appeared to be nearly identical.

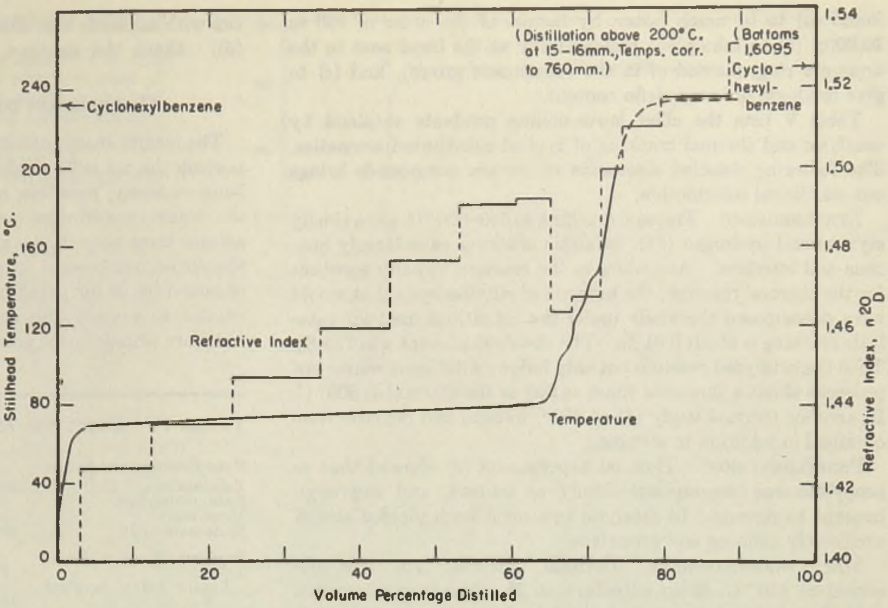

Figure 5. Distillation Curve for the Liquid Product from the Catalytic Cracking of Cyclohexylbenzene at 450° C.

CRACKING OF AROMATICS

The aromatic hydrocarbons show a wide range of stability in catalytic cracking. At one extreme the wholly aromatic compounds, such as biphenyl and certainly benzene and naphthalene in view of the stability of toluene and methylnaphthalenes, are practically inert under normal cracking conditions. At the other extreme the aromatic compounds with large alkyl or cycloalkyl substituents are very reactive. When properly classified according to structure, the aromatics form a consistent picture.

Monoalkylbenzenes crack with increasing ease as the size of the alkyl group increases. Under fixed conditions, at 500° C. decomposition of toluene was about 1%, of ethylbenzene 11%, and of *n*-propylbenzene 43%. Isomeric structure has considerable effect, for isopropylbenzene was 83.5% decomposed under the same conditions. The marked effect of structure was also noted with the butylbenzenes, which at 400° C. were cracked to the following extents: normal, 13.9%; secondary, 49.2%; tertiary, 80.4%. The cycloalkylaromatics, cyclopentylbenzene and cyclohexylbenzene, behave much like the monoalkylbenzenes. All these compounds are cracked primarily at the link joining the substituent group to the aromatic ring, producing benzene nearly quantitatively. The groups removed are frequently altered by secondary reactions.

Polymethylbenzenes also crack with increasing ease as the molecular weight increases, but they are much less reactive than the isomeric monoalkylbenzenes. At 500° C. the cracking of toluene was about 1%, while that of mesitylene or pseudocumene at a higher flow rate and longer process period was about 20%. Pentamethylbenzene may be a little less stable than the trimethylbenzenes. Triethylbenzene appeared to combine the heightened reactivities arising from increased substitution and increased size of the alkyl group. A feature with the polymethylbenzenes is the mobility of the methyl groups, evidenced both by isomerization and by disproportionation. Associated with this phenomenon is the apparent combination of C_1 fragments from the methyl groups to yield C_2, C_3, and C_4 material in small amounts. The transfer of alkyl groups among aromatics in the presence of silica-alumina catalysts was recently described by others (*7*).

Substituted naphthalenes behave in much the same way as the analogous benzene derivatives. Diphenylethane cracked readily; it may be regarded as an analog of isopropylbenzene, with a methyl replaced by a phenyl group. Biphenyl, on the other hand, with no aliphatic groups, was almost inert.

The condensed ring bicyclic aromatics with only one aromatic ring (also designated as naphthene-aromatics) crack fairly readily and yield, as the chief lower-boiling products, benzene and some of its homologs. The ease of cracking evidently depends on the size and structure of the naphthenic ring, for Tetralin cracked more than twice as readily as indan under the same conditions. Although cracking tends to take place at the links to the aromatic ring, it does not occur there so exclusively as with the alkyl- and cycloalkyl- aromatics.

Aromatics are generally considered to be relatively unreactive in cracking, but the results of the present study show that some types are highly reactive over the catalyst. Therefore, it is essential to specify the types of aromatics concerned before attempting to predict the behavior of an aromatic fraction in catalytic cracking.

Table V. Chief Lower-Boiling Products from Catalytic and Thermal Cracking of Aromatics

	Catalytic Cracking		Thermal Cracking		
Compound	Temp., ° C.	Chief products	Temp., ° C.	Chief products	Citation
Ethylbenzene	500	Benzene, ethylene	550–650	Styrene, toluene, benzene, hydrogen, methane	(*2, 9*)
n-Propylbenzene	500	Benzene, propylene	650	Toluene, ethylene	(*2*)
Isopropylbenzene	500–550	Benzene, propylene	600–650	Styrene, methane	(*2*)
Amylbenzenes	500	Benzene, pentenes	600–650	Toluene, styrene, gases	(*2*)
1,1-Diphenylethane	500	Benzene, ethylbenzene	675–700	Toluene, benzene, styrene	(*11*)
Methylnaphthalenes	500	Naphthalene, methane	450[a]	Naphthalene, methane	(*14*)
tert-Butylnaphthalene	500	Naphthalene, butene	650	Naphthalene	(*3*)
Tetralin	500–525	C_6, C_7, C_{10} aromatics	600	C_8, C_{10} aromatics	(*12*)
Cyclohexylbenzene	500	Cyclohexane, benzene	600	Styrene, alkylbenzenes, naphthalene, gases	(*3*)

[a] Autoclave at 25 atmospheres pressure.

COMPARISON WITH THERMAL CRACKING

The accelerative effect of the catalyst on the cracking of alkyl- or cycloalkyl-substituted aromatic compounds is great and comparison must be made with thermal cracking carried out at somewhat higher temperatures. Comparisons at the closest available temperatures used here or in the literature are listed below and followed by substantiative evidence. Compared to thermal cracking, catalytic cracking of these substituted aromatics is found (*a*) to be much faster, by factors of the order of 100 to 10,000; (*b*) to take place preferentially at the bond next to the aromatic ring, instead of in the substituent group; and (*c*) to give products of lower olefin content.

Table V lists the chief lower-boiling products obtained by catalytic and thermal cracking of typical substituted aromatics. The following detailed discussion of certain compounds brings out additional information.

ETHYLBENZENE. Thermal cracking at 550–600° C. gave chiefly styrene and hydrogen (*9*); catalytic cracking gave largely benzene and ethylene. According to the reaction velocity constant for the thermal reaction, the amount of ethylbenzene that would have decomposed thermally under the conditions used for catalytic cracking is about 0.01%. The observed amount was 11.8%. Thus the catalyzed reaction not only follows a different course but proceeds about a thousand times as fast as the thermal at 500° C. In another thermal study (*2*) at 650°, toluene and benzene were obtained in addition to styrene.

PROPYLBENZENES. Thermal experiments (*2*) showed that *n*-propylbenzene decomposed chiefly to toluene, and isopropylbenzene to styrene. In catalytic treatment both yielded almost exclusively benzene and propylene.

METHYLNAPHTHALENES. Thermal cracking (*15*) was observed at 450° C. in an autoclave at 25 atmospheres pressure. α-Methylnaphthalene cracked three to four times as fast as β-methylnaphthalene. Products were about equally divided among lower-boiling compounds, chiefly naphthalene and methane, and higher-boiling condensation products. The rate of thermal cracking at 500° C. is computed to be of the order of one hundredth that of catalytic cracking at the same temperature.

TETRALIN. In thermal cracking (*12*) there was no appreciable reaction at 550° C., with residence times twelve to twenty-four times those used for catalytic cracking. At 580° cracking was noticeable, and at 600–625° it proceeded fairly rapidly. Calculated first-order rate constants corrected to 500° (assuming an activation energy of 60 kg.-cal. per mole) indicate that the catalytic reaction is of the order of ten thousand times as fast as the thermal. Other comparisons, from the data in Table VI, show that catalytic cracking: (*a*) produces less hydrogen per mole cracked; (*b*) gives a gas lower in methane, and containing considerable amounts of C_3 and C_4 components which are virtually absent in the thermal gases, according to Sundgrén's analyses (*12*); and (*c*) gives a somewhat higher ratio of gas to lower-boiling liquid. The liquid products also differ considerably. Approximate analyses follow:

	Catalytic (This Work)			Thermal (*12*)		
Temp., ° C.	500	500	525	580	600	625
Flow rate, moles/l./hr.	6.4	13.7	13.7	0.55	0.55	0.55
Wt. % of lower-boiling liquid to 195° C.						
C_6 (70–95° C.)	29	36	34	10	7	10
C_7 (95–115° C.)	14	16	18	5	3	5
C_8 (115–145° C.)	16	9	18	36	22	48
C_9 (145–175° C.)		9		16	14	10
C_{10} (175–195° C.)	41	30	30	33	54	27
Olefin content, wt. % of fraction C_{10} (175–195° C.)	2	...	2	80	60	85

The catalytic liquid contains large amounts of C_6, C_7, and C_{10}; the thermal is predominantly C_8 and C_{10}. In both cases the liquids are made up of monocyclic aromatics, but in the thermal product the olefin content (C_8 and above) is much higher. It should again be pointed out, however, that the olefin content of the catalytic product is very dependent on operating conditions, and in some circumstances it might be quite high.

CYCLOHEXYLBENZENE. This compound was cracked thermally at 500° C. (Table IV). The rate of cracking was only about one four-hundredth that of catalytic cracking. There was a little lower-boiling liquid, which was not identified but was certainly not the almost exclusively C_6 material found in catalytic cracking. Much hydrogen was formed in thermal cracking. At 600° C. thermal cracking of cyclohexylbenzene gave monocyclic aromatics with aliphatic side chains including styrene and naphthalene (*3*). Again the contrast with catalytic cracking is evident.

COMPARISON OF HYDROCARBON CLASSES

The results accumulated on the cracking of pure hydrocarbons portray the behavior of the principal classes met in virgin petroleum—namely, paraffins, naphthenes, and aromatics. Although the isomers tested were not numerous for some classes, generalizations have been drawn which are felt to be reasonably valid for the structures present in petroleum. Recent unpublished data obtained by us for paraffins do indicate that their cracking may depend to some degree on isomeric structure; our generalizations are primarily for normal paraffins.

TABLE VI. CATALYTIC AND THERMAL CRACKING OF TETRALIN

Type Reaction and Source	Catalytic (This work)			Thermal (*12*)		
Temperature, ° C.	500	500	525	580	600	625
Rate, moles/l./hr.	6.4	13.7	13.7	0.55	0.55	0.55
Time, sec.[a]	7.7	3.6	3.5	92	90	84
% decomposed[b]	30.0	29.3	29.3	2.8	4.3	10.8
Products, % wt. of charge						
Gas	7.0	8.0	7.3	0.44	0.50	1.98
Liquid below original b.p.	21.0	20.2	21.2	1.89	3.22	7.10
Carbon	2.0	1.1	0.8	0.52	0.63	1.69
Gas analysis, vol. %						
H_2	36.4	57.0	35.3	56.2	66.6	84.7
CH_4	7.5	...	...	39.0	29.5	13.3
C_2H_4	2.7	...	3.2	4.1	3.9	2.0
Total olefins	15.9	16.3	23.8	4.1	3.9	2.0
Total saturates	47.7	26.7	40.9	39.0	29.5	13.3
Moles/mole charge decomposed						
H_2	0.37	1.00	0.39	1.31	1.37	4.56
Hydrocarbon gas	0.66	0.77	0.71	1.02	0.69	0.83

[a] Time of contact, assuming catalyst 100% void and allowing for expansion.

[b] To gas, lower-boiling liquid and carbon, on no-loss basis.

Figure 6 shows reactivities of representative hydrocarbons over the cracking catalyst, with percentages decomposed plotted against the number of carbon atoms in the molecule. At a given carbon number the paraffins are the most stable hydrocarbons in the figure, except toluene. Most stable of all are estimated to be the unsubstituted aromatics (not included in Figure 6), such as benzene, naphthalene, and biphenyl. The polymethylaromatics are somewhat more reactive than the paraffins, judging from data for the polymethylbenzenes. Next in order of increasing reactivity are the condensed-ring naphthene-aromatics (not in Figure 6) such as Tetralin, then the naphthenes, and finally the aromatics with large alkyl or alicyclic groups, among which only the monoalkylbenzene series is illustrated.

Olefins are important components of cracked and synthetic petroleum fractions, but cannot be directly compared with the other classes because of the lower reaction temperatures employed. Even at 400° C. the aliphatic olefins cracked more extensively than did the naphthenes at 500° C., an indication of their high reactivity. The alicyclic olefins or unsaturated naphthenes are similar in behavior.

The primary products from catalytic cracking of the several hydrocarbon classes are determined by the carbon-carbon bond ruptures which occur. These may be summarized as follows:

1. Paraffins are cracked preferentially at those links which yield fragments of three or more carbon atoms. With normal paraffins, cracking occurs at gamma carbon-carbon bonds or at those still nearer the center of the molecule, and the product gas is correspondingly low in methane and C_2. Long chains tend to crack simultaneously in several places and result in products comprising a molecular weight range very much lower than that of the feed.
2. Naphthenes also tend to give fragments of three or more carbon atoms. They are cracked in both the ring and the side

chain, especially when the latter contains three or more carbon atoms.

3. In substituted aromatics the link to the ring is selectively attacked, and in the simplest case of monoalkylaromatics the substituent group is sheared off to yield the bare aromatic and the complementary olefin. This reaction is very extensive with substituent groups of three or more carbon atoms.
4. Olefins are cracked in much the same manner as paraffins but much more readily.

In addition to the cracking reactions, there are secondary and auxiliary reactions which are important in determining the nature of the products. These include isomerization, saturation by hydrogen transfer, polymerization and condensation, cyclization to aromatics, dehydrogenation, and coke formation.

Isomerization is most pronounced with olefins, both aliphatic and cyclic. A shift in the position of double bonds has been determined in unreported experiments to be very rapid. Branching of the carbon skeleton of olefins, while less rapid, is also prominent. Saturation of olefins by hydrogen transfer is particularly important, and since it acts selectively on tertiary olefins, it leads preferentially to the formation of branched saturates. It is somewhat favored if high-molecular-weight naphthenes, such as Decalin, are present to act as donors of hydrogen. Direct isomerization of paraffins occurs to a very small extent.

Polymerization and condensation are prominent with olefins, and to a lesser extent with higher aromatics. Cyclization and condensation to aromatics is noticed with paraffins and aliphatic olefins, and seems particularly to lead to aromatics in the range C_8 to C_{10}. Dehydrogenation under catalytic cracking conditions is extensive only for the higher hydroaromatic compounds, such as Tetralin. Coke formation is invariably associated with catalytic cracking but is more marked with certain types of hydrocarbons, as will be outlined below.

Compositions of gases from catalytic cracking are surprisingly uniform, except for compounds such as the alkylbenzenes or the isobutylene polymers where the particular structure is of controlling importance. Gases are, in general, rich in C_3 and C_4 compounds because of the tendency to crack out large fragments. On the other hand, highly methylated chains such as 2,2,4-trimethylpentane tend to give moderately large amounts of methane. The degree of saturation of the gas depends on the conditions of cracking and on the efficacy of the parent hydrocarbon as a hydrogen donor. Hydrogen contents of gases are ordinarily low. This hydrogen does not necessarily imply direct dehydrogenation; often the major portion of it can be accounted for by the elimination of hydrogen in the condensation reactions that lead to coke formation, since most of the hydrocarbons have empirical formulas C_nH_n to C_nH_{2n+2}, whereas coke is about $C_nH_{0.5n}$.

Coke formation, measured by the carbon deposited on the catalyst, is fairly characteristic for different classes. Aliphatic olefins produce more carbon, evaluated as weight percentage of the original hydrocarbon, than do the naphthenes and paraffins, and the aromatics range in an intermediate position. The greatest amounts of coke are formed by cyclo-olefins, diolefins, and unsaturated aromatics such as styrene.

Comparison of catalytic and thermal cracking rates of the different hydrocarbon classes brings out the striking fact that the catalyst markedly changes the relative order of stability of the several classes. Thermally the stability for a given carbon number increases in the order: (1) paraffins and aliphatic olefins, (2) naphthenes, (3) alkyl aromatics, (4) unsubstituted aromatics. In catalytic cracking, stability increases in the order: (1) olefins, (2) aromatics with C_3 or larger substituent groups, (3) naphthenes, (4) polymethyl aromatics, (5) paraffins, (6) unsubstituted aromatics.

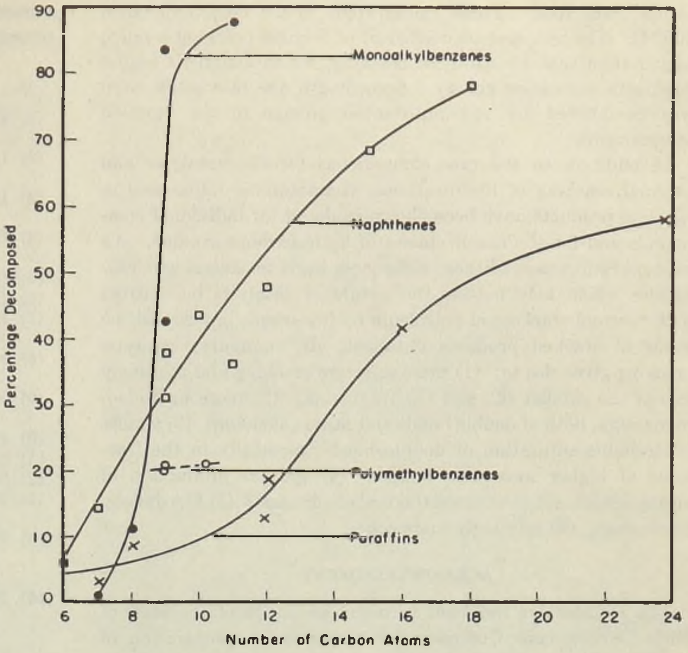

Figure 6. Catalytic Cracking of Various Hydrocarbon Classes

From treatment over silica-zirconia-alumina catalyst at 500° C. with flow rate of 13.7 moles per liter per hour for 1 hour; the percentage decomposed is the sum of gas, liquid boiling below the original b.p., and carbon.

These orders are based upon the assumption that the major portion of the molecule is of the class specified, and they represent only a rough segregation. For example, paraffins and olefins of the same carbon number are not necessarily identical in thermal stability, and actual rate ratios depend on conditions as well as on individual structures. For present purposes, however, the rates of thermal cracking of olefins and paraffins at atmospheric pressure and about 500° C. may be taken as roughly equal.

The change in the order of stability effected by the catalyst explains why petroleum cracking stocks cannot be rated uniformly for both catalytic and thermal cracking. Of particular practical importance is the paraffin-naphthene relation, since many virgin cracking stocks contain large amounts of these two hydrocarbon types. Catalytically, in the range C_{10} to C_{18}, naphthenes crack two to three times as fast as paraffins; thermally the naphthenes crack at about one twentieth the rate of the paraffins[1]. A factor of about 50 is thus introduced in the rate ratio of naphthenes compared to paraffins, in favor of catalytic cracking. This explains the preferred position of naphthenic oils as stocks for cracking with catalysts of these or similar characteristics.

A rough measure of catalysis for any class is obtained by comparing the first-order rate constants computed for catalytic and thermal cracking. As pointed out previously (*4*), such a comparison has only qualitative significance, and the ratios depend on the conditions for the catalytic reaction as well as on the assumptions applied in computing rate constants. Approximate ratios of catalytic to thermal decomposition rates are: paraffins, 6 to 60; naphthenes, about 1000; aromatics, up to 10,000;

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[1] The ratio of rates for thermal cracking of naphthenes and paraffins has been obtained from two sources: (*a*) a survey of the sparse data available from cracking at atmospheric pressure and about 500° C. and (*b*) the collections of Tilicheev (*14*), based largely on cracking in autoclaves. Both sources yield the same naphthene/paraffin rate ratio, although source *b* gives absolute rates two to ten times as high as source *a*.

olefins, over 1000. These values apply in the neighborhood of 500° C. The temperature coefficient of thermal cracking is much higher than that for catalytic cracking, which denotes a higher Arrhenius activation energy. Accordingly, the rate ratios cited will be altered by any substantial change in the reaction temperature.

In addition to the rate comparisons for the catalytic and thermal cracking of hydrocarbons, characteristic differences in reaction products have been shown in detail for individual compounds and for the major classes of hydrocarbons studied. An over-all comparison of these differences leads to several generalizations which help outline the nature of catalytic in contrast with thermal cracking of petroleum hydrocarbons in terms of the kinds of cracked products obtained. In summary, catalytic cracking gives rise to: (1) more selective cracking and relatively less of the smaller (C_1 and C_2) fragments; (2) more olefin isomerization, both of double bonds and carbon skeleton; (3) a more controllable saturation of double bonds, especially in the fractions of higher molecular weight; (4) greater production of aromatics (except at extreme thermal conditions); (5) less diolefin production; (6) relatively more coke.

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ANTISKINNING AGENTS . . . .

DERIVED FROM NITROPARAFFINS

A number of nitroamines and polyamines have been tested as antiskinning agents for a badly skinning tung oil varnish. The results are given and are compared here with those from other antioxidants.

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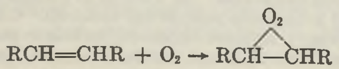
IN THE manufacture of paints and varnishes, the use of tung oil has always been a problem because of the gelling and skinning properties of the finished products before application. Tung oil (*9*, *14*) is obtained from the nuts of the tree, *Aleurites fordii*, which grows chiefly in China. It differs from other drying oils, except oiticica oil, in that it has conjugated double bonds which account for the characteristic waterproofness, fast drying, and durability it imparts to varnishes. The mechanism of drying and oxidation of oil films is still the subject of study and controversy (*12*). It is fairly well agreed that the reaction is complex and involves oxidation, polymerization, and colloidal gel formation. As Bradley (*1*) pointed out, it is generally believed that a certain amount of linear polymerization is characteristic of the fusible polymer which makes up the film-forming material before final application. Drying is then a mechanism by which the linear polymer is converted to a cross-linked polymer. Any agent or means of activation to bring about this conversion may be considered as a promoter.

The first step in the drying of the oil film is the addition of oxygen at the double bonds to form peroxides:

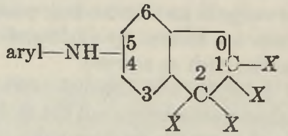


$$\mathrm{RCH{=}CHR + O_2 \rightarrow RCH\overset{O_2}{\frown}CHR}$$

The next steps in the mechanism are not clear. Elm (*6*) showed that, during the physical change of the oil, it is converted from a noncolloidal into a colloidal state upon exposure to oxygen. Just how the polymerization and/or association takes place has not been demonstrated. Later investigators (*1*, *11*) believe that oxidation followed by association is more likely in the light of the study of solvent action on the drying-oil film.

Irrespective of the mechanism, skinning and gelling of the paint or varnish are attributed to oxidation and/or polymerization in the presence of oxygen. The property of air hardening is necessary for the normal use of such paints and varnishes; obviously, then, attempts to eliminate skinning and related phenomena must at the same time avoid objectionable loss of air-hardening properties of the final film.

The literature reveals a number of patents on antioxidant compositions suitable for use in inks, paints, varnishes, and the like. Most frequently mentioned are polyhydroxy phenols and their derivatives (*4*). Other compounds are the azones (*5*)—i.e., organic compounds containing the tetravalent azono group $-\mathrm{C{=}N{-}N}$; the arylaminodihydrobenzofuranes (*7*) of the general formula:



where aryl refers to the aryl nucleus of the benzene, naphthalene, or biphenyl series, and *X* is an alkyl group or hydrogen; and the arylamines (*8*) and alkylamino alcohols (*13*). One patent (*3*) discloses products of a nature somewhat similar to those discussed in this paper.

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TABLE I. TIME FOR SKIN FORMATION WITH VARIOUS AMOUNTS OF INHIBITORS

Inhibitor	Days Required for Skin Formation at Concn. of: 0.3 g./50 ml.	0.1 g./50 ml.	0.05 g./50 ml.
N-(2-Aminoisobutyl)butylamine	21	14	7
N-(2-Nitroisobutyl)butylamine	14	7	4
N-(2-Nitroisobutyl)dibutylamine	6	5	2
N-(2-Aminoisobutyl)piperidine	14	10	3
N-(2-Aminoisobutyl)aniline	30	..	
N-(2-Nitroisobutyl)aniline	20+	5	1
N-(2-Aminoisobutyl)*N*-methylaniline	7+	3	2
N-(2-Nitroisobutyl)*N*-methylaniline	3	3	2
N-(2-Chloro-2-nitrobutyl)aniline	10	7	7
N-(2-Aminoisobutyl)*p*-chloroaniline	15	14	7
N-(2-Nitroisobutyl)*p*-chloroaniline	9	7	4
N-(2-Nitroisobutyl)*p*-toluidine	9	10	7
N-(2-Aminoisobutyl)sulfanilic acid	1	1	1
N-(2-Nitroisobutyl)sulfanilic acid	1	1	1
N,*N*'Diphenyl-2-nitro-2-methyl-1,3-propanediamine	7	4	4
N-(2-Nitroisobutyl)-β-naphthylamine	11	8	10
N,*N*'-bis(2-Nitroisobutyl)benzidine	3	3	3
N,*N*'-bis(2-Aminoisobutyl)*p*-phenylenediamine	20+	..	..
N,*N*'-bis(2-Nitroisobutyl)*p*-phenylenediamine	20+	20+	20+
Blank control	1[a]	1[a]	1[a]
Stabilizer 59 (C.S.C., comparison)	20	1	1
Hydroquinone (comparison)	20+	1	1
2-Nitro-1-butanol (comparison)	1	1	1
p-Phenylenediamine (comparison)	3	3	..

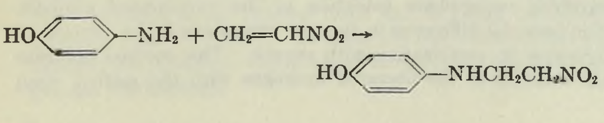
[a] No inhibitor added.

TABLE II. EFFECT OF INHIBITOR ON DRYING TIME OF FILMS

Compound	Concentration, G./50 Ml.	Time for Uniform Film Drying, Hrs.
Blank control	...	5
p-Phenylenediamine	0.15	48 (still tacky)
	0.05	24
Hydroquinone	0.15	10
	0.05	8
Stabilizer 59	0.15	5
	0.05	5
N-(2-Aminoisobutyl)*p*-chloroaniline	0.15	6
	0.05	5
N,*N*'-*bis*(2-Nitroisobutyl)-*p*-phenylenediamine	0.15	12
	0.05	8
N,*N*'-*bis*(2-Aminoisobutyl)-*p*-phenylenediamine	0.15	10
	0.05	8
N-(2-Aminoisobutyl)aniline	0.15	6
	0.05	5
N-(2-Nitroisobutyl)aniline	0.15	5
	0.05	5
N-(2-Aminoisobutyl)-*o*-chloroaniline	0.15	6
	0.05	6
N-(2-Aminoisobutyl)butylamine	0.15	6
N-(2-Aminoisobutyl)butylamine	0.05	5
N-(2-Aminoisobutyl)-*o*-toluidine	0.15	6
N-(2-Aminoisobytyl)-*o*-toluidine	0.05	5

It might be presumed that any antioxidant would be suitable as an antiskinning agent or that any antioxidant might have antigelling or antiskinning properties. However, the results shown by this paper concur with those indicated for the rubber industry. When used in rubber, antioxidants are of different types according to their ability to inhibit static oxidation, flex cracking, sun checking, or reversion of cure (*10*). Wagner and Brier (*15*) point out that the antioxidant uses are different for the rubber industry from those for the paint industry and are not necessarily comparable. The definitions for an antioxidant for gasoline, for rubber, and for paint (*2*) bear out these differences. The terms "antioxidant" and "inhibitor" are frequently confused and used interchangeably.

Dickey and McNally (*3*) describe the synthesis of nitroamines from diamines or aminophenols and nitro-olefins:



The reaction is simple and straightforward. The products described were prepared in the following manner:

$$RNH_2 + HOCH_2C(CH_3)_2NO_2 \rightarrow RNHCH_2C(CH_3)_2NO_2$$

where R is alkyl, aryl, or substituted aryl. Similarly the aromatic diamines yielded:

$$NH_2{-}Ar{-}NH_2 + 2HOCH_2C(CH_3)_2NO_2 \rightarrow NO_2C(CH_3)_2CH_2NH{-}Ar{-}NHCH_2C(CH_3)_2NO_2$$

where Ar is a benzene, naphthalene, or diphenyl nucleus. The nitro compounds can be readily reduced to the corresponding amine derivatives.

It is emphasized that many of the products illustrated here cannot be made by the Dickey process (*3*).

No comparisons have been made with dipentene or pine oil, volatile type inhibitors, in this report.

SKINNING TESTS

The tests were carried out by pouring 50-ml. portions of a limed-rosin tung oil mixing varnish (notably a bad skinner), a commercial varnish, into 8-ounce, wide-mouth jars. The inhibiting or antiskinning agent was added, and the jar left exposed to the atmosphere. The jars were examined every 24 hours. Several controls were run to check the rate of skinning of the uninhibited varnish. The commercial varnish was a highly cooked product that had quick-drying and good body properties. It was prepared from the following formula and directions:

Limed rosin, lb.	100
Tung oil, gal.	35
Boiled linseed oil, gal.	5
Sublimed litharge, lb.	5
Mineral spirits, gal.	75
Liquid drier (6% Co), gal.	1

Heat the tung oil and 80 pounds of limed rosin to 400° F. Sift in the litharge while stirring, and run quickly to 575° F. Pull the kettle from the fire and run to string. Check by the addition of bodied linseed oil and balance of limed rosin. Cool to 400° F. and thin.

The products tested, amount of inhibitor used, and time required for skin formation, both in the jar and on surface films, are given in Table I. The effect on the drying time of the films is shown in Table II. The films of varnish were prepared by adding 10 ml. of the varnish to a glass plate and allowing the liquid to flow down the plate inclined at a 45° angle. The number of hours required for complete drying, not just a tacky film, is recorded. Many of the films were reasonably dry at 3.5 hours.

COMPARISON OF RESULTS

The tables show that the structure of the compounds gives little evidence for correlation and prediction of antiskinning properties. Likewise the evidence is not conclusive that di-, tri-, or tetramines are more effective than nitroamines as antiskinning agents. Amines such as *p*-phenylenediamine have a long history as antioxidants and reducing agents, and it is well known that aniline is difficult to keep colorless because of its affinity for oxygen.

It was not expected that *N*,*N*'-*bis*(2-nitroisobutyl)-*p*-phenylenediamine would exhibit an effect equivalent to the corresponding reduction product, *N*,*N*'-*bis*(2-aminoisobutyl)-*p*-phenylenediamine. Nor, on the other hand, was it expected that *N*,*N*'-*bis*(2-nitroisobutyl)benzidene would have so little effect as an antiskinning agent, especially after some of the other compounds had already been tested.

The presence of an aromatic nucleus in the derivative is not essential, as is well illustrated by the results with *N*-(2-aminoisobutyl)butylamine. Again, however, the results with the corresponding nitro derivative are unexpected and a comparison with *N*-(2-nitroisobutyl)dibutylamine is not enlightening. A number of the compounds tested were ineffective at low concentrations, and some were not even effective at higher concentrations.

The amino derivatives seem to be more effective than do the nitro compounds with most of the products, but not all. A number of comparisons were run with other products known to have antiskinning properties. Although hydroquinone was good at the higher concentration, it was ineffective at the lower concentration in comparison with some of the other products tested.

Two of the higher-molecular-weight compounds increased the drying time of the film but not so much as the basic diamine from which they were derived.

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Production of Methyl Vinyl Ketone from Methylvinylcarbinol

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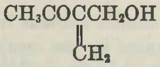
A procedure is described for the catalytic vapor-phase oxidation of methylvinylcarbinol to give methyl vinyl ketone. The catalysts considered consist of combinations of zinc oxide with cupric or cuprous oxide. The yields of methyl vinyl ketone are about 63% of theory under optimum conditions. With adequate equipment to control temperature rise during the reaction, the yields of methyl vinyl ketone would be considerably increased.

IN RECENT years methyl vinyl ketone has received considerable attention as a possible monomer in the preparation of elastomers. Most of the information in regard to the compound is in the patent literature which describes its uses, preparation, methods of polymerization, and stabilization. F. Bayer and Company (*2*) were the first to show autopolymerization of the compound; its copolymerization with butadiene was first described in a patent by the I. G. Farbenindustrie A.-G. (*10*). Methyl vinyl ketone is valuable not only as a monomer for rubber copolymers but also as a synthetic resin intermediate. The ketone condenses with formaldehyde to give water-soluble products which may be converted to resins by the addition of polycarboxylic acids or anhydrides, chlorides, esters, and amides.

One of the earliest syntheses of methyl vinyl ketone was described by Wohl and Prill (*19*). The method involved the condensation of acetone with formaldehyde followed by dehydration:

$$CH_3COCH_3 + HCHO \rightarrow CH_3COCH_2CH_2OH \xrightarrow{-H_2O} CH_3COCH{=}CH_2$$

This procedure was extended and modified by Drinberg and Bulygina (*4*), Morgan and Holmes (*13*), and White and Haward (*17*). Gault and Germann (*6*) emphasized the difficulty in controlling the mode of condensation of the formaldehyde and acetone, as evidenced by the isolation of such compounds as methylene butanolone



$$CH_3CO\underset{\Vert\atop CH_2}{C}CH_2OH$$

which limit the subsequent yields of methyl vinyl ketone. Although the starting materials are readily available, the reaction has never been shown to be practicable on an industrial scale.

Churbakov and Ryazantsev (*3*) claim a high yield of methyl vinyl ketone by the hydrolysis of vinylacetylene in the presence of mercury salts and sulfuric acid as catalysts:

$$CH{\equiv}C{-}CH{=}CH_2 + H_2O \xrightarrow{HgSO_4,\ H_2SO_4} CH_3COCH{=}CH_2$$

The vinylacetylene is prepared by the well known reaction of Nieuwland *et al.* (*14*):

$$2CH{\equiv}CH \longrightarrow CH{\equiv}C{-}CH{=}CH_2$$

N. V. de Bataafsche Petroleum Maatschappij (*15*) patented a method for methyl vinyl ketone by the direct dehydration of acetylmethylcarbinol with sodium bisulfite as catalyst. Since the direct dehydration of an α-keto alcohol is very difficult, indirect dehydration is more generally employed. Allen and Haury (*1*) and Long (*11*) patented methods for the preparation of the ketone by the pyrolysis of acetylmethylcarbinol. The pyrolysis was effected at 500° to 550° C. in the presence of an inert gas such as nitrogen.

Groll (*7*) patented procedures for the production of unsaturated carbonyl compounds by the catalytic dehydrogenation of unsaturated alcohols. He claimed a 33% yield of methyl vinyl ketone by the catalytic dehydrogenation of methylvinylcarbinol. Groll and de Jong (*9*) claimed higher yields were obtained by the catalytic vapor-phase oxidation of the unsaturated alcohols. The essential difference in the two procedures is the removal of hydrogen in combination with oxygen. This method prevents the reaction of the liberated hydrogen with the methyl vinyl ketone to form methylvinylcarbinol. On the other hand, the oxidation method has the disadvantage that it may be difficult to control the extent of the oxidation. Moreover, catalytic oxidations are generally highly exothermic and require more care in maintaining the proper temperature.

The general topic of catalytic vapor-phase oxidation has been treated in detail by Marek and Hahn (*12*). Parks and Yula (*16*) described the preparation of several catalysts for oxidation reactions and made generalizations on the relative degree of oxidative ability of various oxide catalysts. The recent developments in the production of unsaturated alcohols, through high-temperature chlorination of unsaturated hydrocarbons followed by hydrolysis, as described by Groll and Hearne (*8*) and Williams and associates (*18*), will prove a stimulus to further work on this interesting class of compounds.

CATALYTIC PROCEDURE

Equipment. The catalytic reactions were carried out in a Pyrex tube which was heated in a well-insulated, electrically heated furnace. The catalysis tube was 62 cm. in length and 3.2 cm. in diameter; it was packed for a length of approximately 20 cm. with the catalyst to be used. The furnace was 45 cm. in length. Temperatures were measured by thermocouples sealed in the furnace. The thermocouples had previously been calibrated against a thermometer embedded in the catalyst. The relation was established with gas flowing but without addition of the reactant.

The gases were passed through a wet-test flowmeter and then through purification trains before passing into the vaporizing flask. The vaporizing flask was also standard equipment containing a gas inlet tube, side arm, and elongated neck leading to the drop regulator. The drop rate regulator consisted of a valve from a compressed air tank attached by rubber tubing to a reservoir containing the reactant. The materials produced during catalysis were led through a system consisting of a water condenser, ice baths, and dry ice baths.

Catalysts. The catalysts were prepared by mixing the powdered components and homogenizing them with water to form a thick paste. The paste was spread on glass plates to a depth of about 4 mm., was cut into squares 6 to 7 mm. in size, and dried overnight at 50° C. The catalyst was then removed from the plates and dried for 3 hours at the temperature to be used in the catalytic experiment. When used at the same or different temperatures, a single charge of catalyst gave duplicable results up to and including five runs. After the fifth run, the catalyst tended to become powdery and to pack; it was then either reactivated and reformed or replaced by a newly prepared catalyst.

Methyl Vinyl Ketone. The dropping mercury electrode procedure described by Fulmer, Kolfenbach, and Underkofler (*5*) was used to determine methyl vinyl ketone. The results were checked in each case by estimating the fraction boiling between 77° and 84° C. Final yields were based on the amounts of methylvinylcarbinol introduced into the vaporizer flask. The methylvinylcarbinol was purchased from the Shell Chemical Company.

Procedure. In using the zinc oxide–cuprous oxide catalyst, the tube was packed with catalyst and heated, in an atmosphere of nitrogen, to the temperature to be used in the run. The vaporizer flask was heated to 140° C., and the methyl vinyl ketone added a drop at a time under controlled conditions. The flow of nitrogen was cut off, and air was introduced at the desired rate into the vaporizer flask. After all of the carbinol had been introduced, the air flow was continued for 2 minutes to ensure completeness of reaction. Nitrogen was then introduced into the tube to prevent oxidation of the cuprous oxide and to sweep the reaction products from the furnace. In using the zinc oxide–cupric oxide catalyst the procedure was as above except that the use of nitrogen gas was omitted.

Table I. Yields of Methyl Vinyl Ketone (MVK) from Methylvinylcarbinol[a] with Zinc Oxide–Cupric Oxide Catalysts

Run No.	Grams CuO per 100 Grams ZnO	Temp., ° C. Initial	Temp., ° C. Final	Air Flow Ml./Min.	Time, Min.	MVK, % of Theory
1	22	300	320	600	60	59
2	30	235	255	600	60	45
3		275	295	600	60	62
4		300	325	600	60	63
5		310	335	600	60	50
6		335	360	600	60	47
7		300	325	600	60	63
8		300	325	300[b]	60	62
9		300	325	0	60	23
10		275	295	600	30	58
11		275	295	600	60	62
12		275	295	600	120	48
13	40	300	320	600	60	60
14		325	350	600	60	49

[a] 36 grams of methylvinylcarbinol used in each run.

[b] The air flow of 300 ml. per minute, for 60 minutes, furnishes oxygen in the stoichiometric quantity indicated by the equation: $CH_3CHOHCH=CH_2 + 0.5O_2 \rightarrow CH_3COCH=CH_2 + H_2O$.

Table II. Yields of Methyl Vinyl Ketone (MVK) from Methylvinylcarbinol[a] with Zinc Oxide–Cuprous Oxide Catalysts

Grams Cu_2O per 100 Grams ZnO	Temp., ° C. Initial	Temp., ° C. Final	MVK, % of Theory
10	250	250	Trace
	300	300	Trace
20	235	255	45
	250	270	61
	275	295	63
	300	325	53
	310	335	41
30	250	270	51
	300	325	50
40	250	275	46

[a] 36 grams methylvinylcarbinol used in each run at air flow of 600 ml. per minute for 60 minutes.

The condensates from all flasks were combined, and the methyl vinyl ketone was salted out by adding a mixture of sodium chloride and sodium sulfate. The supernatant liquid was measured and analyzed for methyl vinyl ketone. Organic products, other than methyl vinyl ketone, included unconverted methylvinylcarbinol, methyl ethyl ketone, and carbon dioxide. Under conditions giving maximum yields of methyl vinyl ketone, about 10% of the methylvinylcarbinol was unchanged and the by-product methyl ethyl ketone was at a minimum. At higher than optimum temperatures the proportion of carbon dioxide markedly increased.

YIELDS

The yields of methyl vinyl ketone, using the two catalysts are shown in Tables I and II. When appreciable yields of the ketone were obtained, the final temperature was from 20° to 25° C. above the initial temperature. In those instances in which only traces of the ketone were formed (Table II) there was no temperature rise. These data indicate that this rise in temperature is associated with the heat of reaction and is practically constant for the range of ketone yields from 23 to 63% of theory.

Table I gives typical data on the zinc oxide–cupric oxide catalysts. The variables studied included rate of air flow, time of run, ratio of cupric oxide to zinc oxide, and temperature; in all runs 36 grams of methyl vinyl ketone were used. Three ratios of air flow were tested (runs 7, 8, 9) under otherwise identical conditions. While the yields of methyl vinyl ketone were equally good in runs 7 and 8, there was a slight reduction of cupric oxide in run 8. In subsequent experiments an air flow rate of 600 ml. per minute was employed. A reaction time of 60 minutes gave maximum yields for the three proportions of cupric oxide–zinc oxide employed (runs 1, 4, 13); 30 grams of cupric oxide per 100 grams of zinc oxide proved best. Using the above optimum conditions of air flow rate, time, and proportion of cupric oxide, the temperature was varied (runs 2 to 6). The highest yields of methyl vinyl ketone, 62 to 63% of theory, were obtained in the temperature range 275° to 300° C. The drop in yield at 310° was associated with definite evidence of thermal decomposition of the methylvinylcarbinol.

Table II lists data on the zinc oxide–cuprous oxide catalysts. The highest yields of methyl vinyl ketone are obtained at somewhat lower temperatures and lower ratio of cuprous oxide to zinc oxide than with the zinc oxide–cupric oxide catalysts. The temperature range is more critical than with the latter catalysts. The maximum yields of methyl vinyl ketone do not differ greatly with the two. With the zinc oxide–cuprous oxide catalyst, gaseous nitrogen was used at the beginning and end of each run to maintain the copper in the cuprous state. The zinc oxide–cupric oxide catalyst is preferred for continuous use since it is in the maximum state of oxidation and gaseous nitrogen may be omitted. The cupric oxide also furnishes a sort of "storehouse" for available oxygen in that it can be slightly reduced during the run without harmful effect and can be easily reactivated. The reactivation procedure consists simply of a powdering procedure, burning off the carbon, and reforming the cubes.

ACKNOWLEDGMENT

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Stability of Soybean Flours • • • • •

EFFECT OF ACCELERATED OXIDATION

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Various commercially available soybean flours and grits have been subjected to accelerated oxidation studies. The keeping times or stabilities of these flours vary directly with their fat content. A 10° rise in temperature reduces the induction period of the flours by a factor of approximately 2. The loss of diene and triene acids during the course of oxidation is measured spectroscopically. Evidence is obtained to show that the decrease in total unsaturation of the fatty acids is due mainly to the loss of diene acid.

THE nutritive value of soybean products was critically reviewed recently by Payne and Stuart (*10*) who state that the general acceptance of soybean protein by the public is largely dependent upon the control of two factors: "the production of soybean products free from bitter objectionable flavors, and the development of suitable technique for flavoring and blending of soybean products with other foods."

From the standpoint of consumer acceptance of soybean products, the prevention of off-flavors and -odors which result from fat deterioration is of major importance. Fat rancidification occurs in soybean flours, grits, or flakes subjected to long periods of shelf storage or short periods of high-temperature storage. Since soybean flours and grits may be stored for at least one and a half years at room temperature before there is organoleptic evidence of deterioration, accelerated tests conducted at elevated temperatures in the presence of air should serve to evaluate present-day commercial methods of processing and provide a means for the study of factors effective in retarding oxidative rancidity in soybean products.

The development of a test similar to the active oxygen method (*7*) which has been applied to the study of the keeping qualities of separated fats and oils would aid materially in suggesting methods of improving the keeping properties of many fat-containing solid foods. In any test of this type, correlation must be made between organoleptic and chemical tests. Uniformity of results among various laboratories is difficult to obtain when data are compared upon the basis of organoleptic observation. However, chemical tests offer some basis for comparison. The average percentage composition of the three types of soybean flours investigated is given in Table I. Soybean grits and flakes have essentially the same composition as the flours, but vary in particle size due to differences in the degrees of cracking, rolling, grinding, and screening of the beans.

METHOD OF OXIDATION

All oxidations were carried out at 100° or 110° ± 0.2° C. in an apparatus (*6*) designed in the research laboratories of the Ralston Purina Company (Figure 1). A 10-gram sample of flour or other finely ground food was placed in a glass tube, 14 inches long and $1^1/_8$ inches in diameter, in an even layer. This tube, shown in the foreground of Figure 1, was open at both ends so that air could be passed over the sample during the test. The tube was inserted in the stainless steel tank filled with mineral oil, previously raised to the desired temperature of the test, under thermostatic control.

The means of metering the air passing across the surface of the sample was similar to that used in the active oxygen method (*7*). Prior to distribution from a manifold, it was washed in dichromate solution, concentrated sulfuric acid, and solid sodium hydroxide. The flow of air in the tests reported here was approximately 3 ml. per second. It is evident, therefore, that during these accelerated tests the samples contained little or no moisture.

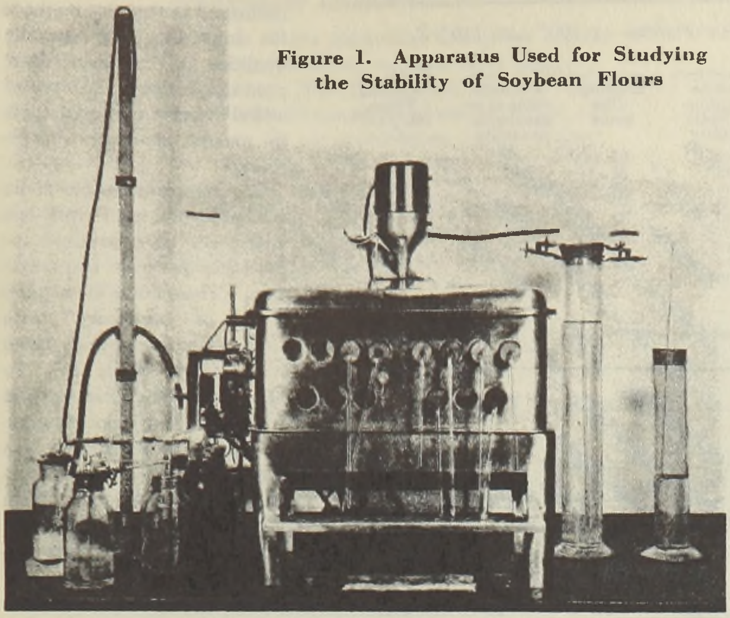


Figure 1. Apparatus Used for Studying the Stability of Soybean Flours

At a given interval during the oxidation, half of the 10-gram sample was removed for chemical and organoleptic tests. The other portion of the sample, whose surface had been undisturbed, was removed for testing at a later time. To determine the effects of surface exposure to the passing air, a 5-gram sample of flour was supported on a cardboard strip to obtain maximum surface per sample weight. This flour had a stability comparable to a 10-gram sample spread evenly within the glass tube.

COLORIMETRIC DETERMINATION OF PEROXIDES

A modification of the colorimetric method of Chapman and McFarlane (*2*) was used to determine the peroxide content of the flours. The method measured the color of a ferric thiocyanate solution formed when fat peroxides reacted with ferrous ions in an acetone solution containing ammonium thiocyanate. The peroxide value was expressed as milliequivalents of ferric ion per kilogram of flour.

A calibration curve was set up for the Evelyn photoelectric colorimeter using a 490 mμ filter and a standard solution of $FeCl_3.6H_2O$. To standardize the method, 1-ml. aliquots of an acetone solution of ferric chloride, whose concentrations range from 2 to 20 μg. per ml., were added to 9 ml. of a solution of 0.4% ammonium thiocyanate in 96% acetone. To prepare the latter solution, 400 mg. of ammonium thiocyanate were dissolved in 4 ml. of distilled water; and 96 ml. of anhydrous acetone, previously distilled from ferric chloride and calcium chloride, were added. A linear relation between concentrations and log I_0/I was observed over the range of concentrations used.

To determine the peroxide content, two 200-mg. samples of each flour were weighed into 8 × 1 inch test tubes fitted with air condensers. These samples were extracted for 20 minutes with 8 ml. of anhydrous acetone at steam-bath temperature. The cooled solutions were filtered through acetone-washed filter paper into 10-ml. volumetric flasks. The flour and filter paper were washed with small successive portions of acetone.

If the flour was suspected of having a high peroxide value, a 2-ml. aliquot of this 10-ml. filtrate was diluted to 25 ml. with anhydrous acetone. A 1-ml. aliquot of either the total filtrate or a dilution of it (2:25) was added to 9 ml. of 0.4% ammonium thiocyanate in 96% acetone previously saturated with ferrous sulfate. The ferrous sulfate (100 mg.) was added to the ammonium thiocyanate solution after the acetone had been added and the flask flushed with nitrogen. After the solution had stood in the dark over the ferrous sulfate for 10 minutes with intermittent shaking, the supernatant solution was then decanted.

The resulting mixture of flour extract and ammonium thiocyanate in acetone containing ferrous sulfate was heated almost to boiling, and then held at 50° C. for 10 minutes to allow time for the fat peroxides to react with the ferrous ions present. The resulting colored solutions were cooled and read in the Evelyn colorimeter at 490 mμ. A blank solution of acetone was used to determine the center setting while a correction was made for color produced in the color reagent by air oxidation.

DETERMINATION OF UNSATURATED FATTY ACIDS

Peroxide-free ether was used to extract the fat from 5-gram samples of tested high-fat flours. The fat so obtained was subjected to mild saponification, and the unsaponifiable portion of the sample was removed in a liquid-liquid extractor. The alkaline solution after ether extraction was acidified and further extracted with ether to recover the fatty acids. The ether solution was dried over anhydrous sodium sulfate and filtered, and the excess solvent was removed in vacuo. The free fatty acids so obtained were analyzed for total unsaturation by the Wijs iodine method. The fatty acid samples were further subjected to a spectrophotometric determination of the total octadecadienoic and -trienoic acids by the method of Mitchell, Kraybill, and Zscheile (*9*) as modified by Baldwin and Longenecker (*1*).

PREPARATION OF METHYL LINOLEATE

The methyl linoleate was prepared from linoleic acid (*4*) obtained by debromination in ether of tetrabromostearic acid (melting point, 115° C.). The distilled methyl linoleate had an iodine value of 171.7 (theoretical, 172.4). Alkali isomerization of this ester and subsequent determination in aqueous medium of its ultraviolet absorption value at 234 mμ yielded an $E^{1\%}_{1\text{ cm.}}$ value of 829.

KEEPING QUALITY

The keeping qualities of various soybean flours and grits at 100° and 110° C. under the conditions of the accelerated test are summarized in Tables II, III, and IV. The end of the induction period was measured both chemically and organoleptically. Rapid peroxide formation typified the end of the induction period. The keeping times of the various soybean flours in Tables II and III were determined by at least two independent tests. The values obtained by the accelerated method were reproducible to within one hour (Figure 2). Since the flour samples were removed at one-hour intervals and a variation of 30 minutes on either side of the end of the induction period causes a considerable change in peroxide value, the peroxide values at organoleptic rancidity are not in exact agreement.

TABLE I. AVERAGE PERCENTAGE COMPOSITION OF SOYBEAN FLOUR TYPES (*10*)

	Full Fat Flour	Expeller Flour	Solvent-Extd. Flour
Moisture	5.5%	5.0%	7.0%
Protein	40.5	50.0	53.0
Fiber	2.5	2.5	2.0
Ash	5.0	5.5	6.0
Fat	22.0	7.0	0.75
N-free ext	24.5	30.0	31.25

Table II. Relative Stabilities of Full-Fat Flours at 100° and 110° C.

Sample No.	Manufacturer	Treatment	Fat Content, %	100° C. Keeping time hours	100° C. Peroxide value at organoleptic rancidity	110° C. Keeping time hours	110° C. Peroxide value at organoleptic rancidity	Ratio of Keeping Times, 100°/110° C.
1	A	....	22[a]	46	85	22.5	46	2.04
2	B	....	22.2	77	85	38	100	2.03
3	B	Bleached	22.2	91	56	45	81	2.02
4	C	....	15.0	104	85	50	250[b]	2.08
5	D	....	22.9	63.5	83	33	79	1.92
6	D	Bleached	22.9	67	87	33	75	2.03
7	E	....	22.2	65	48	28	58	2.32
8	E	Bleached	22.1	67	79	33	59	2.03
9	F	....	22[a]	74	138[b]	37	47	2.00
10[c]	A	....	22[a]	36	....	....	...	...
11[c]	F	....	22[a]	70	....	....	...	...

[a] Approximately. [b] High values explained in text. [c] Purchased on local market.

Table III. Relative Stabilities of Soy Grits and Expeller Bean Flours at 100° and 110° C.

Sample No.	Manufacturer	Type	Particle Size	Fat Content, %	100° C. Keeping time, hours	100° C. Peroxide value at organoleptic rancidity	110° C. Keeping time, hours	110° C. Peroxide value at organoleptic rancidity	Ratio of Keeping times, 100°/110° C.
1	B	Low fat	Flour	6.3	128.5	7	56	31	2.29
2[a]	B	Low fat	Flour	6.3	85	..	....	..	....
3	B	Grit	Coarse	6.4	105	22	52.5	61	2.00
4	D	Low fat	Flour	6.9	108	12	54	44	2.00
5	D	Regular grit	Retained on 16 mesh	6.0	116.5	24	54	31	2.16
6	D	Fine grit	Through 16 mesh	6.4	104	41	48	49	2.17
7	F	Grit	.....	5.7	148	15	75	27	1.97

[a] Purchased on local market.

In keeping with the observation that a 10° rise in temperature doubles the rate of reaction, the ratio of the keeping times at 100° and 110° C. was approximately 2. This ratio is in accord with that reported by Mehlenbacher (*8*) for a series of fats and oils whose stabilities were determined by the active oxygen method (*7*).

The odor of the air escaping from the surface of the samples being tested was indicative of the "sweetness" of the flour. The odor passed through the successive stages of "grassy", "beany", and "rancid". The rancid off-odor always preceded the appearance of a rancid taste in the dried flour. The latter taste appeared at the onset of rapid peroxide formation. Reversion effects were difficult to detect in soybean flours, as the escaping air was never bland. To those experienced in organoleptic testing of soybean flours and soybean intermediates, the samples seemed to possess a toasted taste due to the extreme heat. This effect, however, did not interfere with the detection of oxidative rancidity.

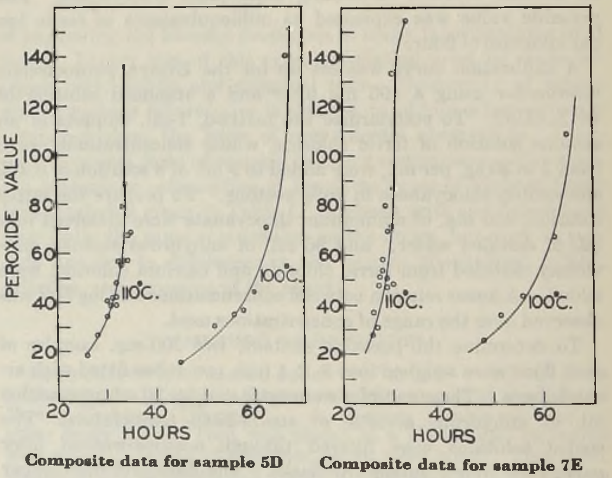
The effect of commercial bleaching upon the stability of high fat soybean flours is indicated in Table II. It appears from the data on the few flours tested that bleaching tended to enhance their stabilities. Additional stability tests upon the same flour bleached by various methods should be carried out, however, before the effect of bleaching can be critically appraised.

Part of the variation in the stability of different soybean flours may be attributed to differences in the methods of processing. Furthermore, differences in stability were also observed in flours obtained directly from the manufacturers as compared to those procured on the local market. The lowered induction periods of flours 10 and 11 (Table II) and flour 2 (Table III), which were purchased in one-pound boxes on local markets, undoubtedly may be attributed to prolonged shelf storage.

Contrary to the usual commercial observations that expeller flours have less stability than full-fat flours, it has been observed that the fat content directly affects the resistance of a flour to oxidative rancidity at high temperatures. This possible objection to an accelerated test is not of major importance if one is interested in studying methods for improving the keeping qualities of soybean flour products, either by the use of added antioxidants or changes in present commercial processes.

The solvent-extracted flours whose fat contents were less than 1.5% never attained appreciable peroxide concentration. These flours did acquire a flat or "cardboard" taste long before the keeping times indicated in Table IV. To the flour miller this taste is indicative of deterioration, although in these studies it was not recognized as a criterion of oxidation rancidity. With a suitable tasting panel, these flours could bear future examination.

The decrease in total unsaturation of the extracted soybean oil during oxidation, as determined by the iodine value, gave no indication of specific fatty acids oxidized. The loss of diene and triene acids, however, may be evaluated from spectral analyses of the alkali-isomerized fatty acids obtained from the extracted oil of full-fat soybean flours. Typical results are summarized in Table V. The loss of diene acid is similar to that reported by Filer *et al.* (*3*) from a study of hydrogenated vegetable oil shortenings and cottonseed oil. There appears to be, however, a more rapid loss of diene unsaturation in the oil of soybean flour at the end of the induction period.



Composite data for sample 5D Composite data for sample 7E

Figure 2. Rate of Peroxide Formation in Full-Fat Soybean Flours at 100° and 110° C.

Calculation of the iodine value expected for the fatty acids of an oxidized flour from the percentage change of diene and triene acids shows good agreement with the iodine values experimentally determined. Furthermore, the major decrease occurs in the linoleic or diene acid. This loss of diene is reasonable in view of the high initial linoleic acid content of soybean oil.

ULTRAVIOLET ABSORPTION

Figure 3 presents plots of the ultraviolet absorption curves for alkali-isomerized methyl linoleate and the fatty acids extracted from soybean flours. Since it had been observed that, during the high-temperature deterioration of soybean flour, an oily distillate collected in the air outlet tubes, highly purified methyl linoleate was added to a solvent-extracted flour to the extent of 10% by weight. Within 6 hours at 110° C., an appreciable quantity of oily distillate appeared in the air outlet tube of the methyl linoleate flour mixtures. A sample of this decomposition product which was alkali-isomerized had a spectral curve (Figure 3).

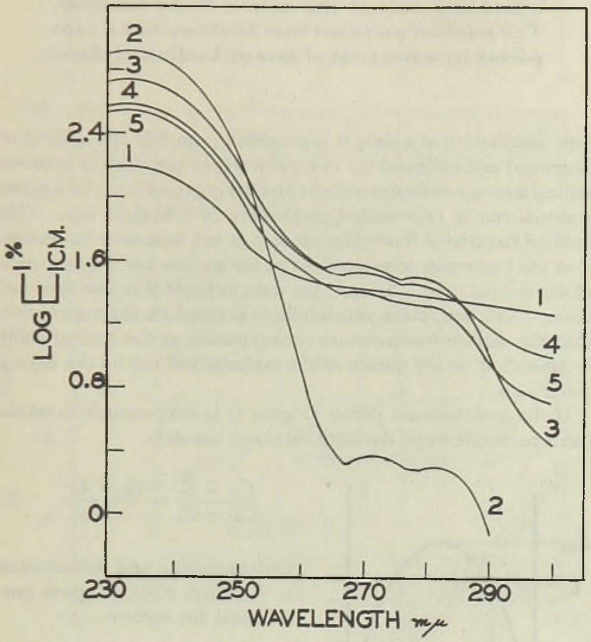


Figure 3. Spectral Absorption Curves

1. Oily distillate from methyl linoleate decomposition.
2. Methyl linoleate.
3, 4, 5. Fatty acids from oil extracted from soybean flour 2B; 3, no aeration; 4, aerated 78 hours; 5, aerated 79 hours.

The marked general absorption of this isomerized distillate in the region 270 to 280 mμ is probably due to carbonyl resonance. Holman *et al.* (*5*) recently investigated oxidation products of unsaturated fatty acids in this region of the ultraviolet. Their experiments indicated that carbonyl resonance served to increase the general absorption in this region.

The inflections at 270 and 280 mμ in the three absorption curves (Figure 3) for the alkali-isomerized fatty acids extracted from soybean flour are indicative of triene acid. Apparently, oxidation reduced the amount of triene acid without the appreciable formation of decomposition products having marked general absorption in this region. The small amount of spectroscopically active triene material in the methyl linoleate represented about 0.5% triene acid.

Since the investigation on the soybean flours was concerned primarily with rancidification under conditions of accelerated oxidation, the reversion effect of the soybean oil in the soybean flour was not considered since it was difficult to detect. Evaluation of reversion in soybean flour requires the use of a suitable tasting panel. Studies are currently in progress on possible correlation of the stabilities of soybean flours as determined by accelerated oxidation with stabilities determined under varying conditions of controlled humidity and temperature.

TABLE IV. RELATIVE STABILITIES OF SOLVENT-EXTRACTED SOYBEAN FLOURS AT 100° C.

Sample No.	Manufacturer	Fat Content, %	Stability at 100° C., Hr.
1	C	0.7	216
2	D	0.6	250
3	E	1.3	232
4	E (grits)	1.3	378
5	E	0.7	310

TABLE V. CHANGES IN THE FATTY ACIDS OF FULL-FAT SOYBEAN FLOURS

Flour Sample	Hours Aerated	Peroxide Value	Iodine Value	Linoleic Acid, %	Linolenic Acid, %	Iodine Value[a]
3B (110° C., 45-hour induction period)	0	..	139	56.6	8.4	...
	36	3	136	55.9	7.7	136
	37	9	133	54.8	7.9	134
	39	15	131	51.5	7.6	128
	43.5	25	130	52.6	7.7	130
2B (100° C., 77-hour induction period)	0	..	138	57.1	8.4	...
	72	29	133	56.1	7.5	134
	76	39	123	45.3[b]	6.9	112
	78	140	102	38.5	7.3	101
	79	168	94	35.3	5.6	91
1A (100° C. 46-hour induction period)	0	..	141	55.4	9.2	..
	44.5	68	135	49.3[b]	8.8	129
	46.5	249	91	27.6	9.0	90
	49	314	55	7.4	8.6	52

[a] Calculated from change in diene and triene acid contents.
[b] Value for diene probably too low.

ACKNOWLEDGMENT

The authors wish to express appreciation to C. B. Shaffer for photographing the apparatus (Figure 1) and also to H. E. Longenecker for continued interest and advice during the investigation. Thanks are also due the Soy Flour Association for supplying many of the soybean flours for the investigation.

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Inhibitors of Corrosion of Aluminum—Correction

An error should be pointed out in this article which appeared in the August, 1945, issue of INDUSTRIAL AND ENGINEERING CHEMISTRY. Two values are given for magnesium in the synthetic tap water analysis near the bottom of the second column of page 738. The second entry at the end of the table (1.4 p.p.m.) should refer to manganese.

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THE DRYING OF SOLIDS . . . . .

Prediction of Critical Moisture Content

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The average moisture concentration at the critical point in the drying of a solid is expressed in terms of the drying conditions and the nature of the material. This relation is developed on the assumption that the surface moisture concentration at the critical point is a function only of the nature of the material. The relation proposed here is shown to be supported by several sets of data on kaolin and clays.

IN THE drying of slabs with air, the process divides itself into two distinct stages. In the first, the rate remains constant at a rate approximating that of evaporation from a free liquid surface. The water distribution becomes nonuniform, with maximum concentration at the center and minimum at the faces. When the integrated average water concentration falls to a certain value, known as the critical average moisture content, the second period is initiated, with a decrease in drying rate. During this period the rate is roughly proportional, at each point in the process, to the average free water content of the solid. These facts allow the complete drying schedule of a material to be approximated, if the critical average moisture content is known. Consequently, it is of considerable importance to be able to predict the critical average moisture content for a particular material being dried under given conditions.

Sherwood and Gilliland (*5*) presented a method of predicting a critical average moisture content from the rate of drying in the constant-rate period and the diffusion constant of liquid through the solid. This method assumes that water migrates within the solid in accordance with the diffusion law, and that the constant-rate period ends when the free water concentration at the surface falls to zero. Use of this method requires one drying test to obtain the diffusion constant and involves a graphical solution of the diffusion equations.

More recent work by Ceaglske and Hougen (*1*) showed that in coarse granular solids, such as sand, water movement does not follow the diffusion equations, which call for development of a parabolic distribution as the constant-rate period continues. The actual distribution curves determined were S-shaped, and were correlated by the assumption that water moves through the solid in response to capillary forces instead of to concentration gradients. However, the data of Sherwood (*4*) show that for a number of materials, including wood, brick clay, and soap, the water distribution follows that predicted from the diffusion equations fairly closely. The method of correlation presented in this paper depends on the validity of the diffusion equations in predicting water distribution and, consequently, would not be expected to apply to materials of the type investigated by Ceaglske and Hougen.

By making use of the fact that in the constant-rate period the diffusion equations indicate rapid approach to a parabolic moisture distribution in a slab, it is possible to simplify the method of Sherwood and Gilliland (*5*) to a point where the relation between critical average moisture content and drying conditions for a given material can be represented graphically by a straight line. This method has added flexibility, since it is not necessary to assume that the free water concentration at the surface has fallen to zero at the critical point. In fact, the data indicate that this does not occur. The derivation which follows is based on the assumption that the surface free-moisture concentration at the critical point is dependent on the nature of the material but not on the drying conditions.

Table I. Data on Drying of Kaolin and China Clay Slabs

Clay	Air Velocity, Ft./Sec.	t_a	t_w	α	W_c	$\frac{\alpha}{1.5t_a-2.3}$
Florida kaolin	10.4	156	. . .	0.346	0.396	1.50
	9.6	132	. . .	0.250	0.372	1.28
	10.4	172	95	0.377	0.360	1.47
	10.4	110	75	0.197	0.388	1.68
	7.5	142	92	0.228	0.350	1.08
	10.8	166	106	0.368	0.369	1.50
	10.8	167	128	0.252	0.337	1.02
	10.2	167	135	0.169	0.258	0.67
	10.4	167	132	0.222	0.297	0.90
English china clay	10.4	140	108	0.242	0.168	1.16
	10.4	166	128	0.341	0.197	1.38
	10.6	117	93	0.168	0.205	0.97
	10.4	167	121	0.236	0.132	0.95
	9.4	167	138	0.134	0.120	0.52
	7.9	167	103	0.233	0.165	0.94

If the constant-rate period (Figure 1) is long enough to establish a parabolic water distribution across the slab,

$$\frac{C_m - C}{C_m - C_s} = \frac{(x - L)^2}{L^2} \tag{1}$$

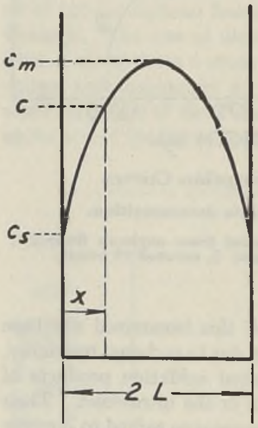

FIGURE 1

Differentiating and substituting $x = 0$ and $x = 2L$ gives gradients at the surface,

$$\left(\frac{dC}{dx}\right)_s = \pm \frac{2\,(C_m - C_s)}{L} \tag{2}$$

At any time,

$$C_{av} = \frac{1}{L}\int_0^L C dx \tag{3}$$

Substituting for C from Equation 1 and integrating,

$$C_{av} - C_s = \frac{2(C_m - C_s)}{3} \tag{4}$$

The diffusion law

$$-L\rho \frac{dW}{d\theta} = -D\left(\frac{dC}{dx}\right)_s$$

combined with Equations 3 and 4 gives:

$$L\rho \frac{dW}{d\theta} = \frac{3D(C_{av} - C_s)}{L} \tag{5}$$

Applying Equation 5 at the critical point and noting that $C = \rho W$ and $\alpha = L\rho(dW/d\theta)_c$,

$$W_c = W_{sc} + \frac{\alpha L}{3\rho D} \tag{6}$$

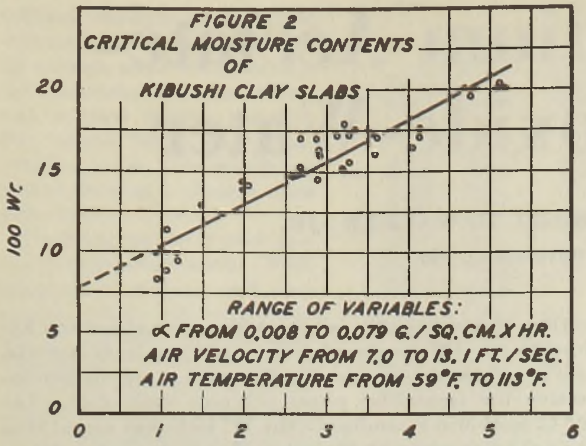

FIGURE 2
CRITICAL MOISTURE CONTENTS OF KIBUSHI CLAY SLABS

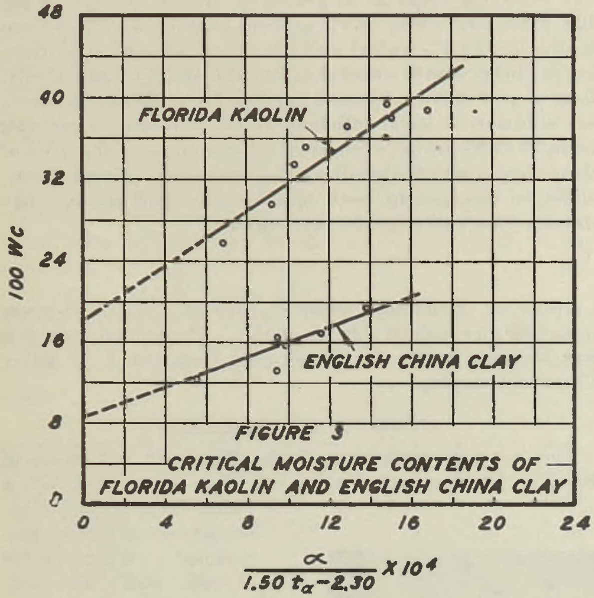

FIGURE 3
CRITICAL MOISTURE CONTENTS OF FLORIDA KAOLIN AND ENGLISH CHINA CLAY

Diffusion coefficient D would be expected to depend on the nature of the stock and the viscosity of the liquid. Assuming that D varies inversely as the viscosity, and making use of the fact that the fluidity of water is practically linear with temperature,

$$D = \frac{K}{\mu} = K(a + bt_a) \tag{7}$$

The data available for testing these relations were obtained on slabs dried from one face only. Consequently, the actual temperature of the slabs would be between the wet- and dry-bulb temperatures of the air. As an approximation, the dry-bulb temperature is used.

Substituting for D in Equation 6,

$$W_c = W_{sc} + \left(\frac{L}{3\rho K}\right)\left(\frac{\alpha}{a + bt_a}\right) \tag{8}$$

For a particular stock of given thickness, $L/3\rho K$ is constant. Consequently, if W_{sc} is independent of drying conditions, a graph of W_c against $\alpha/(a + bt_a)$ should be a straight line, with intercept W_{sc} and slope $L/3\rho K$.

Thirty-nine tests made by Kamei, Mizuno, and Shiomi (*3*) on Kibushi clay slabs under a wide variety of drying conditions are plotted in this manner in Figure 2; values of a and b were taken from viscosity data on water in their temperature range. Considering the fact that the reproducibility of their experimental critical moisture contents was not better than 2% moisture, the points fall fairly close to the predicted straight line.

Figure 3 shows results of a similar test of data obtained by the author on two other types of clay. The slabs were 17.5 × 17.5 × 2.0 cm., and were dried from one face at a variety of air temperatures, humidities, and velocities. All samples were prepared similarly by hand-kneading the clay with enough water to give an initial water content, W, of about 0.55. The clay was dried in a thin sheet metal pan, and the sides and bottom of the slab were covered with tin foil to prevent drying from those surfaces. The data (Table I) fall reasonably close to a straight line in Figure 3. None of these curves extrapolate to an intercept, W_{sc}, of zero, as was assumed in the method of Sherwood and Gilliland. Comings and Sherwood (*2*) observed in some cases a recovery in drying rate following the initial fall, and attribute this to breaking away of the stock from the pan because of shrinkage during drying. This effect was not observed during these tests, presumably because of the ability of the tin foil to shrink with the stock.

Having once established the position of the line on a plot of the type of Figures 2 and 3, the critical average moisture content is readily predicted graphically or by direct use of Equation 8. It would be expected that data for slabs of other thicknesses would fall on lines having the same intercept but slopes directly proportional to the thickness. No suitable data have been found to test this effect.

For other regular shapes, similar relations can be derived from the diffusion equations. Thus, for long cylinders, the analog of Equation 8 is:

$$W_c = W_{cs} + \frac{R}{4\rho K}\left(\frac{\alpha}{a + bt_a}\right) \tag{9}$$

For spheres the corresponding relation is:

$$W_c = W_{sc} + \frac{R}{5\rho K}\left(\frac{\alpha}{a + bt_a}\right) \tag{10}$$

No data for testing these relations are available to the author.

NOMENCLATURE

a, b, K = constants
C, C_{av}, C_m, C_s = moisture concentration, gram/cc.; C corresponds to position x, C_{av} to integrated average in stock, C_m to midplane, C_s to surface
D = diffusivity of liquid through solid, sq. cm./hr.
L = half thickness of slab dried from both sides, cm.
R = radius of cylinder or of sphere, cm.
t_a = air temperature, dry bulb., ° F.
t_w = air temperature, wet bulb., ° F.
W = integrated average free water content, grams water/gram dry stock
W_c = integrated average free water content at critical point
W_{sc} = free water content at surface at critical point
x = distance from one face of a slab, cm.
α = rate of drying in constant rate period, grams/sq. cm. × hr.
ρ = density of stock, grams dry stock/cc.
μ = viscosity, poises
θ = time, hours
Subscript c = critical point
Subscript s = surface

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The System Sodium Acetate–Sodium Hydroxide–Water

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Isotherms at 0.5°, 10°, and 20° C. for the system sodium acetate–sodium hydroxide–water have been determined for the formation of both sodium acetate and sodium hydroxide crystals. Eutectics occur in all isotherms. At 0.5° C. $NaOAc.3H_2O$ is obtained as the crystalline phase at low sodium hydroxide concentrations. At high concentrations the crystalline phase is $NaOH.3.1H_2O$. The eutectic is at 4.92 grams of sodium acetate and 61.5 grams of sodium hydroxide per 100 grams of water (2.9, 37.0, and 60.1%, respectively). At 10° C. $NaOAc.3H_2O$ is again obtained as the crystalline phase at low sodium hydroxide concentrations. A eutectic occurs at 57 grams of sodium hydroxide per 100 grams of water (6.1% sodium acetate, 33.4% sodium hydroxide, 60.5% water). At this point the crystals change to anhydrous sodium acetate and continue until a second eutectic occurs at 94 grams of sodium hydroxide per 100 grams of water (1.2% sodium acetate, 48.0% sodium hydroxide, 50.8% water) at which concentration the crystalline phase becomes $NaOH.H_2O$. The 20° C. isotherm is similar to the 10° isotherm except that the eutectics occur at 53 grams of sodium hydroxide per 100 grams of water (9.3% sodium acetate, 31.4% sodium hydroxide, 59.3% water) and 102 grams of sodium hydroxide per 100 grams of water (1.4, 49.5 and 49.1%), respectively. Recovery of sodium acetate crystals from sodium hydroxide solution is most efficient at concentrations ranging from 20 to 50 grams of sodium hydroxide per 100 grams of water because the solubility of sodium acetate is most sensitive to changes in both temperature and sodium hydroxide concentration in this region.

DESTRUCTIVE distillation of pine stumps for the production of terpenes and other useful materials yields an aqueous fraction containing small amounts of acetic acid. This solution is too dilute with respect to acetic acid to warrant recovery by distillation, but it has been found (*1, 7*) that this small amount of acid can be recovered by passing the solution through a bed of acid-absorbing resin. The acid may be subsequently removed from the resin in a more concentrated form by washing with alkali, and sodium acetate may be recovered from the alkaline solution by crystallization.

However, in order that the crystallization of sodium acetate from alkaline solutions may be carried out efficiently, it is necessary to have some knowledge of the solubility of sodium acetate in sodium hydroxide solutions. The solubility data for the system sodium acetate–sodium hydroxide–water are not available in the literature; therefore, this study was undertaken to determine the proper operating conditions for the precipitation of sodium acetate. The isotherms at 0.5°, 10°, and 20° C. were determined for the formation of both sodium acetate and sodium hydroxide crystals.

Anhydrous sodium acetate was obtained from the Niacet Chemicals Corporation (guaranteed 98–99.5% sodium acetate and maximum impurity, sodium chloride, 0.5%). The sodium hydroxide was technical grade, flaked, obtained from the J. T. Baker Chemical Company.

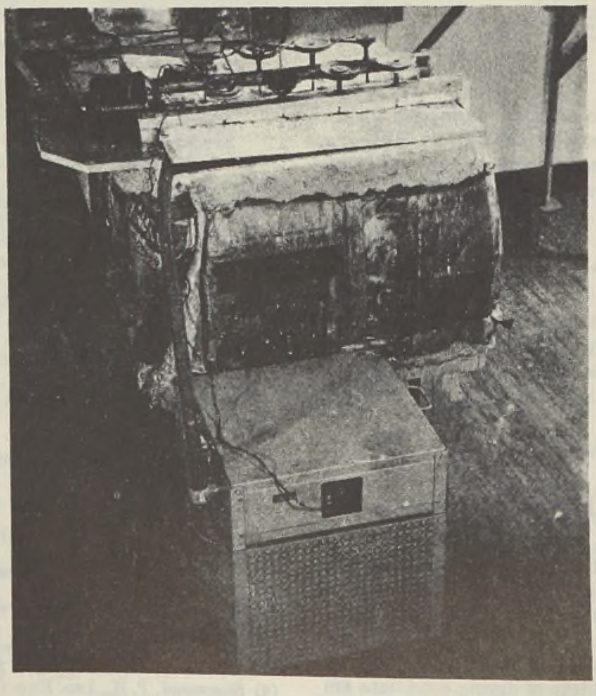

Figure 1. Constant-Temperature Bath

APPARATUS AND PROCEDURE

The constant-temperature bath (Figure 1) was made of wood lined with copper sheeting (*3*). It was insulated with a 1-inch layer of 85% magnesia-asbestos cement surmounted by a 2-inch layer of rock wool. The bath was covered with three removable boards surfaced with a 1-inch layer of 85% magnesia-asbestos cement. Uniform temperature throughout the bath was maintained by adequate circulation with a propeller.

The refrigerator was an Aminco portable cooling unit controlled by an Aminco Quickset bimetal thermoregulator. The regulator was checked against National Bureau of Standards calibrated thermometers and was found to be correct within ±0.35° C. over the range covered, 0° to 20° C.

The apparatus for sampling is shown in Figure 2, as modified from the Walton-Judd apparatus (*10*). The outer vessel is a

Table I. Solubilities of Sodium Hydroxide and Acetate in Water

Solubility, Grams per 100 Grams of Water									
From supersatn.		From undersatn.		Mean		NaOH, %	NaOAc, %	H_2O, %	Crystal
NaOH	NaOAc	NaOH	NaOAc	NaOH	NaOAc				
				0.5° C. Isotherm					
0.00	36.4	0.00	36.2	0.00	36.3	0.0	26.6	73.4	NaOAc.$3H_2O$
0.00	36.3	0.00	36.3	0.00	36.3	0.0	26.6	73.4	
0.282	35.6	0.321	35.6	0.30	35.6	0.22	26.4	73.4	
1.937	33.2	1.815	33.8	1.88	33.5	1.4	24.7	73.9	
4.11	30.8	3.92	30.5	4.02	30.7	3.0	22.8	74.2	
7.94	27.0	7.75	27.8	7.85	27.4	5.8	20.2	74.0	
16.4	19.0	16.9	18.6	16.7	18.8	12.3	13.9	73.8	
23.1	12.4	23.9	12.2	23.5	12.3	17.3	9.1	73.6	
28.6	9.72	28.3	9.30	28.5	9.5	20.6	6.9	72.5	
30.5	8.72	...	...	...	...	21.9	6.2	71.8	
...	...	33.5	7.50	...	...	23.8	5.3	70.9	
44.2	5.58	...	...	...	...	29.5	3.6	66.9	
...	...	...	...	61.5	4.92	37.0	2.9	60.1	Eutectic
61.5	2.77	[a]	[a]	...	...	37.4	1.7	60.9	NaOH.3.$1H_2O$
62.0	5.23	[a]	[a]	...	...	37.0	3.1	59.9	
60.8	5.10	[a]	[a]	...	...	36.6	3.1	60.3	
61.8	0.00	61.8	0.00	61.8	0.00	38.2	0.00	61.8	
				10° C. Isotherm					
0.00	40.5	0.00	40.6	0.00	40.6	0.0	28.9	71.1	NaOAc.$3H_2O$
1.17	39.8	1.11	39.4	1.14	39.6	0.8	28.2	71.0	
3.38	38.5	3.49	36.7	3.44	37.6	2.4	26.6	71.0	
9.07	30.1	8.92	30.5	9.0	30.3	6.5	21.7	72.8	
15.2	25.2	15.8	23.8	15.5	24.5	11.1	17.5	71.4	
21.1	17.7	21.7	18.1	21.4	17.9	15.3	12.8	71.9	
...	...	30.9	11.7	...	...	21.6	8.2	70.2	
...	...	34.2	10.3	...	...	23.6	7.1	69.3	
35.6	10.2	...	...	...	...	24.4	7.0	68.6	
52.3	10.5	...	...	...	...	32.1	6.5	61.4	
54.8	10.2	55.0	10.2	54.9	10.1	33.3	6.1	60.6	
...	...	...	...	55.0	10.0	33.4	6.1	60.5	Eutectic
55.3	10.5	55.2	11.2	55.3	10.9	33.3	6.6	60.1	NaOAc
60.7	8.8	59.5	8.5	60.1	8.6	35.6	5.1	59.3	
67.4	5.6	66.9	5.5	67.2	5.5	38.9	3.2	57.9	
77.0	3.4	76.5	3.8	76.8	3.6	42.5	2.0	55.5	
...	...	...	...	94.5	2.4	48.0	1.2	50.8	Eutectic
94.5	2.3	94.1	2.3	94.3	2.3	47.9	1.2	50.9	NaOH.H_2O
...	...	95.0	2.2	...	...	47.9	1.2	50.9	
...	0.00	...	0.00	100.08	0.00	50.0	0.00	50.0	
				20° C. Isotherm					
0.00	46.3	0.00	46.3	0.00	46.3	0.0	31.6	68.4	NaOAc.$3H_2O$
11.43	36.1	11.65	36.8	11.54	36.5	7.8	24.6	67.6	
22.0	25.0	21.5	24.5	21.8	24.2	14.0	16.6	68.5	
32.5	16.7	31.9	16.9	32.2	16.9	21.6	11.3	67.1	
...	...	43.3	15.8	...	...	26.2	9.9	63.9	
...	...	47.2	16.1	...	...	28.8	9.8	61.4	
...	...	...	...	53.0	15.7	31.4	9.3	59.3	Eutectic
54.1	14.3	...	...	...	...	32.1	8.5	59.4	NaOAc (anhydrous)
...	...	61.5	9.6	...	...	36.0	5.6	58.4	
66.8	7.3	...	...	...	...	38.4	4.2	57.4	
82.0	4.3	80.1	4.3	81.1	4.2	43.7	2.3	54.0	
89.3	3.1	90.5	3.5	89.9	3.4	46.5	1.8	51.7	
...	...	...	...	101.5	2.8	49.5	1.4	49.1	Eutectic
102.0	2.5	101.6	1.7	101.8	2.1	50.0	1.0	49.0	NaOH.H_2O
				107.5 (8)	0.00	51.8	0.00	48.2	

[a] Mixed crystals even after long standing; equilibrium not reached.

1000-ml. tall-form Pyrex beaker without lip, covered with a wooden lid through which are inserted a tube connected to a suction line and a glass stirring propeller. The sample bottle is a 30-ml. weighing bottle. The sample was filtered through a sintered glass disk of medium porosity.

Duplicate samples of most concentrations were made. Both samples were warmed until clear solutions were obtained. One sample was then held at room temperature (supersaturation in Table I) or above until the other sample had been cooled below the temperature at which the measurement was to be made (undersaturation in Table I). Both samples were then placed in the constant-temperature bath, and the individual stirring propellers were started.

The samples were allowed to remain until equilibrium had been reached. It was found that 24 hours were sufficient for those samples where sodium acetate in some form was the solid phase, but 48 hours were required for those samples where sodium hydroxide in some form was the solid phase.

At the conclusion of the proper time the sampling device, which had been precooled to the bath temperature for several hours, was inserted in the beaker. After the bottle was filled, it was removed and the contents transferred to a clean 50-ml. Erlenmeyer flask and stoppered. Duplicate samples were removed for each determination. The samples were allowed to come to room temperature, and the density was determined at 20° C. by a Westphal balance. Analyses were obtained by titrating 10-ml. aliquots with standardized hydrochloric acid.

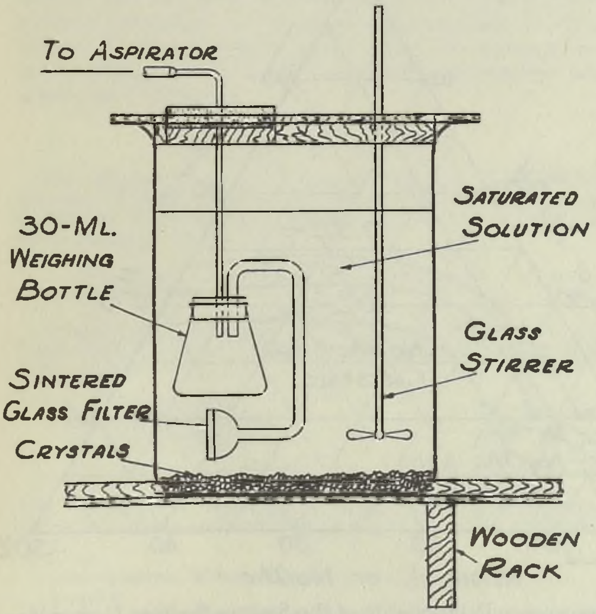

Figure 2. Sampling Apparatus

Samples were titrated with a Beckman pH meter model G. The sodium hydroxide end point, which occurs sharply between pH 8 and 6, agrees with data obtained by Dugger (*2*) and Hull (*5*), using phenolphthalein to indicate the end point. The electrometric method showed that the sodium acetate end point occurs between pH 2.8 and 2.6. Previous data by Dugger (*2*) and Hull (*5*), who used bromophenol blue (pH 3.8–3.1 measured electrometrically) to indicate the end point, were corrected to fit these results and are included in Table I. Bromophenol blue indicator gave results that were low by 11% for sodium acetate.

SOLUBILITY ISOTHERMS

Determinations were made at three different temperatures (0.5°, 10°, and 20° C.) in order to obtain solubility isotherms. The results are shown in two different ways. Figure 3 is plotted on rectangular coordinates as grams of sodium acetate per 100 grams of water against grams of sodium hydroxide per 100 grams of water. Figure 4 is plotted on triangular coordinates to show the percentage relationship of the system sodium acetate–sodium hydroxide–water.

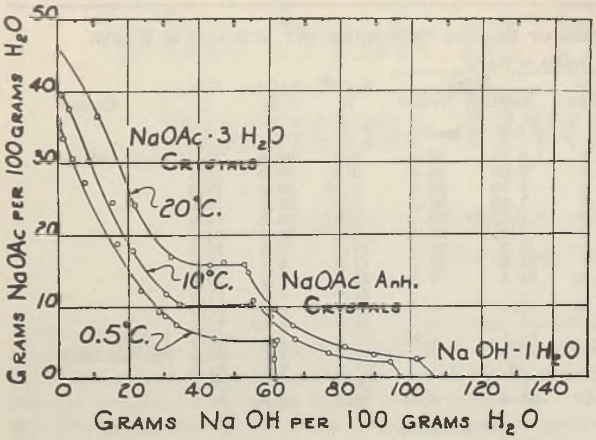

Figure 3. Phase Diagram for the System Sodium Hydroxide–Sodium Acetate–Water

0.5° C. ISOTHERM. In determining this isotherm, it was found that the solubility of pure sodium acetate was 36.3 grams per 100 grams of water. The literature (*4, 6, 9*) gives a value of 36.4 grams of sodium acetate per 100 grams of water, which is within the accuracy of the method. In low concentrations of sodium hydroxide the crystals formed were sodium acetate with 3 molecules of water ($NaOAc.3H_2O$), and in the high sodium hydroxide solutions the crystals were sodium hydroxide with 3.1[1] molecules of water ($NaOH.3.1H_2O$). The eutectic is 61.5 grams of sodium hydroxide per 100 grams of water and 4.92 grams of sodium acetate per 100 grams of water (37.0% sodium hydroxide, 2.9% sodium acetate, and 60.1% water). There is no evidence of mixed crystals or other hydrates at this temperature. The solubility of sodium hydroxide in equilibrium with $NaOH.3.1H_2O$ agrees with the literature (*8*). The data plotted in Figures 3 and 4 are listed in Table I.

10° AND 20° C. ISOTHERMS. At 10° C. the solubility of pure sodium acetate in equilibrium with $NaOAc.3H_2O$ was found to be 40.6 ± 0.1 grams per 100 grams of water, and the solubility at 20° was 46.3 ± 0.1 grams per 100 grams of water. These values agree with those in the literature (*9*). As sodium hydroxide is added, the equilibrium crystals continue to be $NaOAc.3H_2O$ until the concentration of sodium hydroxide reaches 57 and 53 grams per 100 grams of water, respectively, at 10° and 20° C. The compositions of these eutectics are 33.4% sodium hydroxide, 6.1% sodium acetate, and 60.5% water at 10° C. and 31.4 sodium hydroxide, 9.3% sodium acetate, and 59.3% water at 20° C. The curve breaks at this point and the crystals are then anhydrous sodium acetate until a second break occurs at 94 and 102 grams of sodium hydroxide per 100 grams of water, respectively, when the crystals are $NaOH.H_2O$[1]. The latter values are the eutectic points—namely, 48.0% sodium hydroxide, 1.2% sodium acetate, and 50.8% water at 10° C. and 49.5, 1.4, and 49.1%, respectively, at 20°.

CONCLUSIONS

The object of this investigation was to determine the proper operating conditions for the crystallization of sodium acetate from sodium hydroxide solutions in connection with the recovery of waste acetic acid from destructive distillation of pine stumps. The acid may be adsorbed by the proper type of deionizing resin and is regenerated (and concentrated) by passing an alkali solution through the absorbing bed. It has been shown (*1, 7*) that sodium acetate concentrations of the order of 40 to 50 grams per 100 grams of water can be obtained by recycling the regenerant solution after the addition of sufficient sodium hydroxide to maintain the proper alkalinity.

The data presented in this paper indicate that sodium acetate may be most conveniently and efficiently recovered from solutions of the above concentration by crystallizing as $NaOAc.3H_2O$ from sodium hydroxide–sodium acetate solutions containing from 20 to 50 grams of sodium hydroxide per 100 grams of water. Over this range the solubility of sodium acetate is most sensitive to both temperature and sodium hydroxide concentration. Furthermore, equilibrium is reached more quickly, and separation of the crystals from the mother liquor is simpler and easier than with the more viscous solutions of high sodium hydroxide concentration.

The mother liquor from the sodium acetate crystallization still contains appreciable quantities of both sodium acetate and sodium hydroxide. This solution may be used to make up regenerant solution for removing the adsorbed acetic acid. Thus by means of continuous recycling of the regenerant and mother liquor, a recovery of the waste acid in the wood liquors may be very high.

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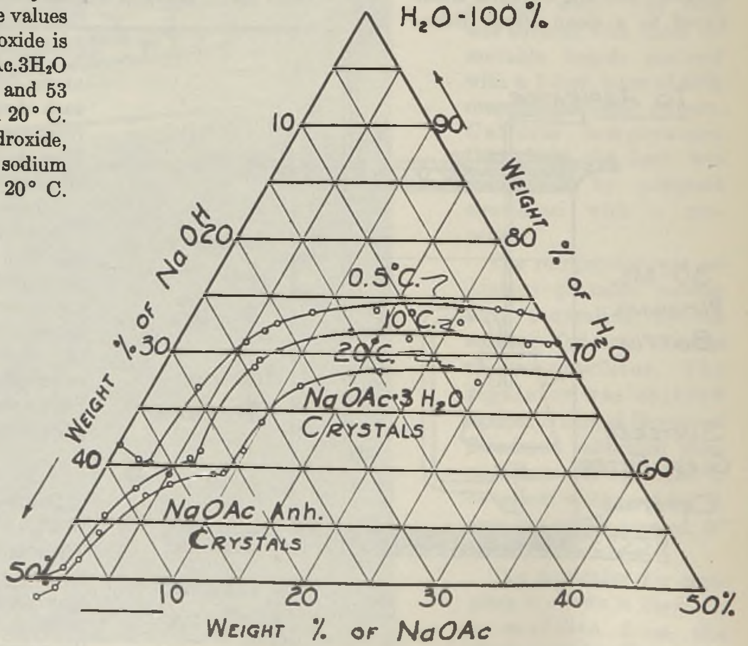

Figure 4. Percentage Relationship of the System Sodium Hydroxide–Sodium Acetate–Water

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[1] This is a metastable form. According to Mathieson Alkali Works (*8*), the stable crystal should be $NaOH.4H_2O$.

Production of 2,3-Butanediol from Acid-Hydrolyzed Starch

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Acid-hydrolyzed starches fermented by *Aerobacter aerogenes* gave 13.5 to 14.0 pounds of 2,3-butanediol per 34 pounds of pure starch (equivalent to one bushel of corn). Proper balance in trace element content was important in determining the efficiency of the fermentation; addition of manganese, cobalt, or molybdenum decreased butanediol production; addition of copper or zinc improved the fermentation of some, but not all, samples. Treatment of starch hydrolyzates by an ion-exchange agent was generally effective in increasing the butanediol yield.

THE fermentation process for the production of 2,3-butanediol from carbohydrates, previously known only on the laboratory scale, has received recent attention from many laboratories. The impetus has come from the wartime urgency of producing 1,3-butadiene for the manufacture of Buna-type synthetic rubbers. A method for producing 1,3-butadiene from 2,3-butanediol, based on the pyrolysis of the diacetate, had previously been disclosed by Hill and Isaacs (*8*).

Bacteria of the *Bacillus polymyxa* type convert unsaccharified starchy substrates to *l*-2,3-butanediol (*14*) and ethyl alcohol, whereas bacteria of the genus *Aerobacter* transform most mono- and disaccharides principally to *m*-2,3-butanediol (*2, 14*) accompanied by small quantities of *d*-2,3-butanediol and ethyl alcohol. Use of the latter bacteria requires that starchy substrates be converted to reducing sugar either by acid or enzymes prior to fermentation. The fermentation of refined sugar solutions and of saccharified grain mashes by *Aerobacter* will be discussed in detail in later communications. The present paper is concerned primarily with the production of 2,3-butanediol from acid-hydrolyzed refined wheat and corn starches, which have not been used previously as a source for butanediol. Starch hydrolyzates were studied as substrates for butanediol production primarily because it was believed that the recovery of butanediol would be more easily accomplished from the resulting fermented liquors than from whole grain mashes. Starches are cheaper than refined glucose but more expensive than grain on the carbohydrate basis.

The object of the present investigations was to determine the proper laboratory cooking conditions for preparing fermentable mashes from starch by acid hydrolysis and to ascertain the yields of butanediol. In the course of the investigation, variations in the fermentation of starch hydrolyzates were observed, and some degree of success was attained in explaining and overcoming these variations.

MATERIALS AND METHODS

The organism used, *Aerobacter aerogenes* NRRL-B199, has been found to be among the best butanediol-producing strains. It was maintained in stock culture on agar slants of the following medium (in grams per liter):

Difco tryptone	5	Difco yeast extract	5
Glucose	1	Agar	15

Inoculum was developed by growing the organism 8 to 20 hours at 30° C. in an unagitated and unaerated medium of the composition:

Glucose, grams	50
$MgSO_4.7H_2O$, gram	0.25
KH_2PO_4, gram	0.60
$CaCO_3$, grams	5.0
Distilled water to make 1 liter	

The medium was dispensed in 100-ml. portions into 200-ml. Erlenmeyer flasks and sterilized by steam at 121° C. for 30 minutes. When the organism was inoculated into this medium from agar slants, 1 ml. of sterile 20% urea solution was also added to each flask. (The urea was sterilized separately from the glucose solution to avoid excessive caramelization of the latter.)

The main fermentation medium was prepared by cooking 3-liter portions of aqueous starch suspensions (usually of about 10% concentration) in 6-liter Florence flasks in a laboratory sterilizer at 22 to 25 pounds steam pressure (128° to 131° C.) for periods up to 4 hours. Hydrochloric and sulfuric acids (C.P.) were used as hydrolysis catalysts. Acid concentrations of the starch slurries during hydrolysis ranged from 0.02 to 0.12 normal. Before steaming, the acidic starch slurries were gelatinized in a hot water bath while being agitated; this procedure avoided lumping and was conducive to a more uniform and efficient saccharification. All production media contained, per liter, besides the saccharified starch: $MgSO_4.7H_2O$, 0.25 gram; KH_2PO_4, 0.60 gram; urea, 2.0 grams; and calcium carbonate 5.0 to 10.0 grams. This salt and urea composition had been found near optimal in previous studies of the fermentation of glucose media. (Extra calcium carbonate was supplied in the one instance where 0.12 *N* hydrochloric acid was employed for hydrolysis.) The first two salts were added to the medium before cooking; the urea and calcium carbonate were each sterilized separately (the former as a 20% aqueous solution, the latter dry) and were added before inoculation. The quantity of calcium carbonate employed was sufficient to neutralize to pH 5.5–6.0 the acid used for hydrolysis, and also to act as a means of pH control during the fermentation. After addition of all the components, each 3-liter lot of medium was inoculated with 100 ml. of an 8- to 20-hour-old inoculum culture.

The fermentations were conducted in rotating aluminum drum fermenters (*7*) which were operated at 30° C., 10–12 r.p.m., 5 pounds gage pressure, and an air flow of 50 to 100 ml. per minute, which had been found near-optimal conditions in previous studies of butanediol production from glucose.

Except for one lot of wheat starch prepared at this laboratory, all wheat and corn starches employed were commercial samples obtained from representative manufacturers.

The progress of the fermentations was followed by analyses for reducing sugar, by the cuprous titration method of Shaffer and Hartmann (*11*). Total sugar was determined by subjecting 5 ml. of the mash to the action of 25 ml. of 0.24 *N* hydrochloric acid in the laboratory sterilizer for 1 hour at 121° C.; reducing sugar was then determined on a portion of the neutralized hydrolyzate. This method was adopted because it was convenient for routine work, produced a near-maximum quantity of reducing sugar from starch, and caused no appreciable destruction of glucose, as measured by copper reduction.

2,3-Butanediol was determined by periodic acid oxidation of an extract or distillate prepared from the culture media, essentially according to the method of Johnson (*9*). A correction for acetoin was necessary. Acetoin was determined by an unpublished colorimetric method, based on the reduction of Folin-Wu phos-

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Table I. Effect of Cooking Conditions on Butanediol Yield from Starch 2778

(Mashes 1 and 2 hydrolyzed 1.25 hours at 130° C.; mashes 3 and 4 hydrolyzed 4 hours at 130° C.; distilled water used throughout)

Fermenter No.	HCl Concentration	Sugar, Grams/100 Ml. Original Free	Sugar, Grams/100 Ml. Original Total	Sugar, Grams/100 Ml. Final (free)	Fermentation Time, Hr.	Products, Grams/100 Ml. Butanediol	Products, Grams/100 Ml. Acetoin	Products, Grams/100 Ml. Ethyl alcohol
1	0.12 *N*	10.04	10.36	0.30	32	3.72	0.20	0.33
2	0.12 *N*	10.35	10.36	0.38	33	3.74	0.11	0.25
3	0.04 *N*	10.25	10.30	0.52	47	4.23	0.21	0.07
4	0.02 *N*	10.22	10.48	0.49	40	4.18	0.16	0.20

phomolybdic acid reagent by this compound. No correction for interfering substances was necessary. Ethyl alcohol was determined by observing the refractive index of a distillate from a long packed column which held back all the 2,3-butanediol. An empirical correction was applied for diacetyl produced from the acetoin present by virtue of its reaction with alkaline copper reagent, which was added to the distillation flask. The analytical methods for 2,3-butanediol, acetoin, and ethyl alcohol mixtures are exacting. They require the application of several correction factors and will be published later.

In so far as possible, all fermentations were terminated as soon as the minimum reducing sugar concentration was reached; previous investigations had shown that maximum 2,3-butanediol production coincided with this point. The yields shown in the tables are expressed as percentages of the theoretical yields, based on reducing sugar consumed. This method of calculation largely avoids deviations between various experiments due to differences in medium concentration or in degree of completeness of fermentation.

HYDROLYSIS CONDITIONS

A hydrolysis procedure that would yield the maximum quantity of fermentable sugar was desired, so as to obtain the highest possible yield of butanediol from a given quantity of starch. Goering (*6*) found that cooking starch 4 hours at 25 pounds steam pressure with 0.02 *N* sulfuric acid yielded hydrolyzates from which high yields of alcohol were obtained. In the industrial production of dextrose by the acid hydrolysis of cornstarch, approximately 0.025 *N* hydrochloric acid is employed 30 minutes at about 45 pounds pressure. Accordingly, it appeared likely that the use of approximately 0.02 *N* acid would yield fermentable mashes which would have a high dextrose equivalent and would not require the addition of a large quantity of neutralizing agent prior to fermentation; thus, a high salt content was avoided which might have an unfavorable effect on the fermentation and on recovery operations.

To compare the effects of different laboratory cooking conditions on butanediol production, mashes were prepared from starch 2778, a refined wheat starch supplied by an industrial concern. This starch contained 8.19% moisture, and analyzed 98% starch on the dry basis, by the A.O.A.C. starch-by-diastase method (*1*). Two mashes (350 grams of starch in 3 liters total volume) were cooked 1.25 hours under pressure at 130° C. with 0.12 *N* hydrochloric acid in distilled water, and two other similar mashes were cooked 4 hours at the same temperature with 0.02 *N* and 0.04 *N* hydrochloric acid in distilled water. After cooling, 40 grams of sterile calcium carbonate and 20 ml. of 5 *N* sodium hydroxide were added to the mashes cooked with 0.12 *N* hydrochloric acid, and 25 grams of sterile calcium carbonate were added to the mashes cooked with the more dilute acid. The sodium hydroxide was required to bring the pH of the more acid cooks up to the range (5.5 to 7.0) known to be desirable for the initiation of fermentation, but no sodium hydroxide was required for the hydrolyzates prepared with the smaller quantities of acid. Table I gives results of fermentation of these mashes; Table II shows yields on the basis of pounds of butanediol per 100 pounds of starch as received and 34 pounds of moisture-free starch (equivalent to one bushel of corn). It is assumed that 0.07 gram of butanediol per 100 ml. of mash was derived from the glucose in the inoculum. The acetoin and ethyl alcohol from this source are ignored, since they were very small in quantity. The yields of butanediol from starch 2778, especially when low acid concentrations were used for hydrolysis, were among the best obtained from acid-hydrolyzed starches.

At the time when these good yields were being obtained from starch 2778, much poorer yields (approximately 10 pounds of butanediol per 34 pounds of starch) were being obtained from another wheat starch, designated as SS, even though it was hydrolyzed and fermented in the same manner. This starch had been prepared by a wet-milling process (*13*) from a soft white winter wheat grown in Michigan. Distilled water had been used in the manufacture of this starch, and the following percentage analyses (dry basis) show that it was of a purity at least equal to that of starch 2778:

	Starch SS	Starch 2778
Ash	0.12	0.15
Starch	98	98
Protein (N × 5.7)	0.19	0.32

Typical results obtained upon fermenting untreated hydrolyzates of starch SS are shown in Table III. Not more than 60% of the fermented sugar appeared as butanediol, and almost 20% was accounted for as ethyl alcohol. This was in marked contrast to the results obtained by the fermentation of starch 2778 (Table II), which gave a 74 to 86% conversion of reducing sugar to butanediol and only about 5% conversion to ethyl alcohol. Hydrolyzates of starch SS fermented much faster than hydrolyzates of starch 2778.

ANAEROBIC FERMENTATION

Table IV presents results of a study of the anaerobic fermentation of hydrolyzates of the two starches, of an unsupplemented glucose-nutrient salt medium, and of a glucose-nutrient salt medium supplemented with concentrated corn steep liquor (5 grams per liter). These fermentations were conducted in the aluminum fermenters, which were revolved but were not supplied with air. The hydrolyzate of starch 2778, like the unsupplemented glucose medium, required about 60 hours to complete the fermentation, whereas the hydrolyzate of starch SS fermented in 31 hours. Starch SS fermented about as fast anaerobically as aerobically, whereas starch 2778 fermented much more slowly anaerobically than it did aerobically. When fermented anaerobically, all mashes produced large quantities of ethyl alcohol; in fact, the ratio between butanediol and ethyl alcohol was approximately 2 to 1, the same as has been consistently obtained in the fermentation of unsaccharified grain mashes by *Bacillus polymyxa* under anaerobic conditions. The addition of 0.5% corn steep liquor to the glucose medium greatly accelerated the rate of fermentation but had virtually no effect on the ratio of products formed under these conditions.

Table II. Yields Calculated from Table I

Fermenter No.	Yield, Lb./100 Lb. Starch (as Received) Butanediol	Yield, Lb./100 Lb. Starch (as Received) Acetoin	Yield, Lb./100 Lb. Starch (as Received) Ethyl alcohol	Yield, Lb./34 Lb. Pure Dry Starch Butanediol	Yield, Lb./34 Lb. Pure Dry Starch Acetoin	Yield, Lb./34 Lb. Pure Dry Starch Ethyl alcohol	Yield, % of Theoretical, Based on Glucose Consumed[a] Butanediol	Yield, % of Theoretical, Based on Glucose Consumed[a] Acetoin	Yield, % of Theoretical, Based on Glucose Consumed[a] Ethyl alcohol
1	32.5	1.8	2.9	12.3	0.7	1.1	75	4	7
2	32.7	1.0	2.2	12.4	0.4	0.8	74	2	5
3	36.8	1.9	0.6	13.9	0.7	0.2	86	4	1
4	36.4	1.4	1.8	13.8	0.5	0.7	85	3	4

[a] "Glucose consumed" is assumed to equal original free sugar minus final free sugar.

Table III. Butanediol Production from Untreated Hydrolyzates of Starch SS

(All mashes cooked 4 hours at 130° C.)

Fermenter No.	Acid and Water Used for Hydrolysis	Fermentation Time, Hr.	Glucose Consumed, G./100 Ml.	Products, Grams/100 Ml. Butanediol	Acetoin	Ethyl alcohol	Yield, % of Theoretical, Based on Glucose Consumed Butanediol	Acetoin	Ethyl alcohol
1	0.03 *N* HCl in distd. water	22	9.05	2.79	0.10	0.86	60	2.4	19.0
2	0.05 *N* H_2SO_4 in tap water	17	8.1	2.29	0.18	0.66	55	4.4	16.0
3	0.05 *N* H_2SO_4 in tap water	18	8.2	2.39	0.17	0.77	57	4.2	18.4

Table IV. Anaerobic Fermentation of Glucose Medium and Hydrolyzates of Starch 2778 and Starch SS

(Distilled water used throughout; media for fermenters 1 and 2 sterilized 0.75 hour at 121° C.; mashes for fermenters 3 and 4 cooked 4 hours at 130° C.)

Fermenter No.	Carbohydrate Employed	Acid for Hydrolysis	Fermentation Time, Hr.	Glucose Consumed, G./100 Ml.	Products, Grams/100 Ml. Butanediol	Acetoin	Ethyl alcohol	Yield, % of Theoretical, Based on Glucose Consumed Butanediol	Acetoin	Ethyl alcohol
1	Glucose	None	63	9.9	2.79	0.02	1.29	55	0.4	26
2	Glucose + 0.5% corn steep liquor	None	39	9.5	2.52	0.07	1.21	52	1.5	25
3	Starch 2778	0.04 *N* HCl	65	10.0	2.99	0.09	1.35	58	1.8	26
4	Starch SS	0.10 *N* HCl	31	9.9	2.58	0.08	1.28	51	1.6	25

Table V. Comparison of Fermentations of Starch 2778 Hydrolyzed in Distilled Water and in Peoria Tap Water[a]

Fermenter No.	Water	Acid for Hydrolysis	Fermentation Time, Hr.	Glucose Consumed, G./100 Ml.	Products, Grams/100 Ml. Butanediol	Acetoin	Ethyl alcohol	Yield, % of Theoretical, Based on Glucose Consumed Butanediol	Acetoin	Ethyl alcohol
1	Distilled	0.08 *N* H_2SO_4	42	11.89	4.43	0.24	0.33	73	4.1	5
2	Peoria tap	0.08 *N* H_2SO_4	37	12.1	3.63	0.20	0.97	59	3.2	15.7
3	Peoria tap	0.03 *N* HCl	24	8.50	2.47	0.10	0.51	57	2.4	11.7

[a] All mashes cooked 4 hours at 130° C. Further examples of distilled water with starch 2778 are given in Table I.

EFFECT OF VARIOUS FACTORS

Growth Factors. No difference in the proportions of ethyl alcohol and butanediol was observed when aerated glucose cultures were supplemented with biotin, nicotinic acid, *p*-aminobenzoic acid, pyridoxin, inositol, thiamine, riboflavin, and sodium pantothenate. Therefore, it was considered unlikely that these compounds were responsible for the anomalous results obtained with some starch hydrolyzates.

Acid, Alkali, Alcohol. Three portions of starch SS were subjected to exhaustive extraction in the cold with 0.1 *N* sodium hydroxide, 0.1 *N* hydrochloric acid, and 65% aqueous ethyl alcohol, and the extracted starch was used for preparing fermentation mashes. Neither alcohol nor hydrochloric acid produced any improvement in this starch, but the sodium hydroxide treatment increased the butanediol yield to about 72% of theoretical and greatly decreased ethyl alcohol production.

Trace Elements. When Peoria tap water instead of distilled water was used in preparing mashes of starch 2778, the yield of butanediol decreased, the yield of ethyl alcohol increased, and the fermentation time was reduced (Table V). This suggested that the fermentation of starch hydrolyzates might be influenced adversely by traces of metallic elements in the Peoria water supply and also in starch SS but absent from starch 2778. Peoria tap water (*4*, *5*, *10*) is reported to contain the following:

Fe	0.1–0.3 p.p.m.	F	About 0.1 p.p.m.
Ca	72–97	SiO_2	13–17
Mg	37–46	HCO_3	420–437
Na	About 25	SO_4	5–52
K	About 4	Cl	14–23
Mn	About 0.12	NO_3	1–4

Spectroscopic analyses of the ashes of the two starches showed striking differences in relative content of inorganic elements. Starch 2778 contained about ten times as much lead, copper, iron, and strontium, about five times as much zinc, about twice as much calcium, about the same quantity of boron, phosphorus, aluminum, tin, silicon, nickel, and vanadium, and about half as much manganese, magnesium, molybdenum, chromium, and titanium as did starch SS. The absolute quantities of the various elements were determined only in the case of nickel, which was found to be present to the extent of 1 to 2 parts per million parts of starch.

Added Ions. These trace element data suggested determining the effect of added ions on the fermentation of hydrolyzates of starch 2778 (Table VI). At the ion concentrations employed, copper, fluorine, or a mixture of iron and zinc had little effect on butanediol or alcohol production; manganese (5 p.p.m.), cobalt, or a mixture of cobalt and molybdenum greatly reduced the quantity of butanediol formed. Alcohol production was stimulated by cobalt and by the cobalt-molybdenum mixture. Nickel, chromium, or fluorine (0.1 p.p.m.) increased butanediol production appreciably above the value obtained from the control culture, but not above the yield obtained in similar control cultures in other experiments. Fluorine and manganese, added together at the concentrations in which they occur in Peoria tap water, had little effect on butanediol or alcohol production, but did appear to accelerate the fermentation appreciably. Increasing the fluorine concentration tenfold, in the presence of the same quantity of manganese, caused no appreciable change in the results obtained. Although these experiments did not fully explain the tap water effect, they showed that traces of certain metallic elements could influence the production of ethyl alcohol and have a pronounced deleterious effect on butanediol production from a starch that otherwise would give a good yield of this product.

IMPROVEMENT IN YIELDS

Ion-Exchange Agents. Removal of the injurious ions by precipitation was adjudged impossible owing to the appreciable solubility of the common compounds, particularly the hydroxides, carbonates, and sulfides, of some of the metals concerned. Ionic substitution by cation-exchange agents was therefore investigated. A hydrolyzate prepared from starch SS was adjusted to pH 5.1 and filtered to remove the slight flocculent precipitate always present at this stage. A 1-liter portion of the filtrate was then stirred for 30 minutes with 20 grams of Zeo-Karb H (regenerated on the hydrogen cycle). After separation

TABLE VI. EFFECT OF ADDED IONS ON BUTANEDIOL PRODUCTION FROM HYDROLYZATES OF STARCH 2778

(All media prepared with distilled water and hydrolyzed 4 hours at 130° C. with 0.03 *N* HCl)

Fermenter No.	Element Added,[a] P.P.M.	Fermentation Time, Hr.	Glucose Consumed, G./100 Ml.	Products, Grams/100 Ml.			Yield, % of Theoretical, Based on Glucose Consumed		
				Butanediol	Acetoin	Ethyl alcohol	Butanediol	Acetoin	Ethyl alcohol
1	None	26	7.61	2.89	0.17	0.12	74	4.6	3.1
2	5 Fe + 5 Zn	32	8.46	2.99	0.21	0.15	69	5.1	3.5
3	5 Mn	27	8.64	2.41	0.37	[b]	54	8.8	[b]
4	0.1 Cu	31	8.50	3.09	0.25	[b]	71	6.0	[b]
5	1 Co + 1 Mo	27	8.46	2.36	0.15	0.75	54	3.6	17.4
6	0.1 Ni	28	7.51	3.04	0.06	0.04	79	1.6	1.1
7	0.1 Cr	26	7.43	3.11	0.06	0.12	82	1.6	3.3
8	1 Co	23	7.86	2.42	0.11	0.63	60	2.9	15.7
9	0.1 F	30	8.85	3.57	0.13	0.26	79	3.0	5.8
10	1.0 F	29	8.83	3.33	0.30	0.26	74	6.9	5.8
11	0.1 F + 0.12 Mn	20	8.58	2.74	0.55	0.23	62	13.1	5.3
12	1.0 F + 0.12 Mn	24	8.30	3.12	0.16	0.22	74	3.9	5.2

[a] The elements were supplied in the form of the following salts: $FeSO_4$, $ZnSO_4$, $MnSO_4$, $CuSO_4$, $Co(CH_3COO)_2$, $(NH_4)_2MoO_4$, $NiSO_4$, K_2CrO_4, and NaF. The salts were added to the starch slurries prior to gelatinization and hydrolysis.

[b] None detected.

TABLE VII. EFFECT OF TREATING HYDROLYZATES OF STARCH SS WITH ZEO-KARB H AND WITH DARCO G-60

(All mashes made with distilled water and hydrolyzed 4 hours at 130° C. with 0.03 *N* HCl)

Fermenter No.	Treatment Prior to Fermentation	Fermentation Time, Hr.	Glucose Consumed, G./100 Ml.	Products, Grams/100 Ml.			Yield, % of Theoretical, Based on Glucose Consumed		
				Butanediol	Acetoin	Ethyl alcohol	Butanediol	Acetoin	Ethyl alcohol
1	Darco G-60 at pH 4.9	18	5.57[a]	1.70	0.04	0.12	59	1.5	4.2
2	Darco G-60 at pH 8.0	19	6.28[a]	1.87	0.06	0.31	57	2.0	9.7
3	Zeo-Karb H at pH 5.1 & separated before fermentation	24	6.32[a]	2.29	0.10	[b]	70	3.2	[b]
4	Zeo-Karb H present during cooking and fermentation	22	8.69	2.43	0.26	0.34	54	6.1	7.7
5	Zeo-Karb H added at pH 1.6 & present in medium during fermentation	23	8.38	2.42	0.12	0.59	56	2.9	13.8
6	Zeo-Karb H contacted at pH 1.6, separated before pH was raised	43	8.13	1.55	0.17	0.02	36	4.3	0.5

[a] These mashes became diluted during the treatments; fermentation was practically complete in all cases.

[b] None detected.

of the Zeo-Karb H by filtration, the solution was supplemented with the usual nutrient salts and sterilized, then inoculated and fermented in the customary manner. The favorable results are shown in Table VII (fermenter 3).

It was found necessary to separate the ion-exchange agent from the treated solution prior to fermentation. Treatment with Zeo-Karb H at pH 1.6 (the pH of the mash immediately after hydrolysis) gave particularly poor results.

Treatment with activated carbon at pH 8.0 was successfully employed by Bortels (*3*) to remove trace elements from nutrient media. Two 1-liter portions of the above hydrolyzate were treated with 20 grams of Darco G-60; one portion was contacted with the carbon at pH 4.9 and the other portion at pH 8.0. After removal of the carbon by filtration, the solutions were supplemented with the necessary nutrient salts and fermented. No improvement resulted from these treatments (Table VII).

The batch treatment with the ion-exchange agent employed in these experiments is less efficient than continuous passage of the solution through a column or tower containing the ion exchanger. In the authors' work the latter method has been successfully employed with many samples of starch hydrolyzate liquors.

The efficacy of the ion-exchange treatment for improving the fermentation characteristics of mashes was further demonstrated by the treatment of starch hydrolyzates prepared in a pilot plant iron cooker. Such liquors, when supplemented with the usual salts, urea, and calcium carbonate, would not ferment, presumably because of the high iron content. However, when these hydrolyzates were subjected to treatment with Zeo-Karb H in the manner described for fermenter 3 (Table VII), fermentation proceeded at a normal rate and normal yields of products were obtained. The fermentation characteristics of starches hydrolyzed in bronze and copper equipment have shown similar improvement after treatment with Zeo-Karb H.

Comparative studies were made on samples of commercial starch-converter liquors that had been prepared continuously in bronze equipment. It was generally observed that such hydrolyzates fermented a little more slowly than hydrolyzates prepared in glass apparatus; some samples showed a marked slowness in initiating fermentation. However, all such commercial samples were more suitable for fermentation than hydrolyzates prepared in our infrequently operated pilot-plant equipment. Starch-converter liquors that had been treated with Zeo-Karb H fermented more rapidly than untreated samples; presumably the copper content was reduced to a noninhibitory level by the ion-exchange treatment.

ION ADDITIONS. Since considerable copper was found in the ash of starch 2778, which had given good yields of butanediol, the effect of added copper ion on the fermentation of hydrolyzates of starch SS was determined. Hydrolyzates prepared with Peoria tap water were treated with copper sulfate at concentrations to yield 0.01, 0.10, and 1.0 part of copper per million parts of medium (Table VIII). It was found that copper greatly improved the yield of butanediol and reduced the yield of ethyl alcohol.

The response of hydrolyzates of twenty-four corn and wheat starches to the addition of copper (0.01 p.p.m.) was investigated to determine if it would be desirable to add this quantity of copper to all hydrolyzed starch mashes to increase the yield of butanediol. None of the starches investigated showed such striking improvement as was noted for starch SS (8 to 14% increase in butanediol yield). Six samples showed 5 to 7% increases in butanediol yield; five samples showed 2 to 4% increases; ten samples showed substantially no change; and three samples showed 6 to 15% decreases.

Studies were conducted to determine if hydrolyzates of some of these commercial starches might be improved for use in the butanediol fermentation by the addition of traces of metallic ions other than copper. Most samples showed no improvement with the limited number of ions tested. Table IX shows results obtained with cornstarch 2892, which showed poorer fermentation efficiency in tap water than in distilled water, no improvement from copper, but considerable improvement from treatment with zinc. Although many of the starches studied gave poorer yields of butanediol in tap water than in distilled water, several samples gave a good as or better yields than in tap water.

DISCUSSION

These studies indicate that trace elements play an important role in the production of 2,3-butanediol from acid-hydrolyzed starch. The presence of certain ions, particularly those of manganese, cobalt, or molybdenum, is reflected in a decreased production of 2,3-butanediol and an increased production of ethyl alcohol under aerobic conditions, and an increased rate of fermentation under anaerobic conditions. As is usually the case with trace-element phenomena, the balance between various ions appears to be a determinative factor. The present investigation has shown that mashes which are unbalanced with respect to ions can be improved, for fermentation purposes, by treatment with an ion-exchange agent or by addition of traces of certain metallic ions, such as copper and zinc. The latter treatment has given satisfactory results for individual samples studied but does not appear to be broadly applicable, since each lot of starch must be tested and prescribed for, according to its needs. The ion-exchange treatment, on the other hand, appears to be generally applicable; it has corrected the naturally existing unbalance of ions in starch hydrolyzates and has also removed excessive quantities of adventitious iron and copper from hydrolyzates prepared in metal equipment.

Metallic ions in starch hydrolyzates may be derived from several sources. They may originate in the grain itself and not be separated from the starch during its manufacture; they may be absorbed or adsorbed from processing water by the starch granules during manufacture; they may be present in the water used for preparing the hydrolyzates; and they may arise from the corrosion of metallic equipment used for the acid hydrolysis.

The precise functions of the injurious and the corrective metallic ions are not understood. Virtually nothing is known regarding the enzyme systems that catalyze the production of the four-carbon compounds, butanediol and acetoin, or that shift the metabolism of *Aerobacter* toward production of these compounds in preference to ethyl alcohol; it may be that some of the metals (copper, zinc, manganese, cobalt, molybdenum) found to influence butanediol production from starch hydrolyzates play some part in these systems. Silverman (*12*) reported that an enzyme preparation, isolated from *Aerobacter aerogenes* and able to effect the quantitative conversion of pyruvic acid to carbon dioxide and acetoin, required the presence of cocarboxylase and either Mn^{++} or Mg^{++}.

The possibility of some minor organic constituent of the starches playing an important role in these enzymic processes cannot be overlooked; increased butanediol production from starch SS, which was treated with sodium hydroxide, might be explained on the basis of inactivation or extraction of some deleterious principle.

The majority of starch samples studied have given yields of butanediol equivalent to approximately 13 pounds per 34 pounds of starch. The theoretical yield is 18.9 pounds. Losses in yield are due to the incomplete conversion of starch to fermentable sugar by the hydrolysis procedure, to reversion and destruction of glucose by the acid treatment, and to the fact that not all of the fermentable sugar is converted to butanediol in the fermentation. According to information received from industrial operators, approximately 95% conversion of starch to glucose is possible in plant operation when relatively low starch concentrations (10%) are used. In the best laboratory fermentations (Table I, fermenters 3 and 4) about 86% of the fermented reducing sugar was converted to butanediol. Using 95 and 86% as the maxima to be expected for glucose formation and butanediol formation, respectively, a possible yield figure of ($0.95 \times 0.86 \times 18.9 =$) 15.5 pounds of butanediol per bushel of grain (34 pounds of starch) is obtained. This value is considerably in excess of the best yields obtained in the present investigations. In the cookers employed, heat penetration through the unagitated mash was relatively slow, and there was evidence that the mash near the walls of the flasks was overconverted before the mash at the center of the flasks was sufficiently heated. Pilot-plant cooking tests, conducted by co-workers, have shown that more efficient hydrolysis can be attained in agitated cookers or continuous cookers. It appears that little trouble would be encountered in fermenting commercially produced starch hydrolyzates, particularly if the hydrolyzing equipment was operated continuously. Bronze converters maintained in continuous operation undergo less corrosion than converters operated at infrequent intervals.

Recently, considerable work has been done on the fermentation of acid-hydrolyzed whole-grain (corn and wheat) mashes by workers at the University of Wisconsin, by the research staff of Joseph E. Seagram & Sons, Inc., and by the Northern Regional Research Laboratory. Such mashes were found to yield 13 to 14 pounds of butanediol per bushel of grain processed, without especial attention being given to the metallic ion content of the mash. The ion content is apparently not determinative in whole grain mashes, possibly because of the much higher concentration of all metallic constituents and probably because of the protective action exerted by the proteinaceous constituents. (It is well known that concentrations of heavy metals, which are toxic to organisms in media low in protein, are not toxic to the same organisms in media that are rich in proteinaceous substances.) Whether starch or whole grain would be preferred for the industrial production of 2,3-butanediol would be dependent upon the ability to recover the 2,3-butanediol from the fermented mashes, and upon the importance attached to the recovery of high-quality by-product feed. From the standpoint of fermentation only, it would appear that better average yields could be obtained from acid-hydrolyzed whole grain mashes, and that such mashes would require less adjustment of composition.

TABLE VIII. EFFECT OF ADDED COPPER ION ON BUTANEDIOL PRODUCTION FROM HYDROLYZATES OF STARCH SS

(All mashes made with tap water and hydrolyzed 4 hours at 130° C. with 0.05 *N* H_2SO_4)

Fermenter No.	Cu Added, P.P.M.	Fermentation Time, Hr.	Glucose Consumed, G./100 Ml.	Products, Grams/100 Ml.			Yield, % of Theoretical, Based on Glucose Consumed		
				Butanediol	Acetoin	Ethyl alcohol	Butanediol	Acetoin	Ethyl alcohol
1	None	16	7.33	1.95	0.29	0.80	51	8.1	21.4
2	0.01	16	7.56	2.69	0.14	0.23	69	3.8	6.0
3	0.1	17	7.53	2.54	0.27	0.10	66	7.3	2.6
4	1.0	17	7.31	2.64	0.15	[a]	70	4.2	[a]

[a] None detected.

TABLE IX. EFFECT OF METALLIC IONS ON BUTANEDIOL PRODUCTION FROM HYDROLYZATES OF CORNSTARCH 2892

(All mashes hydrolyzed 4 hours at 130° C. with 0.033 *N* HCl; metals, supplied as $CuSO_4$ and $ZnSO_4$, were added to starch slurries before gelatinization of hydrolysis)

Fermenter No.	Metal Added, P.P.M.	Water	Fermentation Time, Hr.	Glucose Consumed, G./100 Ml.	Products, Grams/100 Ml.			Yield, % of Theoretical, Based on Glucose Consumed		
					Butanediol	Acetoin	Ethyl alcohol	Butanediol	Acetoin	Ethyl alcohol
1	None	Distilled	18	6.57	2.40	0.11	0.37	71	3.4	11.0
2	None	Peoria tap	19	7.60	2.13	0.22	0.62	54	5.9	16.0
3	1 Cu	Peoria tap	19	7.37	2.04	0.16	0.67	54	4.4	17.8
4	5 Zn	Peoria tap	17	7.03	2.89	0.06	0.43	80	1.7	12.0

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ZEIN FIBERS . . . . .

Preparation by Wet Spinning

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A new method for producing textile fibers from zein and the equipment used in the process are described. Zein fibers which have high tensile strength and wool-like properties are produced from alkaline dispersions of zein. The spinning dispersions are formulated to give a product of high viscosity by the use of denaturing agents, such as alcohol or urea, or by aging the solutions. The filaments are coagulated in an acid bath in which salts may or may not be used. The coagulated filaments are given a mild formaldehyde precure prior to stretching and drying. The influence of the extent of precure on the load-elongation properties of the fiber and on fiber strength is determined. Shrinkage and water resistance of the fibers are controlled by acetylation followed by a strong formaldehyde treatment.

PROCESSES for making protein fibers from zein have been patented by Swallen (*6*) and Meigs (*4*) and reviewed briefly by Harold (*3*). The Swallen process involves the use of organic solvents such as ethyl alcohol in the preparation of the spinning solution. This process also uses 20% or more of plasticizer and 2 to 5% of formaldehyde in the spinning dispersion, and extrudes the solutions through standard spinnerettes. The extruded filaments are solidified by evaporation of the solvent (dry spinning) or by a liquid coagulant (wet spinning).

Meigs described a wet spinning process for a wide variety of proteins—namely, the "globulins, prolamines, and phosphoproteins"—and includes zein among the proteins he uses for examples. The Meigs patent contains rather startling claims for stretching the fibers 300 to 2000%, regardless of the type of protein used.

Zein has been mentioned in other patents as one of the proteins from which fibers can be spun or regenerated. However, the absence in the literature of any information on their strength or other properties makes impossible their practical evaluation or comparison with other fibers.

Zein is the only prolamine which has attained any substantial industrial importance. Its solubility in organic solvents has determined to a large extent its commercial utilization for films and coatings, and at present its largest use is as a replacement for shellac. Likewise, the fiber spinning methods described in the literature use organic solvents in the preparation of spinning solutions.

This investigation was directed toward the development of a practical process for making zein fibers by a wet spinning method and toward evaluation of the fibers. The equipment used in this work differs from that for spinning viscose rayon and other protein fibers only in details of construction and in arrangement. Data are presented on the preparation of zein-spinning dispersions, the effect of treating the fiber with formaldehyde prior to stretching (precure), and the effect of precure on the wet and dry strengths of the fibers.

The use of traditional organic solvents for zein has been temporarily abandoned in the present investigation, and an aqueous alkaline dispersion for wet spinning has been developed. The object in making the change is to avoid the extra cost which arises in recovering organic solvents. It has been known for some time that zein is soluble in alkaline solution, but only recently the details of this type of dispersion have been investigated and its limitations defined by Ofelt and Evans (*5*). In their studies on the solubility of zein in sodium and potassium hydroxide and quaternary ammonium hydroxide, Ofelt and Evans showed that a highly concentrated zein solution can be prepared in the pH range 11.3 to 12.7. A complete description of this dispersion procedure is being prepared for publication.

AQUEOUS SPINNING DISPERSION

High-viscosity zein solutions of 13 to 16.5% concentration are required for spinning fibers, and the upper limits in this range

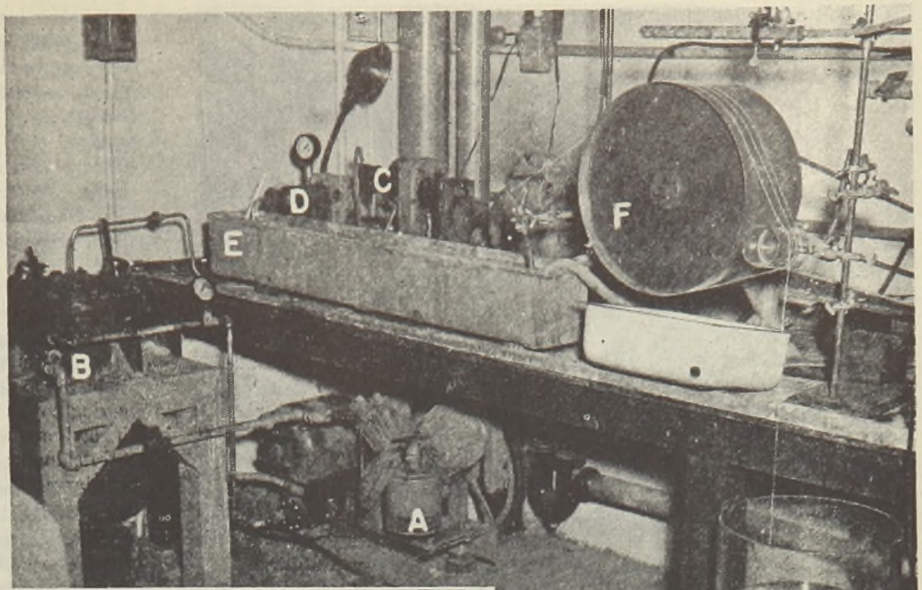

Figure 1 (*Right*). Fiber Spinning Assembly through First Unit Operation

- *A.* Compressor
- *B.* Pressure vessel containing zein solution
- *C.* Metering pump
- *D.* Candle filter
- *E.* Coagulating bath
- *F.* Flat-surfaced reel
- *G.* Precuring bath

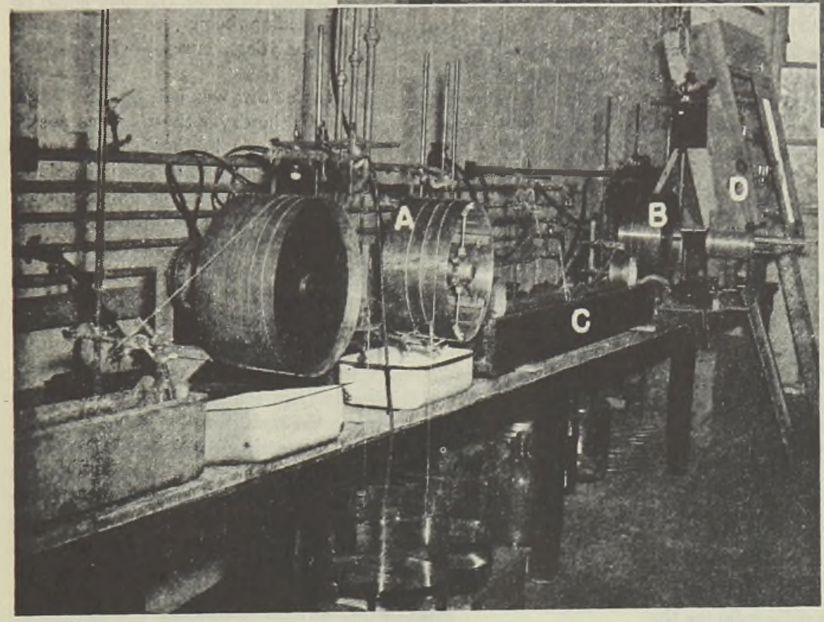

Figure 2 (*Below*). View of Processing Equipment

- *A, B.* Stretching reels
- *C.* Stretching bath
- *D.* Dryer

give the most satisfactory spinnerette operation. The most desirable viscosity for the spinning dispersions is at the incipient gel stage—that is, at the point where the protein mass slowly flows together when cut. Properly aged dispersions are nontacky and appear to be at the point of changing from viscous to plastic flow With this type of dispersion, there will be no formation of "bubbles" on the face of the spinnerette to interfere with continuous operation.

Dispersions of high viscosity were prepared by using (*a*) an initially high zein concentration, (*b*) a dispersion of low concentration and low viscosity with aging, and (*c*) denaturing or gelling agents, such as urea or alcohol, or surface denaturation induced by air bubbles which were stirred into the dispersion. Some dispersions were aged at 25° C. for as long as 7 days with no evidence of ammonia formation or putrefaction. The dispersions of lower concentration and of initial low viscosity were cleared of air bubbles on standing, although dispersion with initial high viscosity required centrifuging to remove the air bubbles. The actual viscosity, after the dispersion had passed through the spinning assembly, was a matter of conjecture because of the temperature changes and of the notable thixotropic property of these protein dispersions.

Urea and alcohol were the most frequently used denaturing agents, and their addition to alkaline dispersions of low zein concentration decreased the required aging time from 7 to 2 days. In addition, the use of urea produced a fiber of improved softness. This result was probably due to the formation of a urea-formaldehyde resin in the fiber during the formaldehyde curing operation. The solvent action of urea was necessary to form a clear spinning dispersion when quaternary ammonium hydroxides were used as the zein dispersing agents.

If dispersions were spun without aging or without chemical denaturation, their spinning properties were improved when a large amount of air or nitrogen was incorporated into them by vigorous stirring. The air was removed prior to spinning the dispersion. From this behavior it was concluded that surface denaturation had an effect on the spinning properties of the zein solution similar to that of chemical denaturation with urea or alcohol. Heat also served as a denaturing agent, but the dispersions were very sensitive to heat treatments; at about 40° C. gelation occurred rapidly and made this method impractical. Likewise, inorganic salts caused rapid denaturation and insolubilization which were difficult to control. Trace quantities of salts, however, may provide adequate means of obtaining the required amount of denaturation. Furthermore, the addition of formaldehyde to the spinning dispersions made the spun filaments very elastic. The spinning dispersion containing formaldehyde and the fibers freshly coagulated from these dispersions exhibited considerable tackiness. The tacky filaments had a tendency to "plaster" or stick together during subsequent handling; the maximum concentration of formaldehyde which

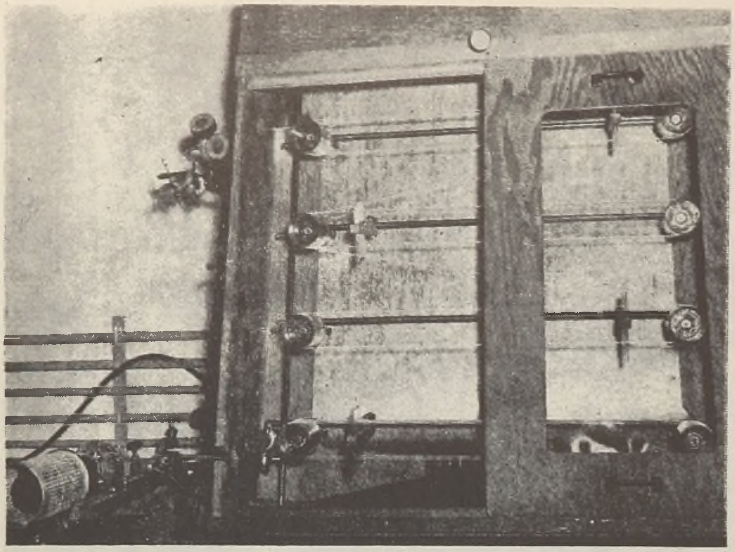

Figure 3. Continuous Fiber Dryer and Wind-up Bobbin

could be used under these conditions was thus limited to about 2% of the weight of zein. However, the plastering difficulty could be overcome by the use of salts in the coagulating bath or by the incorporation of denaturing agents, as mentioned above, in the spinning dispersions, in which case the concentration of formaldehyde could be increased.

Table I gives formulas for preparing satisfactory spinning dispersions. The dry powder zein was first quickly and thoroughly wetted with part of the ice cold water by manual stirring. The remaining cold water was added by mechanical stirring, and after a smooth suspension was attained, the dilute alkali was slowly added through a dropping funnel. If formaldehyde was to be used in the dispersion, it was added with the alkali. A high local concentration of either alkali or formaldehyde precipitated the protein, but solid urea could be added at any stage in the dispersing process without harmful effects. The alcohol had to be added after the zein had been dispersed in the alkali. Before spinning, the dispersions were deaerated by centrifuging or by allowing them to stand until free of bubbles; to remove the last amount of air, the dispersions were subjected to partial vacuum.

EQUIPMENT AND PROCESS FOR SPINNING

Figure 1 is a photograph of the apparatus used for spinning the fibers; Figures 2 and 3 show the equipment for continuous stretching and drying of the fibers. The zein dispersions were forced by air pressure, which could be controlled within a range of 0–200 pounds per square inch, through the metering pump, candle filter, and spinnerette, and into the acid coagulating bath. The spinnerettes were 1.5 inches in diameter and contained 100 to 3000 holes, with hole diameters in the range 0.003 to 0.006 inch. The coagulating bath composition most frequently used consisted by weight of 4.7% sulfuric acid, 3.1% acetic acid, and 4.4% zinc sulfate. The salt was not always necessary, and with many formulations either of the acids, in the proper concentration, gave satisfactory results. When the spinning formulations resulted in tacky fibers, the salt of the coagulating bath hardened the surface of the fibers and prevented them from plastering.

The alkaline zein dispersions behaved differently from other protein dispersions in that they did not provide sufficient lubrication for the metering pump, which would often freeze and shear the drive pin. This difficulty was overcome by cooling the pump with a stream of cold water.

After coagulation, the filaments were pulled through the bath and gathered into a tow on a large solid-faced reel, around which the tow was passed several times before falling into a mild formaldehyde precuring bath. Cold water was sprayed over the fibers on the reel to remove most of the acids and the salts adhering to them. The container holding the precuring mixture was rotated on a turntable at such a rate that the tow entered faster than the peripheral speed of the container. The tow entered the container or "curing pot" near the edge, and settled to the bottom in zigzags which formed a doughnut-shaped cake.

After the fiber had precured for the desired time, the continuous tow was withdrawn from the curing pot in the reverse direction from which it had entered, and was stretched and dried. Stretching was in a 6-foot tank of water between two large reels driven at variable speeds (Figure 2) at a temperature between 45° and 60° C. The maximum amount of stretch before excessive breakage of filaments occurred was between 200 to 350%. The limit to which the fiber could be stretched depended on the nature of the spinning dispersion, the amount of formaldehyde precure, and the temperature of the stretching bath.

From the stretching reel the wet tow was fed into the top of the dryer shown in Figure 3. In the dryer the tow was passed between four pairs of free-moving glass cylindrical reels in such a fashion that about 120 feet of the continuous tow was exposed to a variable-velocity air stream, which entered at the bottom of the dryer and was maintained at about 65° C. An aluminum wind-up bobbin, driven by the same motor which operated the stretching reel, pulled the fiber through the dryer. The speeds of the stretching reel and bobbin, however, could be varied dependently or independently, thus making possible an additional stretching of the fiber in the dryer. The tow was in the dryer for about 5 minutes.

During the preliminary work the fiber was stretched without precure by running it directly from the reel, immediately after the coagulating bath, through the tank of water at about 30° C. to a second reel. Considerable stretch was realized between the two reels, but the elongation obtained was lost when the fiber was removed from the reel for further treatment. The filaments sometimes plastered seriously when fiber was allowed to accumulate on the reel. The continuous stretching and drying procedure prevented shrinkage of the fiber at this stage of its production.

PRECURING AND STRETCHING

The mild formaldehyde treatment introduced after coagulation and before stretching of the fibers has been designated "precure". The precure was found to be a necessary treatment of the fibers before they could be effectively stretched. Noncured filaments were easily broken when handled at room temperature, and stretched indefinitely at elevated temperatures without showing

Table I. Spinning Dispersions of Zein (% by Weight)

Formula No.	Commercial Zein, %	Water, %	0.4 *N* NaOH, %	Formaldehyde, %	Urea, %	Aging, Hr.
I	13.0	69.0	17.5	0.5	...	168
II	16.5	62.5	21.0	...	...	24
III	16.5	59.0	24.0	0.5	...	2
IV	16.5	57.0	24.0	1.0	1.5	3
V	15.5	59.5	22.0	0.5	2.5	7
VI[a]	13.0	68.0	17.0	0.5	1.5	72
VII	15.0	60.0	22.0	...	3.0	4
VIII	16.5	58.0	24.0	...	1.5	2
IX	13.0	65.0	17.5[b]	0.5	...	72
X	8.3	81.4	..	...	8.3[c]	48

[a] Most frequently used dispersion.

[b] Plus 4.0% of ethyl alcohol.

[c] Plus 2.0% of tetraethanol ammonium hydroxide.

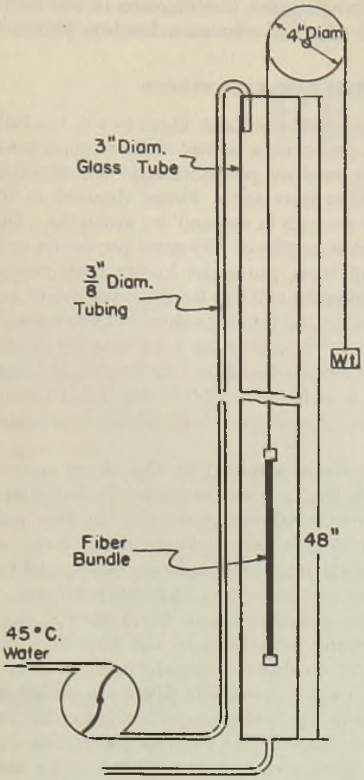

Figure 4. Schematic Diagram of Apparatus for Measuring the Load-Elongation Values of Zein Fibers

a satisfactory increase in strength. The extent of the precure, as determined by the concentration of formaldehyde and by the time and temperature of treatment, greatly influenced the character of the fibers. A low-cured sample could be given a high percentage of stretch which resulted in flexible fibers of small diameter having large shrinkage values in water. A highly cured sample would tolerate relatively less stretching and would produce coarser fibers of higher tensile strength (Figure 5). However, excessive curing resulted in brittle fibers.

The effect of time, concentration, and temperature of the formaldehyde precure treatment on the properties of the fiber was investigated in a series of experiments in which these factors were varied. Temperatures of 25° and 46° C. were used with concentrations of 2.5 to 40% formaldehyde in the precure treatment; then the bundles were washed in warm water and stretched by the direct application of a given weight per filament on the end of the suspended bundle. In these experiments the elongation varied inversely with the amount of cure, and both the amount of stretch and amount of cure influenced the strength of the fibers. As would be expected, increasing the temperature or concentration of formaldehyde increased the rate of cure. From these tests the following generalizations could be made: At 25° C. a treatment of 10% formaldehyde for 7.5 minutes gave a cure almost equivalent to that of 2.5% formaldehyde for 1 hour. Likewise, a treatment of 20% formaldehyde for 15 minutes corresponds to that of 5% formaldehyde for 2 hours. The tensile strength of fibers from all four sets of conditions was about 1.3 grams per denier; however, the stretch for the first two sets of conditions was about 300%, but for the last two it was only 170%. A precure of 2.5% formaldehyde at 46° C. for 30 minutes was similar to that of 10% formaldehyde at 25° C. for 30 minutes.

The precuring solution used most in the present work consisted by weight of 1.3% formaldehyde and 0.2% ammonium chloride added as catalyst. The treatment of fibers by this low concentration of formaldehyde is very mild and eliminates the time of treatment as a critical factor. Good fibers could be recovered from this bath after several days of treatment at room temperature.

In another series of experiments the relation between the load and elongation of wet fibers for different curing treatments was studied. The wet samples of fibers were precured in the regular curing bath (described above) at room temperature for 0, 4.5, 24, 48, and 96 hours. The load-elongation data were obtained in water at 45° C. with equipment illustrated in Figure 4. In making the elongation measurements, increment weights were added every 5 minutes to a 500-filament tow of approximately 4000 deniers, and the increase in length was noted for each added weight. The loading was continued until the fiber broke, and the resulting data are plotted in Figure 5. Fiber *A* used in obtaining curves 1 and 2, and fiber *B* used for the other four curves were from different spinning dispersions.

The load-elongation data are only relative, depending on the rate of loading; nevertheless, they show clearly an increase in tensile strength with increased precure and elongation. The curve for each precured fiber is linear up to a certain load, at which point there is a rather sharp break to another linear portion of greater slope. Except for the transition portion, any curve can be represented quite well by two intersecting straight lines. As the amount of precure was increased, the slope of both of these lines increased, and the point of intersection appears at a higher load value and lower percentage elongation. Comparison of curve 2, for the 18-hour precure of fiber *A*, with the curves of fiber *B* indicates that the spinning conditions had a pronounced effect on the slope of the curve and the properties of the fiber. In contrast to the precured samples, the load-elongation curve for the noncured sample is a straight line with more than 600% stretch, and the fibers exhibit very low tensile strength and very small increase in strength with elongation.

In another series of experiments the increase in the dry and wet strengths of the fiber with increasing stretch was measured. The fibers were stretched in water at 45° C. (with equipment illustrated in Figure 4). After stretching, the wet fiber bundles were fastened to a frame for drying. The strengths were deter-

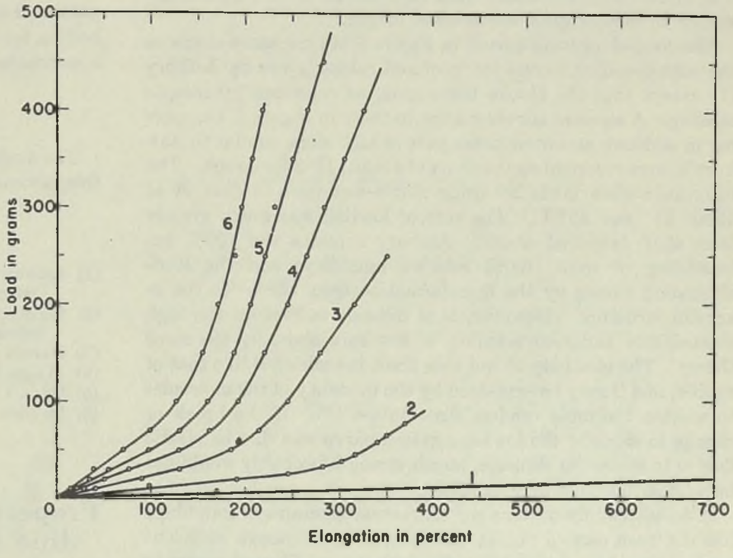

Figure 5. Effect of Amount of Formaldehyde Precure on Load-Elongation Values of Zein Fibers

1. Fiber *A* with no precure
2. Fiber *A* after 18-hour precure
3. Fiber *B* after 4.5-hour precure
4. Fiber *B* after 24-hour precure
5. Fiber *B* after 48-hour precure
6. Fiber *B* after 96-hour precure

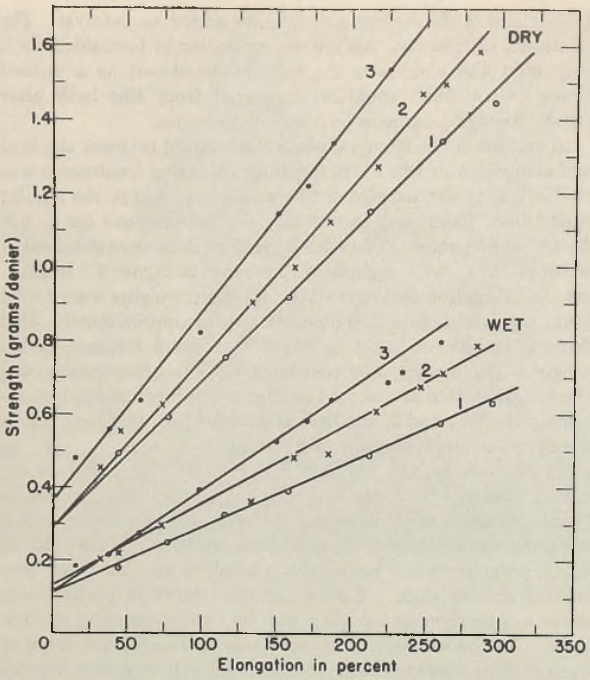

Figure 6. Relation of Tensile Strength of Fibers to Elongation

1. Fiber *B* after 4.5-hour precure
2. Fiber *B* after 24-hour precure
3. Fiber *B* after 48-hour precure

mined at 70° F. and 50% relative humidity on the Scott IP-2 Serigraph by the bundle method. The resulting strength test data (plotted in Figure 6) show a linear relation between elongation and strength. The plotted data show no indication of a change in the slope of the strength curves to correspond to the break in the load-elongation curves of Figure 5. The strongest fibers were obtained at the maximum stretch before breaking. The dried fibers, when immersed in water at 45° C., quickly returned to their original unstretched length.

The load-elongation curves in Figure 5 are the same shape as the corresponding curves for wool and rubber given by Astbury (*1*) except that the Hooke law region, as described by him, is missing. A series of curves similar to those in Figure 5, but having in addition an initial linear part of high slope similar to Astbury's, were recorded on the chart of a Scott IP-2 Serigraph. The recordings were made by using single wet tows of fiber *B* at about 21° and 35° C. The rate of loading was much greater than that described above. Astbury explains the 100% extensibility of wool (100% relative humidity) and the load-elongation curves by the transformation from the α- to the β-keratin structure. However, it is difficult to explain the high extensibility and recoverability of wet zein fibers by the same theory. The elasticity of wet zein fibers is somewhat like that of rubber, and it may be explained by the tendency of the molecules to assume the most random distribution (*2*). If the break or change in slope of the load-elongation curve was due to plastic flow or to molecular slippage, tensile strength probably would not be a linear function of elongation.

A detailed study of the x-ray diffraction diagrams of zein fibers has not been carried out at this laboratory, although sufficient evidence has been secured to indicate that some fibering occurs as evidenced by the arcing in the x-ray pattern of the more highly stretched fibers. Diffraction diagrams of the oriented fibers are similar to the so-called β-pattern obtained from the stretching of hair and wool. The evidence from the x-ray studies, along with the more easily demonstrated birefringence of the fibers, shows that a considerable degree of orientation has been obtained.

PROPERTIES OF ZEIN FIBERS

The process for the production of zein fibers is not yet fully developed. However, a preliminary survey of fiber properties is presented to indicate the excellent possibilities for the establishment of a commercial fiber from zein. Fibers obtained in the manner described above are high in wet and dry strengths. Dry strengths of 1.87 and wet strengths of 0.75 gram per denier have been obtained. In comparison, the better known spun protein fibers have dry tensile strengths of 0.6 to 0.8 gram per denier and wet strengths of about one third the dry values; the dry tensile strength for a good grade of wool is about 1.3 grams per denier. The zein fibers have high resilience and are very flexible, although no plasticizer is used. Fibers finer than 0.6 denier (7.5μ in diameter) have been produced by applying a high stretch in a heated coagulating bath.

As stated earlier, the fibers prepared by the above method shrink to their precured length when immersed in hot water. This shrinkage can be greatly reduced by treating the fiber with strong formaldehyde while it is held under tension. Even so, there is some loss in strength from the maximum values, and the fibers from this "post cure" measure 1 to 1.25 grams per denier.

Preliminary studies on dyeing the zein fibers showed that, after postcuring with strong formaldehyde, the fiber does not withstand the severe acid conditions normally used in dyeing and processing wool. In this respect zein fibers are similar to casein fibers, and like casein, the dyeing properties, in general, are greatly improved by acetylation. The work on acetylation will be reported in a future publication. It is sufficient to say here that acetyl contents above 2% are necessary to give satisfactory resistance to acid-dye bath conditions. Acetylation followed by curing with formaldehyde has given a satisfactory control of shrinkage, and in some cases, the shrinkage has been lowered to 4% as determined by boiling for 15 minutes in water.

From a study of the acid and alkaline peptization curves of zein, the fibers would be expected to offer considerable resistance to the usual alkaline conditions encountered in the use of soaps and scouring powders. Acetylated and properly cured fibers have shown excellent resistance to boiling in buffered solutions of pH 8 to 9 and, in some cases, have shown no loss in strength upon boiling for 2 hours at this alkalinity. Fiber texture, feel, and appearance were not impaired by this boiling treatment.

ACKNOWLEDGMENT

The authors acknowledge the assistance of N. Cyril Schieltz of this laboratory for the x-ray analysis of zein fibers.

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Properties of Granular and Monocrystalline Ammonium Nitrate—Correction

An unfortunate error has been found in this article by W. H. Ross, J. Y. Yee, and S. B. Hendricks in the November issue. On page 1080 the pictures were inadvertently reversed. In other words, as printed, Figure 1 is at the right and Figure 2 is at the left.

SYNTHETIC LIGNIN RESIN AND PLASTIC

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The condensation of lignin preparations with various condensing agents and catalysts has been studied. The most successful reaction found is the condensation of butanol lignin with formaldehyde to produce a thermosetting resin. When the resin is properly compounded with plasticizer and filler, it produces a plastic with flexural strength, modulus of elasticity, and impact strength, in either wet or dry condition, equal to those of plastics now in industrial use. Details for preparing the plastic are given, together with comparative quantitative data of flexural and impact strengths, modulus of elasticity, and water absorption of the lignin plastic and commercial plastics.

WITH wartime shortages of plastics, research was undertaken to develop plastic properties in lignin, to tap an almost unlimited supply of noncritical raw material. The investigation resulted in the production of a lignin plastic which compared favorably in critical laboratory tests with the best commercial plastics. This publication reports the process for preparing the lignin plastic and its physical and mechanical properties. Reviews of lignin plastics have been published by Ellis (*7*), Jahn (*8*), Kline (*9*), Penn (*10*), Schwartz (*11*), Tomlinson (*12*), and others.

In the initial experimental survey of possibilities, a wide range of conditions and reagents was investigated to provide information on various types of reactions. The most promising were then examined in more detail at various temperatures, pressures, and times. Considerable area was explored in the study of lignin condensation and polymerization, including a number of sources of lignin, a large number of condensing agents, various catalysts, appropriate reaction conditions, etc. The most promising reaction found was that between butanol lignin and formaldehyde, and the condensation product of this reaction was developed as a resin and plastic by finding the optimum points of a large number of reaction and processing variables. Although this particular reaction was developed as the most promising, as a result of the information developed in the experimental work on the reaction, it is believed that other reactions set aside as less promising could be reinvestigated profitably.

In addition to the above experiments on isolated lignin preparations, exhaustive attempts were made to carry out condensing reactions without isolating the lignin from the wood, and to combine condensation and polymerization reactions in the mold in a a single-step process. Wood flour of several species of wood was used in conjunction with the most favorable condensing agents, properly catalyzed, under a wide range of reaction conditions. Partial success was obtained in thus molding wood flour with the proper reagents under suitable conditions. The chief obstacles were the difficulty of securing uniformity of reaction in different parts of the mold, and sticking and mold corrosion problems of major magnitude. In view of the knowledge obtained later in studies on the condensation and polymerization reaction velocities, it does not appear promising at present to attempt a one-stage condensation and polymerization of lignin *in situ*.

The following technique is cited as typical of that used to prepare the resin and plastic of butanol lignin and formaldehyde (called "butasin" for convenience, a contraction of butanol lignin and resin). This procedure yielded butasin plastics of optimum physical and mechanical properties.

Samples of butanol lignin (*1–5*) from western hemlock (*Tsuga heterophylla* Sargent) of 15 grams were dissolved in about 200 ml. of water and 15 ml. of 2.5 *N* sodium hydroxide. After the lignin was dissolved, the volume was made up to 750 ml. with water; 33 ml. of 37% formaldehyde and 6 ml. of 28% ammonium hydroxide were added. The electrometric pH of this solution was 10.5 to 11.0. The reaction mixture was placed in a stainless steel autoclave and brought to 140° C. (requiring 30 minutes) with continual stirring through a stuffing box during the entire heating and cooling cycle. The temperature was maintained at 140° for 1 hour and then allowed to cool to room temperature (requiring 2 to 3 hours). The pH of the reaction mixture was then about 6.3; it was made alkaline to a pH of 10.5 to 11.0 with sodium hydroxide (2.5 *N*), and the tan precipitate was filtered off. The precipitate was washed twice with water by removing it from the filter pad, stirring thoroughly with an electric stirrer in 750 ml. of distilled water, and refiltering, and was finally air-dried. This condensation product then constituted the butasin which was modified by filler and plasticizer to form molding powders. The yield of dry butasin was about 80 to 85%, based on the original butanol lignin. The air-dried butasin contained about 8% of volatile material.

About 1 gram of butasin was ground in an agate mortar; 10% (based on the butasin) of plasticizer, dissolved in several ml. of 95% ethanol, was added; and the grinding was continued until the ethanol evaporated. Filler was added to the powder in the amount of 5% (based on the butasin) and was mixed as intimately as possible by hand or in a small jar mill.

This butasin molding powder was added to a rectangular beam mold (*13*), the mold was placed between platens, and the pressure was maintained throughout the molding cycle at 5000 pounds per square inch on the specimen itself. The platens were heated from room temperature to 250° C. (20 minutes), held at 250° for 5 minutes, and cooled to 75° (20 minutes), and the molded butasin was then removed.

MOLDING METHODS

Early in the investigation it was realized that much more rapid progress could be made in the development of a plastic if small quantities could be prepared and tested to indicate the effect of the change of the variable under observation. Such a procedure would permit taking small samples from a single reaction mixture at various stages of the reaction; subsequent molding and testing would permit plotting of the change in the observed variable throughout the entire reaction, from a single reaction experiment. The same considerations applied to the study of fillers, plasticizers, molding temperatures, etc. The necessary molds were designed, constructed, and electroplated. Some of these are more fully described elsewhere (*13*), but were generally of a simple type having an upper and lower force plate and either a conventional or a floating chase. Molded shapes were disks from $^3/_8$ to $2^1/_4$ inches in diameter, or were beams of rectangular cross section, 2 inches long. The former were used for qualitative and the latter for quantitative tests.

The molds were heated by contact, above and below, with electrical heaters containing chambers into which water was forced for cooling at the end of the cycle. The time required to reach 250° C., from room temperature, was about 20 minutes; the cooling period was about 20 minutes from 250° to 75° C., when the pressure was released and the material removed from the mold. Temperatures recorded were measured in thermometer wells in the electrical heaters with the mercury bulbs 1/8 inch from the heater-mold contacts. Temperatures in the paired heaters were maintained at identical levels by suitable switches. Unless otherwise stated, heating periods indicate the time at temperature and do not include heating and cooling. Unless special considerations dictated otherwise, molding pressures were approximately 5000 pounds per square inch. Tabular experimental data were determined under these conditions.

TESTING METHODS

Testing machines and methods were developed to measure flexural strength, modulus of elasticity, impact strength, and moisture absorption on specimens of about one gram. These are described more fully elsewhere (*6*, *13*). In general the methods were patterned after the appropriate methods of the American Society for Testing Materials, but were considerably reduced in scale because of the use of smaller samples. The flexural strength and modulus of elasticity were calculated from data obtained by loading a beam 2 inches long to destruction. The beams had an average rectangular cross section of 0.216-inch width and 0.100-inch height; they were molded in a specially designed mold to form a test specimen which had "skin effect" on all sides and permitted accurate measurement of dimensions. The beam was loaded at a constant rate throughout the test, and the deflections were measured by an optical lever. The accuracy and reproducibility of the flexural test was determined experimentally to be of the order of 1%.

The impact test (*6*) consisted of allowing a polished steel sphere to run down an inclined plane, the path of motion becoming horizontal at the lower end of the inclined plane. Immediately after leaving the inclined plane, the sphere collided with and broke the notched specimen, and continued its flight until it hit the floor. The length of flight after impact was a measure of the residual energy in the sphere. The point of impact and the length of flight were recorded by allowing it to land on carbon paper in contact with the record sheet. Velocity at the time of impact was approximately that recommended by the A.S.T.M. Reproducibility of a free fall of the sphere was of the order of 1%.

MECHANICAL AND PHYSICAL PROPERTIES

The flexural test was used to follow the effects of different experimental techniques; certain variables were changed and checked to determine that improvements in impact and moisture resistance properties did not destroy flexural strength, etc. Table I gives measurements of moduli of rupture and elasticity of butasin, together with comparative data on commercial plastics and the foremost available "lignocellulose" plastics, all molded and tested by the reduced scale methods. These results show that butasin, when plasticized and filled, had a flexural strength, in either wet or dry condition, in the same range as plastics now in widespread use. The leading lignocellulose plastics now available commercially or experimentally had satisfactory dry strengths but unsatisfactory wet strengths unless considerable phenolic resin had been added. The modulus of elasticity of butasin was lower than the phenolic but higher than the acrylic plastic.

The impact test was used to follow the effect of changing experimental variables in much the same way as was the flexural test. Table I also shows the results of impact tests on various laboratory-molded materials, all by the reduced-scale methods. Butasin, when properly plasticized and filled, was equal or superior in impact strength to the other plastics tested.

EFFECT OF PLASTICIZERS

The crude butasin resin, as first isolated and molded, was formed into disks about the size of aspirin tablets, which were easily broken by the fingers. Studies on the kinetics of the reaction, the thermal relations in molding, and related problems increased the strength until considerable effort was required to break a disk held between two wrenches. An extended study of the variables controlling water resistance resulted in such decrease in water absorption that the mechanical properties after 48-hour water immersion were entirely satisfactory and compared favorably to present industrial plastics. Plasticizers were one of the most important variables influencing moisture absorption and were studied in some detail. Plasticizers were selected from the various classes known to have specific effects on the various types of synthetic resins, with a view toward including a representative of each of the potentially useful classes of plasticizers. Various concentrations of plasticizers were employed, and effects on water resistance, flexural strength, modulus of elasticity, flow, etc., were noted. Table II lists some of the more important effects of various plasticizers on butasin.

These data show that tricresyl phosphate produced effects generally superior to those of other plasticizers. Water resistance was improved 200–300%, while the flow point (measured in the heated platen) was reduced from 120–140° C. to 80–100°. Other plasticizers improved water resistance in lesser degree. All of the plasticizers appeared to be completely compatible with butasin in the concentrations employed, except dibutyl phthalate and castor oil which exuded during molding.

There seemed to be little relation between the structure of the plasticizer and the effect it produced; there was a marked similarity and even coincidence between plasticizers for phenolics

Table I. Comparative Flexural and Impact Strengths and Modulus of Elasticity of Butasin and Commercial Plastics

Designation and Composition of Plastic	Modulus of Rupture R, Lb./Sq. In.		Modulus of Elasticity E, Lb./Sq. In. × 10^5		Impact Strength I, Inch-Ounces		Sp. Gr.
	Dry[a]	Wet[b]	Dry[a]	Wet[b]	Dry[a]	Wet[b]	
Butasin alone	8,200[c]	6,000[d]	3.77[c]	Not tested	Not tested	Not tested	..
Butasin alone	12,800	6,700	Not tested	Not tested	Not tested	1.21[c]	..
Butasin with plasticizer and filler[e]	11,400	9,200	5.76	5.38	1.91	1.77	1.21
Commercial plastic A; high-impact phenolic	12,100	12,100	9.21	7.81	1.78	1.62	1.32
Commercial plastic B; acrylic	9,600	9,800	3.57	3.53	1.60	1.50	1.16
Commercial plastic C; maple lignocellulose (hydrolyzed wood)	8,100	[f]	9.60	[f]	2.08	1.72	1.36
Commercial plastic D, same as C but phenolic resin added	9,200	9,300	11.18	10.73	1.13	1.12	1.33
Commercial plastic E; redwood lignocellulose and furfuryl alcohol resin	6,100	2,500	11.00	4.45	1.48	1.79[g]	1.33
Commercial plastic F; lignocellulose	9,400	[f]	[f]	[f]	2.93	[h]	1.23

[a] Twenty-four hours at 105° C.

[b] Immersed 48 hours at room temperature; beam dimensions approximately 2 × 0.2 × 0.1 inch.

[c] Freshly molded, called "green" beams; usually contained about 3% water and 3% other volatile.

[d] Freshly molded beam, immersed 32 hours at 50° C.

[e] Actual ratio, butasin: plasticizer: filler = 100: 10: 5.5.

[f] Too weak to give any value.

[g] High wet impact strength due to excessive filler and fiber rope or cardboard-like effect.

[h] Water immersion caused beam to crumble and disintegrate.

Table II. Effect of Plasticizers on the Strength and Water Absorption of Butasin

Plasticizer	Plasticizer Added, % of Original Butasin	Qualitative Effect (on Molded Disks)	Quantitative Effects: Modulus of Rupture, Lb./Sq. In., Green[a]	Modulus of Rupture, Lb./Sq. In., Wet[b]	Modulus of Elasticity, Lb./Sq. In. $\times 10^6$	% Volatile in Specimen When Tested, Green[a]	% Volatile in Specimen When Tested, Wet[b]	Water Absorption, %[b]
Castor oil	5, 10, 15	Seemed weaker than butasin alone	.....	....	.....	....	..	High
Flexalyn	5, 10, 15	Produced little or no change in strength of butasin	.....	....	.....	....	..	High
Dibutyl phthalate	2, 5, 10, 15	All mixtures improved strength; 5% mixt. was strongest	.....	....	.....	....	..	High
Phenol	5, 10	Both mixtures seemed to improve shattering	.....	....	.....	....	..	High
Butyl phthalyl butyl glycolate	10	....	10,600	Not tested	3.60[a]	6.6	..	..
o- & *p*-toluene sulfonamide	10	....	8,500[c]	Not tested	3.82[c]	3.8[c]	..	2.2
Triethyl citrate	10	....	11,500[c]	Not tested	4.14[c]	4.6[c]	..	4.5
Tricresyl phosphate	10	....	9,000	Not tested	3.33[a]	Not measured	..	1.8
	15	....	8,000	Not tested	4.05[a]	4.1	..	..
None	0	....	10,600	6,000[d]	3.95[a]	6.3	7.4[d]	6.0
	0	....	8,200	Not tested	3.70[a]	6.0	..	..
Tricresyl phosphate (and filler)[e]	10	....	11,400[f]	9,200	5.76[a] 5.38[b]	0.0[f]	2.5	2.5

[a] Freshly molded beam; volatile consisted of water and other volatile material.
[b] Immersed for 48 hours at room temp.
[c] Preconditioned for 48 hrs. at 50° C. before testing.
[d] Immersed 32 hours at 50° C. (severe test).
[e] Butasin–tricresyl phosphate–staple fiber in ratio of 100:10:5.5.
[f] Twenty-four hours at 105° C.

and butasin. There was no consistent relation between the water solubility of the plasticizer and its effect on moisture resistance; in some cases the relation was actually reversed. Generally speaking, the addition of 10% of plasticizer did not greatly affect the flexural strength, modulus of elasticity, or impact strength of the dry butasin beams and preserved these properties after immersion, presumably by preventing water absorption. Plasticizers, in general, markedly improved flow properties, lowered flow point, and reduced the tendency to stain or stick in the mold, although butasin appeared to have less tendency to stain or stick in the mold than phenolics. Corrosive effects on the mold were more noticeable with phenolic than with butasin. The flow properties of phenolic molding powder seemed to be slightly superior to those of butasin.

Table III. Effect of Temperature and Time on Moisture Absorption of Butasin Beams Immersed in Water

Plasticizer, %	% Water Absorption of Butasin: 48 hr., room temp.	24 hr., 50° C.	72 hr., 50° C.
Castor oil, 5	...	Crumbled	...
Flexalyn, 5	...	...	17.3
Dibutyl phthalate, 10	...	...	19.5
Phenol, 5	...	...	16.5
Butyl phthalyl butyl glycolate, 10	...	12.0	14.5
o- & *p*-Toluene sulfonamide, 10	2.2	7.5	9.2
Triethyl citrate, 10	4.5	...	10.0
Tricresyl phosphate, 10	1.8	3.3	5.4
Tricresyl phosphate, 15	...	...	8.8
None	6.0	7.4[a]	15.5
Tricresyl phosphate (+5% staple cotton fiber filler), 10	2.5	...	...

[a] Thirty-two hours at 50° C.

Original intentions in determining water absorption were to use the A.S.T.M. precedent of room temperature. The delay before learning the absorption suggested the utility of an accelerated test at a higher temperature. In such a test 50° C. was accepted as a satisfactory starting point, and certain relative comparisons were made with the test before an attempt was made to learn its absolute value or its exact value relative to the test at room temperature, or before its true drasticity was realized. The degree of severity is illustrated in Table III.

The measurement of water absorption at 50° C. was so drastic that it was discontinued, and the attempt to put an accelerated and standardized absorption test into use was abandoned. As a comparable measure of the drastic nature of the test, acrylic plastic immersed for 72 hours in water at 50° C. absorbed 2.0% of water, became milky in appearance, and acquired a granular surface.

The moisture absorption of butasin, determined by immersion of a 2 × 0.2 × 0.1 inch beam for 48 hours at room temperature, was 1.8%. When determined by immersion of a 2 × 1/8 inch disk for 24 hours at room temperature (A.S.T.M. D 570–42), it was 0.9% (for the phenolic, 0.7%). When the disk was immersed for 48 hours, the absorption was 1.1%, in agreement with the surface-volume ratio of the specimens.

EFFECT OF FILLERS

Although fillers may be used to modify various properties, such as specific gravity, heat resistance, etc., the most urgent function for fillers in butasin is to increase impact strength. Various materials such as high-strength cotton staple and cotton cloth, glass thread, wood flour, etc., were used. For the staple fiber and wood flour, both hand mixing and grinding as well as semimicro ball milling were used before the molding powder was placed in the mold. For fabric and thread, alternate layers of butasin powder and fabric or thread were placed in the mold carefully by hand to obtain as uniform distribution as possible. Somewhat erratic results in tests of such specimens (fabric and thread) indicated that hand distribution was not trustworthy as to reproducibility. Table IV shows some of the fillers used and the effects on impact strength, flexural, water resistance, etc.

It is evident that small proportions of fillers increased impact strength 200–300% without adversely affecting the moduli of rupture or elasticity. This fact is interesting in view of the poor impact strength of any previous high-lignin plastic. Enormously high impact strengths (200% higher than the phenolic plastic) were obtained by the use of larger quantities of filler, but simultaneous loss of flexural strength and stiffness occurred. These high impact strengths were noted in other materials, notably the commercial lignocellulose plastics, which contained an extremely high proportion of fiber and were almost a pressed cardboard; these high impact strengths have been called "cardboard effects" in this laboratory. They were almost invariably accompanied by high water absorption and disintegration upon immersion. It is possible that future research may increase the impact strength of butasin still farther to a point greatly in excess of present industrial standards, without sacrificing either flexural strength or stiffness. Such material would undoubtedly prove exceedingly useful in meeting industrial conditions involving severe impact loads. The combination of butasin, tricresyl phosphate, and 1/4-inch staple cotton in the ratio of 100:10:5.5 gave an impact strength which was higher than that of a phenolic plastic, which was an improved impact material. The flexural strength, modulus of elasticity, moisture resistance, and wet strength of this butasin combination were also satisfactory. The effect of moisture absorption upon the properties of butasin and commercial plastics is shown in Table I.

Table IV. Effect of Fillers on Butasin

Butasin, %	Filling Material, %	Plasticizer, %	Impact Strength, In. Oz.	Modulus of Rupture, Lb./Sq. In.	Modulus of Elasticity, Lb./Sq. In. × 10^3	Volatile Material, %[a]	Remarks
100	None	None	1.06	9,400	382	6.1	Green beam[b]
	Glass thread, 50	None	1.03	3,100	610		12 threads longitudinally in beam of 0.1 × 0.2 in. cross section
50	Wood flour, 50	None	0.64	3,700	321	...	....
50	1/4-in. cotton staple, 50	None	3.02	4,100	330	5.0	Powdered resin did not saturate bulk of fibers
75	Same, 25	None	3.55	7,200	450	6.3	Green beam[b]
83.4	Same, 12.5	Triethyl citrate, 4.1	3.52	7,200	270	8.5	Green beam[b]
86.6	Same, 9.1	Same,4.3	2.45	4,800	375	9.0	Green beam[b]
95	Same, 5	None	2.63	5,100	310	11.2	Green beam + 48 hr. in H_2O before testing
95	Same, 5	None	3.26	8,500	354	7.3	Green beam[b]
85.8	Same, 4.7	Tricresyl phosphate, 9.5	1.91	11,400	576	2.5[c]	Oven-dry beam

[a] Included water and nonaqueous volatile material.
[b] Freshly molded, tested without conditioning.
[c] Absorbed water only.

SPECIAL PROBLEMS

Problems requiring positive solution included water resistance. The 48-hour water absorption of a 2 × 0.2 × 0.1 inch specimen of butasin (without plasticizer) was about 6%. Various means of reducing this absorption were attempted, including reduction of basic hygroscopicity by alkylation with dimethyl sulfate, development of water repellency by changing the contact angle of the material by incorporation of aluminum stearate, decreasing water affinity by resin salt formation through ion exchange, and modification by mutual solubility in protein. The results of some of these experiments were negative, while others were inconclusive or unpromising for various reasons; the use of plasticizers indicated a much more rapid and practical solution to the problem. Their success is best judged by the wet strength values in Table II.

The molding temperatures used initially were selected by experience; 160° C. was used chiefly. To determine the permanency of thermoplasticity of butasin, consecutive molding cycles were conducted upon the same sample, and the molded product was ground to a powder between moldings. Three such cycles of one hour each at 160° caused only a moderate weakening of the (third) molded sample. The fourth and fifth cycles for 20 and 30 minutes at 200° increased the strength somewhat. The sixth cycle for one hour at 220° created fair strength but a slight change from conchoidal to granular structure. The seventh cycle for one hour at 230° caused much loss of strength and dominance of granular structure. In the eighth cycle, flow began at 200°, and complete fusion occurred at 250° in a molding period of 5 minutes. The tenth cycle, after 10 minutes at 250° and 20 minutes at 260°, failed to fuse the molding powder; a crumbly mass was removed from the mold. Molding conditions then adopted were 250° for 5 minutes which produced a thermoset resin of considerably higher strength than that by molding at 160° C.

Freshly molded beams, called "green beams", contained about 6% volatile matter, whereas the original air-dry molding powder contained about 8% volatile. Water and at least one other material appeared to be present since a freshly molded butasin beam placed in a desiccator for 30 days lost 6.1% of its weight and a similar specimen exposed to room conditions for 30 days lost 3.2% of its weight. One series of freshly molded butasin beams lost from 2.8 to 5.5% of volatile material by heating at 105° C. for 24 hours and simultaneously increased in strength. A freshly molded phenolic beam lost 2.5% during the 24-hour period at 105° and showed an even greater increase in strength.

Suggestions for a possible plasticizer were sought by examining the character of the 20% unreacted butanol lignin which, together with the reaction products, was compatible with the butasin but was gummy in nature. It was found that washing the precipitated butasin with dilute alkali to remove the unreacted butanol lignin was essential to high strength. Further extraction of the butasin with acetone isolated a varnish-like resin but substantially reduced the strength of the butasin. Incorporation of the separated varnish-like resin with butasin not extracted with acetone would undoubtedly increase strength.

Butasin was prepared from lignin which was isolated in alkaline butanol-water solutions, neutral butanol-water solutions, and acidic butanol-water solutions. The presence of butanol during the isolation of the lignin appeared to be essential since alkali lignin did not undergo the butasin reaction.

The flow point of butasin at 5000 pounds per square inch was approximately 120° C. The dry flexural strengths of butasin resin alone, molded at 3000, 4000, 5000, and 6000 pounds per square inch, were 9000, 11,200, 12,800, and 13,000 pounds per square inch, respectively.

The bulk factor (compression ratio in molding) of butasin varied from 2 to 3, depending upon the particular sample and particle size. The specific gravity of molded butasin was 1.21. The physical appearance of molded butasin was black, glossy, and of high luster. It polished well and seemed to be about the same as the phenolics in machining properties.

Butasin and the butasin reaction seemed more nearly comparable with the phenolics and the phenol-formaldehyde condensation than with any of the other commercial plastics. Butasin was formed in the presence of both alkaline and acidic catalysts.

Laboratory tests are indicative, but it is desirable to correlate the information obtained with full-scale production and actual service records. In so far as laboratory tests and research data indicate industrial performance and behavior in use, butasin compared favorably in all respects with present industrial plastics. Further research may be expected to change this first "model" of butasin greatly. It is probable that a series of resins can be prepared in which the different properties vary throughout a wide range. It is believed that the information acquired in this study will aid greatly in adapting the process to other sources of lignin, especially to those now in commercial production. There appears to be no reason to doubt that future research can solve these problems or that lignin can be utilized as a plastic.

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DENSITIES OF GR-S LATICES

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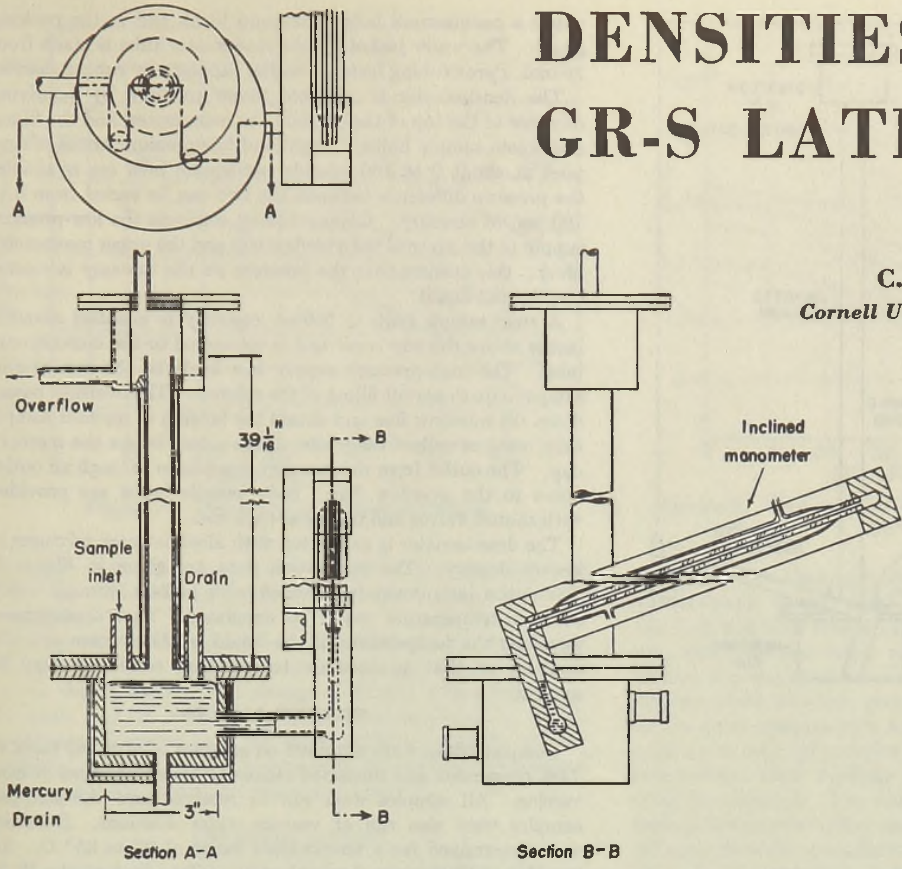

Figure 1. Constructional Details of Densitometer

A densitometer capable of indicating densities of unvented GR-S latices with an absolute accuracy of approximately 0.002 gram per cc. has been developed. The design permits the instrument to operate over a wide range of pressures without affecting its accuracy. The present instruments have been constructed to withstand pressures of 100 to 150 pounds per square inch, but this range can be extended. Complete data have been obtained on samples of stripped and unvented GR-S latices of various degrees of conversion. Above 44.5% conversion the density of the unstripped samples increases linearly with conversion. The slope of this curve is 0.00114 gram per cc. per % conversion, or 0.0035 gram per cc. per % total solids. The data show that below 45% conversion two phases are present. Above 25° C. the density of stripped latex of 75% conversion and of the unvented latices of various conversions decreases linearly with temperature. The rate of decrease for the stripped latex is approximately 0.0004 gram per cc. per ° C. and for unvented latex, approximately 0.0006 gram per cc. per ° C.

THE extremely rapid expansion of the synthetic rubber industry after the start of the war made it necessary to build copolymer plants without a complete knowledge of even the simpler properties of many of the materials being handled. Equipment such as agitators, piping, heat exchangers, and reactors had to be designed without knowledge of the flow or heat transfer properties of the synthetic rubber latices being processed. To obtain as much information as possible regarding the fundamental properties of the various materials involved, the Office of the Rubber Director established and financed research programs in various laboratories.

The Office of the Rubber Director, acting through the government-owned Rubber Reserve Company, assigned to the School of Chemical Engineering at Cornell University the problem of determining the densities of both stripped GR-S latices and the unvented GR-S latices existing in the reactor at various stages of conversion. The density of unvented latices not only gives an indication of the percentage conversion of the monomers to the copolymer, but also is required to correlate heat transfer and fluid flow data.

Since the unvented latices were under butadiene pressure, it was necessary to develop a densitometer that could be operated under relatively high pressures. Although the vapor pressures exerted by the various samples did not exceed 70 pounds per square inch, it was necessary to allow for greater pressures because nitrogen was used to blow the samples from one location to another.

DESCRIPTION OF DENSITOMETER

The densitometer determines the density of a fluid by measuring the pressure exerted by a column of liquid of fixed length. The column is supported on a mercury surface in a cup connected to an inclined mercury manometer. The pressure on the top of the column and in the manometer is equalized so that the manometer reading depends only on the temperature and the density of the fluid and is independent of the absolute pressure. Figure 1 shows the details of the instrument, and Figure 2 is a diagram of the laboratory installation.

The cup is made from a 2-inch length of standard 3-inch pipe. A steel plate, $^3/_8$-inch thick, is welded on the bottom and a $^1/_4$-inch flange, $5^3/_4$ inches in diameter, is welded to the top of the cup. A plate, $5^3/_4$ inches in diameter and $^3/_8$ inch thick, is bolted to this flange. The plate is provided with two $^1/_4$-inch holes, one for liquid inlet and one for outlet, and a $^1/_2$-inch hole for the column. The water jacket for the cup is welded to the flange of the cup. Mercury is drained through a $^1/_8$-inch line in the bottom of the cup. The manometer offtake, a $^1/_4$-inch pipe nipple, is set longitudinally in the side of the cup, $1^1/_2$ inches below the flange. Both lines pass through, and are welded to, the water jacket.

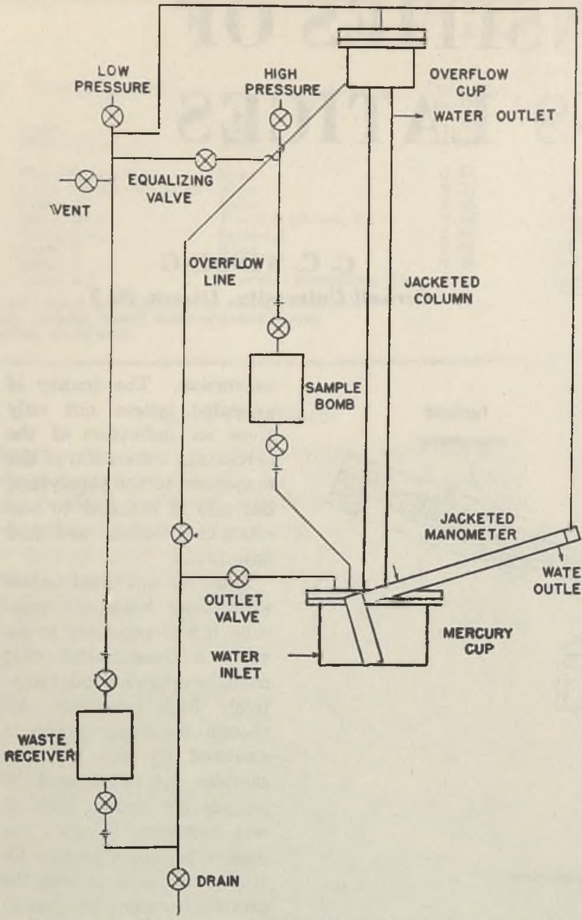

Figure 2. Diagram of Laboratory Installation with Densitometer

The column is a 39 $^{1}/_{16}$-inch length of $^{1}/_{2}$-inch black steel pipe screwed into the cover of the mercury cup and into the bottom of the overflow cup. A water jacket, made of 1$^{1}/_{2}$-inch seamless steel tubing, is welded to the column. The top of the column is 1$^{1}/_{4}$ inches below the overflow cup; the bottom is flush with the lower side of the mercury cup cover.

The overflow cup is constructed from a 2-inch length of 2-inch steel pipe. A $^{3}/_{8}$-inch steel plate is welded on the bottom of the cup; a flange, $^{1}/_{4}$ inch thick and 4$^{1}/_{4}$ inches in diameter, is welded on the top of the cup. The outlet consists of a $^{1}/_{4}$-inch pipe on the side of the cup and level with the bottom. A $^{1}/_{4}$-inch steel plate, 4$^{1}/_{4}$ inches in diameter, is bolted to the flange. A tapped hole is provided in the cover for an equalizing line.

The manometer consists of two end blocks and a glass capillary tube, water-jacketed, held in place by a 1$^{1}/_{2}$-inch channel. The lower end block is a 1-inch-square steel bar, 4$^{1}/_{2}$ inches long. The nipple from the mercury cup is connected to the side of the block near the bottom; the capillary tube is seated in a hole near the top of the block at right angles to the entrance from the mercury cup. These two openings are connected by a $^{1}/_{4}$-inch hole drilled through the length of the block and plugged at the bottom. The upper end block has a hole for the other end of the capillary tube and a tapped hole at right angles to this for an equalizing line. The lower end block is welded to the back of a 1$^{1}/_{2}$-inch channel; the upper block is bolted to the channel to permit the removal of the capillary. The capillary tube is a piece of Pyrex tubing with a 3-mm. bore. A gas-tight joint is formed between the capillary and the end blocks by compressing a $^{3}/_{16}$-inch length of rubber tubing, slipped over the capillary, between a countersunk hole in the end block and in the packing gland. The water jacket for the manometer tube is made from 19-mm. Pyrex tubing fastened to the capillary by rubber sleeves.

The densitometer is operated under pressure by supplying nitrogen to the top of the column, the manometer, and the filling and waste sample bulbs. High- and low-pressure nitrogen supplies at about 0 to 100 pounds per square inch are available; the pressure difference between the two can be varied from 0 to 100 cm. of mercury. Copper tubing connects the low-pressure supply to the cover of the overflow cup and the upper manometer block; this ensures that the pressure on the mercury is caused only by the liquid.

A steel sample bulb of 500-cc. capacity is installed about 9 inches above the cup cover and is connected to the mercury-cup inlet. The high-pressure supply line leads to the top of this sample bulb to permit filling of the column. The overflow passes down the overflow line and enters the bottom of another sample bulb, used to collect the waste, about a foot below the mercury cup. The outlet from the mercury cup passes through an outlet valve to the overflow line. Both sample bulbs are provided with shutoff valves and unions at each end.

The densitometer is calibrated with alcohol-water mixtures of known density. The calibration data are given in Figure 3. The entire instrument is provided with jackets through which constant-temperature water is circulated. This arrangement equalizes the temperature of the liquid in the column and the mercury so that an accurate temperature correction may be applied.

STRIPPED LATICES

Complete data were obtained on samples of stripped latex of 75% conversion and unvented latices of various degrees of conversion. All samples were run as received and the stripped samples were also run at various water dilutions. Densities were determined for a temperature range of 0° to 65° C. All samples of latex were obtained at the pilot plant of the B. F. Goodrich Company. The samples were shipped in 500- and 1000-cubic-inch, stainless steel oxygen bombs.

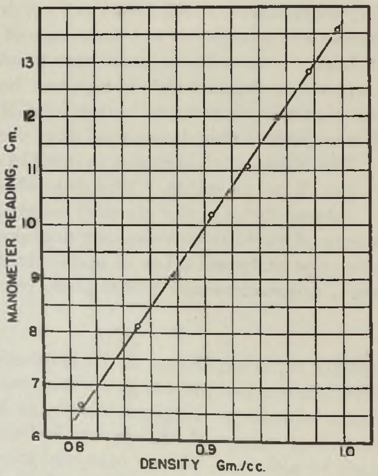

Figure 3. Calibration Curve at 25° C.

Sample 1-0 was completely stripped, Mutual A recipe, GR-S latex of 75.3% conversion, and was used to test the accuracy of the densitometer. Careful measurements were made on this sample, as received and water-diluted, and the data were compared with those obtained with a calibrated 50-cc. pycnometer (Table I). In general, the densitometer data are slightly lower than those from the pycnometer, but they do not show a deviation of more than 0.002. The instrument was designed to cover

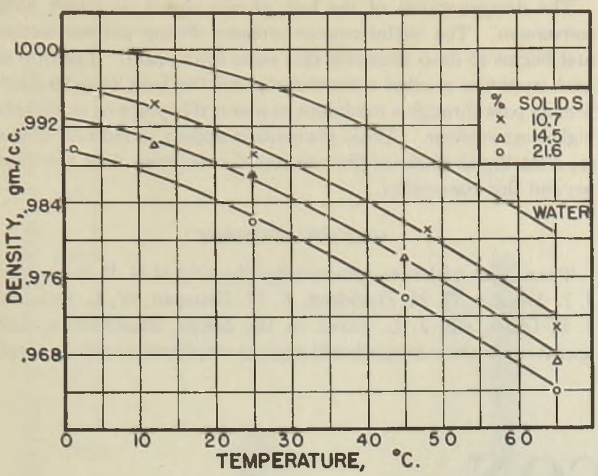

Figure 4. Densities of Stripped Latices

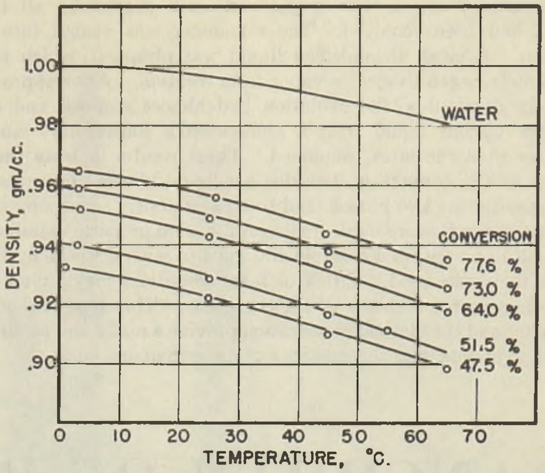

Figure 5. Densities of Unvented Latices above 45% Conversion

the range of densities from 0.800 to 1.000 so that a variation of ±0.002 is equivalent to an error of ±1.0% of the range of the instrument.

Figure 4 shows the variation of the density of water and water-diluted samples of stripped latex with temperature as obtained by the densitometer. The change of density with temperature for water and for latex is nearly the same as shown by the almost parallel curves, but the latex exhibits a slightly greater variation. The change of density with temperature for stripped latex is approximately 0.004 gram per cc. per ° C.

UNVENTED LATICES

Samples of unvented latices were properly stabilized and were received in stainless steel bombs under approximately the vapor pressure of butadiene from the latex. The samples were transferred and the densities obtained under nitrogen pressure. Figure 5 gives the variation of density with temperature for unvented latex of various conversions. The curve for water is included for comparison. The slopes of the unvented latex curves are steeper than that of the water curve, as might be expected since the density of both butadiene and styrene varies more with temperature than does that of water. The decrease in density per ° C. is approximately 0.0006 gram per cc. for unvented latex. Figure 6 shows the variation with percentage conversion. Above 45% conversion the density of the latex increases linearly as the percentage conversion increases; below this value, the density appears to decrease as the percentage conversion increases. The methods employed in handling undoubtedly affected the determinations in the two-phase region. Samples were drawn by gravity from the latex container held in a vertical position while the entire system was under a nitrogen atmosphere at 50 to 100 pounds per square inch. No means were provided for agitating the latex while the sample was being drawn. Thus, if there was separation into two liquid phases, only the heavier phase would be obtained in the small sample bulb which was later attached to the densitometer. This method was used in obtaining the data presented in this report.

Another method of filling was also employed. The larger latex container was shaken vigorously and a sample quickly drawn into an evacuated sample bulb. The bulb was then shaken, a sample forced into the densitometer, and a reading taken as rapidly as possible. When this method was employed for samples below 45% conversion, densities were observed which were much lower than those recorded for the same samples with no agitation. When the same procedure was used for samples above 45% conversion, no difference between these readings and the ones previously recorded could be observed. The data indicate that the density of the well-shaken representative samples below 45% conversion should fall approximately along the extended straight line for the range above 44.5% conversion, but because of the difficulty in obtaining representative homogeneous samples, the data did not fall close to the line. The curves in this region are drawn as dashed lines to indicate that they are not well-defined.

To check the existence of two phases, a container holding a low-conversion sample was allowed to remain in a vertical position for

Table I. Densities of Stripped Latices

Sample No.	% Solids (Total)	Method	Density, Grams per Cc. T_1, ° C.	T_2, ° C.	T_3, ° C.	T_4, ° C.
1-0	21.6	Densitometer	0.990–1.0	0.982–25	0.974–45	0.964–65
		Pycnometer	0.989–1.0	0.983–25	0.975–45	
1-W50	14.5	Densitometer	0.990–12	0.987–25	0.978–45	0.967–65
		Pycnometer	0.992–12	0.988–25	0.980–45	
1-W100	10.7	Densitometer	0.995–14	0.989–25	0.980–48	0.971–64
		Pycnometer	0.993–14	0.990–25	0.980–48	
1-W150	7.0	Densitometer	0.994–1	0.992–25	0.981–45	0.972–65
		Pycnometer	0.996–1	0.992–25	0.984–45	

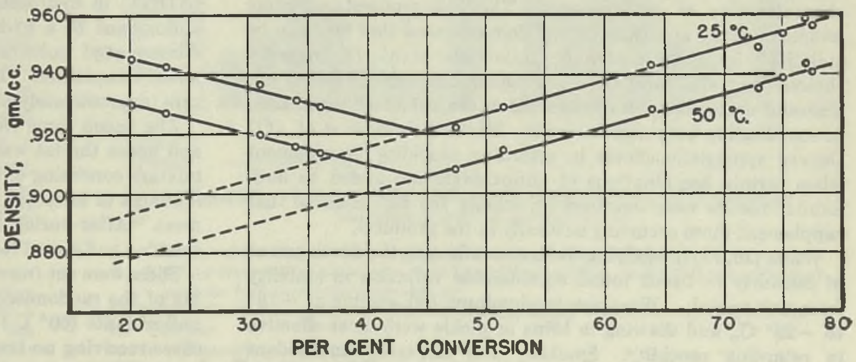

Figure 6. Densities of Unvented Latices *vs.* Conversion

24 hours. Samples were withdrawn until practically all the latex had been removed. The remainder was vented into a beaker. A clear unemulsified liquid was obtained, which immediately began to eject a vapor from solution. After approximately 5 minutes, the evolution had almost stopped and an orange viscous liquid with a molasses-like consistency, much lighter than the latex, remained. These results indicate that, up to 44.5% conversion, two distinct liquid phases are present. Apparently the two phases tend to separate fairly rapidly by the time the samples are used. All samples were properly stabilized and all had been aged from several days to several weeks by the time they were used. Either of these conditions may have had an effect on the stability of the emulsions. This type of densitometer and the method of operation provide a ready and positive method of detecting the existence of more than one phase.

The disappearance of the two phases occurs at about 45% conversion. The initial reactor pressure during polymerization first begins to drop at nearly this same conversion. The rate of heat evolution reaches a maximum, and the heat transfer coefficients pass through a minimum at about this point or at slightly higher conversions. These phenomena appear to indicate that a separate liquid phase of the unreacted monomers does not exist beyond this conversion.

ACKNOWLEDGMENT

The author wishes to acknowledge the help of G. P. Baumann, J. L. Beecher, G. M. Davidson, F. W. Dittman, W. L. Kranich, J. L. Olsen, and J. L. Zabel, in the design, construction, and operation of the various densitometers employed in this project.

RANCIDITY OF BACON . . . .

Effect of Antioxidants

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The effects of antioxidants—(1) nordihydroguaiaretic acid (NDGA), (2) *d*-isoascorbyl palmitate, soybean lecithin, and mixed tocopherols, and (3) gossypol in five different concentrations—in retarding the development of peroxides in slices of unsmoked and smoked bacon were studied and compared with corresponding slices receiving no treatment. The antioxidants dissolved in vegetable oils were applied to the surface of the slices. This study showed that all of the antioxidants were effective in retarding the development of peroxides, the effectiveness of the gossypol varying with the concentration used. The induction or keeping period for the treated slices was three to five times longer than for those receiving no antioxidants. Smoking retards the development of rancidity in bacon, while light promotes its development.

THE development of rancidity, particularly during the warmer months, markedly shortens the time during which cured pork can be stored without becoming unpalatable. The investigation reported here is part of extensive research undertaken to find improved methods of controlling rancidity development in cured pork, which would increase the value of these cured cuts by preventing waste and improving palatability. The quality is determined when served at the table.

Recent studies on and developments in the use of antioxidants (*2–11, 14*) suggest their application in the prevention of rancidity in pork. Certain of these antioxidants have shown remarkable powers in stabilizing lard and oils. Mattill, Olcott, and Golumbic (*1, 2, 7, 9, 10*) made extensive investigations on the chemical characteristics of antioxidants. They determined oxygenic indices of many antioxidants and demonstrated that lard can be stabilized by these materials. Lundberg *et al.* (*5*) recently showed that with lard, nordihydroguaiaretic acid (NDGA) has powerful antioxidant properties which are enhanced when used in combination with ascorbic acid. Riemenschneider *et al.* (*11*) showed synergistic effects in retarding rancidity development when certain combinations of antioxidants are added to lard. Similar results were obtained by adding the antioxidants that supplement those occurring naturally in the products.

White (*16, 17*) in studying the factors affecting the development of rancidity in bacon found considerable variation in stability from slab to slab. Wrapping in aluminum foil, storing at −18° to −23° C., and thawing in brine or pickle were most effective in retarding rancidity. Smoking also imparted antioxidant effects. The changes in rancidity development were determined by the peroxide and free fatty acid content. The peroxides developed rapidly during curing while the free fatty acid developed at a uniform rate during curing and storage. White concluded that rancidity was largely due to oxidation, since the free fatty acid content was low throughout the study. He also found that, of the several methods studied for measuring rancidity, peroxide values were most reliable. A modified Kreis test gave results that were highly correlated with the peroxide values.

The first part of this paper deals with a study of the effects of light and two antioxidants on rancidity development of bacon as estimated by peroxide values, expressed as milliequivalents per kilogram of fat. The second part describes further studies on the use of three antioxidants in controlling rancidity development of the same product.

I. EFFECT OF LIGHT AND ANTIOXIDANTS

This experiment was designed to compare the rate of rancidity development in cured bacon sliced 5 mm. thick: (1) untreated; (2) treated with antioxidant A, 0.02% nordihydroguaiaretic acid (NDGA) in hydrogenated vegetable oil; and (3) treated with antioxidant B, a hydrogenated vegetable oil containing 0.06% *d*-isoascorbyl palmitate, 0.06% soybean lecithin, and 0.01% mixed tocopherols. The comparison was made at room temperature (approximately 80° F.) both in the light and in the dark.

The bacon came from a hog fed a large amount of soybeans, and hence the fat was very oily. The bacon was cured with a mixture consisting of 8 pounds of salt, 3 pounds of brown sugar, 3 ounces of saltpeter, and 5 gallons of water per 100 pounds of meat. After curing for 10 days, the bacon was given a light smoking and stored for 180 days in a dark room at 34° to 36° F.

Slices were cut from the slab and randomized before treatment. Six of the randomized slices were dipped in each of the melted antioxidants (60° C.) and hung on a small rack along with six slices receiving no treatment. This rack was placed on a table and exposed at room temperature to light coming through two

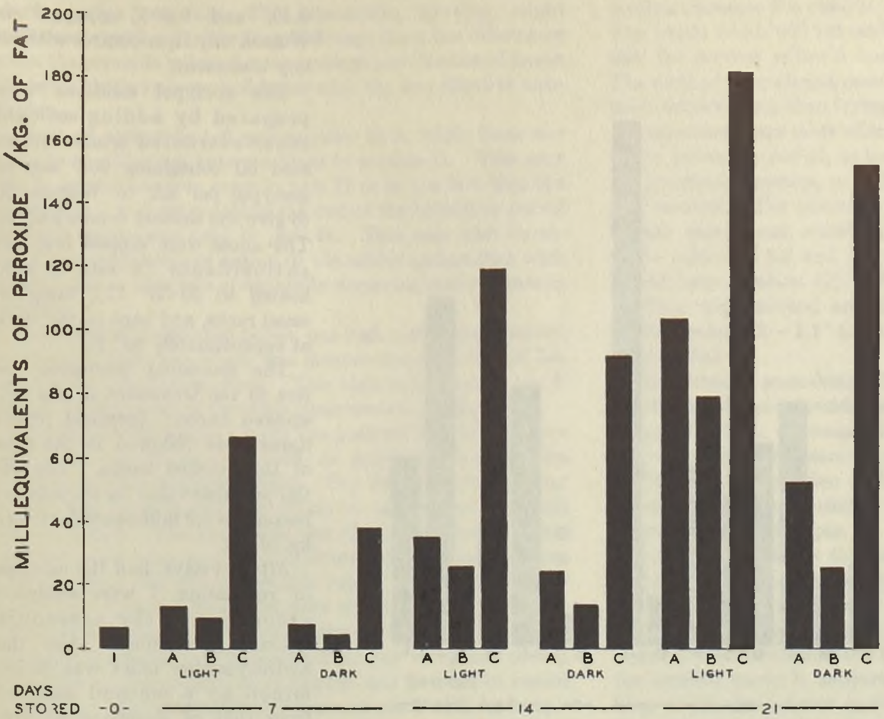

Figure 1. Effect of Antioxidants on Rancidity Development in Sliced Bacon

- **A. 0.02% nordihydroguaiaretic acid in hydrogenated vegetable oil**
- **B. 0.06% *d*-isoascorbyl palmitate, 0.06% soybean lecithin, and 0.01% mixed tocopherols in hydrogenated vegetable oil**
- **C. Control**
- **I. Initial peroxide value of bacon**

large windows. Another rack having the same number of slices with identical treatments was placed in a dark cabinet in the same room. A similar number of slices were treated and stored in the same way on the following day. Eight slices which were used to determine the initial peroxide value at the beginning of the experiment gave an average of 6.8.

At 7, 14, and 21 days, peroxide values were determined on four slices receiving each treatment, stored in both light and dark. After the rinds were removed, the slices were placed in 250-ml. beakers and heated in an oven for 3 hours at 75° C. The fat was then expressed with a small fruit press and filtered, with slight suction, through a small wad of cotton placed in the constricted stem of a funnel. About 1 gram of the melted fat was put in a tared flask, having a ground glass stopper, and weighed. Peroxide values were determined by the hydrochloric acid method of Stansby (*15*) and expressed in milliequivalents of peroxide per kilogram of fat.

The effects of the various treatments are presented graphically in Figure 1.

The average peroxide values for slices treated with antioxidants A and B were significantly[1] lower at all intervals of storage in both light and dark than the controls receiving no treatment. The average peroxide values of the controls increased with time at a uniform rate, and the significantly accountable differences between storage in light and dark were nearly the same at all time intervals. This suggests that the induction period for untreated bacon may be prolonged by storing in the dark; but when this period is over, rancidity develops as rapidly in the dark as in the light. The average peroxide values for the slices of bacon treated with antioxidant B were less at each time interval than for those

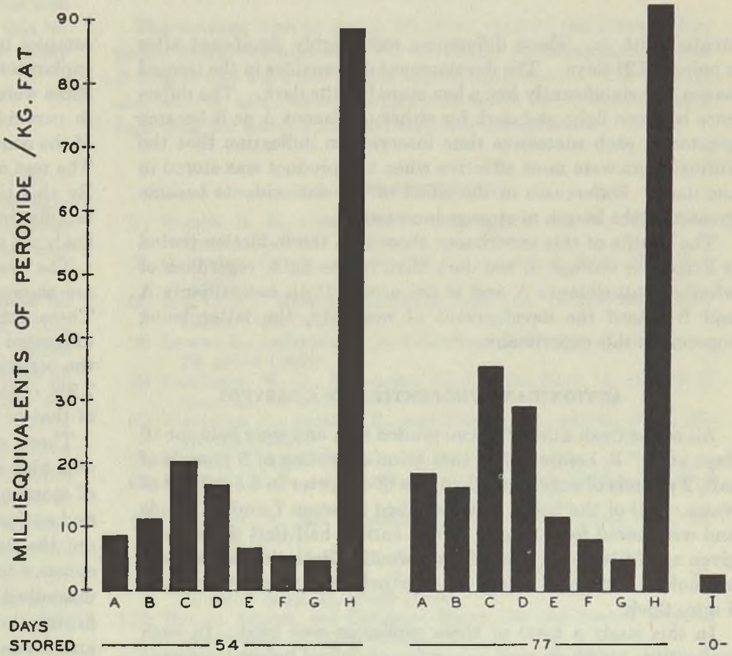

Figure 2. Comparative Effect of Antioxidants on Rancidity Development in Sliced Bacon

- **A. 0.02% nordihydroguaiaretic acid in hydrogenated vegetable oil**
- **B. 0.06% *d*-isoascorbyl palmitate, 0.06% soybean lecithin, and 0.01% mixed tocopherols in hydrogenated vegetable oil**
- **C, D, E, F, G. 0.05, 0.10, 0.20, 0.40, and 0.80% gossypol in Wesson oil, respectively**
- **H. Control**
- **I. Initial peroxide value of bacon**

Least significant difference (p = 0.05), 7.88

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[1] Both this and the following experiment were designed to allow statistical analysis of the resulting data. Differences indicated as significant had a probability of occurrence through chance of less than 5%. Difference stated to be highly significant had a probability of chance occurrence of 1% or less.

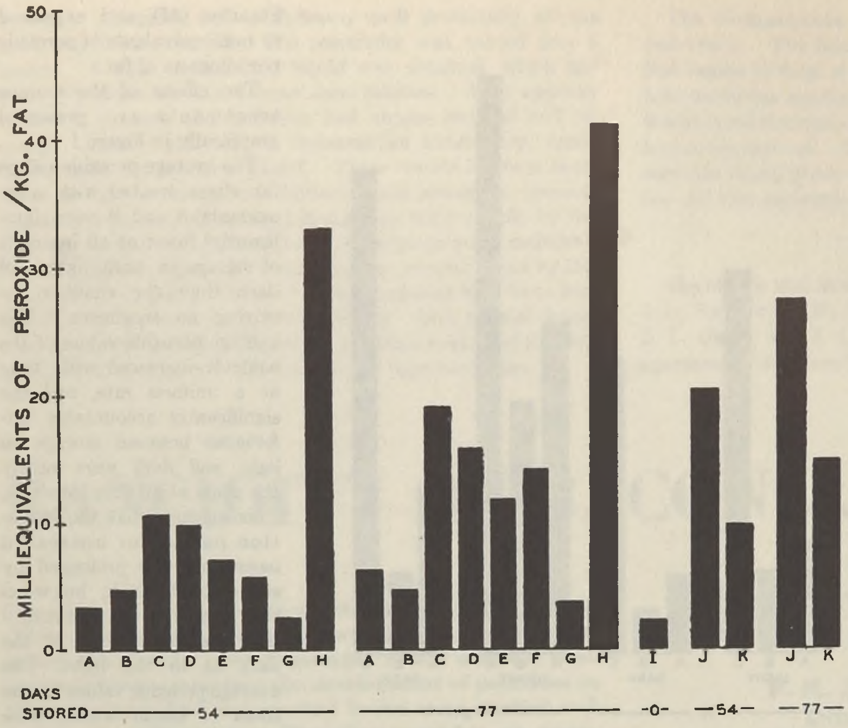

Figure 3. Comparative Effect of Antioxidants and Smoking on Rancidity Development in Sliced Bacon

A to I. Same as in Figure 2
J. Average for all treatments on unsmoked bacon
K. Average for all treatments on smoked bacon
Least significant difference (p = 0.05), 13.44

treated with A. These differences were highly significant after a period of 21 days. The development of peroxides in the treated bacon was significantly less when stored in the dark. The difference between light and dark for either treatment A or B became greater at each successive time interval, an indication that the antioxidants were most effective when the product was stored in the dark. Differences in the effect of the antioxidants became greater as the length of storage increased.

The results of this experiment show that the induction period is longer for storage in the dark than in the light, regardless of whether antioxidants A and B are used. Both antioxidants A and B retard the development of rancidity, the latter being superior in this experiment.

II. ANTIOXIDANT PROPERTIES OF GOSSYPOL

All of the fresh sides of bacon graded firm and were held for 10 days at 34° F. before curing in a brine consisting of 5 pounds of salt, 2 pounds of sugar, and 2 ounces of saltpeter in 4.5 gallons of water. All of the bacon slabs weighed between 7 and 8 pounds and were cured for 10 days. After curing, half (left sides) were given a light smoking with hickory wood. Both the smoked and unsmoked slabs were stored 10 days before being cut into slices 5 mm. thick.

In this study a total of three replicates was used. In each replication, ten slices were cut and randomized before treatment from each of four slabs of unsmoked bacon. Two randomized untreated slices from each slab which were used to determine the initial peroxide values gave an average of 2.9 milliequivalents per kg. of fat. A slice from each slab received one of the following antioxidant treatments: A, 0.02% nordihydroguaiaretic acid in hydrogenated vegetable oil; B, 0.06% *d*-isoascorbyl palmitate, 0.06% soybean lecithin, and 0.01% tocopherols in hydrogenated vegetable oils; C, D, E, F, and G, respectively, 0.05, 0.10, 0.20, 0.40, and 0.80% gossypol in Wesson oil; H, a control without any treatment.

The gossypol solutions were prepared by adding sufficient ether-extracted crude cottonseed oil containing 20.7 mg. of gossypol per ml. to Wesson oil to give the desired concentration. The slices were dipped into the antioxidants (A and B were heated to 50–55° C.), hung on small racks, and kept in the dark at approximately 80° F.

The preceding discussion refers to the treatment of the unsmoked bacon. Identical procedures were followed in the case of the smoked bacon. The initial peroxide value for the smoked bacon was 2.2 milliequivalents per kg. of fat.

After 14 days, half the samples in replication I were analyzed according to the procedure followed in section I. Also, the hydroxylamine index was determined by a method modified from that of Romeo *et al.* (*12*, *13*). Since the peroxide values had not increased except in the controls (the peroxide values of the controls were 21.3 and 2.9, respectively, for unsmoked and smoked bacon), the remaining samples in this replication were reserved in storage for further exploratory work. At the end of 28 days, half the remaining slices were analyzed. At this time there was a slight increase in peroxide values, again being more pronounced in the case of the controls; the unsmoked was 42.1 and the smoked 19.1. The rest of the slices in replication I were analyzed at 49 days. By this time the number of samples approaching rancidity was rapidly increasing; therefore, all slices in replication II were analyzed at 54 days. Replication III was analyzed at 77 days.

The average peroxide values obtained on the unsmoked bacon are shown in Figure 2 and for the smoked bacon in Figure 3. These data show that rancidity developed more rapidly in the untreated bacon (H) than in any other. For example, at 54 days the peroxide value of C on the smoked bacon is 31.2 and of G is 7.9% of that of the control; at 77 days, C is 45.5 and G is 9.5% of that of the control.

There were significant differences in the effects of the seven antioxidants at both 54 and 77 days. For example, after 54 days of storage, A, B, E, F, and G were significantly superior to C; and antioxidants A, E, F, and G were significantly superior to D on the unsmoked bacon. Antioxidant G was significantly superior to C for the smoked bacon. After 77-day storage of the unsmoked bacon, A, B, E, F, and G peroxide values were significantly lower than that for C; E, F, and G were lower than D, and G was lower than A. In the smoked bacon only antioxidants B and G gave significantly lower values than C.

Figure 3 shows the average peroxide values for all slices in all treatments of the unsmoked series (J) and that for all treatments in the smoked series (K) for both 54 and 77 days. The difference between the smoked and unsmoked series was highly significant When H (no antioxidant) treatment was omitted, the differences due to smoking were consistent for all antioxidants; i.e., the interaction of the antioxidants with smoking was nonsignificant for both storage intervals. This interaction, however, might have become significant after longer storage since the differences between the peroxide values for the smoked and unsmoked bacon would probably have increased faster with the less effective antioxidants.

In section I antioxidant B was superior to A, while there was no significant difference between them in section II. This may be due to greater random error in part II or to the fact that the bacon used in I was approaching the end of the induction period while fresh bacon was used in part II. This may also be attributed to supplementary action of the added antioxidant with different kinds or amounts of naturally occurring antioxidants in the bacon.

In treatment F for smoked bacon, one high value was obtained after 77 days of storage which was greater than the sum of the values for the other three slices. This high value throws bar F (Figure 3, 77 days) out of line with treatments C, D, E, and G.

All significant differences among the gossypol treatments were accounted for by linear regression on gossypol concentration transformed to a logarithmic scale. The deviation from linear regression was actually less than would be expected on the basis of random errors. The regression was highly significant. This means that within the range of concentrations used each increase in gossypol resulted in lower peroxide values.

Essentially comparable results were obtained from both the hydroxylamine and peroxide determinations. The hydroxylamine index (milligrams of hydroxylamine per 100 grams of fat) is a measure of the content of aldehydes and ketones in rancid fats and oils. The aldehydes and ketones react with hydroxylamine hydrochloride forming oximes and liberating free hydrochloric acid which may be titrated with standard alcoholic potassium hydroxide using bromophenol blue as an indicator. The correlations between the hydroxylamine and the peroxide values were: replication I, 0.951; replication II, 0.983; and replication III, 0.985. Thus, the peroxide and hydroxylamine values told the same story within the range of rancidity studied in this investigation. The peroxide values are, however, more easily determined than the hydroxylamine index.

DISCUSSION

Peroxides develop first on the exposed surfaces of the cuts of meat. If these peroxides do not develop too rapidly, it is possible to trim the surface and leave the edible portion. It is, therefore, desirable to know the rate at which the peroxides form on the surface even after a value of 20 milliequivalents is reached.

Controls for the hydrogenated vegetable oil and Wesson oil were not included in these studies even though it is known that they contain tocopherols (*9*) which stabilize animal fats. Since either hydrogenated vegetable oil or Wesson oil was added to all samples except the negative controls, the stabilizing effect obtained with all the antioxidants may have been supplemented by the constituents of the vegetable oils. The stabilizing effect from this source should be about the same in all treated samples; hence the differences observed are attributable to the antioxidants or amount of antioxidant used. The results with gossypol in varying concentrations indicate that it contributes the principal stabilizing effects rather than the constituents of Wesson oil. Only traces of gossypol remain on the surface of the bacon slabs after trimming and removing the rind. These traces would largely be destroyed by frying.

The usual method of extracting the fat from the samples was not used in these studies because the large number of samples involved required more expeditious methods, and the complete removal of the solvent from the extracted fat is not easy. Heating in the oven for 3 hours at 75° C., followed by the expression of the fat, are conditions readily reproducible. The peroxide values of samples near or at the end of the induction period may increase rapidly during the period of heating, but that is immaterial because the quality of bacon is judged when consumed. Any bacon which will not undergo the usual methods of preparation for serving without becoming rancid is not satisfactory. The method of rendering used is much less drastic and yields peroxide values lower than frying bacon.

Antioxidants are more effective when applied at the beginning of the induction period, as indicated in sections I and II. It is not practical, however, to add them until after the meat is cured and smoked. The peroxide values, after these operations are usually carried out, remain low as indicated by the initial peroxide values of 2.9 and 2.2 for unsmoked and smoked bacon, respectively (section II). White (*18*) obtained similar values working with smoked and unsmoked bacon. He found that holding bacon at −1.1° C. for 10 days prior to smoking was not detrimental.

These studies were designed for statistical analysis to show the differences in the antioxidants rather than for determining antioxygenic indices. Because of the differences in time elapsing between the time the controls and treated samples became rancid, it is difficult to determine just when the induction periods end. Moreover, the susceptibility to rancidity of bacon varies considerably from pig to pig.

Our studies indicate that smoking approximately doubles the keeping time of bacon, which is in agreement with White (*18*). Unsmoked bacon (section II) treatments A, B, E, F, and G show that they should keep four to five times as long as the untreated; C and D should keep about three times as long. In the case of the smoked bacon it appears that treatments C and D should keep about three times as long as treatment H. With smoking and antioxidants, the bacon should keep five times as long as with no treatment; for some treatments it keeps even longer.

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ALKYLATION OF ISOPARAFFINS

Application of the Carbonium-Ion Theory

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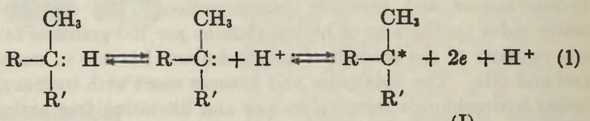
The reactions of paraffin and olefin hydrocarbons in concentrated sulfuric acid indicate that the intramolecular hydrogenation-dehydrogenation properties of this catalyst play an important role in the alkylation of isoparaffins with olefins. The marked similarity of the carbon skeletons of the hydrocarbons produced in the alkylation of isobutane with butenes and the copolymerization of isobutene with normal butenes in less concentrated acid suggest the formation of a carbonium-ion intermediate during the alkylation reaction, similar to that postulated by Whitmore for the polymerization reaction. The products predicted by the carbonium-ion mechanism for the alkylation of isobutane with olefins are in good agreement with those found experimentally. This mechanism also offers a logical explanation for the presence of secondary products and the reaction conditions necessary to obtain satisfactory alkylation of isoparaffins with olefins.

IN RECENT years the alkylation of isoparaffins with olefins in the presence of concentrated sulfuric acid and anhydrous hydrogen fluoride has become an important commercial process for the production of high-octane constituents of aviation fuels. Although many of the practical aspects of the process are well known, no satisfactory mechanism of the chemical reaction has been proposed which accounts for both the products formed and the role of the catalysts.

Birch and Dunstan (*1*) suggested that the initial step in the alkylation reaction is the formation of a complex compound between the catalyst and isoparaffin which reacts with the olefin to form the products. McAllister and co-workers (*18*) and Caesar and Francis (*5*) postulated that the alkylation occurs as a result of the initial carbon-to-carbon cleavage of the isoparaffin prior to reaction with the olefin.

A critical survey of the literature on the reactions of paraffin and olefin hydrocarbons with concentrated sulfuric acid suggested that the mechanism of the alkylation reaction is more intimately connected with the hydrogenation-dehydrogenation properties of this catalyst than is generally realized. The amphiprotic nature of sulfuric acid and the large value of its autoprotolysis constant (*10*) indicate that concentrated sulfuric acid is an excellent catalyst for proton transfer reactions such as hydrogenation-dehydrogenation, hydrogen exchange, isomerization, polymerization, and depolymerization. Since many of the observed products appear to result from intramolecular rearrangements similar to those found in the polymerization of olefin hydrocarbons in less concentrated sulfuric acid, the formation of a carbonium ion intermediate similar to that postulated by Whitmore (*22*) for the polymerization reaction would offer an explanation for many of the experimental results reported on the alkylation reaction. Considerable support for this view is found in the marked similarity of the carbon skeletons of the more highly branched octanes found in the alkylation of isobutane with butenes (*18, 19*) and the octenes reported for the copolymerization of isobutene with normal butenes (*21, 26*).

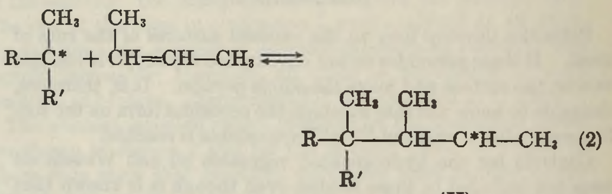
The experimental data reported in the literature indicate that with sulfuric acid the hydrogenation-dehydrogenation reactions of hydrocarbons occur only in the more concentrated acids (*1, 16*). The work reported by Ingold and co-workers (*13*) on the hydrogen exchange of paraffins in concentrated deutero-sulfuric acid showed that paraffins which contain a tertiary hydrogen atom exchange hydrogen much more readily than normal paraffins. The reduction of olefinic hydrocarbons in concentrated sulfuric acid observed by Ipatieff and Pines (*16*) revealed that this acid possesses the necessary properties for the transfer of hydrogen and electrons from one molecule to another. Since activation of the isoparaffin is necessary for the alkylation reaction (*1*), these facts suggest that the initial step is the ionization and partial dehydrogenation of the isoparaffin dissolved in the acid to form a carbonium ion:



$$R-\overset{CH_3}{\underset{R'}{C}}:H \rightleftharpoons R-\overset{CH_3}{\underset{R'}{C}}: + H^+ \rightleftharpoons R-\overset{CH_3}{\underset{R'}{C^*}} + 2e + H^+ \quad (1)$$

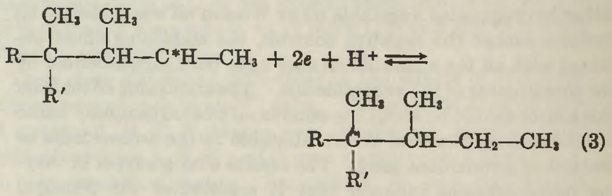
(I)

where C* indicates the carbon atom deficient in electrons. The carbonium ion (I) formed from the isoparaffin then adds to the olefin to form a higher-molecular-weight carbonium ion (II) as postulated by Whitmore (*22*); its hydrogenation then follows (the proton and two electrons may be supplied by the original isoparaffin or by other molecules in the reaction mixture) to give the saturated product (III):



$$R-\overset{CH_3}{\underset{R'}{C^*}} + \overset{CH_3}{CH}=CH-CH_3 \rightleftharpoons R-\overset{CH_3}{\underset{R'}{C}}-\overset{CH_3}{CH}-C^*H-CH_3 \quad (2)$$

(II)



$$R-\overset{CH_3}{\underset{R'}{C}}-\overset{CH_3}{CH}-C^*H-CH_3 + 2e + H^+ \rightleftharpoons R-\overset{CH_3}{\underset{R'}{C}}-\overset{CH_3}{CH}-CH_2-CH_3 \quad (3)$$

(III)

The carbonium ion (II) would be subject to the postulates of the Whitmore theory including instantaneous rearrangement of the carbon skeleton and depolymerization (*30*). These reactions of the carbonium ion throw considerable light on the mechanism of formation of the primary products found in the alkylation reaction and also explain the formation of secondary products.

The proposed mechanism is supported by the experimental results reported in the literature on the reactions of hydrocarbons in concentrated sulfuric acid and also by the conditions necessary for the alkylation reaction.

REACTIONS OF OLEFINS IN CONCENTRATED SULFURIC ACID

POLYMERIZATION. Ipatieff and Pines (*16*) made a thorough study of the effect of sulfuric acid in the polymerization of isopropylethylene, trimethylethylene, normal butenes, monomer, dimers, and trimers of isobutylene, and trimers and tetramers of propylene at various temperatures, concentrations of acid, and ratios of sulfuric acid to olefin treated. Employing 96% sulfuric acid, an acid to olefin ratio of 1.5 to 7 by weight, and a temperature of 0° C., they found that in all cases the hydrocarbon layer boiling up to 225–250° C. (approximately 30–40% of the product) contained only paraffin hydrocarbons as shown by the stability of the fraction to nitrating mixture. Even with 91% acid they found that the fraction boiling up to 200° C. contained 63% paraffins. However, with 87% acid only traces of paraffins were found in the same fraction, while with 77% acid only olefins were present.

The formation of paraffins by "conjunct polymerization" of olefins indicates that concentrated sulfuric acid possesses the necessary properties for the transfer of hydrogen and electrons from one hydrocarbon to another. This reduction of olefins by sulfuric acid may occur by a mechanism similar to that proposed by Burton and Ingold (*4*) for the chemical reduction of multiple carbon-carbon bonds which involves the addition of protons and electrons to the unsaturated carbon atoms.

HYDROGEN EXCHANGE. It has been known for some time that olefin hydrocarbons exchange hydrogen for deuterium in the presence of deutero-sulfuric acid (*12*). Recently Farkas and Farkas (*7*) showed that one of the reactions occurring during the polymerization of isobutylene over liquid deutero-phosphoric acid was the deuteration of isobutylene and its polymers; this indicates that hydrogen exchange in the case of olefins is rapid and a common phenomenon.

These results show that polymerization catalysts such as sulfuric and phosphoric acid can act as acceptors and donors of protons and hence effect hydrogen exchange.

DEPOLYMERIZATION. Several investigators have reported this reaction. Ipatieff and Pines (*16*) obtained the same products in the conjunct polymerization of isobutylene, diisobutylene, or triisobutylene in concentrated sulfuric acid. In the alkylation of isoparaffins it makes little difference whether isobutylene or its polymers (*2*, *3*, *18*) are used as the olefin feed, since the products obtained are essentially the same. Ipatieff and Pines (*15*) reported the depolymerization of isobutylene polymers in the presence of benzene using concentrated sulfuric acid as a catalyst, to give *tert*-butylbenzene instead of the expected octyl- or dodecylbenzene. Whitmore and Mosher (*28*) found that the decenes formed from isoamylenes in 75% sulfuric acid gave isobutylene and isohexenes on depolymerization, an indication that the products of the reaction may not necessarily be those forming the polymer.

ISOMERIZATION. The isomerization of olefins in the presence of acidic catalysts is a well known reaction. The isomerization may involve only a shift of the double bond, as illustrated by the conversion of 1-butene to 2-butene, or it may involve the rearrangement of the carbon skeleton. The latter type of isomerization will be discussed in more detail in another part of this paper.

REACTIONS OF PARAFFINS IN CONCENTRATED SULFURIC ACID

DEGRADATION OF ISOPARAFFINS. Birch and Dunstan (*1*) observed that 2,2,4-, and 2,2,3-, and 2,3,4-trimethylpentanes, 2,2,5-trimethylhexane, and 2,3-dimethylbutane were decomposed when stirred alone with concentrated sulfuric acid at room temperature. A complex mixture of isoparaffins of higher and lower molecular weight was obtained, together with acid-soluble compounds similar to those found during conjunct polymerization of olefins. The formation of appreciable amounts of isobutane when 2,2,4-trimethylpentane was treated with acid, coupled with the rapid darkening of the acid, suggested that the following reaction occurred:

$$C_8H_{18} \rightarrow C_4H_8 + \text{iso-}C_4H_{10}$$

that is, the alkylation reaction is to some extent reversible and certain isoparaffins can break down to give olefins and isoparaffins of lower molecular weight.

Grosse, Mavity, and Ipatieff (*9*) found that benzene reacted with 2,2,4-trimethylpentane in the presence of aluminum chloride and hydrogen chloride to give only *tert*-butylbenzene and pure isobutane which apparently confirmed the suggestion of Birch and Dunstan.

These results indicate that the degradation of isoparaffins in concentrated sulfuric acid can take place to a certain extent during the alkylation reaction and that some of the products can be formed in this manner.

HYDROGEN EXCHANGE. Ingold and co-workers (*13*) carried out a number of investigations on the hydrogen exchange of hydrocarbons in the presence of deutero-sulfuric acid. Their results indicate that, in concentrated sulfuric acid, hydrogen exchange takes place more readily in the case of saturated hydrocarbons containing a tertiary carbon atom.

PROPERTIES OF CONCENTRATED SULFURIC ACID

PROTOLYTIC PROPERTIES. In acid-base catalysis, solvents classified as amphiprotic are those which have the ability to add a proton to form lyonium ions or lose a proton to form lyate ions. Aprotic solvents are those with negligible acidity or basicity (*10*). In concentrated sulfuric acid the lyonium ion is $H_3SO_4^+$ and the lyate ion is HSO_4^-. For solutions of constant ionic strength in any solvent, the product of the concentrations of lyonium and lyate ions is a constant, the autoprotolysis constant of the solvent. In sulfuric acid we have the following equilibrium,

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

where the autoprotolysis constant is

$$K = (H_3SO_4^+)\ (HSO_4^-)$$

since the activity of the solvent does not vary greatly.

Concentrated sulfuric acid differs from other amphiprotic solvents in the large magnitude of its autoprotolysis constant so that effects due to the presence of the lyonium and lyate ions of the solvent are much more pronounced than they are in aqueous solutions. This ability of concentrated sulfuric acid to add protons to form lyonium ions and give off protons to form lyate ions explains why this acid is an excellent catalyst for proton transfer reactions.

DIELECTRIC CONSTANT. It is known that the interionic forces operating in concentrated sulfuric acid are of small magnitude (*11*), which is evidenced by freezing point, solubility, and indicator data; according to theory, sulfuric acid probably has a high dielectric constant, although this has not been measured. Anhydrous liquid hydrogen fluoride also has been reported to have a high dielectric constant (*20*).

The fact that the two best alkylating catalysts are reputed to have high dielectric constants does not seem to be mere coincidence. The ionizing abilities of these highly polar solvents undoubtedly play a part in the reactions of hydrocarbons in these solvents.

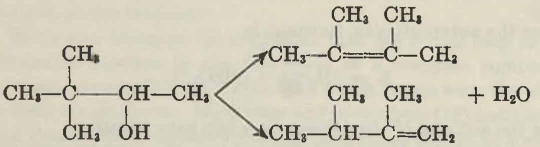
These chemical and physical properties of concentrated sulfuric acid suggest that the alkylation of isoparaffins with olefins is intimately connected with the hydrogenation-dehydrogenation properties of the acid. McAllister and co-workers (*18*) observed in several reactions that this property of concentrated sulfuric acid played a prominent role in the products obtained.

INTRAMOLECULAR REARRANGEMENTS

Any mechanism assigned to the alkylation reaction must consider the occurrence of intramolecular rearrangements during the reaction since many of the products found experimentally cannot be formed by simple addition of the olefin to the isoparaffin. Whitmore (*22, 23*) suggested that the formation of an intermediate carbonium ion in the polymerization of olefins and the dehydration of alcohols in the presence of acid catalysts may satisfactorily account for the known rearrangements which occur in these reactions. Instantaneous redistribution of the electronic structure of the positive ion, which involves a shift of the alkyl group or hydrogen atom, together with its bonding pair of electrons from a neighboring carbon atom to the carbonium carbon atom, forms the basis of this theory. Therefore if the alkylation reaction passes through the intermediate formation of a carbonium ion as the present mechanism suggests, rearrangements similar to those found in the polymerization of olefins and the dehydration of alcohols probably will be found.

The experimental results of the alkylation of isoparaffins with olefins in the presence of catalysts show that many of the primary products formed are the result of intramolecular rearrangements. Thus, the alkylation of isobutane with ethylene in the presence of anhydrous aluminum chloride and hydrogen chloride (*8*) is known to give mainly 2,3-dimethylbutane and 2-methylpentane; only a small amount of the expected 2,2-dimethylbutane is formed. The alkylation of isobutane with propylene (*18*) has been found to give mainly 2,3- and 2,4-dimethylpentanes instead of the expected 2,2-dimethylpentane, an indication that intramolecular rearrangement has taken place. Similar rearranged products are found in the reaction of isobutane and butenes (*18*).

A survey of the literature on the acid-catalyzed reactions of olefins and alcohols shows that such rearrangements are common and occur most readily in molecules containing a quaternary carbon atom. Thus, Whitmore and Rothrock (*29*) observed in the acid dehydration of *tert*-butylmethylcarbinol that the product consisted mainly of the rearranged olefins, 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene:



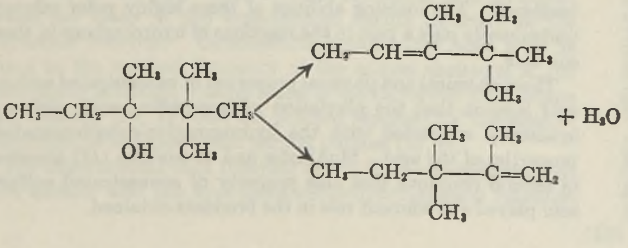
$$CH_3-C(CH_3)_2-CH(OH)-CH_3 \rightarrow \begin{cases} CH_3-C(CH_3)=C(CH_3)-CH_2 \\ CH_3-CH(CH_3)-C(CH_3)=CH_2 \end{cases} + H_2O \quad (4)$$

Cramer and Glasebrook (*6*) confirmed these results in their study of the vapor-phase dehydration of *tert*-butylmethylcarbinol and the rearrangement of 3,3-dimethyl-1-butene over the acidic catalyst, aluminum sulfate:

Reactant	Yield of Olefin, Volume %		
	3,3-Dimethyl-1-butene	2,3-Dimethyl-1-butene	2,3-Dimethyl-2-butene
3,3-Dimethyl-2-butanol	3.5	34.0	62.5
3,3-Dimethyl-1-butene	4.3	33.3	62.4

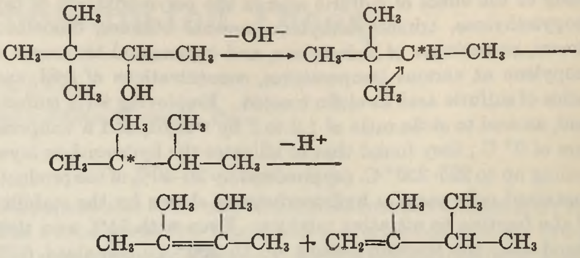
Only a small amount of the unrearranged olefin was obtained. Hydrogenation of the products would give mainly 2,3-dimethylbutane, one of the primary hydrocarbons found in the alkylation of isobutane with ethylene.

In the acid dehydration of methylethyl-*tert*-butylcarbinol, Whitmore and Laughlin (*25*) found that the product contained 80% of the expected olefin, 3,4,4-trimethyl-2-pentene and 20% of a rearranged olefin, 2,3,3-trimethyl-1-pentene:

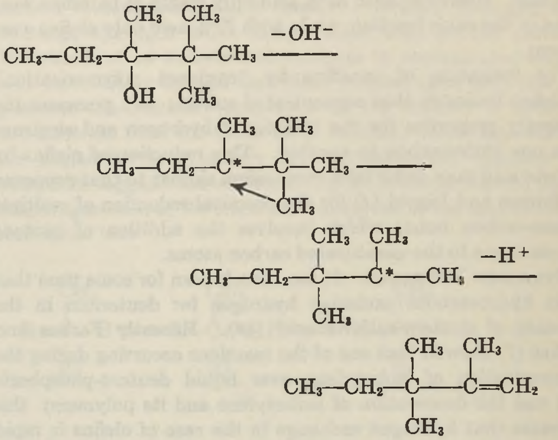


$$CH_3-CH_2-C(CH_3)(OH)-C(CH_3)_2-CH_3 \rightarrow \begin{cases} CH_3-CH=C(CH_3)-C(CH_3)_2-CH_3 \\ CH_3-CH_2-C(CH_3)_2-C(CH_3)=CH_2 \end{cases} + H_2O \quad (5)$$

These reactions indicate that rearrangement of the carbonium ion occurs as follows:



$$CH_3-C(CH_3)_2-CH(OH)-CH_3 \xrightarrow{-OH^-} CH_3-C(CH_3)_2-C^*H-CH_3 \longrightarrow CH_3-C^*(CH_3)-CH(CH_3)-CH_3 \xrightarrow{-H^+}$$
$$CH_3-C(CH_3)=C(CH_3)-CH_3 + CH_2=C(CH_3)-CH(CH_3)-CH_3 \quad (6)$$



$$CH_3-CH_2-C(CH_3)(OH)-C(CH_3)_2-CH_3 \xrightarrow{-OH^-} CH_3-CH_2-C^*(CH_3)-C(CH_3)_2-CH_3 \longrightarrow$$
$$CH_3-CH_2-C(CH_3)_2-C^*(CH_3)-CH_3 \xrightarrow{-H^+} CH_3-CH_2-C(CH_3)_2-C(CH_3)=CH_2 \quad (7)$$

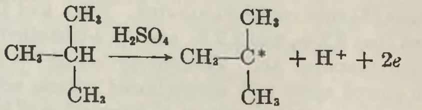
In these reactions the methyl group with its bonding pair of electrons shifts to the carbonium carbon atom to form a new carbonium compound which, by loss of a proton, gives the rearranged olefin.

In addition to this simple rearrangement, a hydrogen atom with its bonding pair of electrons may shift to the carbonium ion (*23*) prior to the shift of the methyl group. Thus, in the study of the dimers formed from tetramethylethylene and its isomers, Whitmore and Meunier (*27*) found that 25% of the product consisted of 2,2,4,6,6-pentamethyl-3-heptene which, he suggested, was formed in the manner shown on page 1213 from *tert*-butylethylene. The shift of a hydrogen atom with its pair of electrons from a neighboring carbon atom to the carbonium carbon atom has been observed in other reactions (*24*).

The factors controlling the nature and the extent of the rearrangement of the carbonium ion in the presence of acid catalysts are not fully understood; however, the experimental data show that rearrangements of the types mentioned above occur, and should be considered in any acid-catalyzed reactions, such as the polymerization of olefins, dehydration of alcohols, and alkylation of isoparaffins with olefins.

APPLICATION OF CARBONIUM-ION MECHANISM

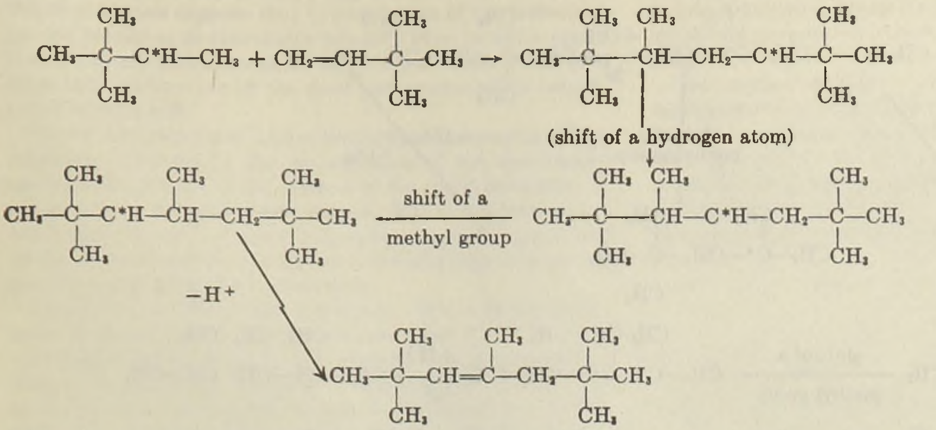
The proposed mechanism postulates that the first step in the alkylation reaction is the formation of a carbonium ion by the isoparaffin. Therefore, using isobutane,



$$CH_3-CH(CH_3)-CH_3 \xrightarrow{H_2SO_4} CH_3-C^*(CH_3)-CH_3 + H^+ + 2e \quad (I)$$

The second step in the reaction is the addition of the carbonium ion to the olefin to form a higher-molecular-weight positive ion as postulated by the Whitmore theory of acid polymerization of olefins (*22*). The addition of the

(From *tert*-Butylethylene)



positive ion to the olefin occurs on the carbon atom of the double bond containing the greater number of hydrogen atoms in accordance with the known polarization of the double bond. Intramolecular rearrangements similar to those discussed above may then occur subject to the following limitations:

1. The ease with which a methyl group shifts decreases in the following order:

$$(CH_3)_3C- > (CH_3)_2CH- > CH_3-CH_2-$$

2. A hydrogen atom may shift from a $-CH_2-$ or $-CHR-$ group, but the rate of shift from a methyl group is practically negligible.

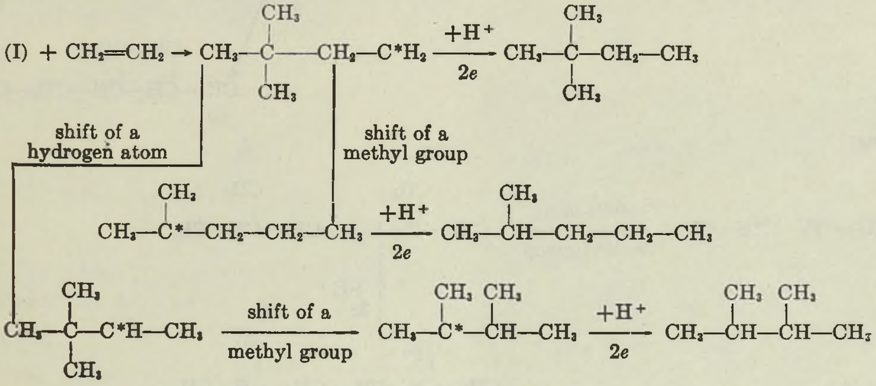
The alkylation of isobutane with ethylene, propylene, and butylenes may then occur as follows:

1. Reaction with Ethylene. The alkylation of isobutane with ethylene in the presence of concentrated sulfuric acid has not been observed, but the reaction proceeds in the presence of an aluminum chloride–hydrogen chloride catalyst (*14*).

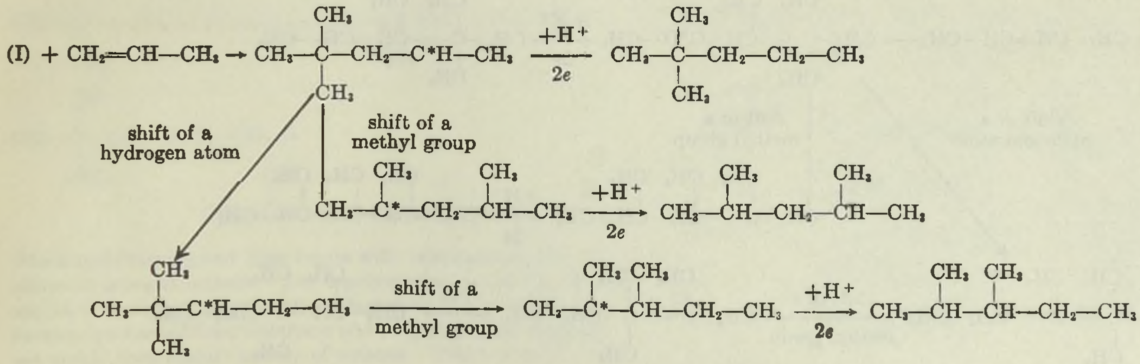
Table I compares hydrocarbons having the expected number of carbon atoms predicted by the carbonium-ion mechanism with those found experimentally in the alkylation of isobutane. The products predicted using the butenes are grouped together since the experimental data show that the hydrocarbons obtained using either normal butenes or isobutene are very similar. McAllister and co-workers (*18*) suggested this is due to isomerization of the olefins prior to reaction with the isoparaffin although no experimental evidence is available to substantiate this suggestion.

The expected isomers predicted for these reactions by the carbonium-ion mechanism are in good agreement with those found

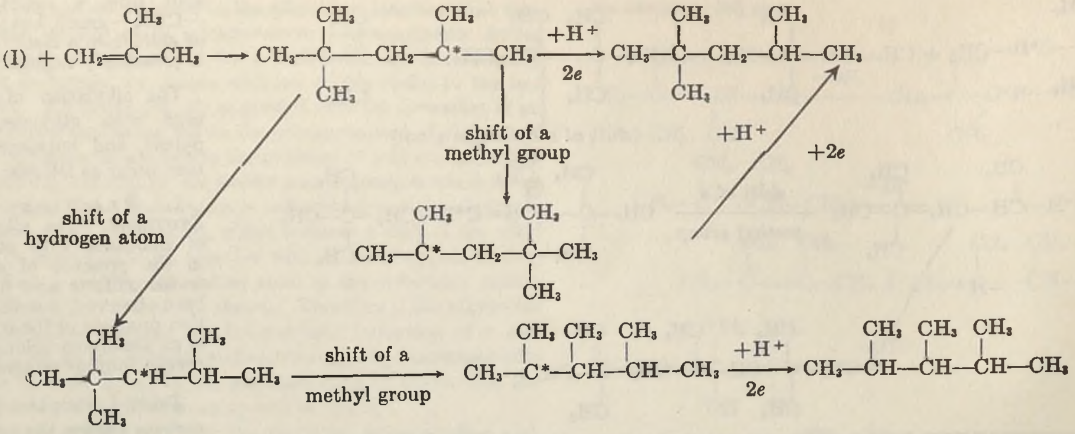
1. Reaction with Ethylene



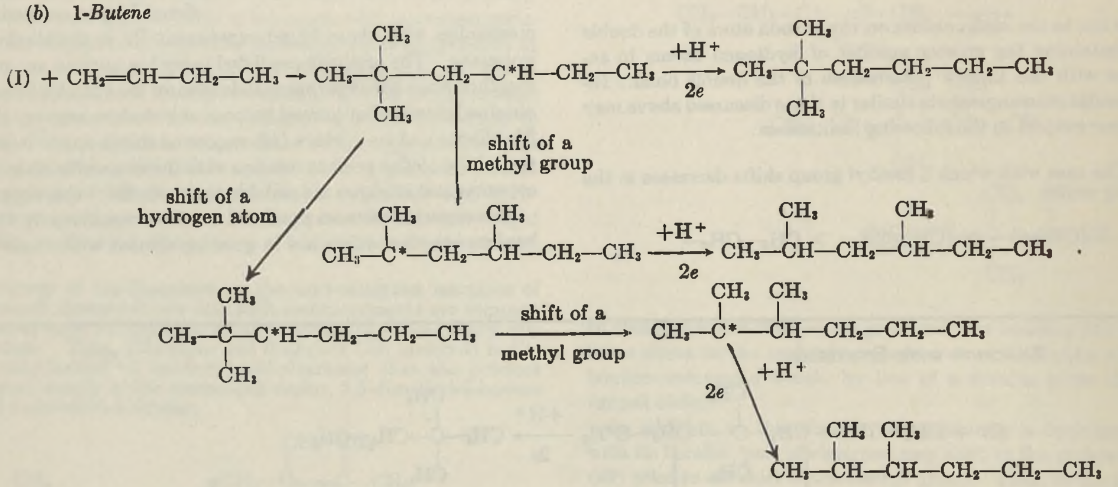
2. Reaction with Propylene



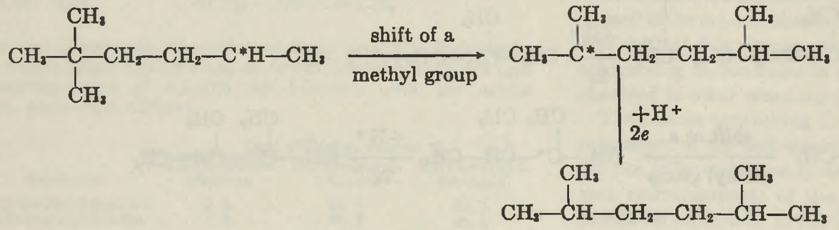
3. **Reaction with Butenes.** (*a*) *Isobutene*



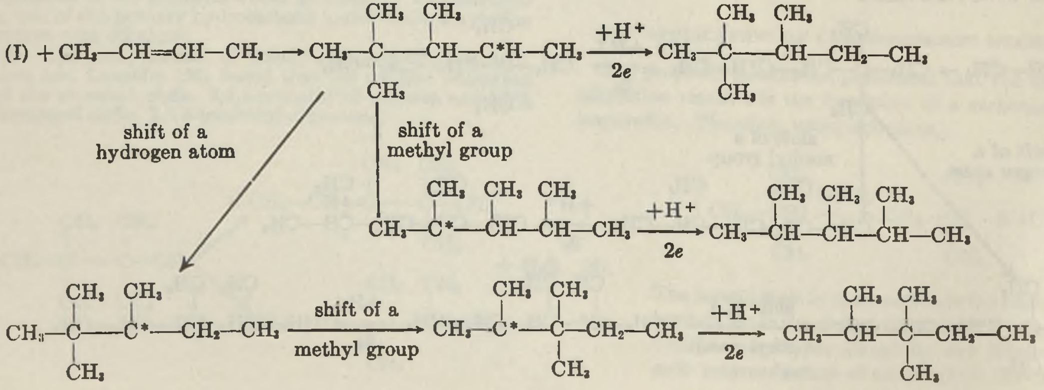
(*b*) 1-*Butene*



or the following:



(*c*) 2-*Butene*



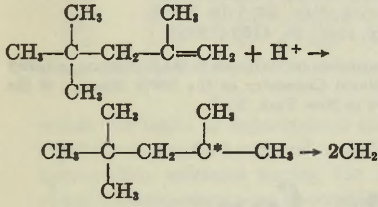
experimentally. The presence of only small amounts of the 2,2-dimethyl isomers suggests that hydrogenation of the carbonium ion can proceed at an appreciable rate only when its active center is on a tertiary carbon atom, so that the ions which would give these hydrocarbons are for the most part rearranged in concentrated sulfuric acid.

The smaller quantity of 2,2,3-trimethylpentane found in butene alkylates, compared to the concentration of the structurally similar olefin present in the product of the copolymerization of isobutene with normal butenes, suggests that the carbonium ion which gives this carbon skeleton is rearranged to a larger extent by the more concentrated acid used in the alkylation reaction to give 2,3,3- and 2,3,4-trimethylpentanes.

FORMATION OF SECONDARY PRODUCTS. The early investigations of the alkylation reaction revealed that many products were formed in various amounts which were entirely unexpected. Thus in the alkylation of isobutane with propylene (*18*) 5–10% of the product was identified as 2,2,4-trimethylpentane and 5–10% as 2,3,4- and 2,3,3-trimethylpentanes. Similarly in the alkylation of isobutane with 2-methyl-2-butene, these octanes were found to make up approximately 30% of the product and with 2-pentene about 20%. Any mechanism for the alkylation reaction must satisfactorily account for the presence of these isooctanes in these reactions.

Previous investigators (*8*, *18*) assumed that these products were formed by the dehydrogenation of isobutane to isobutene which then reacted with more isobutane to give the isomeric octanes. This explanation has been generally accepted because of the lack of a better one. The proposed mechanism gives a more satisfactory and logical reason for the presence of these octanes and also many of the other secondary products found in the alkylation reaction.

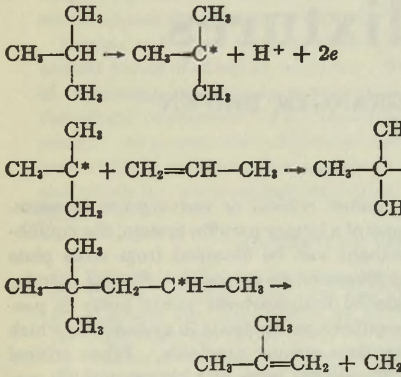
As mentioned previously, one of the reactions of olefins in concentrated sulfuric acid is depolymerization. It has been suggested (*30*) that the depolymerization reaction includes the formation of a carbonium ion as shown below:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH_2 + H^+ \rightarrow$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C^*}-CH_3 \rightarrow 2CH_2=\overset{CH_3}{C}-CH_3 + H^+$$

In the alkylation of isobutane with propylene, the depolymerization reaction may occur as follows:



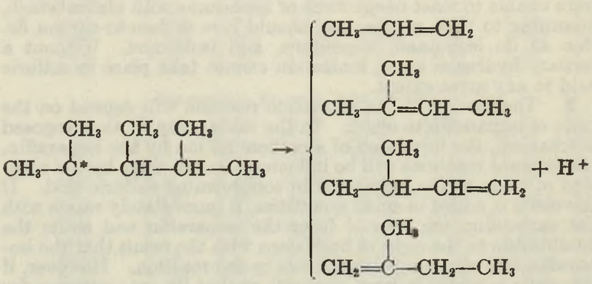
$$CH_3-\underset{CH_3}{\overset{CH_3}{CH}} \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C^*}} + H^+ + 2e$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C^*}} + CH_2=CH-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-C^*H-CH_3$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-C^*H-CH_3 \rightarrow CH_3-\overset{CH_3}{C}=CH_2 + CH_2=CH-CH_3 + H^+$$

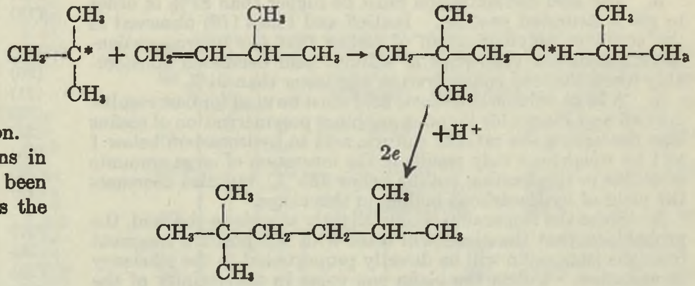
The isobutylene formed then reacts with isobutane to give the observed isomeric octanes. The depolymerization reaction cannot be the primary reaction of the higher molecular weight carbonium ion formed from isobutane and propylene since the product would then consist mainly of octanes. This is contrary to experimental observations which show that the product consists largely of heptanes. Since the depolymerization is a side reaction, unlimited production of isobutene from isobutane could not occur.

The product obtained in the alkylation of isobutane with butenes contains, in addition to the expected octanes, a number of lower and higher molecular weight hydrocarbons. The presence of isopentane and 2,2,5-trimethylhexane, for instance, may be explained by the partial depolymerization of the carbonium ion which gives 2,3,4-trimethylpentane on hydrogenation, into a mixture of propylene and pentenes:



$$CH_3-\overset{CH_3}{C^*}-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3 \rightarrow \left\{\begin{array}{l} CH_3-CH=CH_2 \\ CH_3-\overset{CH_3}{C}=CH-CH_3 \\ CH_3-\overset{CH_3}{CH}-CH=CH_2 \\ CH_2=\overset{CH_3}{C}-CH_2-CH_3 \end{array}\right. + H^+$$

These olefins may then react with the carbonium ion from isobutane to form heptanes and nonanes. Thus, 3-methyl-1-butene gives 2,2,5-trimethylhexane as shown below:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C^*}} + CH_2=CH-\overset{CH_3}{CH}-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-C^*H-\overset{CH_3}{CH}-CH_3$$

$$\xrightarrow[2e]{+H^+} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{CH_3}{CH}-CH_3$$

Rearrangement of the intermediate carbonium ion gives 2,3,5-trimethylhexane which has also been identified as one of the nonanes. The presence of isopentane could be accounted for by the reduction of the isopentenes formed above by the mechanism of conjunct polymerization.

This same reaction (i.e., depolymerization) explains why McAllister and co-workers (*18*) obtained isohexanes in the alkylation of isopentane with 2-butene. As mentioned before, Whitmore and Mosher (*28*) found that isohexenes were formed in the polymerization of isoamylenes, which resulted from the depolymerization of one of the decenes in the product.

The extent of the depolymerization reaction will be determined primarily by the structure of the carbonium ion and the rate at which it is hydrogenated to give the corresponding saturated hydrocarbon. This side reaction is probably one of the chief

TABLE I. COMPARISON OF PREDICTED AND EXPERIMENTAL RESULTS

OLEFIN	PREDICTED PRODUCTS	FOUND EXPERIMENTALLY
Ethylene	2,2-Dimethylbutane 2,3-Dimethylbutane 2-Methylpentane	2,2-Dimethylbutane 2,3-Dimethylbutane 2-Methylpentane
Propylene	2,2-Dimethylpentane 2,3-Dimethylpentane 2,4-Dimethylpentane	2,2-Dimethylpentane 2,3-Dimethylpentane 2,4-Dimethylpentane
Butenes	2,2,4-Trimethylpentane 2,3,4-Trimethylpentane 2,2,3-Trimethylpentane 2,3,3-Trimethylpentane 2,2-Dimethylhexane 2,4-Dimethylhexane 2,3-Dimethylhexane 2,5-Dimethylhexane	2,2,4-Trimethylpentane 2,3,4-Trimethylpentane 2,2,3-Trimethylpentane 2,3,3-Trimethylpentane Not reported 2,4-Dimethylhexane 2,3-Dimethylhexane 2,5-Dimethylhexane

causes for the complexity of the products found in all alkylation reactions.

Reaction Conditions. An understanding of the above mechanism and the reactions of olefins in concentrated sulfuric acid can explain the necessity for employing certain reaction conditions to obtain satisfactory alkylation of paraffins with olefins:

1. Only those paraffins which possess a tertiary hydrogen atom will take part in the reaction. To date no one has observed that normal paraffins react with olefins in the presence of concentrated sulfuric acid. This explains why McAllister and co-workers (*18*) were unable to react neopentane or neohexane with olefins which, according to their mechanism, should give carbon-to-carbon fission as do isobutane, isopentane, and isohexane. Without a tertiary hydrogen atom, ionization cannot take place in sulfuric acid to any great extent.
2. The success of the alkylation reaction will depend on the ratio of isoparaffin to olefin. In the initial step of the proposed mechanism, the formation of a carbonium ion by the isoparaffin, the forward reactions will be influenced in two ways by the addition of olefin to the isoparaffin in concentrated sulfuric acid. If the olefin is added in small quantities, it immediately reacts with the carbonium ion formed from the isoparaffin and shifts the equilibrium to the right in both steps with the result that the isoparaffin will play a substantial role in the reaction. However, if the olefin is added in large amounts so that its concentration far exceeds that of the carbonium ion formed from the isoparaffin, it can also form a positive ion as postulated by Whitmore. Increasing the concentration of the positive ion will shift the equilibrium to the left and result in a poor conversion of the isoparaffin.
3. The acid concentration must be higher than 87% in order to get a saturated product. Ipatieff and Pines (*16*) observed in the conjunct polymerization of olefins that the hydrogenation-dehydrogenation properties of sulfuric acid decreased considerably when the acid concentration was lower than 91%.
4. A large volume of sulfuric acid must be used for best results. Ipatieff and Pines (*16*) found in conjunct polymerization of olefins that decreasing the ratio of sulfuric acid to hydrocarbon below 1 to 1 by weight not only results in the formation of large amounts of olefins in the fraction boiling below 225° C. but also decreases the yield of hydrocarbons boiling in this range.
5. Since the isoparaffin is only slightly soluble in the acid, the probability that the olefin will react with the positive fragment from the isoparaffin will be directly proportional to the efficiency of agitation. Unless the olefin can come in the vicinity of the carbonium ion formed from the isoparaffin, it will form its own ion and combine with more olefin, and consequently low yields of alkylate will be obtained. This fact was recognized early in the development of the alkylation process when it was found that effective dispersion of the hydrocarbons in the acid is essential to obtain high yields of product.
6. Since concentrated sulfuric acid is a hydrogenation-dehydrogenation agent, the presence of diolefins in the olefin feed should have no effect on the character of the alkylate since they are readily hydrogenated to olefins. The presence of butadiene in concentrations as high as 22% (*1*, *17*) caused no change in the composition or yield of alkylate. The only observed effect was the more rapid deterioration of the catalyst due to dehydrogenation of part of the unsaturated hydrocarbon to form cyclic olefins as in conjunct polymerization.

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Equilibrium Constants for Methane in Paraffin Mixtures

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VAPOR-liquid equilibrium data for a number of binary systems of methane and various paraffin hydrocarbons have been reported (*4–7*, *9*, *10*). Sage and Lacey presented a correlation of methane equilibrium constants on the basis of the molecular weight of the paraffin hydrocarbon in the binary system with methane (*8*). As these authors point out, a correlation on the basis of molecular weight does not differentiate between the isomers.

The above-mentioned equilibrium constant data for methane have been correlated on the basis of critical or convergence pressures. *K* values from this correlation are presented in Table I. For illustrative purposes, Figure 1 shows a plot of the equilibrium constants at 160° F. against critical or convergence pressure. Knowing the critical locus of a binary paraffin system, the equilibrium constants for methane can be obtained from cross plots based on the *K* values presented in the table. Similar correlations for the other paraffin hydrocarbons would make it possible to estimate their equilibrium constants in systems for which vapor-liquid equilibrium data are not available. When critical data are not available, the critical locus of a binary paraffin system can be estimated by means of the correlation reported by Mayfield (*3*).

The correlation of the equilibrium constants for methane on the basis of convergence pressure can also be applied to complex mixtures. Data reported by Hanson and Brown (*1*) indicate that,

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Table I. Equilibrium Constants for Methane in Paraffin Mixtures

Pressure, Lb./Sq. In. Abs.	Equilibrium Constants 100° F.	160° F.	220° F.	280° F.	340° F.	400° F.	460° F.
Convergence Pressure, 1000 Lb./Sq. In. Abs.							
100	19.5	23.5	23.5	23.5	23.5	23.5	23.5
200	9.47	10.75	10.9	10.9	10.9	10.9	10.9
400	4.4	4.78	4.98	5.00	5.02	5.03	5.03
600	2.615	2.95	3.1	3.17	3.18	3.185	3.185
800	1.71	1.965	2.12	2.21	2.235	2.245	2.25
Convergence Pressure, 1500 Lb./Sq. In. Abs.							
100	24.3	27.8	28.0	28.0	28.0	28.0	27.3
200	12.1	13.45	13.77	13.77	13.77	13.77	13.45
400	5.965	6.39	6.63	6.79	6.82	6.83	6.68
600	3.9	4.19	4.37	4.49	4.53	4.54	4.46
800	2.89	3.07	3.21	3.31	3.33	3.34	3.34
1000	2.245	2.395	2.495	2.585	2.615	2.625	2.625
1250	1.69	1.765	1.815	1.847	1.848	1.85	1.85
Convergence Pressure, 2000 Lb./Sq. In. Abs.							
100	26.85	29.65	30.4	30.9	31.0	31.0	29.6
200	13.5	14.83	15.33	15.6	15.65	15.65	14.95
400	6.83	7.36	7.63	7.80	7.90	7.88	7.58
600	4.62	4.93	5.13	5.26	5.3	5.29	5.10
800	3.49	3.73	3.87	3.94	3.96	3.95	3.90
1000	2.84	2.985	3.085	3.16	3.175	3.175	3.14
1250	2.27	2.865	2.445	2.54	2.52	2.52	2.495
1500	1.865	1.935	1.995	2.015	2.02	2.02	2.02
1750	1.515	1.565	1.60	1.61	1.61	1.61	1.61
Convergence Pressure, 3000 Lb./Sq. In. Abs.							
100	28.8	31.1	33.15	34.6	35.55	35.3	32.3
200	14.7	16.0	16.9	17.6	18.0	17.9	16.47
400	7.54	8.18	8.64	8.99	9.23	9.16	8.53
600	5.21	5.6	5.93	6.18	6.25	6.23	5.89
800	4.005	4.335	4.520	4.695	4.75	4.72	4.545
1000	3.31	3.57	3.7	3.815	3.86	3.86	3.75
1250	2.735	2.94	3.04	3.12	3.14	3.145	3.10
1500	2.345	2.52	2.605	2.635	2.655	2.67	2.66
1750	2.075	2.20	2.25	2.275	2.30	2.33	2.35
2000	1.86	1.945	1.98	2.005	2.035	2.065	2.095
2500	1.46	1.51	1.54	1.565	1.585	1.61	1.63
Convergence Pressure, 4000 Lb./Sq. In. Abs.							
100	29.0	31.9	34.8	37.15	38.9	38.4	34.2
200	14.95	16.48	17.73	18.8	19.6	19.45	17.6
400	7.81	8.54	9.22	9.76	10.12	9.96	9.18
600	5.48	5.91	6.33	6.72	6.86	6.83	6.4
800	4.26	4.62	4.90	5.16	5.28	5.25	4.99
1000	3.55	3.83	4.02	4.2	4.30	4.30	4.13
1250	2.97	3.195	3.34	3.47	3.53	3.53	3.46
1500	2.57	2.77	2.885	2.96	3.01	3.015	2.995
1750	2.29	2.455	2.53	2.595	2.64	2.66	2.65
2000	2.09	2.20	2.275	2.325	2.355	2.375	2.38
2500	1.765	1.84	1.89	1.925	1.945	1.96	1.975
3000	1.52	1.57	1.605	1.63	1.645	1.66	1.675
3500	1.30	1.33	1.365	1.38	1.40	1.415	1.43
Convergence Pressure, 5000 Lb./Sq. In. Abs.							
100	29.0	32.2	36.0	39.2	41.5	40.9	33.75
200	15.0	16.6	18.3	19.9	21.0	20.55	18.4
400	7.96	8.69	9.50	10.25	10.75	10.6	9.64
600	5.61	6.08	6.59	7.1	7.38	7.28	6.79
800	4.40	4.79	5.12	5.465	5.69	5.635	5.32
1000	3.69	3.98	4.235	4.48	4.65	4.62	4.42
1250	3.10	3.325	3.535	3.70	3.81	3.81	3.70
1500	2.7	2.895	3.04	3.17	3.26	3.29	3.21
1750	2.42	2.58	2.69	2.79	2.85	2.89	2.85
2000	2.2	2.335	2.435	2.51	2.56	2.59	2.565
2500	1.89	1.995	2.065	2.11	2.14	2.16	2.15
3000	1.675	1.75	1.81	1.85	1.87	1.89	1.89
3500	1.515	1.565	1.605	1.645	1.67	1.695	1.695
4000	1.38	1.405	1.440	1.47	1.49	1.51	1.52
4500	1.245	1.26	1.275	1.29	1.303	1.317	1.325
Convergence Pressure, 6000 Lb./Sq. In. Abs.							
100	29	32.6	36.55	40.9	43.8	42.9	37.0
200	15	16.7	18.65	20.65	22.0	21.55	19.1
400	8.0	8.82	9.71	10.6	11.3	11.15	10.05
600	5.7	6.2	6.77	7.38	7.79	7.69	7.07
800	4.51	4.89	5.29	5.7	6.0	5.97	5.6
1000	3.79	4.05	4.37	4.67	4.90	4.89	4.67
1250	3.2	3.41	3.65	3.85	4.01	4.01	3.89
1500	2.8	2.97	3.15	3.31	3.41	3.45	3.37
1750	2.5	2.65	2.8	2.93	3.00	3.03	2.99
2000	2.28	2.4	2.535	2.645	2.69	2.71	2.70
2500	1.955	2.075	2.16	2.235	2.26	2.285	2.285
3000	1.75	1.85	1.91	1.97	2.00	2.015	2.020
3500	1.615	1.68	1.725	1.77	1.79	1.805	1.815
4000	1.50	1.54	1.575	1.605	1.625	1.64	1.65
4500	1.41	1.425	1.445	1.46	1.472	1.485	1.495

within the limits of experimental error, the curves of log *K vs.* log *P* for a paraffin hydrocarbon in binary and complex paraffin hydrocarbon mixtures having the same convergence pressure at a given temperature can be considered coincident.

The convergence pressure of a mixture at its critical temperature is its critical pressure. At any other temperature the convergence pressure is the pressure at which the equilibrium constants appear to converge to unity (*11*).

Kurata and Katz (*2*) published a method for estimating the critical points of complex mixtures. No straightforward method of estimating convergence pressures at temperatures other than the critical temperature of a complex mixture has yet been determined. At present the authors use the critical pressure of a mixture which is similar in composition to the mixture being studied and which has a critical temperature at the temperature in question.

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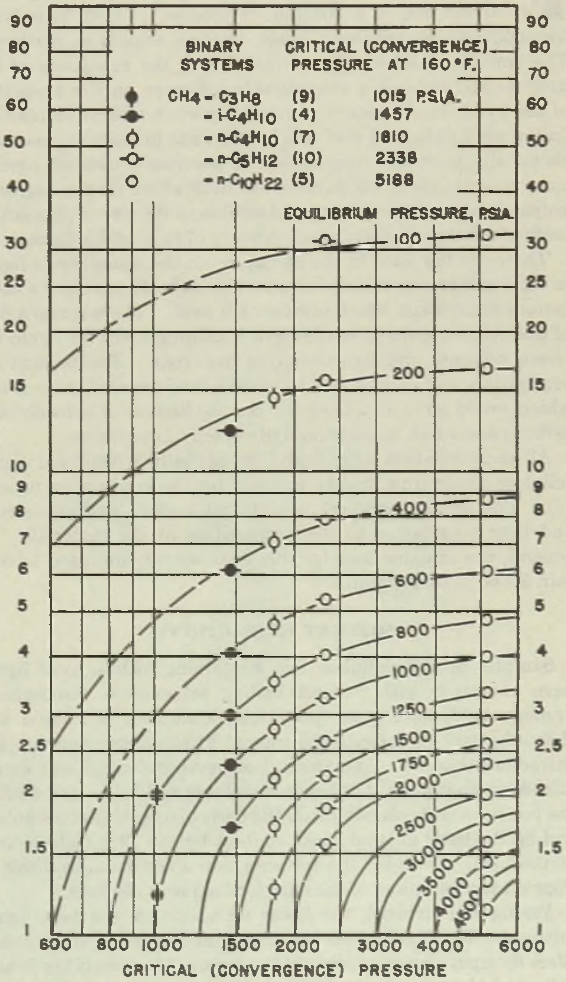

Figure 1

Extraction of Lignin from Hydrolyzed Lignocellulose

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The solubility characteristics of lignin present in acid-hydrolyzed lignocellulose were observed. Methanol was chosen as the most practical solvent for the separation and recovery of soluble lignin. Batch extraction experiments with methanol yielded lignin solutions of low concentration. The method of extraction, however, did not affect appreciably the nature of the lignin. Ninety-eight per cent of the lignin extracted was recovered by concentrating the extract to 25% lignin content and precipitating in 3 parts of water per part of concentrate. Ternary equilibrium data were obtained for the system methanol–methanol-soluble lignin–insoluble lignocellulose. Application of continuous countercurrent extraction methods based on these data yielded extracts containing as high as 11% lignin. Higher concentrations were shown to be feasible by re-use of the extract on fresh lignocellulose feed. Calculations are presented, indicating a steam consumption of 2500 pounds for solvent recovery per 100 pounds of lignin recovered. Actual methanol losses could not be determined in the apparatus used.

EARLIER work (*1*) indicated that rapid hydrolysis of wood, carried out in a continuous process, yielded hydrolyzed lignocellulose containing a lignin fraction soluble in methanol. The amount of soluble lignin varied with the conditions of hydrolysis and showed a considerable influence on the properties of the hydrolyzed product, particularly when utilized in plastics. Initial work indicated that this fraction was practically unaltered chemically from the composition of previously isolated lignins; since the method of production has little effect on the degree of polymerization, it was deemed desirable to develop a practicable method for the separation and recovery of this soluble lignin.

There are few data in the literature on the solubility of lignin in various solvents, mainly because it is difficult to isolate a satisfactory material on which to base such data. There is also a lack of distribution data or methods of obtaining them for lignin between solvents and lignocellulosic materials. The present investigation was carried out to obtain fundamental information which would serve as a basis for the production of substantially carbohydrate-free lignin from hydrolyzed lignocellulose.

All data reported were based on partially hydrolyzed lignocellulose made from maple sawdust by the continuous process (*1*). The sample numbers refer to pilot plant hydrolysis runs and bear no relation to the composition of the materials. In general, the samples used for this work were hydrolyzed to contain 50–60% total lignin.

SOXHLET EXTRACTIONS

Samples of lignocellulose 328 containing 55.0% total lignin were extracted with various boiling solvents at atmospheric pressure in Soxhlet type apparatus. Complete extraction was shown by lack of color in the solvent after passing through the extraction thimble. The amount of lignin extracted was determined by drying the thimble and contents at 105° C. and finding the loss in weight, calculated on the basis of original lignocellulose and on the basis of total lignin content by the 72% sulfuric acid method (*3*). Data for the solvents tested are listed in Table I. Figure 1 is a bar graph of the data for the lower alcohols.

Among the alcohols, the lower members are the best lignin solvents. The high values for normal and isobutyl alcohols are offset by signs of degradation of the lignin; the possibility is also indicated that the lignin-cellulose linkage itself is attacked to free more lignin. Higher-boiling alcohols (2-ethyl hexyl and cyclohexyl) attacked the lignin and lignocellulose so severely that satisfactory data could not be obtained. After allowance for excessive values caused by degradation, it may be concluded that lignin solubility decreases with increase in the number of carbon atoms in monohydric alcohols. The lignin solubility also decreases with increasing number or complexity of the side chains in the alcohol molecule.

The simple esters are poor lignin solvents, but dioxane is comparable with methanol as a lignin solvent. The ethylene glycol monoalkyl ethers are even better; this is surprising, in view of the fact that no decomposition was noted with these solvents, despite their elevated boiling points. Apparently, then, lignin degradation, decomposition, or cleavage is not necessarily a function of temperature alone, but is affected by the nature and structure of the solvent. This information emphasizes the sensitivity of the lignin molecule or building unit to mild or nonreactive materials.

More reactive solvents such as diacetone alcohol also yield degraded lignins; an even more reactive solvent, ethylene chlor-

TABLE I. SOXHLET EXTRACTION OF LIGNIN

Solvent	Boiling Point, ° C.	% Lignin Dissolved, Based on: Hydrolyzed wood	% Lignin Dissolved, Based on: Total lignin in hydrolyzed wood
Methyl alcohol	65	20.00	36.35
Ethyl alcohol	78	19.65	35.70
n-Propyl alcohol	97	18.85	34.30
Isopropyl alcohol	83	15.36	27.90
n-Butyl alcohol	116	20.92[a]	38.00[a]
Isobutyl alcohol	108	16.90[a]	30.70[a]
sec-Butyl alcohol	99	11.10	20.20
tert-Butyl alcohol	83	6.48	11.80
2-Ethyl hexyl alcohol	186	[a]	[a]
Cyclohexyl alcohol	160	[a]	[a]
Methyl acetate	57	10.80	19.65
Ethyl acetate	77	8.78	15.96
Dioxane	102	21.30	38.70
Ethylene glycol monomethyl ether	124	28.00	50.90
Ethylene glycol monoethyl ether	134	27.40	49.80
Ethylene glycol monobutyl ether	169	28.20	51.25
Diacetone alcohol	164	17.90[a]	32.50[a]
Ethylene chlorhydrin	127	86.00[a]	156.2[a]

[a] Degradation of lignin indicated by evolution of noncondensable gases or precipitation of resinous material from the extract.

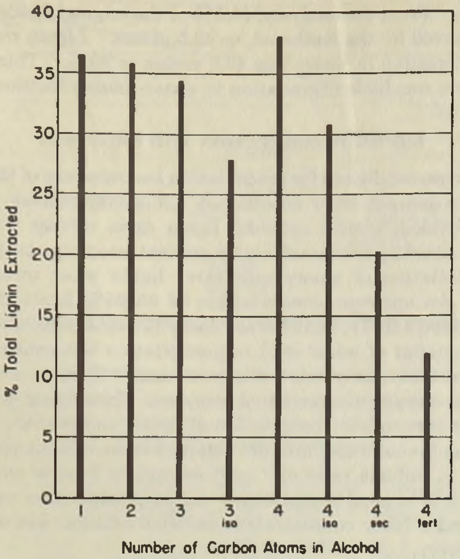

Figure 1. Extraction of Lignin with Boiling Alcohols (760 Mm.)

hydrin, evidentally decomposes cellulose as well as lignin. Qualitative experiments indicated that acetone and ethyl ether were relatively poor solvents for lignin.

On the basis of good solvent properties, lack of reactivity, low boiling point, low cost, and ease of recovery, further work was carried on with methanol as the solvent for lignin.

SOLUBILITY OF LIGNIN IN METHANOL

In order to check the effect of temperature on the solubility of lignin in methanol, one-gram samples of lignocellulose 333 (methanol-soluble lignin content, 22.9%) were mixed thoroughly with 10 grams of methanol in a constant-temperature bath for 30 minutes at temperatures up to 50° C. The extract was removed, centrifuged to clear it of suspended solids, weighed, and dried at 50° C. for 48 hours, and the lignin residue was weighed. Figure 2 gives the results.

Lignin solubility in methanol is limited at room temperature but rises rapidly at 35–40° C. The apparent leveling off at 50° C. was due only to limits of the amount of methanol-soluble lignin in the sample. It is indicated that at 50° C. and above, lignin solubility in methanol is not a limitation in the extraction process.

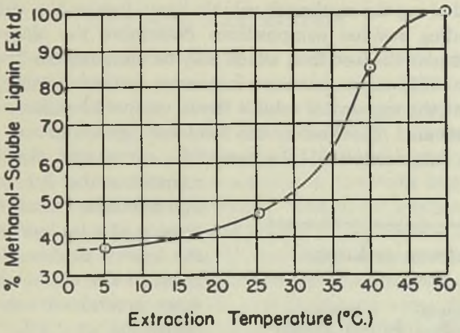

Figure 2. Effect of Temperature on Solubility of Lignin in Methanol

Temp., ° C.	Gram Lignin/ Gram Methanol	% of Methanol-Sol. Lignin Extracted
5.0	0.0086	37.7
25.5	0.0107	46.6
40.0	0.0195	85.1
50.0	0.0229	100.0

As further proof, a methanol-lignin solution concentrated to 28% lignin content by evaporation of solvent was used to extract lignin from lignocellulose 326 (methanol-soluble lignin content, 21.2%). At the end of 24 hours at room temperature, the lignin content had increased to 29.5% and after an additional 48 hours, to 30.0%; all due precautions had been taken to prevent evaporation of methanol.

PERCOLATION EXPERIMENTS

In an attempt to develop a batch method of extraction which would yield higher concentrations of lignin in the solvent, a Silex coffee percolator was charged with 1000 ml. of methanol in the lower chamber, and 300 grams of lignocellulose 326 wetted with 600 ml. of methanol (previously determined as the minimum retention) in the upper chamber.

Ten successive percolations with the same batch of methanol were then made, 10 ml. being withdrawn each time and tested for lignin content by drying and weighing. Presentation of the data in Figure 3 indicates the probability that the extracted lignin is a heterogeneous material, one part being extracted at a higher rate than the other. The semilogarithmic plot also shows that time, and not concentration, is the limiting factor in this extraction.

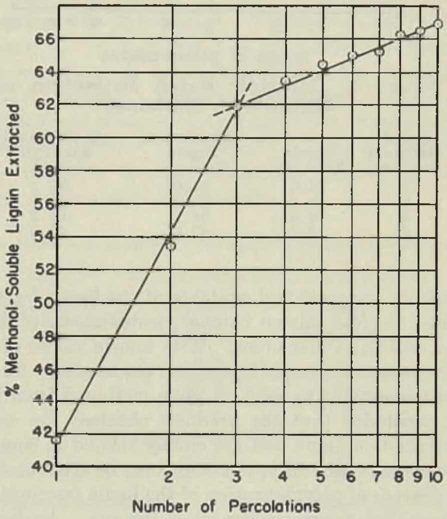

Figure 3. Rate of Extraction of Lignin with Methanol

No. of Percolations	Gram of Lignin/Ml. Ext.	% of Methanol-Sol. Lignin Extracted
1	0.0166	41.7
2	0.0214	53.5
3	0.0249	61.9
4	0.0258	63.5
5	0.0264	64.5
6	0.0267	65.0
7	0.0270	65.3
8	0.0276	66.3
9	0.0278	66.5
10	0.0282	66.9

Because of the relatively poor efficiency of extraction in this experiment, it was decided to utilize the most efficient part of the curve—namely, the first five percolations (allowing a safety factor)—and to use multiple batches of solvent.

Data of Figure 4 cover extraction of another batch of lignocellulose 326 under the conditions noted above, except that after each five percolations the extract in the lower chamber was withdrawn and a fresh batch of 1000 ml. of methanol was added. Lignin extraction was determined by concentrating each batch of extract to 25–35% lignin content by evaporation, pouring the concentrate into three times its own volume of slightly acidified water, filtering, drying the residue at 50° C. for 48 hours, and weighing.

The straight-line semilogarithmic plot again indicates the time limitation on lignin extraction. With poor contact and agitation inherent in the percolation apparatus, ten batches of methanol would be required to remove 90% of the lignin. The resulting low lignin concentration would result in high recovery costs.

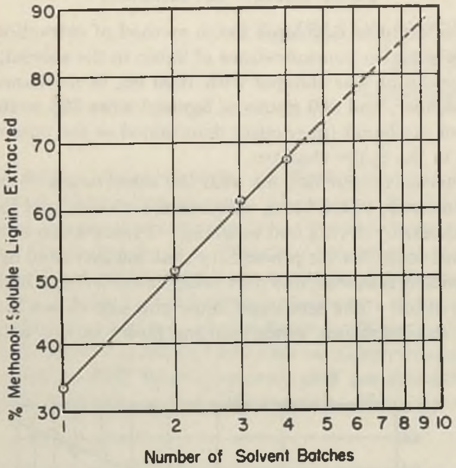

Figure 4. Multiple Batch Extraction of Lignin with Methanol

No. of Methanol Batches	Lignin Extd., G.	Cumulative Lignin Extd., G.	% Methanol-Sol. Lignin Extd.
1	21.0	21.0	33.1
2	11.5	32.5	51.1
3	6.4	38.9	61.2
4	3.7	42.6	67.0

A check on the methoxyl contents of the lignin fractions obtained from the four solvent batches yielded values of 19.5, 18.7, 19.2, and 19.7%, in that order. With known values of 20–21% methoxyl content for maple lignin, and the tendency for the acid hydrolysis treatment to split off some methoxyl from lignin, it may be concluded that the products obtained are essentially carbohydrate-free lignin and are closely related in composition. The differences in solubility, therefore, may be attributable to the varying degrees of polymerization of the lignin fractions.

A material balance was drawn up on this run. Analyses of the raw material and extracted residue were:

Ligno-cellulose	% Methanol-Sol. Lignin	% Insol. Lignin	% Cellulose (by Difference)
Original	21.2	33.4	45.4
Extracted	8.1	38.5	53.4

On a methanol-soluble lignin-free basis, the insoluble lignin is 42.3% for the original lignocellulose and 42.0% for the extracted lignocellulose. This proves that there was no appreciable effect of the method of extraction on the lignin-cellulose linkage or on the degree of polymerization of the insoluble lignin during extraction. From the analyses, 14.5% of the original lignocellulose was removed by the methanol, or 43.5 grams. Lignin recovered by precipitation in water was 42.6 grams or 98%. This proves that there was little degradation to water-soluble fractions.

LIGNIN PRECIPITATION AND RECOVERY

Optimum conditions for precipitation and recovery of the lignin from the extract were determined. A dilute extract yielded finely divided, almost colloidal lignin upon mixing with cold water. On the other hand, highly concentrated extracts resulted in precipitation of amorphous, tarry lignin when mixed with water. An optimum concentration of 25–35% lignin in methanol yielded a fluffy, light-brown, easily filterable lignin.

The amount of water used in precipitation was controlled, as excessive amounts yielded dilute methanol filtrates which resulted in uneconomic methanol recovery. Insufficient water resulted in incomplete precipitation of lignin, as the more concentrated methanol-water mixture retained some solvent power for lignin. A volume ratio of 1 part extract to 3 parts water was found to be a good compromise; lignin precipitation was complete, and a fairly concentrated methanol solution was obtained for recovery.

DISTRIBUTION DATA

Since initial batch extraction methods had proved inefficient as a result of excessive dilution of the extract when appreciable proportions of the methanol-soluble lignin were dissolved, development of a continuous countercurrent method was undertaken. To obtain fundamental data for design calculations, a ternary distribution plot was set up on the basis of the three-phase system (two solid, one liquid) soluble lignin–insoluble lignocellulose–methanol.

Samples of lignocellulose 333 (22.9% methanol-soluble lignin) were mixed with varying amounts of methanol, the mixture was held at 50° C. for 30 minutes, the extract was decanted and the methanol and lignin contents were determined by evaporating to dryness at 50° C. for 48 hours. It was found that the maximum retention of methanol by lignocellulose with this procedure was 3 parts methanol to 1 part of solid. From this point ratios of solvent to solid were increased up to 40:1. Table II gives data for the material balances in these determinations; actual distribution data are listed in Table III and plotted in Figure 5.

In the ternary diagram, feed compositions for methanol–lignocellulose 333 mixtures are indicated by the line starting at the 100% methanol apex and extending toward the point 22.9% methanol-soluble lignin, 77.1% insoluble lignocellulose on the left-hand side. Extract compositions for any given mixture are located along the methanol–soluble lignin line on the right. Corresponding residue compositions determine the shape of the curve under the feed line, which may be designated a "retention" curve. This curve reaches a minimum methanol value, indicating that the amount of soluble lignin retained has some effect on the methanol retention by the insoluble lignocellulose.

The intersection of the retention curve and the feed line represents the 3:1 methanol: lignocellulose mixture. Extension of a tie line parallel to the known tie lines from this point to the extract line indicates a retained extract concentration of 7.8%. By calculation based on the lignocellulose analysis, this composition should be 7.6%. Similar checking of the other extract concentrations showed that extraction of methanol-

Table II. Effect of Methanol-Lignocellulose Ratio on Extraction of Lignin

Ratio, Methanol: Ligno-cellulose	Ratio, Extract: Ligno-cellulose	Concn. of Lignin in Ext., %	Separated in Ext. % methanol-sol. lignin	Separated in Ext. % of methanol	Ratio, Lignin Separated: Methanol Separated	Concn. of Methanol in Residue, % Exptl.	Concn. of Methanol in Residue, % Calcd.	Ratio, Extract: Residue Exptl.	Ratio, Extract: Residue Calcd.
3.5:1	1.73:1	6.93	52.3	46.0	1.14	68.3	68.2	0.62:1	0.59:1
4:1	2.41:1	6.28	66.2	56.5	1.17	67.2	67.1	0.93:1	0.85:1
5:1	3.54:1	4.95	76.5	68.4	1.12	66.4	65.7	1.44:1	1.45:1
8:1	6.16:1	3.21	86.5	74.6	1.12	71.4	71.7	2.17:1	2.33:1
10:1	7.99:1	2.47	86.3	77.9	1.18	73.3	73.4	2.66:1	2.84:1
20:1	17.4:1	1.29	98.0	85.8	1.14	78.3	78.6	4.84:1	4.79:1
40:1	34.4:1	0.77	116	85.3	1.36	88.2	89.1	5.25:1	5.21:1

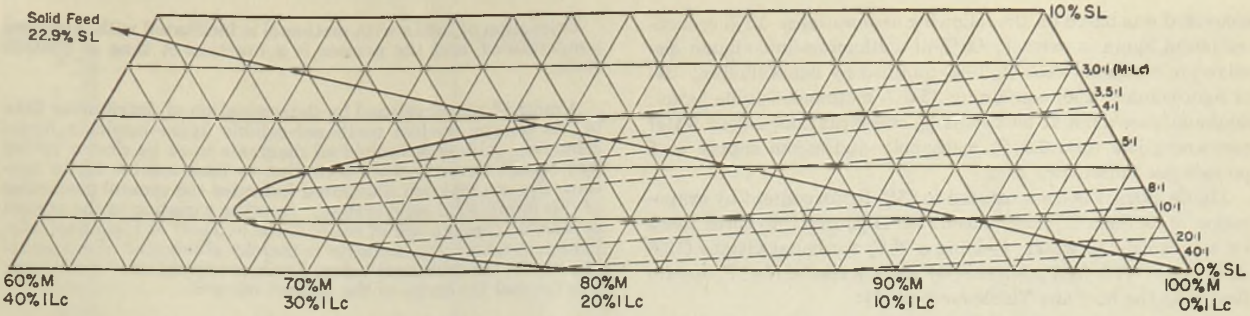

Figure 5. Distribution Equilibria for the System Methanol–Methanol-Soluble Lignin–Insoluble Lignocellulose

Table III. Ternary Extraction Data for System Methanol (M)–Soluble Lignin (SL)–Insoluble Lignocellulose (ILc)

Ratio, Methanol: Lignocellulose	Compn. of Mixture, %			Compn. of Extract, %		Compn. of Residue, %		
	M	SL	ILc	M	SL	M	SL	ILc
3.5:1	77.8	5.1	17.1	93.1	6.9	68.3	4.0	27.7
4:1	80.0	4.6	15.4	93.7	6.3	67.2	3.1	29.7
5:1	83.4	3.8	12.8	95.0	5.0	66.4	2.3	31.3
8:1	88.9	2.5	8.6	96.8	3.2	71.4	1.1	27.5
10:1	90.9	2.1	7.0	97.5	2.5	73.3	1.0	25.7
20:1	95.2	1.1	3.7	98.7	1.3	78.3	0.1	21.6
40:1	97.5	0.6	1.9	99.2	0.8	88.2	0	11.8

soluble lignin was complete in every instance. Discrepancies between experimental and calculated values can be accounted for as errors in plotting the experimental points and the curve.

These data signify that extraction of soluble lignin from lignocellulose with methanol is an unidirectional process, not subject to any equilibrium limits. This would indicate further that the methanol-soluble fraction is not chemically but is physically combined with the balance of the lignocellulose.

Although all of the soluble lignin dissolved in the methanol, not all of it is readily recoverable. A large proportion of the dissolved lignin is retained along with the methanol in the residue. Much of the retained extract can be recovered by pressing the residue, but in a countercurrent system it would be removed by contact with more dilute extract. The extract concentration is not limited to 7.8%, as lignocellulose could be mixed with a higher concentration of extract and solution of lignin would still occur. In this case the feed line would run from the initial extract composition point on the methanol–soluble lignin line to the same lignocellulose composition point noted on the left-hand side of Figure 5.

CONTINUOUS EXTRACTION

An experimental unit was set up for continuous extraction of lignin with methanol. A vertical Pyrex tube, 40 inches long and $^3/_4$ inch in inside diameter, was equipped with a spiral-screwfeed device at the top to feed 20-mesh lignocellulose 333. The extract overflowed just below the solid feed point, but solids carry-over was minimized by use of an inner concentric glass tube immersed to a depth of 6 inches in the methanol. Methanol was provided by evaporating solvent continuously from an electrically heated flask, condensing, and returning the hot liquid through a trap to the bottom of the extractor. Agitation was maintained in early runs by a stream of compressed air entering the extractor through a perforated glass distributor placed above the methanol feed point. Excessive cooling of the methanol, loss of solvent, and carry-over of lignocellulose particles by the air stream led to modification of the operation, in which methanol vapor and liquid were fed to the extractor. The vapor served to agitate the solids in the column, maintained the methanol at the boiling point at the base of the column, and was finally condensed and cooled by an air stream carried across the top of the extractor. Data for the runs listed in Table IV were obtained only after the extractor had been brought into balance for a given set of conditions. Extracts were measured and tested for lignin content over the period required to feed 20-gram lignocellulose samples, the feed being maintained as constant as possible with a manually controlled feed device.

Examination of Table IV shows that agitation is most important for extraction of lignin from lignocellulose. Use of even a moderate flow of air (25 ml. per minute) increased substantially the proportion of lignin extracted. The feed rate of lignocellulose did decrease, but the reduction was not sufficient to account for increased extraction as a function of retention time of lignocellulose in the column. Higher rates of air flow indicated a peak value which would effect maximum extraction of the lignin under the operating conditions at about 325 ml. per minute. Higher flow rates probably decrease extraction efficiency by lowering excessively the methanol temperature.

Table IV. Continuous Extraction Runs

Feed Rate per Min.		Extract Rate, G./Min.	Extract Concn., % Lignin	% of Lignin Extd.
Air, ml.	Lignocellulose, grams			
0	1.05	24.9	0.27	27.6
25	0.86	25.3	0.40	51.5
325	1.14	25.5	0.63	61.0
400	1.25	25.0	0.60	53.2
		Methanol Vapor Agitation		
...	2.11	35.6	0.68	48.9
...	1.51	27.7	0.87	68.5

The first run made with methanol vapor agitation was evidently fed at too fast a rate. The second run, however, although faster in lignocellulose feed rate than the foregoing air-agitated runs, was considerably more efficient in lignin extraction; 68.5% of the soluble lignin in the lignocellulose was removed. This value is comparable with results of the ten percolation and four multiple-batch percolation extractions. Lignin concentration in the extract, although higher in the last continuous extraction run than in the preceding ones, is still too low for practical purposes. This factor was limited by lignocellulose and methanol feed rates. The former could not be increased because the capacity of the extractor was small; the latter could not be decreased appreciably without interrupting continuous flow of solvent to the extractor with the feed system.

Similar operation in a larger continuous extractor (1.75 inches i.d. and 16 feet 2 inches high) yielded extracts containing as high as 11% lignin.

STEAM CONSUMPTION FOR METHANOL RECOVERY

As an indication of the economic feasibility of the process developed, calculations were made for steam requirements in methanol recovery. Consumption of steam per 100 pounds of lignin recovered was based on the following assumptions: 10% concentration of lignin in extract; 90% of methanol-soluble lignin dissolved in methanol extract, 10% retained by lignocellulose; use of lignocellulose 256, containing 33.3% methanol-soluble lignin; methanol recovered at 98.2 mole % concentration; spent water containing less than 0.01% methanol; and steam supply at 5 pounds per square inch gage.

Lignin extract is concentrated to 25% lignin content by evaporation of methanol. The concentrate is poured into three times its own weight of water, yielding a 25% methanol filtrate (15.8 mole %). With feed preheated by spent water to 156° F. and referring to the McCabe-Thiele method (*2*):

$q = 1.043$
slope of q-line $= 24.3$
minimum reflux $= 1.04$
practical minimum reflux $= 1.04 \times 1.5 = 1.56$
$V/D = 2.56$

Approximately twenty theoretical plates are required, according to the methanol–water vapor liquid equilibrium diagram. The heat requirements are:

Evaporation of methanol	313,170 B.t.u.
Distillation of filtrate	415,400
Distillation of washings[1]	1,661,600
Total	2,390,170 B.t.u.

$$\frac{2{,}390{,}170}{960} = 2500 \text{ lb. steam per 100 lb. lignin recovered}$$

[1] Methanol retained in lignocellulose recovered by countercurrent washing with water, yielding a 25% methanol solution.

CONCLUSIONS

Although the ethylene glycol monoalkyl ethers were the best solvents tested as extractants of lignin from acid-hydrolyzed lignocellulose, methanol was chosen as the most practical because of its low cost, ease of recovery, and good solvent power.

Extraction of lignin with methanol is facilitated with increased temperatures, and the process is a function of time of contact alone.

A method was developed for determination of distribution data in the ternary system methanol–soluble lignin–insoluble lignocellulose. Although individual diagrams must be drawn up for hydrolyzed lignocelluloses according to their soluble lignin content, the one diagram illustrated indicates the general properties of this liquid-solid-solid system. Another variation in the system is possible through use of recirculated extracts at higher soluble-lignin contents; the necessity is thereby eliminated of evaporating any of the methanol before lignin precipitation. Such work was beyond the scope of the present research.

Optimum conditions were set up for precipitation and recovery of the lignin extracted, and data were presented indicating that, although the lignin is practically unchanged in composition (particularly methoxyl content) by the method of extraction, the products obtained are probably part of a polymeric series.

Operation of a continuous laboratory extractor has shown the feasibility of continuous operation, although equipment must be developed to feed lignocellulose at a uniform rate. A larger extractor yielded extracts containing as high as 11% lignin.

Calculations on methanol recovery show a steam consumption of 2500 pounds per 100 pounds of lignin recovered, but pilot plant operations will be required to determine methanol losses, which are the most critical factors in the economy of the process. (The process described is the subject of patent applications.)

ACKNOWLEDGMENT

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Nomograph for Absorption Factor Equation

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CERTAIN methods for the design of countercurrent absorbers (*1, 2*) involve the use of the absorption factor equation

$$E = \frac{A^{N+1} - A}{A^{N+1} - 1}$$

where E = "efficiency" of operation
A = absorption factor
N = number of theoretical plates in system

Figure 1 is developed from the transformed equation,

$$1 - E = \frac{A - 1}{A^{N+1} - 1}$$

by the combination of the two simplest types of nomograph—namely, the Z-type and the logarithmic type.

Because of the kind of equation involved, no reading is obtainable from the chart when $A = 1$. In this case, however,

$$E = \frac{N}{N+1} \text{ or } N = \frac{E}{1-E}$$

The nomograph can be used to solve for any of the variables E, N, or A, the other two being known:

Method I. To solve for E, A and N being given: Connect the values of A and N to give A^{N+1}. Make the simple calculations $(A - 1)$ and $(A^{N+1} - 1)$. Connect the values of $(A - 1)$ and $(A^{N+1} - 1)$ to intersect the E scale at the appropriate value of E.

Method II. To solve for N, A and E being given: Make the simple calculation $(A - 1)$. Connect $(A - 1)$ and E, and extend to give the appropriate value of $(A^{N+1} - 1)$. Compute A^{N+1} from the value of $(A^{N+1} - 1)$. Connect A and A^{N+1} to obtain the appropriate value of N.

Method III. To solve for A, N and E being given: In this case the solution is by trial and error. Successive values of A are chosen, and method I is applied until a value of A is found which, when the known value of N is used, gives the known value of E.

Occasionally values of A or $A - 1$ are required which do not appear on the scale of the chart. In order to handle these values,

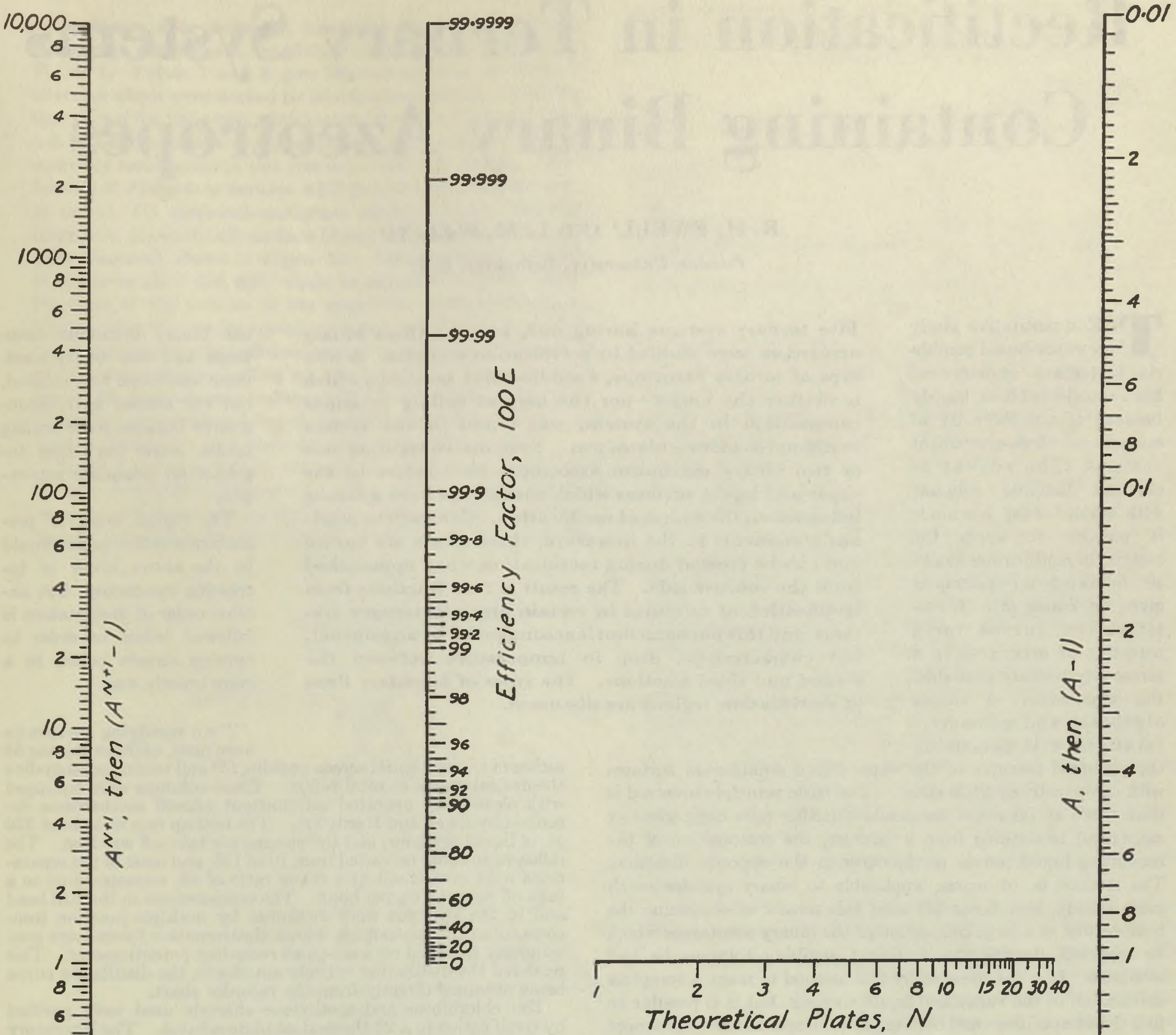

Figure 1. Nomograph for the Absorption Factor Equation

a factor of 10 or some power of 10 may be employed to bring them onto the scale. The necessary correction to the corresponding scale value of A^{N+1} or $(A^{N+1} - 1)$ must be made before proceeding.

ACKNOWLEDGMENT. The writer acknowledges with thanks the permission granted by the managenent of National Oil Proprietary Ltd. for the publication of this paper.

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Rectification in Ternary Systems Containing Binary Azeotropes

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Five ternary systems having one, two, or three binary azeotropes were studied by rectification analysis. A new type of ternary azeotrope, a saddle-point azeotrope which is neither the lowest- nor the highest-boiling invariant composition in the system, was found in the system methanol-acetone-chloroform. Systems containing one or two binary maximum azeotropes have ridges in the vapor and liquid surfaces which sometimes have a strong influence on the course of rectification. Contrary to previous statements in the literature, these ridges are curved and can be crossed during rectification when approached from the concave side. The result is four fractions from rectification of mixtures in certain areas in ternary systems, and this phenomenon is accompanied by an unusual, but characteristic, drop in temperature between the second and third fractions. The types of boundary lines of rectification regions are discussed.

THE quantitative study of vapor-liquid equilibria in ternary systems has been a neglected field, largely because of the difficulty of analysis of three-component mixtures. The advent of efficient distilling columns with small holdup has made it possible to apply the method of rectification analysis following the principles given by Young (*8*). If rectification curves for a number of mixtures in a ternary system are available, the application of simple algebraic and geometric relations will determine the principal features of the vapor-liquid equilibrium surfaces with comparatively little effort. The basic principle involved is that, when an invariant composition (either pure component or azeotrope) is distilled from a mixture, the composition of the remaining liquid moves rectilinearly in the opposite direction. The method is, of course, applicable to binary systems much more simply, and Lecat (*2*) used this means to determine the composition of a large proportion of the binary azeotropes which he reported, despite the inefficient distilling columns he had available. It is not possible by this method to make a complete delineation of the vapor and liquid surfaces, but it is possible to find the compositions and boiling points of any ternary azeotropes in the system and to locate the boundary lines of the rectification regions.

The studies reported in this paper include some of the principal types of ternary systems containing binary azeotropes, and the results serve to clarify some fundamental ideas pertaining to rectification in such systems. The systems studied include the following types of ternary systems:

1. One binary maximum azeotrope
    - *a.* Component opposite binary maximum azeotrope is lowest boiling of three components
    - *b.* Component opposite binary maximum azeotrope is highest boiling of three components
2. Two binary minimum azeotropes
3. Two binary minimum azeotropes and one binary maximum azeotrope
4. Two binary maximum azeotropes and one binary minimum azeotrope

The simplest type containing one binary minimum azeotrope was not studied since the course of rectification in such systems is well known. Types containing two binary maximum azeotropes, three binary minimum azeotropes, and three binary maximum azeotropes were not studied. One system containing one binary minimum azeotrope and one binary maximum azeotrope was studied, but the results were inconclusive because some boiling points were too close together for adequate separation.

The logical order of presentation in this paper would be the above order of increasing complexity, but another order of presentation is followed below in order to develop certain points in a more orderly way.

Two rectifying columns were used, each containing 65 inches of $^1/_2$-inch spiral screen packing (*3*) and testing seventy-five theoretical plates at total reflux. These columns were equipped with electrically operated intermittent takeoff mechanisms described by Ewell and Hardy (*1*). The boil-up rate was about 320 cc. of liquid per hour, and the volume per take-off was 2 cc. The reflux ratio could be varied from 10 to 125, and most of the separations were carried out at a reflux ratio of 80, corresponding to a take-off rate of 4 cc. per hour. The temperatures in the still head and in the still pot were measured by multiple-junction iron-constantan thermocouples, whose electromotive forces were continuously recorded on a six-point recording potentiometer. This rendered the distillation entirely automatic, the distillation curve being obtained directly from the recorder chart.

The chloroform and methylene chloride used were purified by rectification in a 20-theoretical-plate column. The laboratory acetone and methanol after drying were found to be sufficiently pure for the purpose. Mixtures were made up by measuring the volumes of the pure components and using the densities to calculate the weight compositions. Compositions within 1% by weight of the components were considered satisfactory.

The compositions and boiling points of the binary azeotropes involved were taken from Lecat (*2*) or Timmermans (*7*) and checked when questionable by the distillation method or by direct determination of the vapor-liquid equilibrium curves using standard methods.

METHANOL-ACETONE-METHYLENE CHLORIDE

This ternary system contains two binary minimum azeotropes: one in the methanol-acetone system which contains 86.5% acetone and boils at 54.6° C., and one in the methanol-methylene chloride system which contains 94% methylene chloride and boils at 39.2°. The other binary system, acetone-methylene chloride, has no azeotrope. Methylene chloride is the only liquid known to the writers that makes a minimum azeotrope with methanol which boils lower than acetone and still does not make a binary azeotrope with acetone. It was this unique property of methylene chloride that led to a study of this system in order to determine whether the methanol-acetone azeotrope could be separated into methanol and acetone by azeotropic distillation, since this azeotrope is of interest in the wood distillation industry.

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The binary data presented, together with the boiling points of the pure components, are plotted on a triangular diagram in Figure 1. Points 1 and 2 give the compositions of synthetic mixtures which were studied by rectification analysis. Rectification curves for these two mixtures are shown in Figures 1-1 and 1-2. These studies revealed no ternary azeotropes, so that the course of rectification in this system is relatively simple. Rectification of mixtures in the area *ADE* gave the following fractions, in order: (1) methanol–methylene chloride binary minimum azeotrope, (2) methanol–acetone binary minimum azeotrope, (3) pure methanol, shown in Figure 1*A*. Rectification of mixtures in the areas *DEB* and *EBC* would be expected to give the three fractions at the vertices of the respective rectification region. The rectification results agreed with this expectation in general, but the column was not efficient enough to make good separations of the compositions boiling at 54.6° and 56.4° in area *DEB* nor of the compositions boiling at 39.2° and 41.5° in area *EBC*. However, compositions lying on lines *ED* and *EB* were separated into the respective two fractions quite easily (Figure 1*B*).

Table I shows a typical example of a material balance in a ternary rectification (mixture 1). The values given in the first column of Table I are experimental. The weights of the individual components were calculated from the known azeotropic compositions, assuming that the true azeotropic compositions were obtained. It will be noted that about 1.5% of the total charge was not recovered. Experience showed that this represented largely the liquid which could not be drained from the column at the end of a run. It is therefore credited to the last fraction along with the liquid holdup of the column. The first fraction was very close to the true azeotropic composition, but the second fraction was lower in acetone than the true value of 86.5% acetone on account of the flat structure in the vapor and liquid surfaces near the minimum azeotrope. This was shown in a binary test with a mixture of methanol and acetone in the same column. A first fraction containing 84% acetone instead of 86.5% was obtained, but this does not imply that the azeotropic composition is 84% instead of 86.5% acetone. In many systems we have approached binary azeotropes from both sides by rectification to find indicated differences of 5 or 6% by weight in the composition. The efficiency of the rectifying column and the relative volatility of the components determine the spread in the composition of the azeotropic fractions obtained by distillation. If a correction for the composition of fraction 2 is applied to the sums in Table I, the weights of methanol, acetone, and methylene chloride become 78.3, 81.5, and 40.2 grams, respectively, which are in satisfactory agreement with the amounts charged.

Table I. Material Balance for Rectification of Mixture 1 (in Grams)

		Theoretical Weights of Components		
	Exptl.	Methylene chloride	Methanol	Acetone
Fraction 1	42.7	40.2	2.5	..
Fraction 2	97.0	..	13.0	84.0
Fraction 3	57.4	..	57.4	..
Lost	2.9	..	2.9	..
Total recovered	200.0	40.2	75.8	84.0
Corrected (84% acetone in fraction 2)	...	40.2	78.3	81.5
Charged	200.0	40.0	80.0	80.0

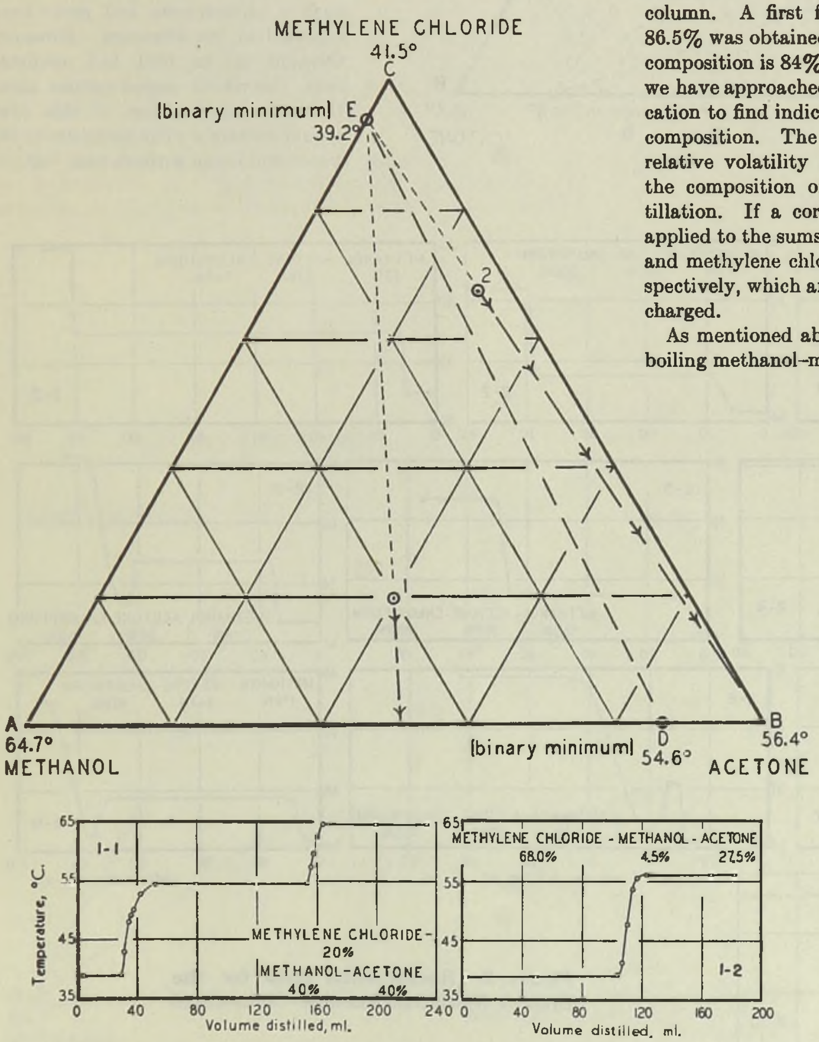


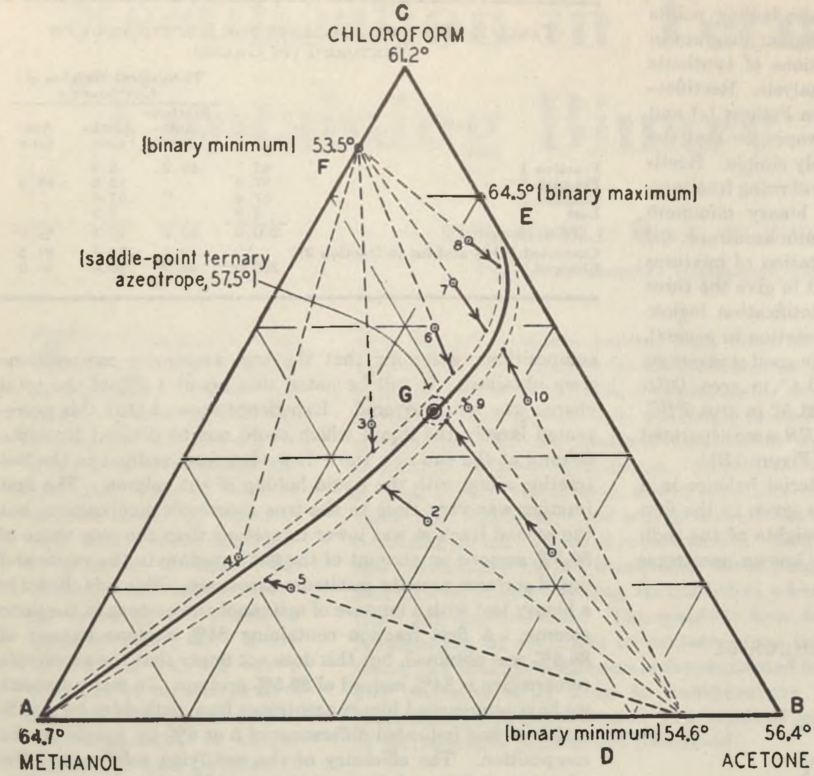
Figure 1. Rectification Data and Rectification Regions for System Methanol-Acetone-Methylene Chloride

As mentioned above, rectification of mixture 2 gave the low-boiling methanol–methylene chloride binary minimum azeotrope and pure acetone as fractions. This result provides a method of separating the components of the methanol-acetone azeotrope by azeotropic distillation. If methylene chloride is added to the azeotrope until the composition reaches line *BE* of Figure 1, it is possible to separate pure acetone by rectification.

It is often stated that, whenever two binary minimum azeotropes occur in a homogeneous ternary system, there will be a ternary minimum azeotrope. This system is one exception, and there are many more. Furthermore, Lecat (*2*) reports several ternary systems having three binary minimum azeotropes but no ternary azeotrope. Therefore, it seems that the existence of ternary azeotropes cannot be predicted on the basis of the binary azeotropes alone.

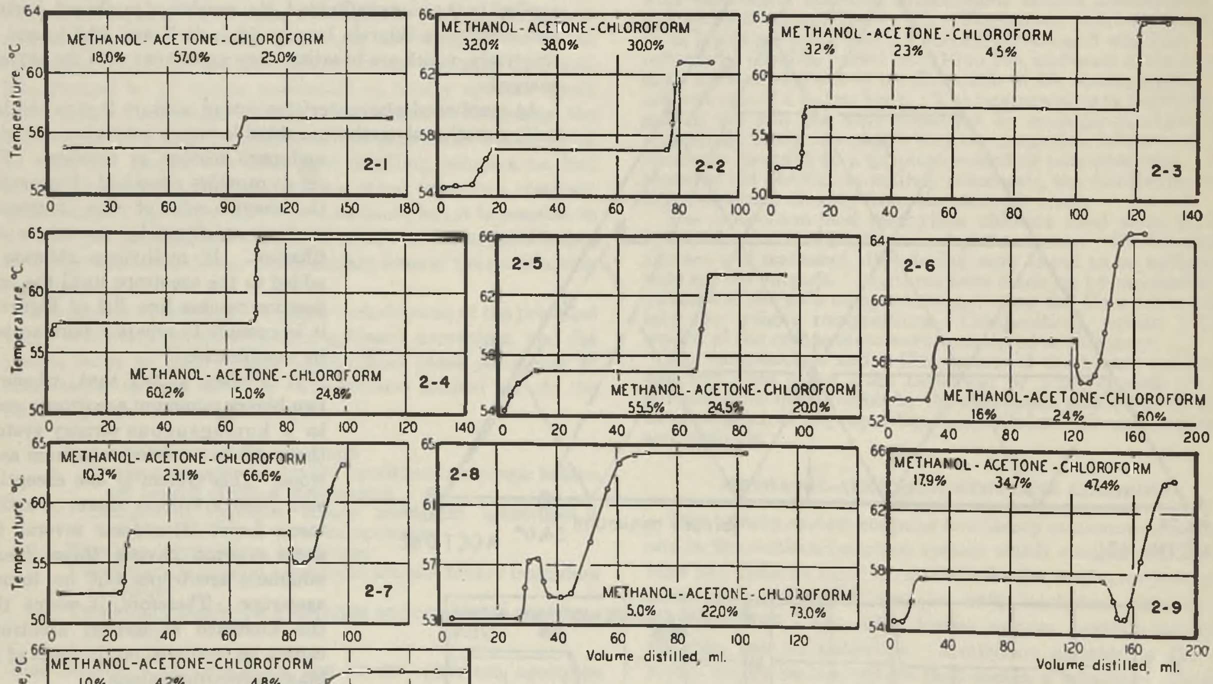
METHANOL-ACETONE-CHLOROFORM

This ternary system contains two binary minimum azeotropes and one binary maximum azeotrope: a minimum in the methanol-acetone system which contains 86.5% acetone and



boils at 54.6° C., a minimum in the methanol-chloroform system which contains 87.5% chloroform and boils at 53.5°, and a maximum in the acetone-chloroform system which contains 79.5% chloroform and boils at 64.5°. These data are plotted on a triangular diagram in Figure 2. The diagram exhibits low points on two sides of the triangle and high points on the third side and the opposite vertex (methanol).

Figures 2-1 to 2-10 show rectification curves for mixtures 1 to 10 of Figure 2. Rectification of mixture 1 gave a first fraction boiling at 54.6° C., which was the methanol-acetone minimum azeotrope, and a second fraction boiling at 57.5° which, from its composition, appeared to be a ternary azeotrope. This at first seemed to be out of the question since the recorded temperature was neither the lowest nor the highest in the ternary system. As far as the writers are aware, such a phenomenon had never been reported in the literature. However, Ostwald (*5*) in 1901 had predicted from theoretical considerations alone that a ternary system of this type should contain a ridge structure in the vapor and liquid surfaces and, further-



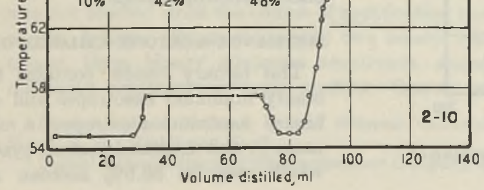


Figure 2. Rectification Data for the System Methanol-Acetone-Chloroform

more, that the ridge would have a low point which he termed a *sattelpunkt*. The ternary azeotrope in Figure 2 boiling at 57.5° C. is, therefore, called a "saddlepoint azeotrope" to distinguish it from ternary minimum or maximum azeotropes. The vapor and liquid surfaces are undoubtedly tangent and have zero slope at this point, just as in the case of ternary minimum or maximum azeotropes. While Ostwald had predicted this phenomenon in general terms, this is the first time it has been demonstrated experimentally, as far as the writers are aware. Contrary to Ostwald's predictions, however, the ridge was found to be strongly curved, particularly from the saddlepoint, *G*, to the acetone-chloroform binary maximum, *E*, as shown in Figure 2. Furthermore, Ostwald called boundary lines connecting components and azeotropes *unüberschreitbare* lines, predicting that it would be impossible to cross them during rectification. However, the results in this paper demonstrate that if such lines are curves (and it is not necessary that they be straight), it is possible to cross them during rectification, when they are approached from the concave side. Under these circumstances four fractions result, whereas Ostwald had assumed that there would never be more than three fractions from rectification in a three-component system.

Simple algebraic analysis of rectification curve 2-1 gave a composition for the saddlepoint azeotrope of 21.8% methanol, 32.2% acetone, 46% chloroform. Subsequent studies showed that the vapor and liquid surfaces near the ternary azeotrope are quite flat so that compositions for the azeotrope differing by several per cent were obtained by approaching it from different directions. A weighted average of a number of determinations gave 23% methanol, 30% acetone, 47% chloroform as a best value for the composition of this azeotrope.

The rectification curves for mixtures 2 and 3 are similar except for the first fractions. For mixture 2 the first fraction was methanol-acetone minimum azeotrope, but for mixture 3 it consisted of methanol-chloroform minimum azeotrope. The same relation exists between mixtures 5 and 4. Thus, a rectification barrier divides this system into two main regions—one on the chloroform side and the other on the acetone side of the saddlepoint azeotrope. Although the methanol-chloroform minimum azeotrope, boiling at 53.5° C., is the most volatile invariant composition in the system, it does not appear in the rectification curves for mixtures on the acetone side of the system.

The position of the rectification barrier in Figure 2 was determined by calculating the composition of each liquid mixture after the first fraction was removed. The heavy lines with arrows show the change of liquid compositions as the first fractions were being removed. The ends of these lines show the liquid compositions which began to yield the saddlepoint ternary azeotrope. These points, at the end of the rectification lines, locate the position of the rectification barrier which is undoubtedly a ridge as predicted by Ostwald. The rectifications for mixtures 2 and 3 or for 4 and 5 did not give a common point on the ridge. This indicates that the vapor and liquid surfaces are rather flat, as is frequently the case near binary and ternary azeotropes. On the methanol side of the saddlepoint azeotrope the rectification curves were quite straight forward (rectification curves 2-2, 2-3, 2-4, and 2-5). After the liquid compositions reached the ridge, or nearly reached it, further rectification proceeded to give ternary saddlepoint azeotrope and pure methanol in that order. This section of the ridge is, therefore, fairly straight.

However, the section of the ridge from the saddlepoint azeotrope to the acetone-chloroform azeotrope has considerable curvature, as Figure 2 shows. Rectification curves 2-6, 2-7, 2-8, 2-9, and 2-10 showed a peculiar drop in temperature and curves 2-6, 2-7, and 2-8 exhibited four fractions. These results were puzzling at first, but when the curved nature of the ridge was established, the interpretation of these results was quite simple. Mixture 6, for example, gave first the methanol-chloroform minimum azeotrope at 53.5° C. and next the ternary saddlepoint azeotrope at 57.5°, as would be expected. After a certain amount of the saddlepoint azeotrope was removed, the temperature in the still head began to drop until it reached approximately 54.6°, which corresponds to the methanol-acetone minimum azeotrope. Analysis of this fraction by the refractive index showed that the composition was nearly the same as the methanol-acetone azeotrope. This phenomenon is not difficult to explain qualitatively. As the saddlepoint azeotrope fraction is removed, the liquid composition must move rectilinearly in the opposite direction. Since the ridge is curved, the liquid composition cannot follow the ridge but must cross it. After the ridge is crossed, the liquid composition lies in a new rectification region in which the most volatile invariant composition is methanol-acetone azeotrope boiling at 54.6° C. Therefore, the temperature must drop from 57.5° to 54.6°. After a small volume of binary azeotrope is removed, the temperature rises to 64.5° C. Apparently in crossing the ridge the liquid composition fortuitously moved over to a point approximately on a line between azeotrope *D* (54.6° C.) and azeotrope *E* (64.5° C.). Rectification curves 2-7 and 2-8 show the

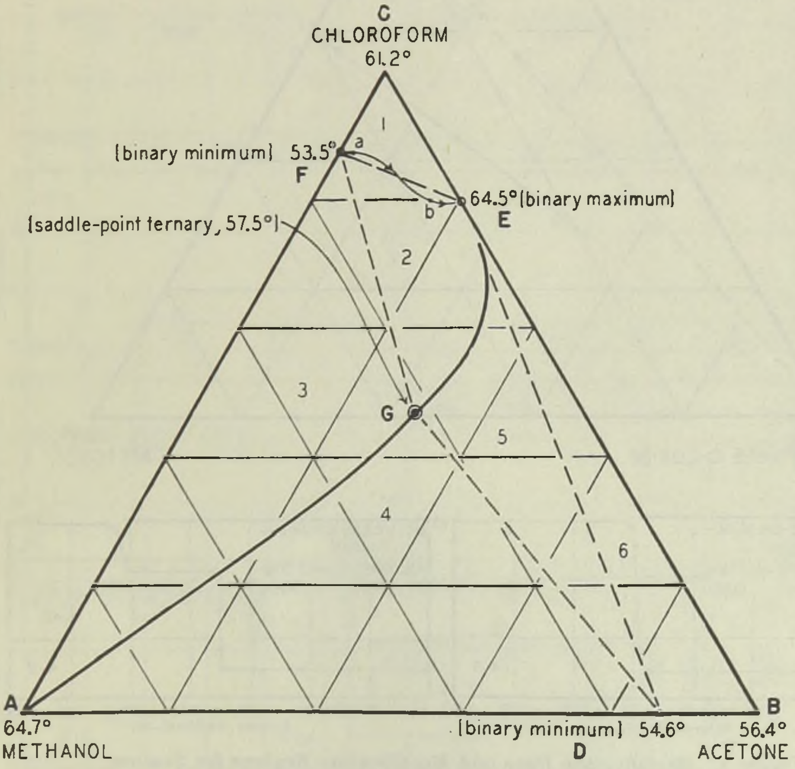


Figure 3. Rectification Regions for System Methanol-Acetone-Chloroform

same phenomenon. In all of these cases the ridge was crossed and four fractions were obtained.

Mixtures 9 and 10 are on the acetone side of the ridge and therefore show slightly different rectification curves. The first and second fractions in Figure 2-10, for example, correspond to the methanol-acetone minimum azeotrope and the ternary saddlepoint azeotrope, respectively. Again the temperature drops after a certain amount of the saddlepoint azeotrope has been removed, but this time the third fraction at the low temperature was the same as the first fraction. Figure 2 shows that such must be the case since the ridge was approached from the convex side. The same is true for mixture 9, shown in Figure 2-9.

The preceding explanation gives a qualitative picture of what happens during rectification in this system. As previously mentioned, the vapor-liquid surfaces are rather flat along the ridge and in the region of the azeotrope. For this reason the true saddlepoint azeotropic composition was difficult to reach. However, a synthetic mixture containing 23% methanol, 30% acetone, and 47% chloroform gave only one fraction upon distillation. After the system was fairly well established, it was possible to calculate beforehand the volume of distillate which must be removed before the temperature would drop during rectification. A total of twenty-three rectifications verified the results which have been presented.

Any area in a ternary diagram which gives the same fractions upon rectification of any mixture lying within it may be called a "rectification" area or region. By this definition the methanol-chloroform-acetone system has six rectification regions (Figure 3). The fractions which each region will give correspond to the composition at the corners of the areas, except that region 2 provides an additional fourth fraction as discussed above.

This system illustrates two types of boundary lines of rectification regions: (*a*) *DG*, *DE*, *FG*, and *EF* which are straight lines, and (*b*) *AG* and *GE* which are curved. Boundary lines *DG*, *DE*, *FG*, and *EF* are all straight lines by virtue of the simple geometrical fact that, when azeotrope *D* (54.6° C.) or azeotrope *F* (53.5°) is removed during rectification, the liquid composition has to move rectilinearly in the opposite direction. *DG* and *FG* differ from *DE* and *EF* in a minor way in that the former two lines are associated with physical valleys in the liquid and vapor surfaces, although the projections of these valleys on the base plane may not necessarily be straight lines coincident with *DG* and *FG*. On the other hand, *DE* and *EF* are not associated with any particular structure of the surfaces but are purely geometrical results.

While *DG*, *DE*, *FG*, and *EF* are all straight-line boundaries of rectification regions and it is impossible to cross them during rectification, it may be possible to cross them during simple distillation. Figure 3 shows a hypothetical case using boundary *EF* as an example. If a mixture, *a*, is placed in a still pot and the vapors in equilibrium with the liquid are continuously removed, the liquid will follow a curved path toward some point *b* and finally to azeotrope *E* (64.5°). This curve is one of a family of curves representing paths of liquid composition for simple distillation which terminate at azeotrope *E*. However, such a curved line cannot be the boundary line for rectification because the liquid composition must move rectilinearly. Schreinemakers (*6*) investigated the course of simple distillation in the system water-phenol-acetone, and showed that the line connecting the water-phenol minimum azeotrope and acetone was curved as far as simple distillation was concerned.

The second type of boundary line of rectification regions is illustrated by curved lines *AG* and *GE*, of which the latter is an especially good example. This type differs from the first in that it is

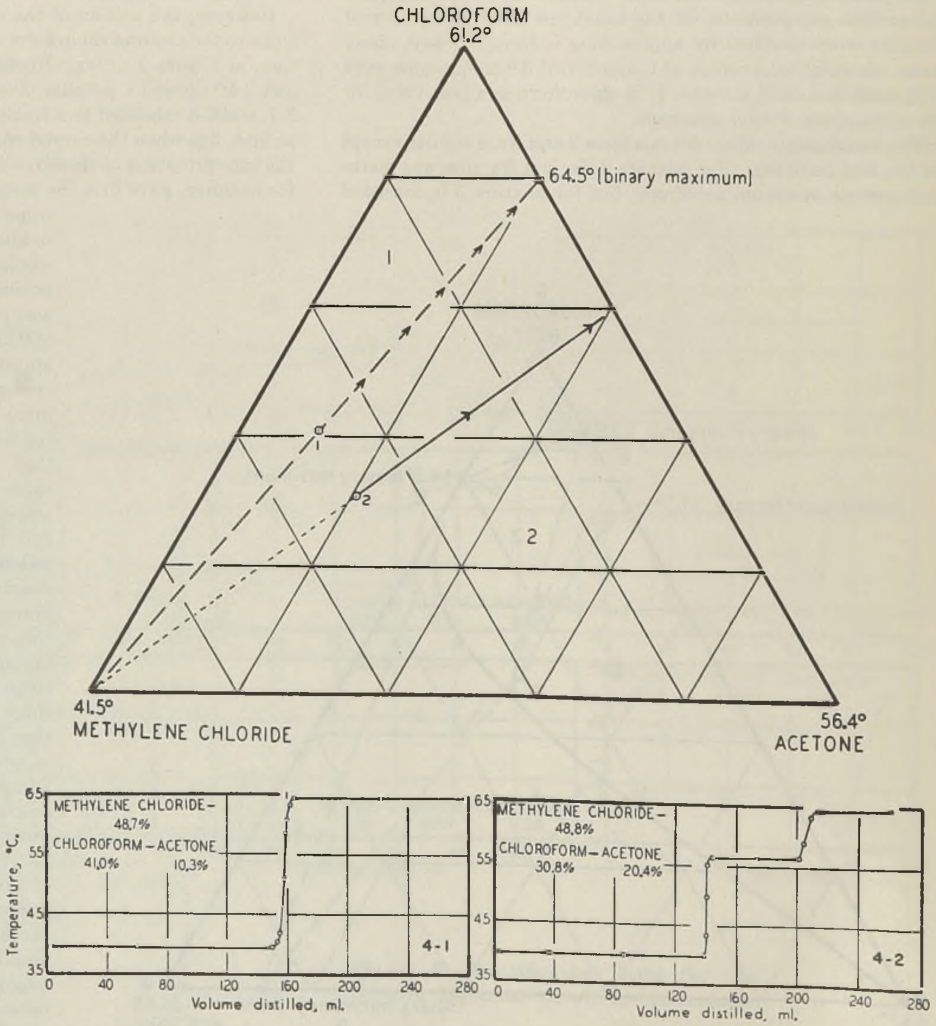
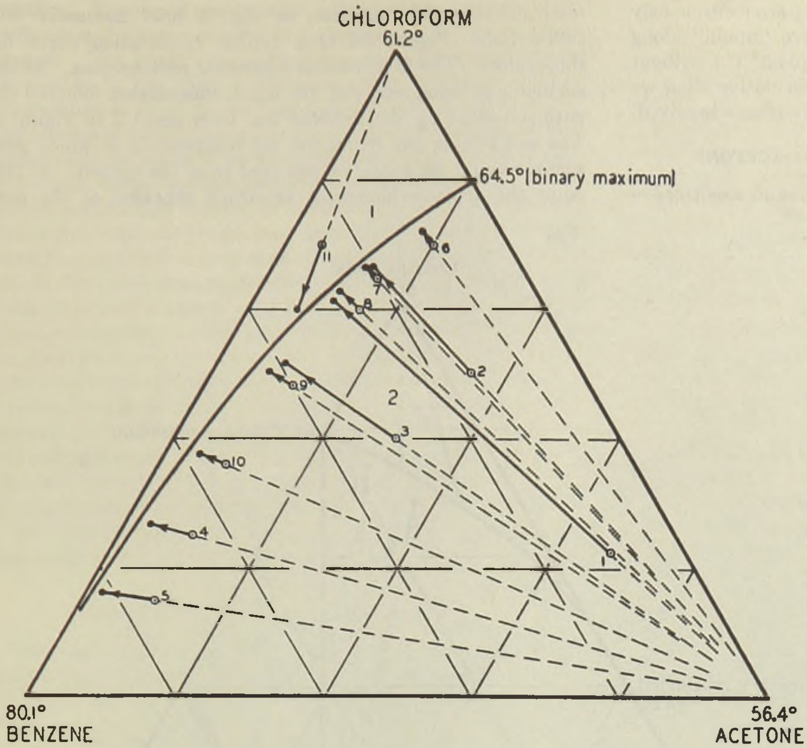


Figure 4. Rectification Data and Rectification Regions for System Methylene Chloride–Chloroform–Acetone



curved and in that it can be crossed during rectification, as shown above. The unique property of this type of boundary line arises from a combination of the geometrical result of rectification and the curved ridge construction of the vapor and liquid surfaces. Actually a mixture in region *EFG* passes over into region *DEG* during rectification and completes its rectification as though it had started in region *DEG*. However, region *EFG* can still be called a "rectification region" since any mixture in it gives the same fractions even though there are four fractions instead of three as in all the other rectification regions of this system.

While this second type of boundary line can be crossed during rectification, it may or may not be possible to cross it during a simple distillation. This would depend on the structure of the vapor and liquid surfaces in the region around the boundary curve. In view of the ridge structure it seems likely that *AGE* would not be crossed in a simple distillation. For example, if a mixture in area *DEG* or *EFG* is subjected to simple distillation

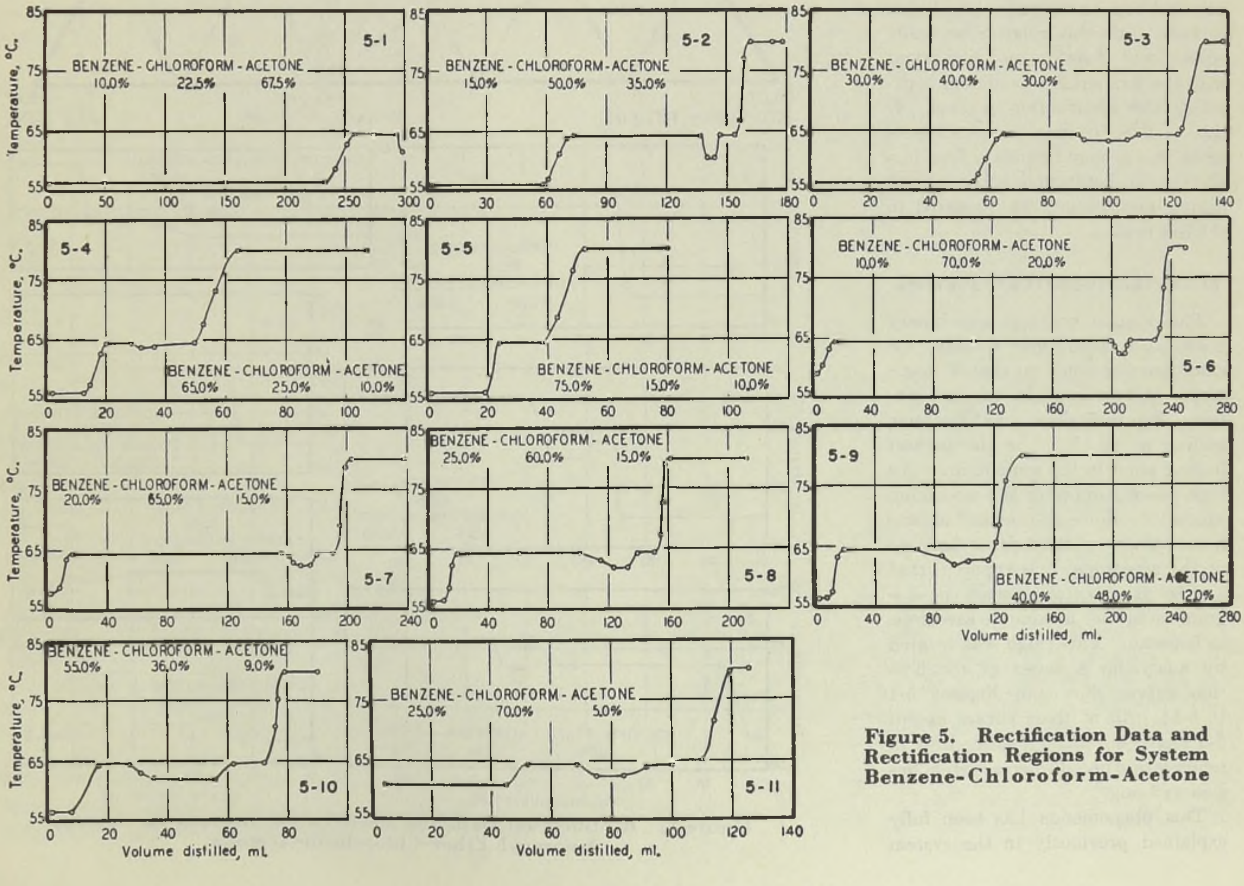


Figure 5. Rectification Data and Rectification Regions for System Benzene-Chloroform-Acetone

(i.e., the vapors in equilibrium with the liquid are continuously removed), the liquid composition would move "uphill" along some curved path approaching azeotrope *E* (64.5° C.) without ever having crossed *GE*. However, this is speculative since we really do not have sufficient knowledge of the surfaces involved.

METHYLENE CHLORIDE-CHLOROFORM-ACETONE

This ternary system contains one binary maximum azeotrope—namely, the chloroform-acetone maximum azeotrope which contains 79.5% chloroform and boils at 64.5° C. The component opposite the binary maximum azeotrope is the lowest boiling of the three components. The first fraction from the rectification of any mixture in this ternary system is methylene chloride, the next fraction is either acetone or chloroform, and the third fraction is the acetone-chloroform maximum azeotrope. Figure 4 shows the triangular diagram of the system. Rectification curves 4-1 and 4-2 are typical of the experimental data obtained. The system is divided into two simple rectification regions separated by a straight line from methylene chloride to the acetone-chloroform maximum azeotrope. This straight line boundary is dictated by the fact that methylene chloride is the first fraction from any mixture in the system and the geometrical result of this fact. This boundary is associated with a physical ridge in the vapor and liquid surfaces, but this ridge is probably curved and therefore not coincident with the straight line boundary separating the rectification regions. If this is true, it may be possible to cross this type of boundary line during simple distillation, although not during rectification, as discussed in the last system.

BENZENE-CHLOROFORM-ACETONE

This system contains one binary maximum azeotrope—namely, the chloroform-acetone maximum azeotrope, the same as in the last system. Figure 5 shows that benzene, boiling at 80.1° C., is the highest boiling point in the system, and this high point is opposite the maximum azeotrope. Since acetone and chloroform boil lower than either benzene or the azeotrope, it is apparent that a ridge must extend across the diagram from the maximum azeotrope to benzene. This ridge was located by analyzing a series of rectification curves shown in Figures 5-1 to 5-11. All of these curves except 5-5 have the characteristic drop in temperature noted when a system has a curved ridge.

This phenomenon has been fully explained previously in the system methanol-chloroform-acetone, so that a brief discussion will suffice here. Figure 5-2 is a typical rectification curve for this system. The first fraction represents pure acetone. As the acetone was being removed, the liquid composition followed the path indicated by the arrowed line from point 2 in Figure 5. The end of this line represents the composition at which pure acetone could no longer be removed from the system. At this point the acetone-chloroform azeotrope appeared as the next

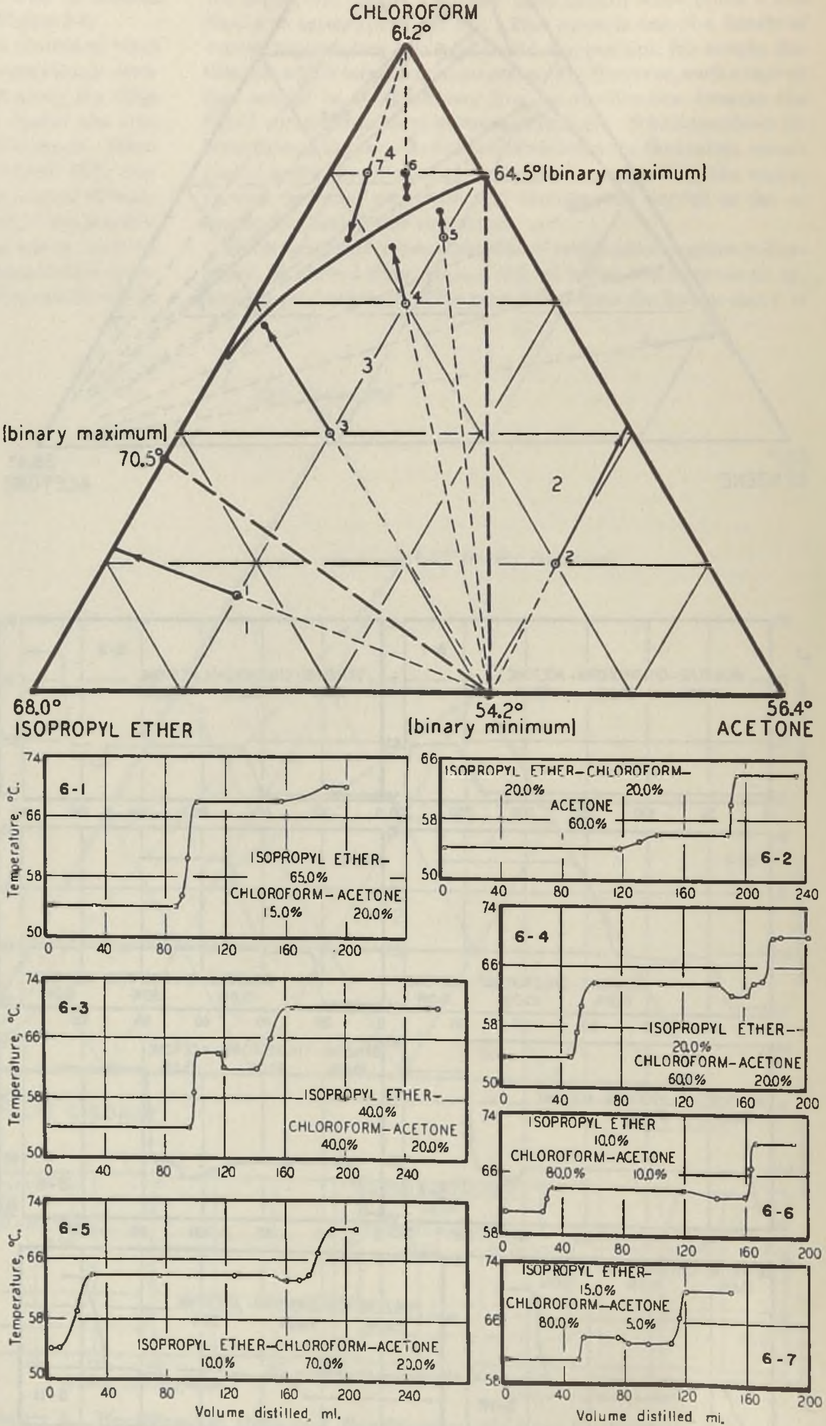


Figure 6. Rectification Data and Rectification Regions for System Isopropyl Ether–Chloroform–Acetone

fraction. The liquid composition, consequently, moved rectilinearly away from the azeotropic composition until the ridge was crossed. The liquid composition was then in region 1 where chloroform is the most volatile invariant composition. The temperature in the still head then dropped down to about 61.2° C. and a small volume of chloroform was removed. This moved the liquid composition back to the ridge and some of the azeotrope came over before the temperature finally reached 80.1° C. A similar explanation applies to rectification curves 5–3 to 5-10, although mixture 5 did not show the temperature drop, probably because of the difficulty in making complete separations at that point. The first fraction in curve 5-11 was chloroform because mixture 11 lies in region 1 on the chloroform side of the ridge. When a ridge is approached from the convex side, it is not crossed by distillation, so the second low-temperature fraction in this curve was rich in chloroform.

Reinders and de Minjier (*4*) studied the course of simple distillation in the benzene-chloroform-acetone system and located the position of the ridge. The line used by them to represent the ridge almost coincides with that in Figure 5 which we obtained by the method of rectification analysis.

The cyclohexane-chloroform-acetone system was found to give a ridge similar to that of the benzene-chloroform-acetone system.

ISOPROPYL ETHER-CHLOROFORM-ACETONE

This system contains two binary maximum azeotropes and one binary minimum azeotrope: a maximum in the isopropyl ether–chloroform system which contains 36.5% chloroform and boils at 70.5° C., a maximum in the acetone-chloroform system which contains 79.5% chloroform and boils at 64.5°, and a minimum in the isopropyl ether–acetone system which contains 61% acetone and boils at 54.2°. These data and the boiling points of the pure components are plotted in Figure 6. It was found that a ridge between the two binary maximum azeotropes divides the diagram into two parts. The position of the ridge was determined in the same manner as previously described.

By drawing straight lines from the isopropyl ether–acetone minimum azeotrope to each of the two maximum azeotropes, one may divide the diagram into four rectification regions. The two straight boundary lines thus obtained do not have any relation to the vapor and liquid equilibrium surfaces, but are a result of the definition of rectification regions. However, the curved boundary line is associated with a physical ridge in the vapor and liquid surfaces and has the characteristics described in detail under the methanol-acetone-chloroform system.

Each of the four regions gave the expected rectification curves as shown by the following examples: Figure 6-1 illustrates a typical curve for region 1. Since this region is enclosed by straight boundary lines, one would expect three fractions corresponding to the compositions at the vertices of the triangle—namely, isopropyl ether–acetone minimum azeotrope, pure isopropyl ether, and isopropyl ether–chloroform maximum azeotrope. There are three distinct plateaus in Figure 6-1, although the separation between the last two fractions was difficult. Region 2 also gave a normal distillation curve as shown in Figure 6-2. The three fractions were isopropyl ether–acetone minimum azeotrope, acetone, and chloroform-acetone maximum azeotrope, respectively.

Regions 3 and 4 are separated by the ridge. It is this structure which gives rise to the peculiar distillation curves already discussed in connection with the previous systems. The curves for region 3 are shown in Figures 6-3, 6-4, and 6-5. The effect of the ridge is clearly seen. Any mixture in region 4 gives chloroform as the first fraction, which is followed by the chloroform-acetone azeotrope fraction and a lowering of temperature before the isopropyl ether–chloroform composition is reached. Figures 6-6 and 6-7 are typical curves for region 4. The interpretation of these curves is similar to that of previous systems which have a ridge in the vapor and liquid surfaces.

CONCLUSIONS

Five ternary systems were studied in detail by the method of rectification analysis. An effort was made to select different types of systems to illustrate the effect of binary maximum and minimum azeotropes on rectification. The following conclusions were drawn:

1. Methylene chloride is a suitable third component for the separation of acetone from the methanol-acetone azeotrope.
2. The occurrence of a ternary azeotrope cannot be predicted on the basis of binary azeotropes alone. Ternary systems containing two binary azeotropes or even three binary azeotropes do not necessarily have a ternary azeotrope.
3. A maximum azeotrope in one or more of the binary systems in a ternary system causes a ridge to appear in the vapor and liquid equilibrium surfaces of the ternary system. The position of the ridge was located in three systems: methanol-chloroform-acetone, benzene-chloroform-acetone, isopropyl ether–chloroform–acetone.
4. If the system has only one binary maximum azeotrope, the ridge extends from that azeotrope to the opposite vertex. If the component at the opposite vertex is the highest boiling of the three components, the ridge can be located by rectification analysis and is shown to be curved in general—e.g., systems methanol-acetone-chloroform and benzene-chloroform-acetone. If the component at the opposite vertex is the lowest boiling of the three components, the ridge cannot be located by rectification analysis—e.g., system methylene chloride–chloroform–acetone. The case where the component at the opposite vertex is the intermediate boiling of the three components was not studied.
5. If the system has two binary maximum azeotropes, the ridge extends from one maximum to the other—e.g., system isopropyl ether–chloroform–acetone. This type of ridge can be located by rectification analysis and is curved.
6. The system methanol-acetone-chloroform contains a ternary saddlepoint azeotrope which boils at 57.5° and contains about 23% methanol, 30% acetone, and 47% chloroform. The saddlepoint azeotrope is neither the lowest- nor the highest-boiling invariant composition in the system.
7. Three types of boundary lines of rectification regions were noted in the systems studied: (1) straight lines connecting binary minimum azeotropes with higher-boiling invariant compositions, which lines may or may not be associated with physical valleys in the vapor and liquid surfaces; (2) straight lines connecting binary maximum azeotropes with low-boiling invariant compositions, which are always associated with physical ridges in the vapor and liquid surfaces; (3) curved ridges connecting binary maximum azeotropes with other high-boiling invariant compositions. The first two types cannot be crossed during rectification but may be crossed during simple distillation. The third type can be crossed during rectification when approached from the concave side, but probably cannot be crossed during simple distillation.
8. When a ternary system possesses a curved ridge structure, rectification of mixtures on the concave side of the ridge yields four fractions, and this result is accompanied by a characteristic drop in boiling point between the second and third fractions.
9. When a ternary system possesses a ridge structure, the first fraction obtained upon rectification may not necessarily be the most volatile invariant composition in the system.

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Improvement in the Color of Peanut and Cottonseed Proteins

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Data are presented to show that protein preparations can be obtained from the meals of white-skin peanuts and blanched red-skin peanuts, without the use of bleaching agents, that are as light or lighter in color than commercial samples of soybean protein. The color of proteins prepared from meals of unblanched red-skin peanuts and cottonseed is improved considerably through the use of controlled protein extraction and precipitation techniques and by washing the moist protein precipitates with organic solvents such as dioxane, acetone, and methyl ethyl ketone. Procedures are given for obtaining, from meal of unblanched red-skin peanuts and from cottonseed meal, satisfactory yields of protein preparations that are lighter in color than those obtained heretofore from similar raw materials, and that approach in color very close to the range of practical usefulness for the production of adhesives and fibers. The use of heat in drying is shown to exert inappreciable influence upon the color of dried peanut protein.

THE suitability of a given preparation of protein for industrial use depends upon its color, solubility, viscosity characteristics, tackiness, and adhesive strength. The relative importance of each of these properties or combinations of them is determined by the particular application of the protein. In products such as fibers, films, paper coating adhesives, gummed tape adhesives, flexible glues, cold water paints, plywood glues, plastics, and related products, the ideal balance between these properties must be determined experimentally.

Several of the properties mentioned have been considered in detail in previous publications—for example, reports on the factors that influence peptization of protein in solvent-extracted and hydraulic-pressed peanut meal (*4, 8*) and cottonseed meal (*9, 15*). As a result of experiments described previously (*10*), conditions have been defined for producing hydraulic-pressed peanut meal from which the protein is readily extracted in high yield; once isolated, this protein has a high degree of solubility.

Viscosity data on relatively concentrated solutions of peanut and cottonseed proteins were reported recently (*6*), together with data on the working range of solutions of modified and unmodified peanut proteins at various concentrations, temperatures, and pH values. This information has made possible the development of peanut protein preparations that are suitable for the production of fibers, gummed tape adhesives, and flexible glues (*3, 5*).

For many industrial purposes lack of color in protein preparations is not only advantageous but frequently a prerequisite to their successful application. The present publication is concerned primarily with the methods developed for obtaining light-colored proteins from peanuts and cottonseed and the application of the trichromatic system of the International Commission on Illumination in evaluating the color of these and soybean proteins.

The seed coats of some varieties of peanuts are almost devoid of color while others vary from light to deep red or even to dark purple. When peanuts are not blanched, as is usually the case in commercial processing, the seed coat remains in the meal after the oil is removed. In the case of white-skin peanuts the presence of the seed coat in the meal is of no consequence since nearly pure white protein can be readily obtained from such material. However, attempts to prepare a light-colored protein from meal of red-skin peanuts have met with little success because of the presence of the highly pigmented skins.

Whereas most of the pigment in the peanut is concentrated in the skin, the highly pigmented portions of the cottonseed occur as pigment "dots" which are distributed throughout the seed. The spectrophotometric nature of some of the pigments contained in these pigment dots has been investigated by this laboratory (*1, 2*). Expression of the oil from cooked cottonseed does not remove any appreciable amount of color, and the solubility of the proteins is greatly decreased (*14*). Solvent extraction of cottonseed with ethyl ether removes a large percentage of the pigments but is not economically feasible. While petroleum naphtha can be used commercially as a solvent for removal of oil from cottonseed, this solvent does not remove an appreciable amount of color and the resulting meal is highly pigmented.

Results are presented here to show that light-colored proteins can be prepared not only from white-skin and blanched red-skin peanuts, but also from unblanched red-skin peanuts by controlling the extraction conditions and pH of protein precipitation. Light-colored proteins have been obtained also from cottonseed by washing the freshly precipitated protein with various organic solvents.

PEANUT SKIN EXTRACTS

Preliminary spectrophotometric examination was made of extracts from peanut skins, which are responsible for most of the color in the meal. White skins were extracted with sodium hydroxide (pH 12.2), and red skins with both sodium hydroxide and 95% ethanol.

Spectral transmittance measurements of these extracts were made with a Coleman spectrophotometer (Model 10S DM, nominal slit width 7.5 millimicrons), using cells 1.27 cm. thick and either 95% ethanol or 0.02 *N* sodium hydroxide as a reference standard. Determinations were made at each 10 millimicrons between 380 and 770 millimicrons except where the curves were flat, when some interpolations were made.

Figure 1 shows the results. There are no distinctive absorption bands in curve *A* for the alkali extract of white skins. The curve is relatively flat, since the extract had almost no color. On the other hand, curve *B*, for the corresponding extract of red skins, shows moderate absorption in the blue region, and has distinctive absorption bands at about 420 and 500 millimicrons.

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Table I. Isolation of Peanut, Cottonseed, and Soybean Protein Preparations

Protein No.[a]	Skins	Blanched	Meal Used[b]	Extraction Agent	Extraction pH	Precipitation Agent	Precipitation pH	Drying Agent
				Peanut Preparations				
1	Red	No	PE-17	Water	..	HCl	4.8	Air, 25° C.
2	Red	Yes	HP-16	Water	..	HCl	4.8	Air, 25° C.
3	Red	Yes	PE-17B	Water	..	HCl	4.8	Air, 25° C.
4	White	No	PE-18	Water	..	HCl	4.8	Air, 25° C.
5	Red	No	HP-11	NaOH	9.8	HCl	4.8	Air, 25° C.
6	Red	Yes	HP-16	NaOH	9.2	HCl	5.4	Air, 25° C.
7	Red	Yes	PE-17B	NaOH	9.8	HCl	4.8	Air, 25° C.
8	Red	No	PE-17	Na_2SO_3	7.6	HCl	4.8	Air, 25° C.
9	Red	No	HP-11	Na_2SO_3	7.4	HCl	5.4	Air, 25° C.
10	Red	Yes	HP-16	Na_2SO_3	7.6	HCl	5.4	Air, 25° C.
11	Red	Yes	PE-17B	Na_2SO_3	7.6	HCl	4.8	Air, 25° C.
12	White	No	PE-18	Na_2SO_3	7.6	HCl	4.8	Air, 25° C.
13	Red	No	PE	NaOH	7.0	CH_3COOH	6.0	Air, 25° C.
14	Red	No	PE	NaOH	7.0	SO_2	6.0	Air, 25° C.
15	White	No	PE	NaOH	7.0	HCl	6.0	Air, 25° C.
16	Red	No	PE	NaOH	11.0	SO_2	4.5	Air, 25° C.
17	Red	No	PE	NaOH	7.8	SO_2	5.0	Air, 25° C.
18	Red	No	PE	NaOH	7.0	SO_2	6.0	Ethanol
18A	Red	No	PE	NaOH	7.0	SO_2	6.0	Lyophylized[c]
18B	Red	No	PE	NaOH	7.0	SO_2	6.0	Vacuum, 30° C.
18C	Red	No	PE	NaOH	7.0	SO_2	6.0	Vacuum, 50° C.
18D	Red	No	PE	NaOH	7.0	SO_2	6.0	Air, 50° C.
19	White	No	PE	NaOH	7.0	HCl	6.0	Air, 25° C.
19A	White	No	PE	NaOH	7.0	HCl	6.0	Ethanol
20	Red	No	PE	NaOH	7.0	HCl	4.5	Air, 25° C.
20A	Red	No	PE	NaOH	7.0	HCl	4.5	Ethanol
21	Red	No	PE	NaOH	8.2	HCl	5.5	Air, 25° C.
21A	Red	No	PE	NaOH	8.2	HCl	5.5	Dioxane
21B	Red	No	PE	NaOH	8.2	HCl	5.5	Acetone
21C	Red	No	PE	NaOH	8.2	HCl	5.5	Methyl ethyl ketone
22	Red	No	PE	NaOH	8.2	HCl	4.5	Air, 25° C.
22A	Red	No	PE	NaOH	8.2	HCl	4.5	Dioxane
22B	Red	No	PE	NaOH	8.2	HCl	4.5	Acetone
22C	Red	No	PE	NaOH	8.2	HCl	4.5	Methyl ethyl ketone
23	Red	No	PE	NaOH	10.0	HCl	5.5	Air, 25° C.
23A	Red	No	PE	NaOH	10.0	HCl	5.5	Dioxane
23B	Red	No	PE	NaOH	10.0	HCl	5.5	Acetone
23C	Red	No	PE	NaOH	10.0	HCl	5.5	Methyl ethyl ketone
24	Red	No	PE	NaCl, 1 *N*	6.4	HCl	4.0–4.8[d]	Air, 25° C.
24A	Red	No	PE	NaCl, 1 *N*	6.4	HCl	4.0–4.8	Dioxane
24B	Red	No	PE	NaCl, 1 *N*	6.4	HCl	4.0–4.8	Methyl ethyl ketone
24C	Red	No	PE	NaCl, 1 *N*	6.4	HCl	4.0–4.8	Acetone
				Cottonseed Preparations				
25	...	...	EE	NaOH	11.0	HCl	7.0	Air, 25° C.
26	...	...	EE	NaOH	11.0	HCl	4.0	Air, 25° C.
27	...	...	PE	NaOH	11.0	HCl	4.0	Air, 25° C.
27A	...	...	PE	NaOH	11.0	HCl	4.0	Dioxane
27B	...	...	PE	NaOH	11.0	HCl	4.0	Acetone
28	...	...	EE	NaCl, 0.5 *N*	6.3	HCl	4.0[e]	Air, 25° C.
28A	...	...	EE	NaCl, 0.5 *N*	6.3	HCl	4.0	Dioxane
28B	...	...	EE	NaCl, 0.5 *N*	6.3	HCl	4.0	Methyl ethyl ketone
28C	...	...	EE	NaCl, 0.5 *N*	6.3	HCl	4.0	Acetone
29	...	...	PE	NaCl, 0.5 *N*	6.3	HCl	4.0[e]	Air, 25° C.
29A	...	...	PE	NaCl, 0.5 *N*	6.3	HCl	4.0	Dioxane
29B	...	...	PE	NaCl, 0.5 *N*	6.3	HCl	4.0	Methyl ethyl ketone
29C	...	...	PE	NaCl, 0.5 *N*	6.3	HCl	4.0	Acetone
Soybean proteins 30, 31, 32, 33, 34, 35, commercial products[f]								

[a] Protein numbers 1–12 correspond to those of Table IV in a former publication (*4*).
[b] PE denotes petroleum-ether (Skellysolve F or B)-extracted meal; EE, ethyl-ether-extracted meal; HP, hydraulic-pressed meal.
[c] Frozen, then dried in vacuo.
[d] Protein precipitated at pH 4.0 then washed one time with water at pH 4.8.
[e] Protein washed one time with water.
[f] Methods of preparation unknown to authors.

Curve *C*, for the ethanol extract of red skins, is unlike curve *B* in that it has two plateaus at 410–450 and about 570 millimicrons. To determine the cause of this difference, a portion of the ethanol extract was dried at 65° C. in vacuo, and the solids were completely redissolved in sodium hydroxide at pH 12.2. The transmittance curve for this solution (curve *D*) has the same general shape and absorption minima as does curve *B;* this indicates that ethanol extracts the same pigment(s) or pigment precursors as does alkali, and possibly that the absorption characteristics of these alcohol-soluble compounds are altered in the presence of alkali.

ISOLATION AND EXAMINATION OF PROTEINS

By the methods indicated in Table I, forty-two samples of peanut protein were isolated from petroleum-ether-extracted and hydraulic-pressed meals prepared from blanched and unblanched red-skin peanuts and unblanched white-skin peanuts. In addition, thirteen samples of cottonseed protein were prepared from petroleum- and ethyl-ether-extracted meals. Water, sodium chloride, sodium sulfite, and sodium hydroxide were the extracting agents at pH values from 6.3 to 11.0. Hydrochloric and acetic acids and sulfur dioxide were used to precipitate the protein at pH values from 7.0 to 4.0.

Since some question had arisen as to the effects of drying upon color, certain of the foregoing samples were dried after precipitation by methods shown in Table I. The stability of the pigments to heat was determined by drying in different ways and at various temperatures. Portions of the same moist protein cake were washed with various organic solvents not only to remove water, but also to ascertain the most effective method of removing color. Ethanol, dioxane, acetone, and methyl ethyl ketone were chosen because the pigments were soluble in these solvents. Six samples of commercially produced soybean protein also were included in the investigation for comparison.

Spectrophotometric Examination of Solutions. Solutions of the various proteins were prepared for spectrophotometric analysis by dissolving 100 mg. in 25 ml. of 0.02 *N* sodium hydroxide (pH 12.2). Occasionally it was necessary to centrifuge to obtain clear solutions of peanut and soybean proteins; for clear solutions of cottonseed protein it was nearly always necessary to centrifuge. Protein solutions having transmittance readings of less than 98% at 1000 millimicrons were considered too cloudy for proper evaluation. Spectral transmittance measurements were made as previously described for the analysis of the peanut skin pigments.

Figure 2 shows representative transmittance curves (400 to 700 millimicrons). They are essentially smooth. The curves for proteins 5, 8, and 26 indicate that considerable pigment was retained in the protein, whereas proteins 4, 7, and 30 show only slight pigmentation.

Colorimetric Evaluation of Solutions. Although spectrophotometric data are recognized as the fundamental basis for the specification of color, even to an experienced observer they permit no more than a qualitative comparison of the chromaticities of various materials. To obtain a graphical comparison of the colors of the foregoing protein solutions, the spectrophotometric data were therefore converted, by means of I.C.I. tristimulus values (*11, 12*), into trichromatic coefficients. Standard illuminant C, an approximation of average daylight, was chosen as the source of radiation. Table II lists the trichromatic coefficients *x, y* for a number of peanut protein preparations. Data for all protein preparations are shown in Figure 3.

Many workers prefer to conceive of color in terms of a monochromatic system of color specification rather than in terms of a

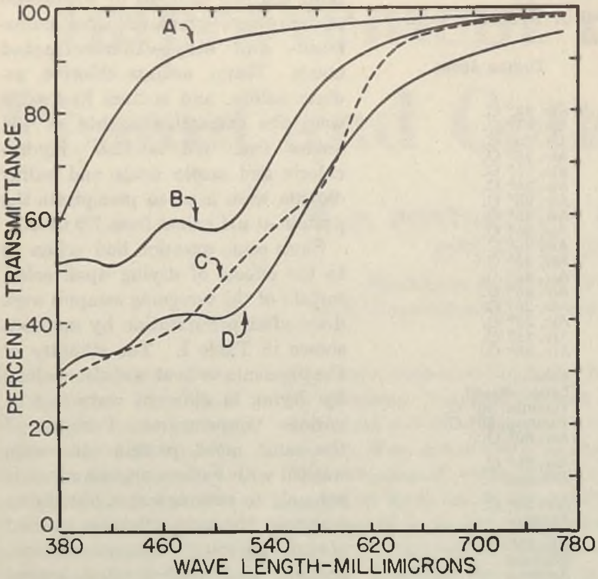

Figure 1. Spectral Transmittance Curves for Peanut Skin Extracts

A. Sodium hydroxide extract of white skins
B. Sodium hydroxide extract of red skins
C. Ethanol extract of red skins
D. Ethanol extract of red skins evaporated to dryness, and pigment redissolved in sodium hydroxide

trichromatic system. In a monochromatic color system it may be considered that the specimen is compared with heterogeneous radiation, such as average daylight, combined with homogeneous (monochromatic) radiation, the wave length of which can be varied at will. The intensity of the heterogeneous radiation, and the intensity and wave length of the monochromatic radiation, are adjusted until a match is obtained. The color is then defined in terms of its luminosity (total radiation required to produce the match), dominant wave length (wave length of the monochromatic radiation), and purity (ratio of monochromatic to total radiation).

In a trichromatic color system it may be imagined that a colored specimen is illuminated by light from a standard source, such as average daylight. Light from the same source also passes through three standard primaries or filters (as red, green, and blue) and is then recombined into a single beam. The amount of light passing through each filter (R for the red filter, G for the green, and B for the blue) is independently adjusted until the sample is matched. Then the chromaticity of the specimen is defined as

$$r = \frac{R}{R + G + B} \text{ and } g = \frac{G}{R + G + B}$$

Table II. Illustrative I.C.I. Tristimulus Data on Alkaline Solutions of Peanut Protein Preparations

Protein No.[a]	x	y	Luminous Transmittance, %	Dominant Wave Length, mμ	Purity, %
1	0.3661	0.3684	68.3	578.5	29.0
2	0.3180	0.3289	95.9	571.0	5.2
3	0.3181	0.3302	96.6	570.0	5.8
4	0.3198	0.3337	97.1	570.0	7.2
5	0.4123	0.3940	49.1	581.4	48.3

[a] Correspond to those in Table I.

It is unnecessary to specify the third coefficient, b, since $r + g + b = 1$. The brightness (or luminosity or transmittance) is defined as the ratio of the total energy passing through the three filters to the energy incident upon them. In the particular case of the I.C.I. trichromatic system the three filters or primary stimuli are imaginary, as is the observer, who has fixed powers of visual perception. The trichromatic coefficients x, y, and z are calculated from spectrophotometric data.

Accordingly, to aid in the interpretation of results, the trichromatic data were converted to the psychophysical values of luminous transmittance, dominant wave length, and purity (*12*, *16*). These values are listed in Tables II and III. Since only a few dominant wave length and purity values are given in Table II, it is necessary to refer to Figure 3 for additional data, where lines of dominant wave length and purity have been superimposed upon the chromaticity diagrams. In interpreting the chromaticity diagrams, it should be remembered that the lower the colorimetric purity of the protein solution and the nearer its x, y plot approaches the plot for illuminant C, the less color it has.

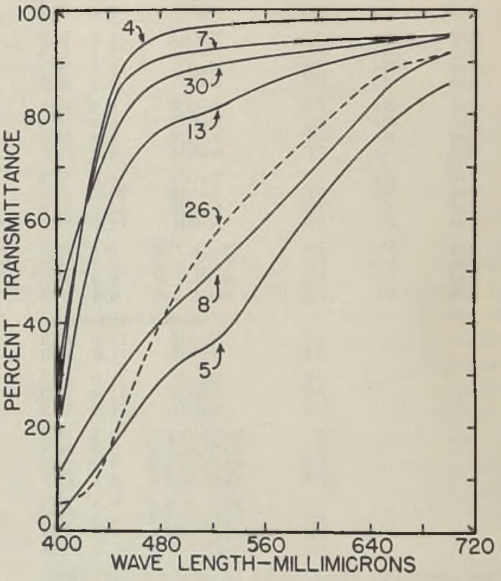

Figure 2. Spectral Transmittance Curves for Alkaline Solutions of Peanut, Cottonseed, and Soybean Proteins

4, 5, 7, 8, 13. Peanut proteins
26. Cottonseed protein 30. Soybean protein
(Curve numbers correspond to protein numbers in Table I)

As the pigment concentration increases, there is a progressive shift to longer dominant wave lengths. This phenomenon was previously observed to occur at wave lengths longer than 570 millimicrons by Newhall and associates (*13*) in the case of the Munsell colors and by Detwiler and associates (*7*) in the case of soybean oils containing varying concentrations of carotenoid pigments.

OPTIMUM COLOR CONDITIONS

The calculated values given in Tables II and III and shown graphically in Figure 3 for the trichromatic coefficients (x and y) and for the psychophysical values of luminous transmittance, dominant wave length, and purity show the differences in color between the white- and red-skin peanut and cottonseed proteins prepared under different conditions. The protein obtained from unblanched white-skin peanuts was lighter than that prepared from unblanched red-skin peanuts but was no better in color than the protein prepared from blanched red-skin peanuts. The proteins prepared from white or blanched red-skin peanuts had about the same color characteristics as did the samples of commercial soybean protein that were examined. Cottonseed protein, in contrast to peanut and soybean proteins, is generally much more highly colored.

The effect of bleaching agents has been investigated only indirectly in these experiments—namely, in those cases where sulfur dioxide was used for protein precipitation, or where sodium sulfite was used for extraction of the protein and sulfur dioxide was accordingly liberated when the extracts were acidified to precipitate the protein. This mild treatment with sulfur dioxide does improve slightly the color of the protein obtained from white-skin peanuts and from blanched red-skin peanuts by precipitation at or near the pH of minimum protein solubility (compare proteins 2 and 10, 3 and 11, 4 and 12); but it exerts no bleaching action upon the color of the protein obtained in a similar manner from unblanched red-skin peanuts (compare proteins 1 and 8).

The results in Tables II and III and Figure 3 make it obvious that, with two exceptions, none of the treatments employed for the separation of protein from the meal of unblanched red-skin peanuts was so effective as blanching in improving the color of the final product. However, in the case of proteins 13 and 14, prepared from the meal of unblanched red-skin peanuts by extraction at pH 7.0 and precipitation of the protein at pH 6.0 with acetic acid and sulfur dioxide, respectively, the proteins were lighter in color than were those prepared by precipitation with hydrochloric acid at pH values lower than 6.0 (compare proteins 13 and 14 with 20). In the case of the protein precipitated at pH 6.0 also, sulfur dioxide exerted an appreciable bleaching action.

The improvement in protein color obtained by precipitation at pH 6.0 was probably due to the elimination in the final product of part of the seed-coat pigments, inasmuch as proteins 15 and 19, prepared from practically unpigmented white-skin peanuts by precipitation at pH 6.0, had practically the same color characteristics as proteins 4 and 12 prepared from the same material by precipitation at pH 4.8. Apparently, the red-seed-coat pigments of the peanut are more soluble at pH 6.0 than at pH 4.5 or are less strongly adsorbed on the protein at pH 6.0.

The yield of protein obtained by precipitation at pH 6.0 was approximately three fourths of that obtained by

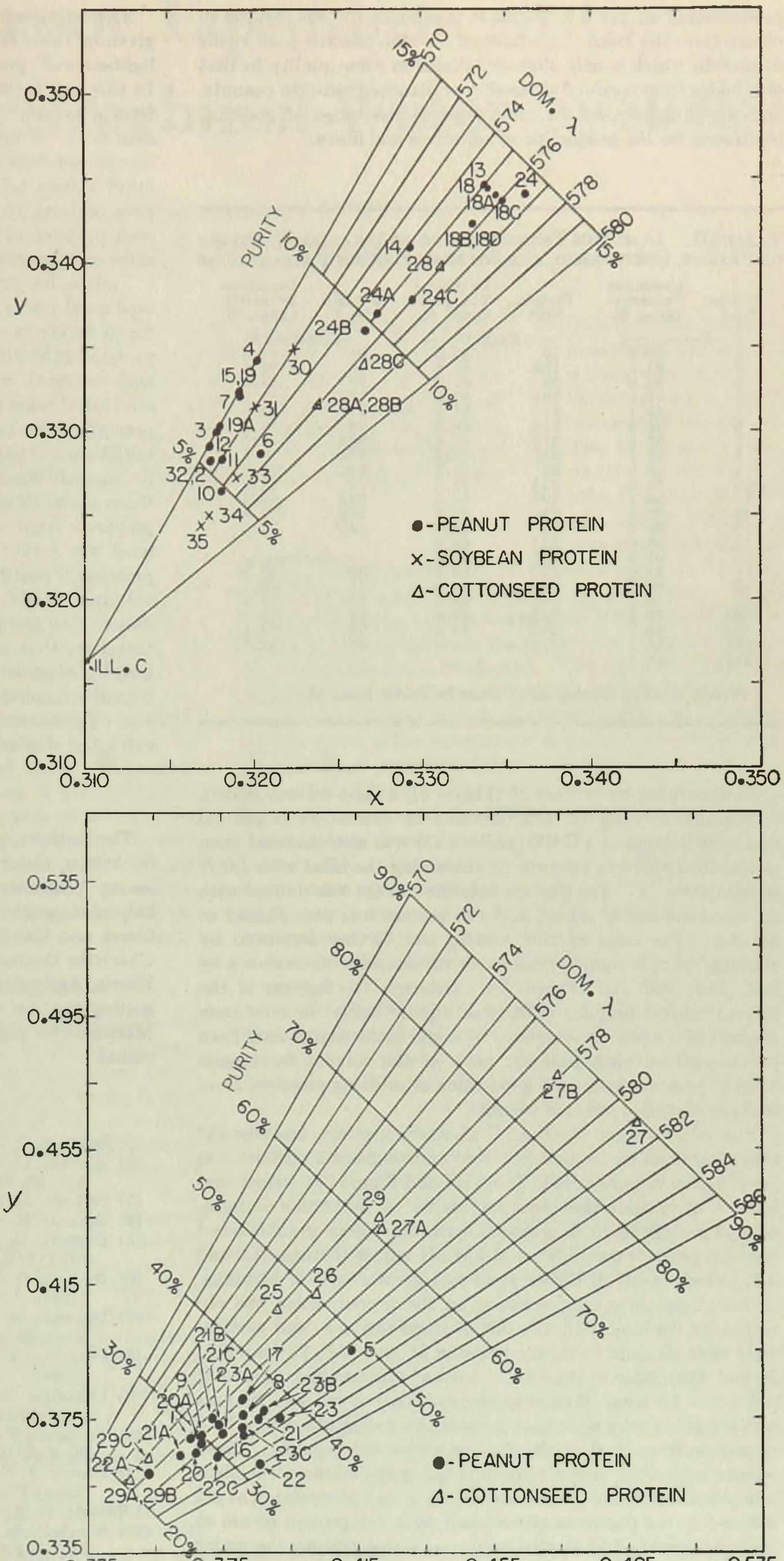

Figure 3. Chromaticity Diagram for Alkaline Solutions of Peanut, Cottonseed, and Soybean Proteins

The lower the colorimetric purity of the protein solution and the nearer its x,y plot approaches the plot for illuminant C, the less color it has.

precipitation at pH 4.5. Thus it is possible by this method to obtain from the meal of unblanched red-skin peanuts good yields of protein which is only slightly inferior in color quality to that obtainable from meals of white-skin or blanched red-skin peanuts, and which approaches in color close to the range of practical usefulness for the production of adhesives and fibers.

TABLE III. LUMINOUS TRANSMITTANCE OF ALKALINE SOLUTIONS OF PEANUT, COTTONSEED, AND SOYBEAN PROTEIN PREPARATIONS

Protein No.[a]	Luminous Transmittance, %	Protein No.[a]	Luminous Transmittance, %	Protein No.[a]	Luminous Transmittance, %
Peanut		Peanut		Cottonseed	
1	68.3	19	95.3	25	67.8
2	95.9	19A	95.8	26	65.1
3	96.6	20	67.2	27	41.9
4	97.1	20A	67.1	27A	61.3
5	49.1	21	57.4	27B	45.5
6	91.5	21A	69.0	28	84.5
7	92.9	21B	62.6	28A	87.6
8	59.7	21C	63.1	28B	87.6
9	66.0	22	61.7	28C	86.3
10	93.5	22A	74.5	29	61.9
11	94.1	22B	65.4	29A	78.4
12	95.6	22C	67.6	29B	78.4
13	84.9	23	53.9	29C	77.5
14	91.6	23A	62.8		
15	95.3	23B	56.2	Soybean	
16	58.0	23C	59.7	30	90.3
17	68.2	24	82.5	31	96.2
18	85.5	24A	86.3	32	93.1
18A	86.4	24B	89.0	33	92.0
18B	85.7	24C	87.1	34	94.4
18C	85.2			35	92.5
18D	84.8				

[a] Protein numbers correspond to those in Tables I and II.

As illustrated by protein 24 (Figure 3), a light-colored protein comparable in color to that obtained by extraction at pH 7.0 and precipitation at pH 6.0 (protein 13) was also obtained from unblanched red-skin peanuts by extracting the meal with 1.0 *N* sodium chloride. The sodium chloride extract was diluted with an equal volume of water, and the protein was precipitated at pH 4.0. The color of this protein was further improved by washing the moist protein cake with various solvents as shown by 24A, 24B, and 24C (Figure 3). Although the lightest of the solvent-washed proteins (24B) was slightly lighter in color than the best of the proteins prepared by alkali extraction of meal from unblanched red-skin peanuts, none of the solvent treatments yielded proteins with such good color as proteins prepared from white or blanched red-skin peanuts.

The effectiveness of ethanol, dioxane, acetone, and methyl ethyl ketone in removing color from various peanut proteins was investigated in some detail (Table III and Figure 3); it was considered of considerable practical value to determine if light-colored protein could be prepared from the protein of unblanched red-skin peanuts precipitated at low pH values (between 4.0 and 5.5), which result in higher yield and greater ease of handling. Although significant improvement in the protein color was obtained by washing with any one of these solvents, and particularly with dioxane (compare proteins 21 and 21A, 22 and 22A, 23 and 23A), none of the solvent-washed proteins precipitated at pH 4.5 or 5.5 from alkaline extracts of meal of red-skin peanuts was so light in color as protein prepared by precipitation at pH 6.0 or protein from meal of blanched or white-skin peanuts. These results show that, if the peanut proteins are extracted at alkaline pH values in the presence of red skins and precipitated at pH 4.5 or 5.5, the pigments either react with the protein or are so strongly adsorbed by it that solvents cannot remove the major part of the color.

Under the conditions investigated, the method of drying the protein obtained from meal of unblanched red-skin peanuts has no appreciable influence upon its color (compare proteins 18, 18A, 18B, 18C, and 18D, Figure 3).

The colorimetric data on the cottonseed protein preparations given in Table III and Figure 3 show that in only one case was a light-colored protein obtained without additional treatment. In this case (protein 28), the protein was precipitated at pH 4.0 from a sodium chloride extract of ethyl-ether-extracted cottonseed meal. Subsequent washing of the moist protein cake with organic solvents further improved the color, dioxane and methyl ethyl ketone being slightly more effective than acetone (compare proteins 28, 28A, 28B, and 28C). The best of the cottonseed proteins (28A and 28B) compare favorably in color with some samples of peanut and soybean protein (Figure 3).

Protein 29, prepared from petroleum-ether-extracted cottonseed meal under exactly the same conditions as protein 28, was much darker in color than the latter. As shown in Figure 3 for proteins 29A, 29B, and 29C, washing of this moist protein cake with solvents was relatively more effective in reducing the amount of color present than was solvent washing of the protein prepared from ethyl-ether-extracted meal. However, since the initial color of protein 29 was high, the best of the solvent-washed proteins obtained from it (29A) was markedly inferior in color to those of the 28 series. Similarly, the color of cottonseed protein prepared from alkaline extracts of petroleum-ether-extracted meal was greatly improved by washing with dioxane (compare proteins 27 and 27A), but since the initial color of protein 27 was extremely high, the solvent-washed product was considerably darker than the proteins of the 28 series. It may be concluded, therefore, that the best conditions found in these experiments for obtaining cottonseed protein with a color which approaches that of commercial proteins consists in the dioxane washing of the moist protein cake obtained at pH 4.0 from a sodium chloride extract of ethyl-ether-extracted cottonseed meal.

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Liquid-Vapor Equilibria in the Acetylmethylcarbinol-Water System

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Liquid-vapor equilibrium data have been determined for the acetylmethylcarbinol-water system at atmospheric pressure. The acetylmethylcarbinol which was used in this work was prepared by the vapor-phase oxidation of 2,3-butylene glycol. The purification of the carbinol is also described. Composition and boiling point of the acetylmethylcarbinol-water azeotrope at a pressure of 760 mm. of mercury have been established.

ACETYLMETHYLCARBINOL is produced by the action of certain bacteria on fermentable substrates. In particular, *Aerobacter aerogenes* produces substantial quantities of the carbinol when the fermenting mash is subjected to intense aeration (*6*, *12*). A process has been developed through the cooperative efforts of the Northern Regional Research Laboratory and Joseph E. Seagram & Sons, Inc., for the production of 2,3-butylene glycol by the fermentation of grain mashes with *A. aerogenes.* By carefully controlling the aeration during fermentation, it is possible to limit the formation of acetylmethylcarbinol. For example, a typical beer would contain butylene glycol and acetylmethylcarbinol in quantities equivalent to 14.0 and 0.5 pound, respectively, per bushel of grain fermented. Consideration has been given to the recovery of the by-product carbinol and to its interference in the butylene glycol recovery process. In these deliberations, liquid-vapor equilibrium data for the acetylmethylcarbinol-water system were of the utmost importance. The purpose of this paper is to present these data. Because pure acetylmethylcarbinol is not readily obtainable, the preparation and purification of the compound will be described.

PROPERTIES AND PREPARATION

Acetylmethylcarbinol is an alpha keto-alcohol and has the formula $CH_3CHOHCOCH_3$. A colorless liquid at ordinary temperatures, it is miscible with water in all proportions and is soluble in most other common solvents. Values for the boiling point of the carbinol, ranging from 140° to 145° C., have been reported by various investigators (*1*, *5*, *11*). Acetylmethylcarbinol solidifies over a period of several days, at temperatures approximating 0° C., to form a white crystalline compound which has been proved to be a dimer of the carbinol (*2*). Zinc catalyzes the reaction. The dimer has no definite melting point. Acetylmethylcarbinol dimer is a stable material and is an excellent source of pure monomer. The preparation of the dimer is a simple method for the purification of crude distilled carbinol.

No liquid-vapor equilibrium data for the acetylmethylcarbinol-water system are available in the literature. It has been observed at this laboratory and by Fulmer and co-workers (*3*) that it is difficult to recover acetylmethylcarbinol from weak water solutions by distillation methods; i.e., it has not been possible to make quantitative separations of water and carbinol by atmospheric fractional distillation.

The carbinol was prepared by catalytic vapor-phase oxidation of 2,3-butylene glycol. Butylene glycol has been catalytically oxidized in the vapor phase by McAllister and de Simo (*9*) and Kolfenbach (*7*) to produce diacetyl as the principal product. McAllister and de Simo reported the formation of acetylmethylcarbinol by the oxidation.

The oxidation apparatus is shown in Figure 1. Butylene glycol from reservoir *A* was fed at a constant rate to heater *B* where the glycol was vaporized and mixed with a measured stream of air. The hot gases were then passed through catalyst tube *C* which was packed with clean copper turnings and maintained at a temperature exceeding 270° C. Thermometer *D*, immersed in the gas stream, and thermocouples *E*, placed on the outside of the catalyst tube, were used to measure the temperature of the vapor during its passage through the apparatus. After oxidation, the vapor was cooled and condensed. The product from the oxidation apparatus was then analyzed for acetylmethylcarbinol, diacetyl, and butylene glycol. Operating data and analytical results for a few of the runs are given in Table I. For preferential production of acetylmethylcarbinol, low oxygen-glycol ratios were used. Glycol which was oxidized or lost in one pass over the catalyst averaged 25 to 30%. In general, combined yields of carbinol and diacetyl, based on glycol disappearance, amounted to 70 to 80%. The average ratio of acetylmethylcarbinol to diacetyl in the product was approximately 4. With higher oxygen-glycol ratios, more glycol is oxidized per pass, but the ratio of carbinol to diacetyl in the product is much less.

Acetylmethylcarbinol was recovered from the glycol oxidation product by fractional distillation. The fraction which boiled from 139° to 145° C. was redistilled, and a heart cut was taken. This material was dimerized in the presence of zinc at approximately 4° C. The crude dimer was filtered from undimerized material, washed with diethyl ether, and vacuum-dried over calcium chloride. It was found that, if the liquid carbinol was exposed to the atmosphere for 12 to 24 hours before it was dimerized, an acetylmethylcarbinol dimer resulted which was crystalline, white, and very stable. The finished material was stored at room temperature with no apparent reversion to the monomer. It was analyzed for carbon and hydrogen: found 54.7% carbon, 9.21% hydrogen; theoretical 54.5% carbon, 9.15% hydrogen. The refractive index of the melted dimer was $n^{23}_{D} = 1.4190$.

EQUILIBRIUM DETERMINATIONS

An equilibrium still similar to the one described by Othmer (*10*) was used in this work. To prevent oxidation of the acetylmethylcarbinol, an atmosphere of carbon dioxide was maintained in the still during distillation. Air was swept from the apparatus with the inert gas, and a stream of carbon dioxide was passed across the vent during the distillation. A thermometer with 1° subdivisions was used to determine the temperature of the vapor. The still was charged with distilled water and acetylmethylcarbinol dimer in amounts calculated to make a solution of the approximate desired composition. When the mixture was heated, the dimer was converted to the monomer (*2*, *11*) which dissolved to form a clear solution. All distillations were conducted for 2 hours with an evaporation rate of approximately 200

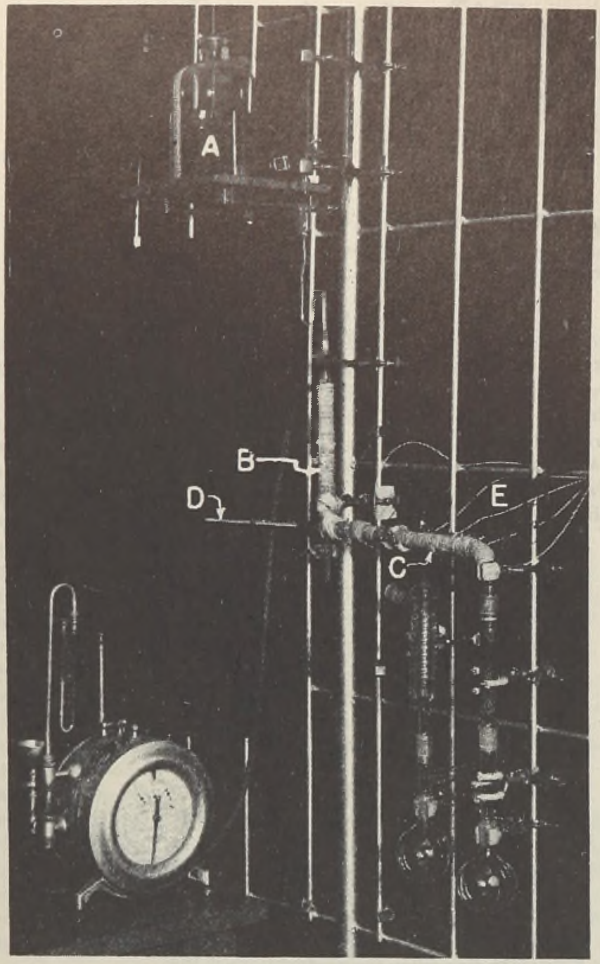

Figure 1. Oxidation Apparatus

cc. of liquid per hour. Since the distillate receiver had a capacity of 25 cc., the rate of circulation was approximately eight cycles per hour.

Samples of the liquids in the boiler and distillate receiver were taken at the end of the distillation period. Those samples containing less than 93% acetylmethylcarbinol were analyzed for their carbinol content by a periodic acid-oxidation method used for the determination of butylene glycol. One mole of acetylmethylcarbinol is oxidized by the acid to one mole of acetaldehyde and one mole of acetic acid. The acetaldehyde is distilled into a solution of sodium bisulfite to form the stable addition compound. Excess bisulfite is destroyed with iodine, and the combined bisulfite is then liberated with alkali and determined by titration with iodine. A sample of acetylmethylcarbinol dimer was dried at room temperature for several days over anhydrous magnesium perchlorate. The loss in weight, presumed to be water, was determined to be 0.2%. Analysis of dilute solutions of this dried sample by the periodic acid method, by the direct titration method of Johnson (*4*) and by the iodoform method of Langlykke and Peterson (*8*) indicated that the method used in this work gave slightly low results. The factor of 1.027 was calculated and used to convert analytical values for acetylmethylcarbinol to the reported values. The carbinol contents of those samples containing acetylmethylcarbinol in excess of 93% were obtained by difference; i.e., water was determined by the method of Karl Fischer, the water values were corrected for the interference of acetylmethylcarbinol in the method, and the corrected values were deducted from 100 to give the carbinol content. Table II gives results of the equilibrium determinations, and Figure 2 shows the equilibrium diagram. Figure 3 presents the phase diagram for the acetylmethylcarbinol-water system at 750 mm.

COMPOSITION AND BOILING POINT OF AZEOTROPE

Several mixtures of carbinol and water, each mixture of approximate azeotropic composition as deduced from the previous work, were boiled at total reflux under a 1 × 48 inch Stedman fractionating column. An atmosphere of carbon dioxide was provided to minimize oxidation of the acetylmethylcarbinol. The still-head pressure was kept constant at 762 mm. of mercury by venting the still through a water-sealed bubbler. A Beckmann differential thermometer, graduated to 0.01° C., was used to measure the boiling temperature at the top of the column. The thermometer had been standardized at the boiling point of water at 762 mm. of mercury. The distillation was conducted until steady-state conditions were established as indicated by constancy of the temperature. A small sample of overhead con-

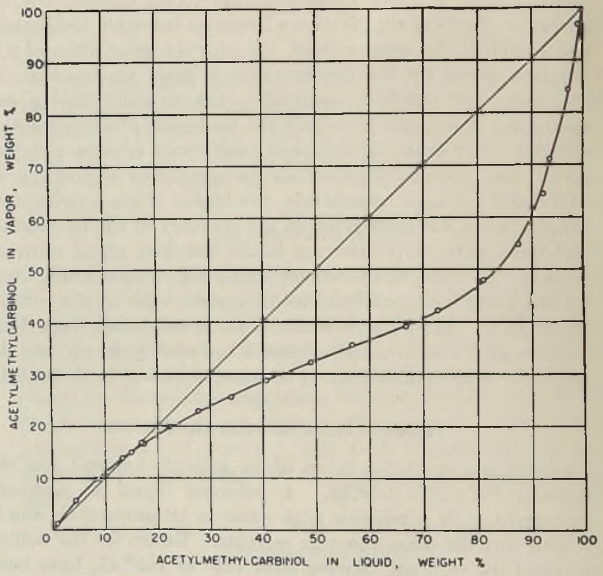

Figure 2. Liquid-Vapor Equilibrium Diagram for the Acetylmethylcarbinol-Water System at 750 Mm. of Mercury

Table I. Vapor-Phase Oxidation of 2,3-Butylene Glycol

Run No.	1	3	4	9	10
Average glycol rate, g./hr.	180	207	230	325	315
Average air rate, l./min.	0.57	1.16	1.17	1.16	1.13
Temp. to catalyst, ° C.	297	295	298	291	290
Catalyst temp., ° C.	307	319	358	314	374
Feed, moles oxygen/mole glycol	0.142	0.252	0.228	0.160	0.161
Space velocity[a]	1240	1870	1970	2340	2280
Product rate, g./hr.	174	202	220	326	304
Product analysis, %					
Butylene glycol	76.3	79.1	75.1	79.6	72.0
Acetylmethylcarbinol	17.4	9.53	14.8	12.5	19.6
Diacetyl	0.65	4.9	4.1	3.5	3.1
Glycol oxidized or lost, % of feed	26.5	23.1	28.2	20.0	30.5
Acetylmethylcarbinol yield, %[b]	64.9	41.1	51.3	64.3	63.2
Diacetyl yield, %[b]	2.5	21.9	14.4	18.3	10.2
Glycol unaccounted for, % of feed[c]	8.6	8.5	9.7	3.5	8.1
Acetylmethylcarbinol-diacetyl weight ratio	26.7	1.9	3.6	3.6	6.3

[a] Volume of gas at standard conditions passed in contact with 1 volume of catalyst per hour.

[b] Per cent of theory, based on glycol which disappeared during oxidation.

[c] Most of this loss was as fog from the condensing system.

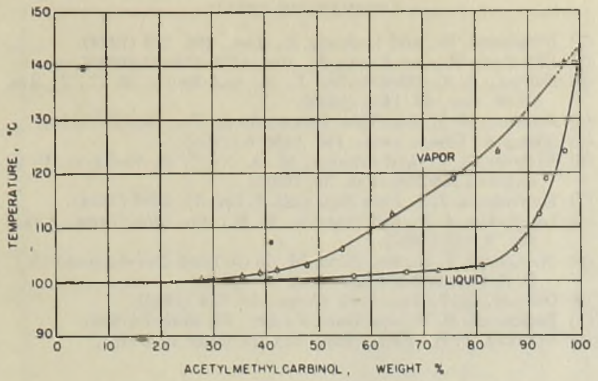

Figure 3. Phase Diagram for Acetylmethylcarbinol-Water System at 750 Mm. of Mercury

densate was then slowly withdrawn. This sample and a sample of the liquid in the boiler were analyzed for acetylmethylcarbinol by the periodic acid method. Table III gives analytical results and observed temperatures. The boiling points at 760 mm. of mercury are based on the assumption that $\Delta T/\Delta P$ for the azeotrope is equal to $\Delta T/\Delta P$ for water. The results show that the azeotrope contained 15.0% by weight of acetylmethylcarbinol, which is in agreement with the value obtained from the equilibrium determinations The boiling point of the azeotrope at 760 mm. of mercury was 99.87° C.

DISCUSSION OF RESULTS

The unusual behavior of dilute acetylmethylcarbinol-water solutions during atmospheric distillation is caused by the formation of a minimum constant-boiling mixture which has a boiling point close to that of water. It is apparent from consideration of the liquid-vapor equilibrium data that dilute solutions of acetylmethylcarbinol will distill practically unchanged in composition. Simple distillation was utilized by Langlykke and Peterson (*8*) in their method for determining carbinol in fermentation liquors. They report that, for solutions containing up to 0.1% carbinol, the distribution of acetylmethylcarbinol during simple distillation is constant and independent of the concentration in the solution. In order that the distribution may be independent of concentration, the equilibrium relation between the liquid and vapor composition must be linear. That the relation is linear for concentrations of acetylmethylcarbinol in the liquid up to 1.0% by weight is shown in Figure 4. The equilibrium line is straight and follows the equation

$$y = 1.345x$$

where x and y represent the concentrations of carbinol in the liquid and vapor, respectively. Table IV compares a portion of Langlykke's data and calculated data based on liquid-vapor equilibrium. The calculated results were obtained by the Rayleigh equation with the relation between x and y as given above. The two sets of values are in good agreement. It is estimated that the application of Langlykke's method can be safely extended to fermentation liquors containing up to 1.0% acetylmethylcarbinol.

Figure 2 shows that it is difficult to separate water and the azeotrope by fractional distillation at atmospheric pressure.

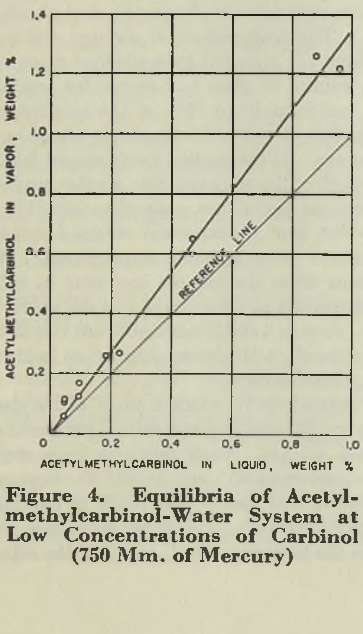

Figure 4. Equilibria of Acetylmethylcarbinol-Water System at Low Concentrations of Carbinol (750 Mm. of Mercury)

Table II. Liquid-Vapor Equilibrium Data for Acetylmethylcarbinol-Water System at 750 mm. of Mercury

Observed[a]				Smoothed[a]		
Detn. No.	x, wt.%	y, wt.%	Temp., ° C.	x, wt.%	y, wt.%	Temp., ° C.
1	0.0454	0.0594	99.8	0.2	0.27	99.8
2	0.0482	0.115	[b]	0.5	0.67	...
3	0.0933	0.127	[b]	1.0	1.35	...
4	0.0987	0.167	[b]	2.0	2.6	...
5	0.184	0.262	[b]	5.0	6.2	...
6	0.230	0.270	[b]	7.0	8.3	...
7	0.469	0.651	[b]	10.0	11.1	...
8	0.471	0.599	[b]	13.0	13.5	...
9	0.882	1.26	[b]	15.0	15.0	(99.87)[c]
10	0.960	1.22	[b]	17.0	16.3	...
11	4.48	5.65	[b]	20.0	18.2	...
12	8.88	9.91	[b]	25.0	21.2	100.0
13	13.4	13.7	[b]	30.0	23.8	100.1
14	15.1	14.9	99.8	40.0	28.3	100.4
15	17.0	16.8	[b]	50.0	32.4	100.8
16	17.4	16.5	100.0	60.0	36.3	101.2
17	22.4	19.8	[b]	70.0	40.5	101.8
18	27.8	22.8	[b]	80.0	46.7	102.7
19	34.1	25.5	[b]	85.0	51.3	104.6
20	40.9	28.7	100.5	90.0	60.1	109.5
21	49.2	32.1	[b]	95.0	76.7	119.8
22	56.9	35.5	101.0	98.0	89.6	131.2
23	66.9	39.0	101.7	99.0	94.8	137.3
24	72.8	42.2	102.0			
25	81.2	47.9	103.0			
26	87.6	54.7	106.0			
27	92.2	64.2	112.5			
28	93.4	75.9	119.0			
29	97.0	84.3	124.0			
30	98.9	96.8	140.5			

[a] x = acetylmethylcarbinol in liquid; y = acetylmethylcarbinol in vapor.
[b] Neither the apparatus nor the thermometer was sensitive enough to detect the small temperature changes in these regions.
[c] At 760 mm. Hg.

Table III. Boiling Point and Composition of Acetylmethylcarbinol-Water Azeotrope

Run No.	Beckmann Temp., ° C.	Boiling Point, ° C.		Acetylmethylcarbinol, Wt.% in:	
		762 mm.	760 mm.	Boiler	Overhead
Standardization	5.24	100.07	100.00	...	...
1	5.11	99.94	99.87	13.0	15.0
2	5.12	99.95	99.88	14.5	14.8
3	...	...	...	15.9	15.2
Av. 1, 2, 3	...	99.94	99.87	...	15.0

Table IV. Observed and Calculated Volatility of Acetylmethylcarbinol in Aqueous Solutions

Fractions, % of Total Distilled	Acetylmethylcarbinol in Distillate, % of Carbinol in Total Distilled		
	Langlykke's obsvd. (av.[a])	Calculated[b]	Difference, based on obsvd.
25	31.8	32.0	0.63
50	59.7	60.7	1.67
75	83.6	84.7	1.32

[a] For solutions containing <0.1% acetylmethylcarbinol.
[b] For solutions containing <1.0% acetylmethylcarbinol.

Calculations indicate that the high reflux ratio and the large number of plates which are required make the operation impractical. Mixtures which are richer in acetylmethylcarbinol than is the azeotrope can be fractionally distilled to carbinol and azeotrope with comparative ease. The product made by the vapor-phase oxidation of butylene glycol was a mixture of this type in that the carbinol-water ratio was high.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of the Analytical and Physical Chemical Division of this laboratory in conducting some of the analyses.

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Nutritive Value of Canned Foods

INFLUENCE OF TEMPERATURE AND TIME OF STORAGE ON VITAMIN CONTENTS[1]

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The effect of storage on the vitamin content of tomato juice, green lima beans, and whole-kernel yellow corn has been studied at 30° to 110° F. over a 365-day period. The vitamin content of each food is affected adversely by prolonged storage at the higher temperatures. The amount of vitamins retained varies with the type of product and the particular vitamin. Both time and temperature affect the retention of ascorbic acid. When corn and lima beans are stored at higher temperatures for long periods, spurious reducing substances are formed which interfere with ascorbic acid determination. Temperature of storage has a limited effect on carotene retention but a marked effect on thiamine retention. Riboflavin retention is not seriously affected by the conditions employed. Pantothenic acid retention is affected adversely by both time and temperature of storage, the temperature effect being most significant. Storage at extremely high temperatures (110° F.) for relatively short periods results in marked losses of vitamins, especially ascorbic acid and thiamine. These data emphasize the necessity of storing canned foods under the most favorable conditions in order to retain maximum vitamin content. It is suggested that the vitamin content of canned foods is preserved most effectively at storage temperatures ranging from just above the freezing point of the respective food to approximately 42° F.

NUMEROUS investigators have reported on the nutritive value of canned foods, but relatively little information is available regarding the previous history of the canned products described. It is reasonable to conclude (*1, 2, 6, 11, 15*) that many conditions are operating which affect the nutritive value of the finished product; among them are such factors as variety, growing conditions, stage of maturity at time of harvest, methods of handling between harvesting and canning, and methods of blanching and processing.

Information is also lacking on the changes in nutritive value which are likely to occur from the time commercially canned foods are processed until they reach the consumer. Time and temperature of storage are factors which may cause significant changes in the nutritive value of canned foods. This is true, particularly, with reference to changes in vitamin content.

Daniel and Rutherford (*4*) showed that home-canned tomato juice, stored at room temperature for 6 months, sustains an appreciable loss of ascorbic acid. Roberts (*12*) reported that grapefruit juice, stored for 9–15 months, lost about 25% of the ascorbic acid. The temperature of storage was not specified. Fellers and Buck (*5*) reported that strained peas, spinach, and tomato juice, packed in glass and stored for one year at room temperature, lost from 10 to 25% of the original ascorbic acid and that little loss of this vitamin occurs after the first 2 or 3 months of storage. Glass-packed foods stored for one year at 36° F. lost but 5% of the ascorbic acid; similar products stored at 90° F. for a similar period lost approximately 21%. These investigators report that glass-packed strained spinach, carrots, peas, and tomato juice retained approximately 85% of the original carotene after storage for one year in subdued light. While the temperature of the storage was not given, the authors conclude that "there is a small but significant loss of vitamin A in canned peas, spinach, and tomato juice when held under rather adverse storage conditions".

Moore and co-workers (*7*) made a study of the changes occurring in orange and grapefruit juices during commercial processing and subsequent storage. Both products were stored in glass and in tin containers at 40° and at 80° F., respectively, for 6 months. Ascorbic acid assays were made at monthly intervals. Their data show that ascorbic acid retention was greater in the canned than in the bottled product, and that the retention of this

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[1] This is the thirteenth of a series of papers dealing with the general subject. Previous articles have appeared in *The Journal of Nutrition*, *Journal of the American Dietetic Association*, and ANALYTICAL EDITION OF INDUSTRIAL AND ENGINEERING CHEMISTRY (August issue, page 531; November issue, page 710).

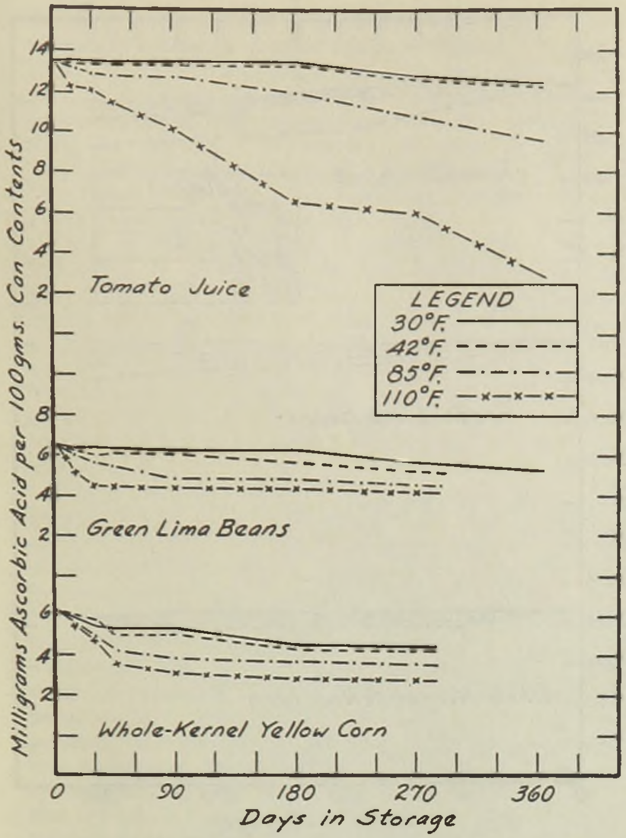

Figure 1. Effect of Time and Temperature of Storage on Ascorbic Acid Content of Canned Tomato Juice, Lima Beans, and Yellow Corn

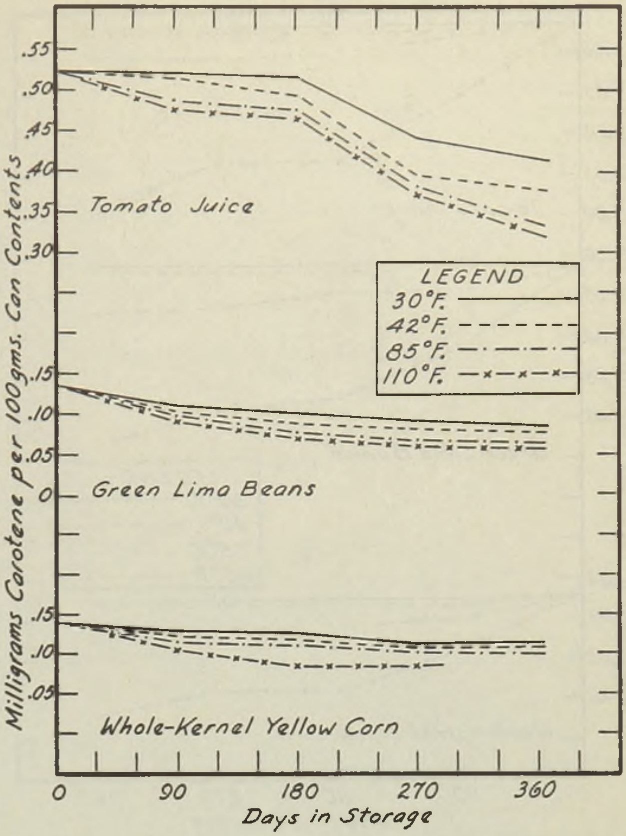

Figure 2. Effect of Time and Temperature of Storage on Carotene Content of Canned Tomato Juice, Lima Beans, and Yellow Corn

nutrient was considerably greater at the lower storage temperature (40°) than at the higher (80° F.).

It seems evident that both time and temperature of canned food storage play a role in determining the vitamin content of the retail product. Temperature of storage appears to have a more significant effect on the retention of ascorbic acid than time of storage; the reverse appears to be true with carotene. Little or nothing is known about the effect of these factors on the retention of some of the other vitamins. The influence of storage temperatures in excess of 80° F. and of storage periods lasting more than 6 months on the vitamin content of canned foods have not been sufficiently investigated.

The armed forces were frequently confronted with the problem of storing vast quantities of canned foods for extended periods and sometimes under adverse conditions as far as temperature was concerned. The present report covers some of the findings obtained in a preliminary investigation of this problem.

STORAGE CONDITIONS

Three canned food products were used in these studies. Each of the three represented a commercial pack.

Tomato Juice was prepared and canned in No. 300 cans on August 20 from tomatoes (Rutgers) grown on sandy loam soil in the state of Delaware. Because of the comparatively wet growing season, the tomatoes arrived at the cannery in what was considered "fair" condition. They were processed within 10 hours of the harvesting time. Before processing, the tomatoes were washed in an Ayars washer, then spray-rinsed in a reel washer. The juice was processed for 20 minutes at 212° F. in a three-crate vertical retort and was then canal-cooled. The finished product graded "fancy" in accordance with the canner's standard.

Whole Kernel Yellow Corn (Golden Cross), grown in Maryland during a rather wet season, was prepared and canned on August 23. The corn was processed within 6 hours after harvesting. The product was washed in a combination flotation and reel washer. The corn was brine-packed in No. 2 cans, processed in a vertical retort for 50 minutes at 240° F., and then canal-cooled. According to the canner's standard, the product graded "fancy".

Green Lima Beans (Henderson's bush limas) grown on sandy loam soil in the state of Maryland, were prepared and canned on August 22. The product arrived at the cannery in average condition due in part to the unusually damp season. The beans were canned within 10 hours after harvesting. After being shelled, the beans were dry-cleaned, washed in a universal washer, and subjected to quality separation. The storage studies reported concern only that portion of the batch which came from the quality separator under the classification "medium greens". The beans were water-blanched for 2.5 minutes at 190° F., brine-packed, and processed in a vertical retort for 20 minutes at 240° F. The processed product was canal-cooled. In accordance with the canner's grading system, the finished product graded "fancy".

More uniformity of product was achieved by selecting cans of foods which were being processed in sequence from the same batch of canning stock. The canned foods were delivered at the laboratory as soon as possible after processing; there the cans were redistributed among the various cases so as to effect a uniform allocation of the canned product under the various conditions of storage. After representative cans were selected for the initial vitamin assays, the foods were stored at 30°, 42°, 85°, and at 110° F. The highest temperature (110° F.) was selected with extreme conditions of Army storage in mind; it is considerably above what would be expected domestically. At specified intervals, representative cans were removed from storage; the con-

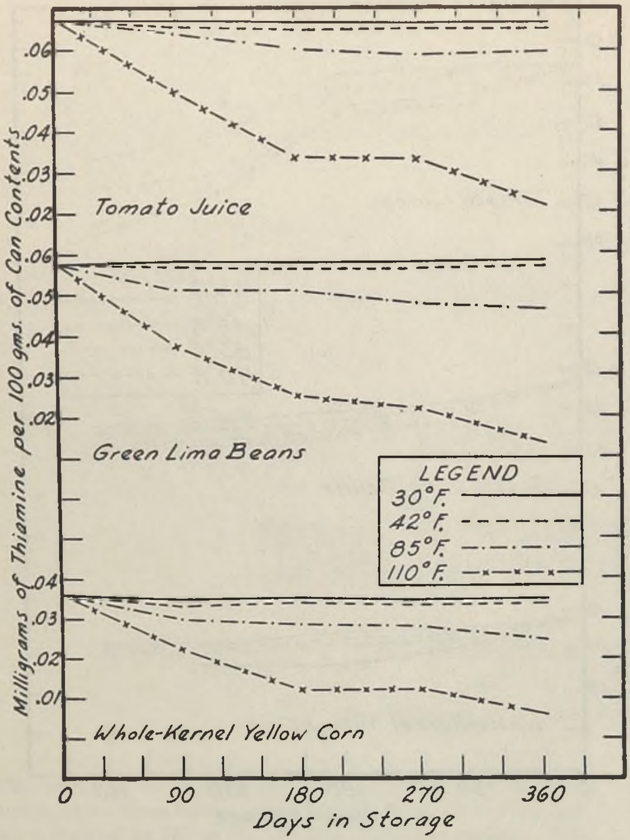

Figure 3. Effect of Time and Temperature of Storage on Thiamine Content of Canned Tomato Juice, Lima Beans, and Yellow Corn

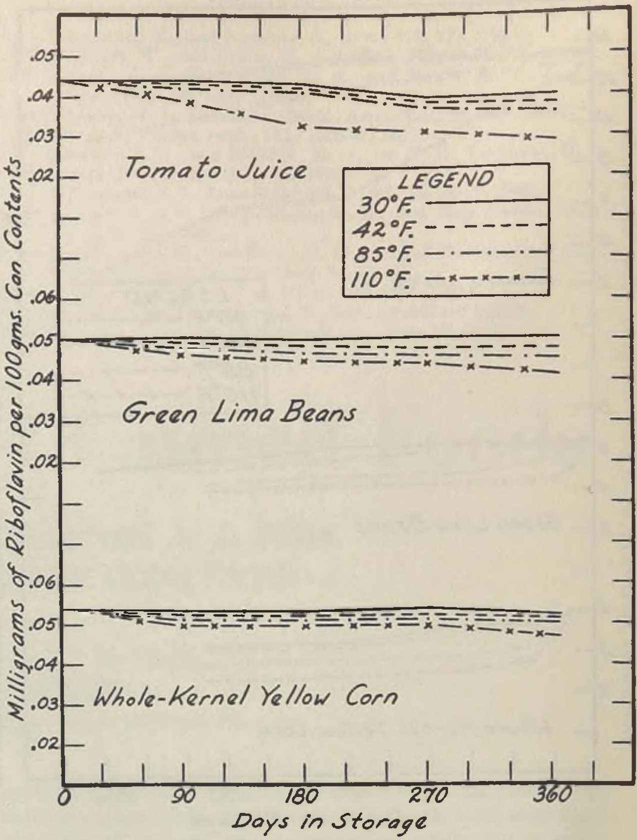

Figure 4. Effect of Time and Temperature of Storage on Riboflavin Content of Canned Tomato Juice, Lima Beans, and Yellow Corn

tents were assayed for ascorbic acid, carotene, thiamine, riboflavin, and pantothenic acid, and also examined as to quality and solid-liquid distribution. In addition, each can was examined as to vacuum and condition.

In most instances assays were made on aliquots from a well-mixed composite consisting of the contents of six cans. With the exception of those used in the ascorbic acid determinations, all aliquots were reduced to a uniform consistency by blending in a Waring Blendor before the samples were weighed. Aliquots used in the ascorbic acid determination were mixed with a known amount of metaphosphoric acid solution of definite concentration before blending.

Each of the three products was assayed for the above-mentioned vitamins when placed in storage. Additional ascorbic acid assays were made after 15, 30, 45, 90, 180, 270, and 365 days of storage. Assays for the other vitamins were made after 90, 180, 270, and 365 days of storage.

Ascorbic acid was determined by the procedure essentially as outlined by Morell (*9*); metaphosphoric acid was employed as the preservative and an Evelyn photoelectric colorimeter as the measuring instrument. Carotene was determined by the method outlined by Moore and Ely (*8*), petroleum ether (boiling range 35–60° F.) being used as the solvent. In the early part of the investigation carotene measurements were made with a Cenco-Sheard spectrophotelometer, but during later stages a Beckman quartz spectrophotometer was employed. All carotene measurements were made at a wave length of 450 microns.

Thiamine and riboflavin were determined by the method of Conner and Straub (*3*). In each instance the fluorescence was measured in a Model 12, Coleman electronic photofluorometer. Riboflavin was also determined by the microbiological procedure of Snell and Strong (*14*). Pantothenic acid was determined by the method of Pennington, Snell, and Williams (*10*).

VITAMIN CONTENTS

The data are presented in condensed form in Figures 1 to 5. They indicate that the vitamin content of each canned food was affected adversely by storage at the higher temperatures for relatively short periods. The amount of the original vitamin retained by the three products varied somewhat with the food under investigation and also with the different vitamins. In general, the effect of time of storage on vitamin retention was less marked than that of temperature.

Tomato juice retained 92% of the original ascorbic acid after storage for one year at 30° F.; only 20% of this vitamin was present after the product had been stored for the same period at 110° F. (Figure 1). Green lima beans retained 83% of the original ascorbic acid when stored for 270 days at 30° F., and 65% appeared to be present after storage at 110° for the same period. Yellow corn showed favorable retention of ascorbic acid (92%) when stored at 30° F. for 270 days but rather poor retention when stored at 110° (47%).

In general, storage at 42° F. for 270 days resulted in a favorable retention of ascorbic acid by all three products. When stored for the same period at 85° F., the loss in ascorbic acid appeared to be approximately half of that occurring while the products were maintained at 110° F. For some unknown reason the apparent ascorbic acid content of the yellow corn and of the lima beans not only ceased to decrease throughout the course of the storage period but actually appeared to increase as a result of prolonged storage (9 to 12 months) at the higher temperatures. These apparently anomalous ascorbic acid values appeared to be due to the formation of nonascorbic acid compounds which reacted with the dye during the course of the assay and therefore indicated abnormally high ascorbic acid contents. Attempts to check the reliability of the ascorbic acid values through additional analyses by the method of Roe and Oesterling (*13*) did not reveal either the nature of the interfering substances or their probable concentration in the various samples.

When the indicated ascorbic acid values for both corn and lima beans were greater after 365 days of storage at the higher temperatures than they were after a 270-day storage period, the former values were considered unreliable and, therefore, are not indicated on the graph. It is impossible to state at what stage of the storage period this spurious reduction began to vitiate the true values; therefore the data obtained for the ascorbic acid content of corn and lime beans after prolonged storage especially at the higher storage temperatures, are of questionable accuracy.

With all three products carotene retention appeared to be less affected by temperature of storage than was ascorbic acid (Figure 2). Each of the products, regardless of storage temperature, showed measurable losses of carotene. In general, the losses increased with increase in storage temperature. Tomato juice, lima beans, and yellow corn retained 79, 78, and 74%, respectively, of the original carotene when stored at 30° F. for one year. Tomato juice and lima beans retained only 62 and 54%, respectively, of the original carotene content when stored for a similar period at 110°. Yellow corn, for some unknown reason, reacted peculiarly to prolonged storage at the higher temperatures in that its carotene content decreased rather consistently with respect to both time and temperature of storage throughout the first 180 days of storage. At this date, corn stored at 30° F. retained approximately 90% of the original carotene, whereas corn stored at 110° retained only 58%. With continued storage, however, yellow corn held at the higher temperatures appeared to increase slightly in carotene content; the same product, maintained at the lower temperatures (30° and 42°), continued to decrease in carotene content throughout the remainder of the 365-day period. Further investigation is being carried out with the hope that an explanation may be found for this anomaly.

Of the several vitamins studied, thiamine retention proved to be least affected by time of storage but one of the most severely influenced by temperature of storage (Figure 3). At the end of a 365-day period at 30° F., all three foods retained essentially 100% of their original thiamine content. Thiamine retention at the 42° storage was also favorable. However, when the three products (tomato juice, lima beans, and yellow corn) were stored at 110° for one year, only 31, 25, and 20%, respectively, of the original thiamine was retained. Measurable losses of thiamine were also detected as the result of storage at 85° F.

Retention of riboflavin by each of the three products, although affected by both time and temperature of storage, remained relatively satisfactory during the entire period. Both fluorometric and microbiological methods of assay were used in determining the riboflavin content of these foods; however, only those data obtained by the microbiological method are given (Figure 4), owing to similarity of values and of trends in riboflavin retention as indicated by the results obtained by the two methods. For the tomato juice the two methods of assay yielded almost identical results for all periods. With the lima beans and the yellow corn, the fluorometric method yielded slightly but consistently higher riboflavin values. The data show that, under the most unfavorable storage condition employed in this investigation, approximately 60% of the original riboflavin content was retained after 365 days. Of the three products studied, the riboflavin content of yellow corn was least adversely affected by storage; that of tomato juice was most severely affected.

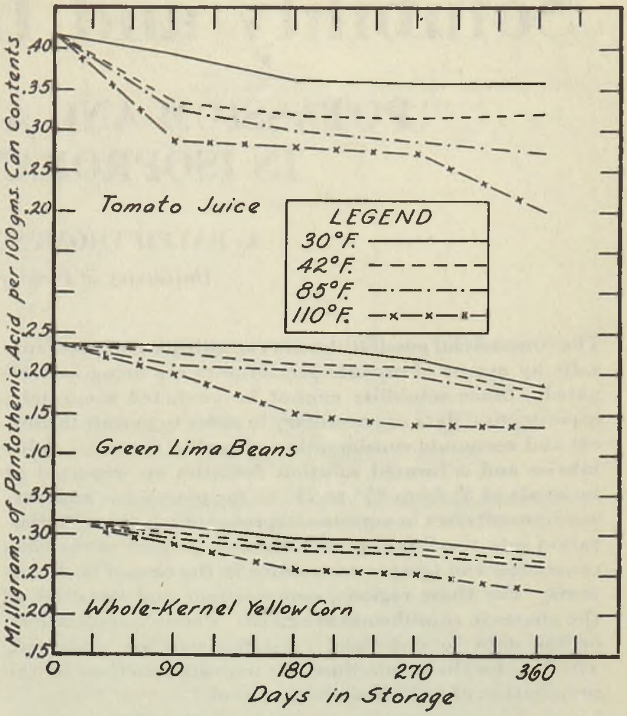

Figure 5. Effect of Time and Temperature of Storage on Pantothenic Acid Content of Canned Tomato Juice, Lima Beans, and Yellow Corn

The pantothenic acid content (Figure 5) of the three foods was not seriously affected by time of storage, but the temperature effect was somewhat significant in the case of lima beans and yellow corn and definitely significant for tomato juice. When stored for one year at 30° F., tomato juice retained approximately 85% of its pantothenic acid content while 45% of the original pantothenic acid remained after storage at 110° F. for the same period.

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Solubility and Density Isotherms

POTASSIUM AND AMMONIUM NITRATES IN ISOPROPANOL SOLUTIONS

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The commercial possibilities of crystallization of inorganic salts by means of organic precipitants are being investigated. Since solubility cannot be predicted accurately, experimental data are necessary in order to permit technical and economic consideration of such a process. Solubilities and saturated solution densities are reported at intervals of 5° from 25° to 75° C. for potassium and ammonium nitrates in aqueous isopropanol solutions. Separation into two liquid phases occurs over part of the concentration and temperature range in the case of both systems. For these regions, compositions and densities of the phases in equilibrium are given. Possible applications of the data to industrial crystallization are discussed. The data for the ammonium salt indicate a method for the preparation of anhydrous isopropanol.

A PROGRAM has been initiated to investigate the commercial possibilities of crystallization by means of organic precipitants, which should be reasonably priced liquids such as the common alcohols. It is realized that this idea is not new, since advantage has been taken of "salting out", both in the separation of organic liquids from aqueous solution by the addition of an inorganic salt and in the laboratory preparation of pure salts by the application of an organic precipitant. However, little consideration has been given to the possibility of crystallizing salts on a commercial scale by this method.

As solubility cannot be predicted accurately, the first step in such a program is to obtain solubility data for systems of the suggested type in order to estimate the economic feasibility of the proposed method. In the present work the solubilities, phase equilibria, and densities of saturated solutions were determined for potassium and ammonium nitrates in aqueous solutions of isopropanol over the temperature range from 25° to 75° C.

Both potassium and ammonium nitrates are very soluble in water, both show a pronounced increase in solubility in water as the temperature is raised, and the anhydrous salt is formed on crystallization in both cases. These factors provided a simple analytical method for the determination of the salt content of the solution (namely, evaporation to dryness) which gave a high degree of precision.

Not many measurements of the solubility of inorganic salts in aqueous solutions of isopropanol have been made, and in very few cases was more than one temperature employed. Larson and Hunt (*11*) gave data for sodium and potassium halides at 25° C. in absolute isopropanol. Data for potassium chloride, ammonium acid phosphate and sulfate, sodium bromide and carbonate at 25° C. in aqueous isopropanol solutions have been reported by Ginnings and Chen (*6*). Frankforter and Temple (*3*) investigated the systems consisting of the aqueous alcohol and potassium carbonate or fluoride at 20° C. The solubilities of sodium chloride and of sodium sulfate in absolute alcohol are reported by Kirn and Dunlop (*7*) over the temperature range from 20° to 50° C. The solubility of sodium chloride in aqueous alcohol solutions was also determined at several temperatures by Kraus and Seward (*9*) and by Ferner and Mellon (*2*). The latter also studied the solubility of potassium chloride in aqueous isopropyl alcohol at a few temperatures (*2*). The solutions of magnesium bromide and iodide in absolute isopropanol were studied from 0° to 140° C. by Menschutkin (*12*). The solubility of mercuric iodide in pure isopropanol at the boiling point was determined by Sulc (*16*). The solubility of cupric chloride in the absolute alcohol at 40° and 80° C. is reported by Seidell (*15*). Silver bromate was investigated at 25° C. by Neuman (*14*), and silver nitrate dissolved in pure isopropanol at 20° was studied by Müller (*13*).

PREPARATION OF MATERIALS

ALCOHOL SOLUTIONS. It was decided that commercial isopropanol would be used for making up the aqueous solutions, provided the solubility in a test solution of given composition was the same as that in a solution of the same composition prepared from purified alcohol. Since only traces of organic compounds, in addition to water, are present as impurities in the commercial alcohol product, it was believed that these would have a negligible effect on the solubility of the inorganic salts in the aqueous alcohol solutions.

This was found to be true. The solubilities of the salts in approximately 50% alcohol by weight were determined, using solutions prepared from commercial alcohol and from purified alcohol. The purification was carried out by the method proposed by Gilson (*5*) and reported by Weissberger and Proskauer (*17*). Values obtained by using the commercial and purified alcohol solution for two different temperatures showed excellent agreement. At both temperatures the differences were less than 0.01% salt by weight. Since these checks were within the limits of the experimental measurements, it was decided that data obtained using aqueous solutions prepared from commercial alcohol would be satisfactory.

Originally, isopropanol solutions of approximately 10, 20, 30, 50, and 70% by weight were used in addition to the commercial "91% by volume" product. Later it was found necessary to employ several more solutions at the lower and upper ends of the alcohol composition range for the purpose of determining the alcohol (solvent) compositions in the two-phase regions. The methods employed will be explained in detail later. Analyses

TABLE I. ANALYSES OF ISOPROPANOL SOLUTIONS (IN VACUO)

Solvent No.	Density at 35° C., G./Ml.	Mole % Alcohol	Weight % Alcohol
I- 5	0.98510	1.58	5.07
I- 7	0.98186	2.21	7.01
I-10	0.97726	3.21	9.96
I-14	0.97136	4.57	13.76
I-20	0.96112	6.93	19.89
I-30	0.94087	11.33	29.88
I-50	0.89417	23.03	49.94
I-64	0.86044	34.81	64.02
I-70	0.84647	41.00	69.84
I-80	0.82248	54.33	79.86
I-87	0.80358	67.94	87.60
I-93	0.78924	81.01	93.43
I-95	0.78382	86.63	95.58

Table II. Smoothed Values for Solubility and Density Isotherms

KNO_3–Isopropanol–Water		
Temp., ° C.	Wt. % KNO_3 in satd. soln.[a]	Density of satd. soln., g./ml.[a]
	Water as Solvent	
25.00	27.24	1.1864
30.00	31.49	1.2167
35.00	35.40	1.2458
40.00	39.02	1.2740
45.00	42.64	1.3059
50.00	46.11	1.3358
55.00	49.28	1.3640
60.00	52.33	1.3905
65.00	55.20	1.4137
70.00	57.87	1.4390
75.00	60.50	1.4629
	I-5 as Solvent	
25.00	22.86	1.1416
30.00	26.62	1.1681
35.00	30.38	1.1951
40.00	34.13	1.2219
45.00	37.85	1.2503
50.00	41.50	1.2792
55.00	45.03	1.3090
60.00	48.39	1.3381
65.00	51.56	1.3665
70.00	54.56	1.3930
75.00	57.52	1.4186
	I-7 as Solvent	
25.00	21.16	1.1255
30.00	24.91	1.1506
35.00	28.64	1.1764
40.00	32.34	1.2034
45.00	36.03	1.2304
50.00	39.72	1.2571
55.00	43.36	1.2850
60.00	46.84	1.3166
65.00	50.38	1.3502
	I-10 as Solvent	
25.00	18.96	1.1046
30.00	22.44	1.1256
35.00	25.98	1.1478
40.00	29.53	1.1720
45.00	33.32	1.1998
50.00	37.13	1.2294
55.00	41.14	1.2610
	I-20 as Solvent	
25.00	13.14	1.0448
30.00	16.06	1.0610
35.00	19.11	1.0790
40.00	22.42	1.0988
45.00	26.15	1.1218
	I-30 as Solvent	
25.00	9.53	1.0021
30.00	11.85	1.0131
35.00	14.27	1.0242
40.00	17.00	1.0380
45.00	20.25	1.0550
	I-50 as Solvent	
25.00	4.44	0.9277
30.00	5.78	0.9296
35.00	7.09	0.9318
40.00	8.33	0.9348
45.00	9.50	0.9380
	I-70 as Solvent	
25.00	1.495	0.8626
30.00	1.785	0.8597
35.00	2.099	0.8570
40.00	2.456	0.8545
45.00	2.876	0.8524
50.00	3.346	0.8505
55.00	3.847	0.8486
	I-80 as Solvent	
25.00	0.488	0.8341
30.00	0.603	0.8297
35.00	0.720	0.8256
40.00	0.837	0.8216
45.00	0.956	0.8177
50.00	1.075	0.8140
55.00	1.213	0.8103
60.00	1.425	0.8068
65.00	1.675	0.8032
70.00	1.841	0.7996
	I-87 as Solvent	
25.00	0.126	0.8130
30.00	0.151	0.8088
35.00	0.178	0.8041
40.00	0.206	0.8000
45.00	0.237	0.7948
50.00	0.271	0.7896
55.00	0.312	0.7851
60.00	0.365	0.7806
65.00	0.411	0.7766
70.00	0.443	0.7727
75.00	0.477	0.7689

[a] In vacuo.

NH_4NO_3–Isopropanol–Water		
Temp., ° C.	Wt. % NH_4NO_3 in satd. soln.[a]	Density of satd. soln., g./ml.[a]
	Water as Solvent	
30.00	69.86	1.3295
35.00	71.84	1.3376
40.00	73.58	1.3449
45.00	75.35	1.3520
50.00	76.99	1.3586
55.00	78.61	1.3653
60.00	80.14	1.3713
65.00	81.72	1.3768
70.00	83.20	1.3818
75.00	84.56	1.3872
	I-7 as Solvent	
30.00	67.65	1.3079
35.00	69.74	1.3173
40.00	71.76	1.3255
45.00	73.71	1.3332
50.00	75.55	1.3406
55.00	77.29	1.3478
60.00	79.01	1.3548
65.00	80.65	1.3619
70.00	82.26	1.3690
75.00	83.79	1.3754
	I-10 as Solvent	
30.00	66.69	1.2996
35.00	68.99	1.3097
40.00	71.10	1.3187
45.00	73.10	1.3272
50.00	75.00	1.3354
55.00	76.81	1.3434
60.00	78.50	1.3509
65.00	80.26	1.3581
70.00	81.97	1.3650
75.00	83.51	1.3717
	I-87 as Solvent	
30.00	8.70	0.8461
35.00	9.52	0.8453
40.00	10.37	0.8444
	I-93 as Solvent	
30.00	4.57	0.8162
35.00	5.01	0.8130
40.00	5.50	0.8099
45.00	6.01	0.8070
50.00	6.53	0.8044
55.00	7.07	0.8021
60.00	7.66	0.8005
65.00	8.29	0.7999
70.00	8.97	0.7995
	I-95 as Solvent	
30.00	3.23	0.8025
35.00	3.47	0.7993
40.00	3.81	0.7962
45.00	4.19	0.7930
50.00	4.59	0.7902
55.00	5.00	0.7872
60.00	5.45	0.7848
65.00	5.90	0.7830
70.00	6.37	0.7817
75.00	6.89	0.7806

[a] In vacuo.

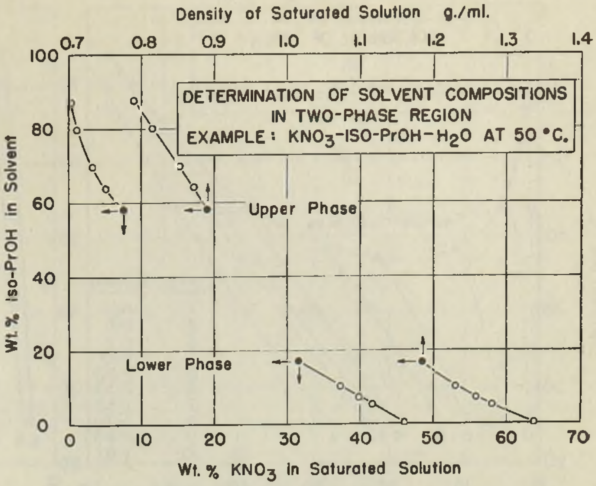

Figure 1. Illustration of Indirect Analytical Methods for Determining Solvent Compositions in Two-Phase Region

of these isopropanol solutions were made by density measurements at 35° ± 0.02° C., using the density-composition data of Langdon and Keyes (*10*). For all isopropanol solutions used, the average values of the density in vacuo at 35° C. are given in Table I, with the corresponding compositions in mole and weight per cent alcohol.

Salts. The potassium and ammonium nitrates were Baker's c.p. grade. They were further purified by recrystallizing twice from water. After drying to constant weight in an oven at 105° C., the recrystallized salts were stored in a vacuum desiccator over anhydrous calcium chloride until used.

MEASUREMENT OF TEMPERATURE, DENSITY, AND SALT CONTENTS

In order to control the temperature from 25° to 75° C., a constant-temperature bath, provided with an adjustable thermoregulator, was constructed. The 1-liter equilibrium cell, which was simply a tall-form Pyrex beaker without pouring lip, was supported in this bath. The cell was equipped with a stirrer connected through a mercury seal, a thermometer, and a sampling tube. After the temperature had been adjusted to the desired value, with a given solvent and excess salt in the cell, stirring was continued at about 400 r.p.m. for at least 5 hours. This period was found by numerous tests to be more than enough time for equilibrium to be reached within the accuracy of the experimental measurements, whether the equilibrium temperature was approached from above or below. Usually it was convenient to allow considerably more time than this, so there was no doubt that a saturated solution was obtained.

The temperature was determined by means of a calibrated thermometer, and it is considered that the temperature was known to 0.02° C.

The density was determined by weighing a definite volume of the solution in weighing pipets designed especially for handling saturated salt solutions at elevated temperatures. These pipets, similar to large-sized Lunge pipets with the cap on the tip only, were made in two sizes (approximately 15 and 55 ml.). The smaller was used for solutions with a high solid content and the larger for solutions with a low solid content, the dividing line being about 10% by weight. The pipets were calibrated over the temperature range 25° to 75° C. by weighing the quantity of boiled distilled water required to fill the pipets to the mark at a definite temperature. Before filling, the pipets were heated in an

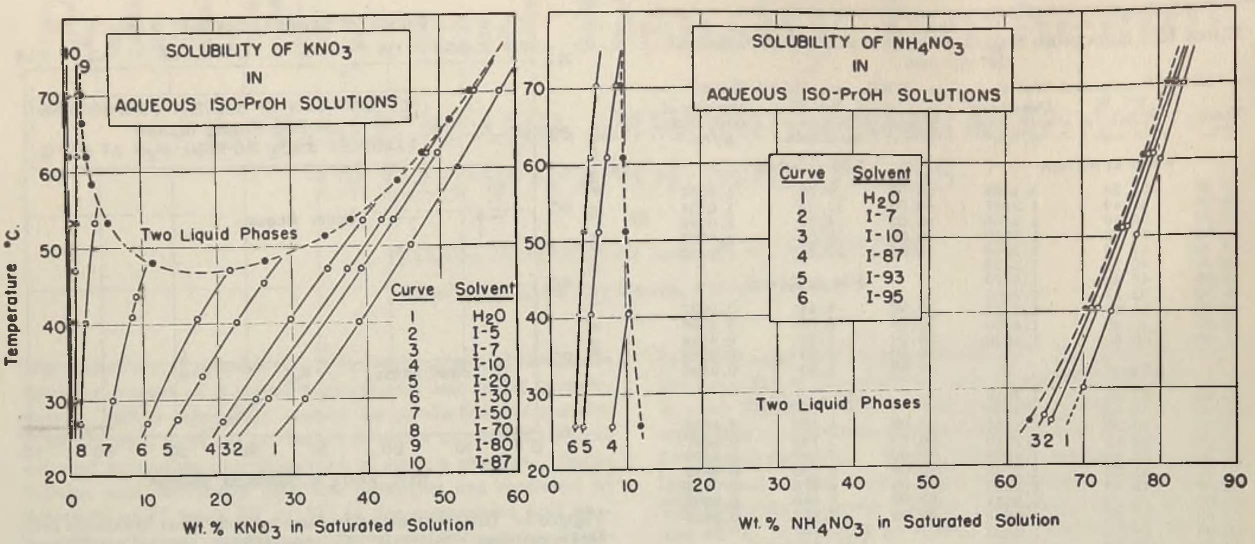

Figure 2. Solubility of Potassium and Ammonium Nitrates in Aqueous Isopropanol Solutions

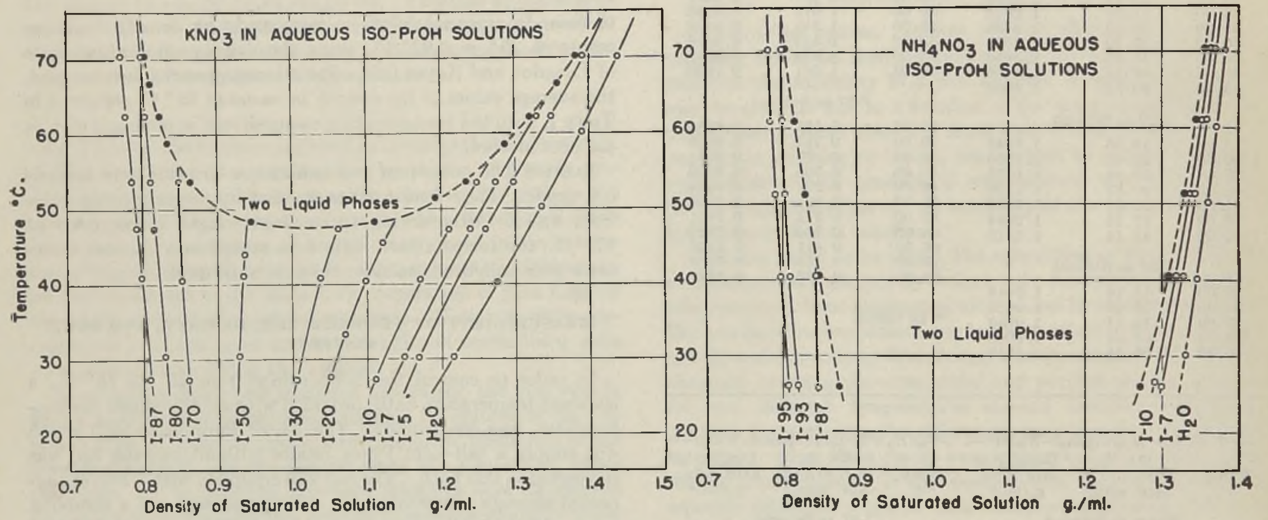

Figure 3. Density of Saturated Solutions of Potassium and Ammonium Nitrates in Aqueous Isopropanol

Table III. Data from Two-Phase Region

	Upper Phase			Lower Phase		
Temp., ° C.	Wt. % salt in satd. soln.	Density of satd. soln., g./ml.	Wt. % alcohol in solvent	Wt. % salt in satd. soln.	Density of satd. soln., g./ml.	Wt. % alcohol in solvent
System KNO_3–Isopropanol–Water						
50	7.52	0.8892	59.3	31.55	1.1852	17.5
55	4.197	0.8531	68.7	40.22	1.2510	11.2
60	3.185	0.8293	73.1	45.82	1.3043	8.4
65	2.491	0.8150	76.4	50.25	1.3486	6.9
70	2.090	0.8036	78.9	54.11	1.3862	5.8
75	1.75	0.7932	80.8	57.43	1.4125	5.1
System NH_4NO_3–Isopropanol–Water						
30	11.32	0.8638	84.5	65.44	1.2840	14.5
35	10.89	0.8542	..	67.90	1.2964	..
40	10.56	0.8456	87.4	70.12	1.3072	14.7
45	10.31	0.8380	..	72.25	1.3171	..
50	10.11	0.8305	89.5	74.20	1.3269	15.3
55	9.96	0.8234	..	75.99	1.3360	..
60	9.83	0.8167	91.3	77.70	1.3442	16.6
65	9.72	0.8102	..	79.39	1.3504	..
70	9.62	0.8033	92.8	81.09	1.3552	18.3
75	9.52	0.7990	..	82.81	1.3604	..

auxiliary oven held at a temperature 1° C. higher than that of the constant-temperature bath. The same procedure was followed when salt solution samples were being taken. This precaution was sufficient to prevent precipitation within the pipet. Using these pipets, it was possible to determine the density of a solution within ±0.0003 gram per ml.

The salt content was found by evaporating the solution to dryness in an oven at 100-105° C. It was thought that ammonium nitrate might decompose or vaporize when subjected to this treatment unless special precautions were taken. In spite of the indication of Cohen and Kooy (*1*) that substantial sublimation losses might be encountered at these temperatures, such was not found to be the case in the present work. Several tests showed that the loss of salt was not greater than 0.015% when aqueous and alcoholic solutions were evaporated at 105° C. for 96 hours. This period of time was at least four times that employed for evaporations during solubility measurements. These observations confirm those of Klevke (*8*) who found that there

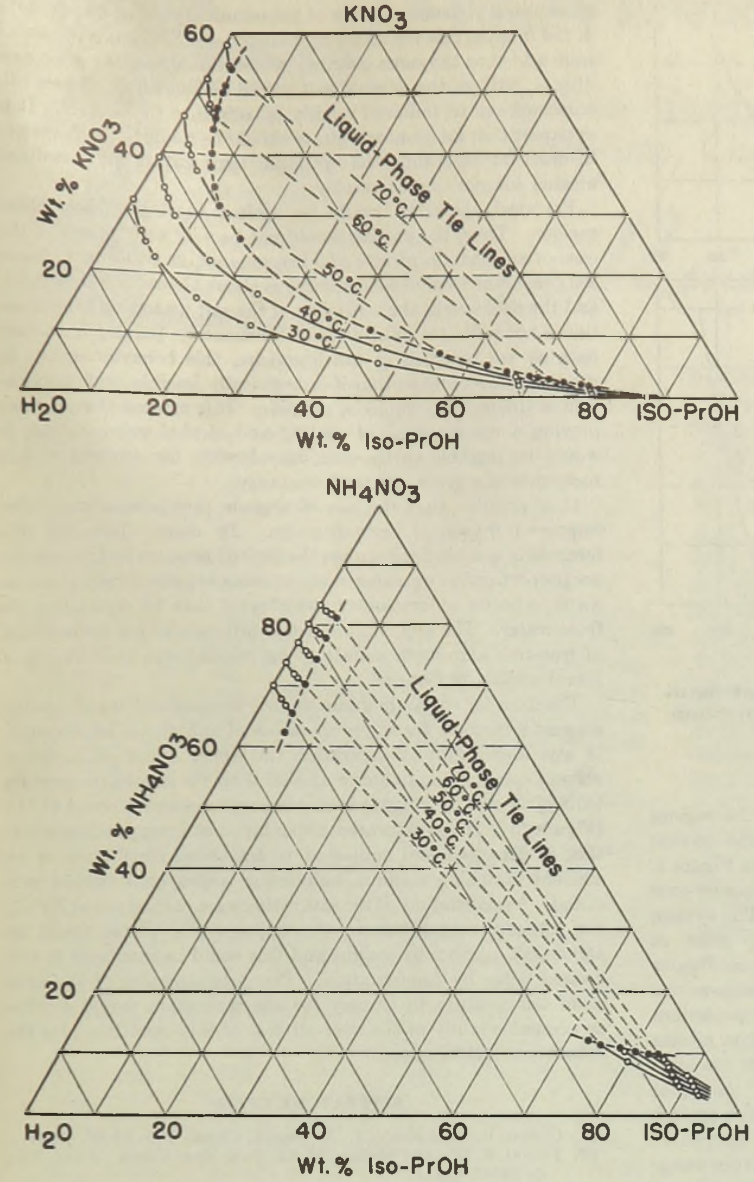

Figure 4. Composition Isotherms for Systems of Potassium and Ammonium Nitrates with Isopropanol and Water

is almost no decomposition of ammonium nitrate during evaporation of its solutions.

Immediately after filling the pipet to the mark, the solution was ejected into a tared weighing bottle. The difference in weight gave the quantity of solution to be evaporated. After drying the outside carefully with a cloth, the pipets were weighed to ascertain the weight of the residue. The sum of the weight of this residue and that of the solution in the weighing bottle gave the total weight of solution required to fill the pipet to the mark. From this, the density of the solution was calculated. Weights were obtained to the nearest milligram and, using the respective pipets, it was possible to evaluate the percentage of salt within ±0.03% at all values above 5% solids and ±0.003% below this figure for the potassium salt. In the case of ammonium nitrate, the precision was ±0.02% above, and ±0.01% below, 5% by weight.

When two liquid layers were present, the samples from the upper (high-alcohol) layer were taken first in the usual manner with the larger pipet. Sampling from the lower phase required a slight modification of the procedure. A glass tube with an inside diameter slightly greater than the outside diameter of the weighing pipet stem was inserted in the sample tube so that its lower end came within one inch of the bottom when placed in the equilibrium cell. This tube was used in sampling by lowering it through the upper phase while air, dried by a calcium chloride tube, was blown gently through by means of a rubber tubing connection. With the tube in position, the rubber connection was removed, and the tube then filled with liquid from the lower phase only. The pipet was inserted in the tube, and samples of this phase were taken.

SOLVENT COMPOSITION IN REGIONS WITH TWO LIQUID PHASES

The composition of the solvent in each layer, when two liquid phases were present, was determined by two independent indirect analytical methods. When there are two liquid phases and a solid phase in equilibrium at a given temperature, each liquid phase must contain solute in the concentration corresponding to its saturation condition and each solvent composition is definitely fixed.

To determine the alcohol content of each phase for a given temperature, large-scale plots of density *vs.* solvent composition or solubility *vs.* solvent composition were extrapolated to the values found when two liquid phases were present. Since these extrapolations were short and almost straight lines for solubility at low alcohol content and for density at high alcohol content, the methods were considered satisfactory. They are illustrated for a single isotherm in Figure 1. The values obtained by the two methods differed in no case by more than 0.2% alcohol by weight in the solvent, with most of the differences being less than 0.1%.

EXPERIMENTAL RESULTS

Plots of the experimental points for salt content against temperature, with alcohol composition as parameter, are shown in Figure 2. Similar plots for density of saturated solution are presented in Figure 3.

In all figures, open circles represent analyses of samples taken when only one liquid phase was present; solid black points are used to give the same information for regions where there were two liquid phases.

All density and solubility data were interpolated to give values at intervals of 5° C. by a frequently used graphical method which involved such magnification that the values could be read easily to the same number of decimal places as the original data. The equation of a straight line which passed close to the experimental points was determined. For all experimental temperatures the deviation from the straight line, Δ (data value minus equation value) was calculated, and a plot was made of Δ against temperature. For temperatures at intervals of 5° C., Δ was found on the plot and the interpolated value obtained by adding Δ to the equation value for the temperature in question.

These smoothed values for solubility and density isotherms are presented in Table II for the salt-isopropanol-water

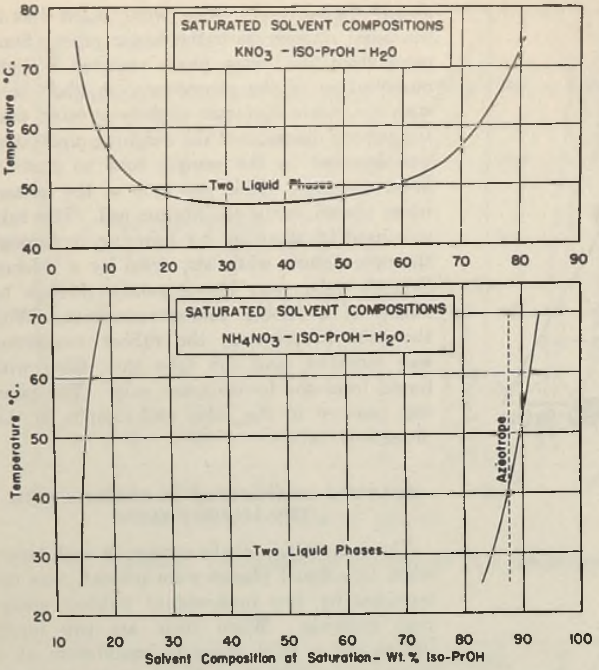

Figure 5. Two-Phase Solvent Compositions at Saturation for Systems of Potassium and Ammonium Nitrates with Isopropanol and Water

systems. Table III gives similar data obtained in the regions where two liquid phases were present, as well as the solvent compositions determined by the methods illustrated in Figure 1.

In these systems separation into two liquid phases occurs over part of the concentration and temperature range. The system potassium nitrate–isopropanol–water shows a plait point at 47.2° C. (determined from large-scale plots similar to Figures 2 and 3). At the plait point the salt content is 18% (determined from the equal distribution point on a plot of per cent potassium nitrate in the alcohol phase against per cent potassium nitrate in the water phase), and the alcohol content is 29% of the total solution or 35.5% of the solvent (determined from the equal alcohol point on a plot of the alcohol content of one phase against that of the other). The system ammonium nitrate–isopropanol–water does not exhibit a plait point in the temperature range investigated. These facts are shown on the triangular composition diagrams for the two systems in Figure 4. The plots of solvent composition in each phase against temperature (Figure 5) also indicate the presence of the plait point in the case of the potassium salt and its absence for the system with the ammonium salt.

POSSIBLE INDUSTRIAL APPLICATIONS

The fact that most inorganic salts are relatively insoluble in alcohols suggests that commercial crystallization could be carried out satisfactorily for these salts by adding alcohol at a controlled rate to a saturated aqueous solution of the salt. Presumably, an industrial installation would consist of a tank with agitator in which the crystallization would take place. After separation of the crystals the diluted alcohol solution would be concentrated in a fractionating column for re-use, to complete the cycle. Owing to the rapid increase in solubility as the water content of a solution is raised, it is not expected that any difficulty would be encountered by salt precipitating on plates below the feed.

As an example of the quantity of salt precipitated by alcohol addition, if 15 pounds of isopropanol were added to 100 pounds of a saturated aqueous solution of potassium nitrate at 40° C., 44% of the original salt would be crystallized. If 50 pounds of alcohol were added to the same quantity of solution under the same conditions, 68% of the original salt would be recovered. These calculations can be followed readily by reference to Figure 4. It is apparent that an economic study should be made for each system in order to determine the optimum temperature and resultant alcohol composition to employ.

Practical operation would be limited to single liquid-phase regions. Thus, the process would not be very satisfactory in the case of ammonium nitrate and isopropanol, as two liquid phases are present at alcohol concentrations above about 15% by weight, and the decrease in the solubility of the salt up to this concentration is not sufficient to be useful. Fortunately, judging from such data as are reported in the literature, this behavior occurs in relatively few cases so that if economically feasible, wide application of the method would be possible. It is evident that, by employing a combination of cooling and alcohol precipitation, it would be possible to increase considerably the amount of salt recovered in a given temperature range.

It is possible that the use of organic precipitants may offer improved fractional crystallization. In cases where the differences in solubilities between the desired product and impurities are proportionately greater in the aqueous organic solution than in water, a better separation can be effected than by crystallization from water. The application of this principle to the preparation of iron-free aluminum sulfate using ethanol was indicated in a recent article by Gee (*4*).

The data for the ammonium nitrate–isopropanol–water system suggest a method for the preparation of anhydrous isopropanol. It was found that at saturation the upper liquid phase has a solvent composition richer in alcohol than the azeotropic mixture (87.6% alcohol by weight) at all temperatures above about 41° C. (Figure 5). If the saturated upper layer, at a temperature above this, is decanted and subjected to fractional distillation in an efficient enriching column, anhydrous isopropanol can be produced. As an example, if the saturation were carried out at 70° C., the solvent composition in the upper liquid phase would be about 93% alcohol by weight and this could be increased to any desired value by fractionation. The determination of the optimum temperature to employ for the saturation would involve an economic study of the over-all cost of this operation plus the subsequent fractionation.

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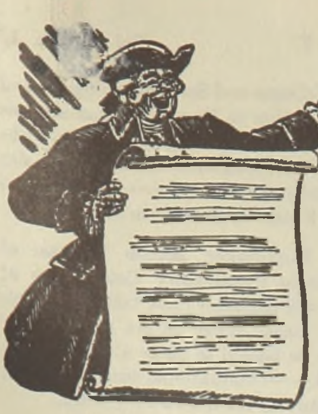
Presented before a special meeting of the Philadelphia Section, American Chemical Society, June 13, 1945. Based on a dissertation presented by A. R. Thompson to the Graduate School, University of Pennsylvania, in partial fulfillment of the requirements for the degree of doctor of philosophy.



NOVEMBER'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ **November 1.** President Truman sends new Anglo-American petroleum agreement providing for 6-man international commission to Senate for ratification.∼∼U.S. Senate hears demands that atomic bomb be outlawed.∼∼Bernard M. Baruch predicts before Senate subcommittee that Germans and Japanese will endeavor through science, technology, and engineering to wage a third world war.∼∼Union members Columbia Chemical Division, Pittsburgh Plate Glass, file suit for portal-to-portal pay.∼∼General Tire and Rubber purchases Pennsylvania Rubber Co.

¶ **November 2.** Harvard's President James B. Conant endorses proposed National Science Foundation.∼∼WPB Chairman Krug says all except 12 of the 215 antitrust law immunity certificates permitting wartime pooling of industrial facilities, patent rights, and technical information have been revoked.∼∼House Military Affairs Committee reports five objections to committee's atomic energy control bill.

¶ **November 3.** Petroleum Industry War Council approves revised Anglo-American petroleum agreement.∼∼Willard H. Dow, president Dow Chemical, says company will spend $15,000,000 in plastics production expansion.

¶ **November 4.** Presidents of eight colleges and universities write President Truman requesting deferment for college students majoring in science on a quota basis.∼∼Eastman Kodak announces new color printing process which reduces by two thirds to three quarters time required for color printing.

¶ **November 5.** U. S. Supreme Court refuses to rule whether Government was right or wrong in seizing Montgomery-Ward properties.∼∼Edward U. Condon sworn in as director of National Bureau of Standards and also becomes scientific adviser to Senate Special Committee on Atomic Energy.∼∼House Military Affairs Committee reports atomic energy control bill, majority recommending quick action.∼∼Senators and Representatives call on top atomic scientists for more guidance before legislation on atomic energy comes up for vote.∼∼ Discovery of antimalarial drug paludrine announced by Lord Leverhulme at annual meeting of Liverpool School of Tropical Medicine.

¶ **November 6.** Senator Ball introduces atomic energy bill designed to ease research restrictions and give scientists larger voice in control measures.∼∼Attorney General Clark says FBI will conduct antitrust investigations.∼∼Department of Commerce says economic survey disclosing for first time method of operation of I. G. Farbenindustrie is available for distribution.∼∼Foreign Commissar Molotoff promises Russians that Soviet Union will have atomic energy and many other things.

¶ **November 8.** Federal Judge Charles E. Wyzanski, Jr., orders Alien Property Custodian to return to Standard Oil of New Jersey all patents company bought prior to 1939 for $35,000,000 from I. G. Farbenindustrie.∼∼Captain Harold E. Stassen, USNR, former Governor of Minnesota, proposes United Nations solve differences among Big Three powers by outlawing production or possession of atomic bomb.∼∼John L. Collyer, president B. F. Goodrich, says U. S. should maintain a total standby general purpose synthetic rubber production capacity of 600,000 to 700,000 tons annually to insure military security.∼∼ACS reports Secretary of War Patterson has proposed new draft policy whereby students who have been engaged in war work can continue their scientific and technological studies.

¶ **November 9.** Celanese Corp. opens negotiations for acquisition of Tubize Rayon Corp.∼∼Vannevar Bush, testifying before Senate Civil Service Committee, endorses proposals to set up two scientific classifications in Civil Service, one at salaries from $12,000 to $14,000 a year and the other $15,000.∼∼Robert S. Wilson, former director Rubber Bureau, WPB, predicts comeback for natural rubber in meeting postwar needs.

¶ **November 10.** British Prime Minister Attlee and Canadian Prime Minister W. L. Mackenzie King arrive in Washington and enter upon atomic energy discussions with President Truman. ∼∼Nine members of House Military Affairs Committee say establishment of permanent federal atomic energy commission "would undermine the very foundation upon which our national life is built."∼∼Metropolitan Section, American Physical Society, at special meeting urges removal of secrecy on atomic energy immediately and international control of all armaments.

¶ **November 12.** Reconstruction Finance Corp. announces special listing of large quantities of chemicals now declared surplus and offered for sale through 31 RFC regional offices.

¶ **November 14.** S. C. Moody, general manager Calco Chemical Division, American Cyanamid, says ground has been broken for first units of new research and technical sales service at Bound Brook, N. J.∼∼Surplus Property Administrator Symington recommends to Congress prompt disposal of government-owned chemical plants which cost $3,400,000,000.∼∼Senator Harley M. Kilgore says all industry should get results of federally financed research.∼∼Secretary of War Patterson doubts that secret of atomic bomb can be kept from other nations.

¶ **November 15.** President Truman, Prime Ministers Attlee of Great Britain and W. L. Mackenzie King of Canada in joint statement offer to share, on a reciprocal basis with others of the United Nations, detailed information on practical industrial application of atomic energy as soon as effective enforceable safeguards against its use for destructive purposes can be devised. They are of opinion that United Nations Organization should work out rules to govern the atomic age and propose earliest possible creation of United Nations Commission to survey entire problem and make recommendations to the UNO on two vital aspects of problem—(1) how to outlaw use of atomic weapons and establish effective safeguards by inspection; (2) how to promote exchange of basic scientific knowledge for peaceful ends and devise controls to limit use to peaceful purposes.∼∼Otto Hahn of Berlin and Wolfgang Pauli of Zurich, Switzerland, receive Nobel prizes for their research in atomic fission, the former the 1944 prize for chemistry and Prof. Pauli the 1945 prize for physics.∼∼Artturi Virtanen of Helsinki receives 1945 chemistry award for his discoveries on a method of fodder conservation.∼∼One out of every 5.5 trees on U. S. Rubber Co.'s plantations in Malaya and Sumatra have been destroyed, according to John W. Bicknell, managing director of company's plantations. He says U. S. must depend on synthetic rubber for next 3 to 5 years.

¶ **November 16.** Secretary of State James F. Byrnes predicts United Nations atomic energy commission proposed in British-American atomic control program can be set up within 60 days and disclaims suggestion to use atomic bomb as diplomatic or military threat against any nation.∼∼Party of 88 Germans, reputedly with top war secrets, arrive in New York guarded by military intelligence officers.∼∼Irving Langmuir, Nobel prize physical chemist and associate director of G.E.'s Research Laboratories, says at joint meeting of American Philosophical Society and National Academy of Sciences held at University of Pennsylvania that if atomic bomb war ever occurs whole world may become uninhabitable.∼∼Federation of Atomic Scientists through J. H. Rush, representing Association of Oak Ridge Scientists, Clinton Laboratories, makes public resolution urging President Truman "immediately to invite into conference Governments of Britain and Russia".∼∼University of Chicago approves resolution warning that government control of atomic research might shackle all science.∼∼British seize powerful Krupp munitions dynasty.∼∼J. Robert Oppenheimer, University of California, who directed development of atomic bomb at Los Alamos, says it is impossible for U. S. to have nationalistic policy of atomic energy.∼∼Glenn T. Seaborg, professor of chemisty, University of California, at Technical Conference Chicago Section ACS[1] announces discovery of elements 95 and 96.

¶ **November 18.** Civilian Production Administration urges distributors of nitrate of soda to place orders immediately to forestall possible cutbacks in output.∼∼James C. White, president Tennessee Eastman, says expansion of production facilities under way calls for expenditure of more than $5,000,000 during each of years 1946 and 1947.

¶ **November 19.** Shell Oil unveils in its Sewaren, N. J., testing laboratory newly designed combustion head for domestic oil burners which it claims will cut fuel consumption 20%.

¶ **November 20.** President Truman tells newsmen U. S. is still making atomic bombs for experimental purposes. He suggests that General Assembly of UNO name atomic safeguards board at its meeting January 2.∼∼Representatives of 4 nations—United States, Britain, Holland, and France—open rubber meeting in London to discuss policies to govern rubber industry in light of developments in synthetics.

¶ **November 21.** Libbey-Owens-Ford Glass Co. announces $500,000,000 construction program for its Plaskon division.∼∼CPA authorizes use of Butyl rubber in production of inner tubes for tires for passengar cars and small trucks and tractors after January 1.∼∼Reynolds Metals acquires Aluminum Products Co.∼∼Karl T. Compton, president MIT, tells House Military Affairs Committee, growing role of science in war increases rather than diminishes need for large Army reserve.

¶ **November 22.** Anthony Eden in House of Commons in view of atomic energy urges revision of UNO charter to remove large powers' veto right.∼∼Du Pont plans to open plastic research laboratory and offices in Columbus, Ohio, January 1.∼∼Allied Chemical and Dye continues its graduate chemistry and chemical engineering fellowship plan for academic year 1945–46.

¶ **November 23.** Arthur H. Compton, chancellor Washington University, St. Louis, and Nobel prize winner in physics, tells Middle States Association of Colleges and Secondary Schools and Affiliated Associations in convention in New York that controls can be exerted over science on regional basis only and that to withhold or restrict further scientific investigation in nuclear physics would weaken U. S. and eventually entire world.∼∼U. S. Marines seize and begin destruction of 3 large cyclotrons in Japan.

¶ **November 24.** Philip J. Noel-Baker, British Minister of State, in welcoming delegates to Preparatory Commission of UNO, says General Assembly will probably have task of controlling atomic energy and that means must be set up whereby brains of our greatest men can be pooled to make atomic energy serve and not destroy mankind.∼∼International study group on rubber forecasts great rubber surplus for next 2 or 3 years.

¶ **November 25.** Secretary of Interior Ickes says Federal Government plans to carry on peacetime experimentation in production of synthetic gasoline from oil and shale at a converted war plant in Louisiana, Mo.∼∼War Department announces award of distinguished service medal to 54 officers for work on atomic bomb project.

¶ **November 26.** CPA says all orders for penicillin from American civilian hospitals, U. S. Veterans Hospitals, and U. S. Public Health Service must be treated by suppliers as though they bear CC preference ratings.∼∼Howard W. Smith, professor of physiology, N. Y. College of Medicine, at press conference in N. Y., discloses that 43 American scientists in letter ask President Truman to endorse Magnuson bill (S.1285) for federal support of scientific research and development.

¶ **November 27.** Secretary of Commerce says instead of competing with established commercial research organizations, Department of Commerce's program for expanding technological aids for business should increase commercial research.∼∼Commerce Department says DDT output—2,750,000 pounds per month—is under demand.∼∼J. Howard Pew, president Sun Oil, urges end of all war agencies to ensure industrial future of U. S.∼∼Reynolds Metal leases from TVA nitrate plant No. 1 at Sheffield, Ala.∼∼Alexander Sachs, economist and informal adviser to President Roosevelt on atomic energy, appears before Senate Special Committee on Atomic Energy, reveals how he interested President Roosevelt in 1939 in atomic energy, and gives early history of organization of work.

¶ **November 28.** Maj. General Leslie R. Groves, appearing before Senate's Special Committee on Atomic Energy, approves Truman-Attlee approach to world supervision of atomic energy but does not think international inspection system would be foolproof.∼∼At dinner of Americans United for World Organization Senator McMahon, chairman of Senate Special Committee on Atomic Energy, says our domestic policy must be adaptable to purposes of proposed UNO atomic energy commission but must not stifle research.∼∼Deputy Petroleum Administrator Davies, appearing before Senate Petroleum Committee, urges extensive postwar oil legislation.∼∼Representative Coffee tells House that Government must provide incentives if it expects to sell its billion dollars worth of aluminum plants and introduces legislation to authorize federal stock piling of metal.

¶ **November 29.** Selective Service recommends that local boards defer registrants studying or teaching physical science or engineering.∼∼Harold Urey, University of Chicago, tells Senate Special Committee on Atomic Energy that U. S. should stop making and stock piling atomic bombs, yield control of nuclear energy to United Nations, and be willing to sacrifice our national sovereignty for world peace.

¶ **November 30.** Irving Langmuir, appearing before same committee, stresses importance of prompt action by world powers to set up mechanization for atomic energy control.

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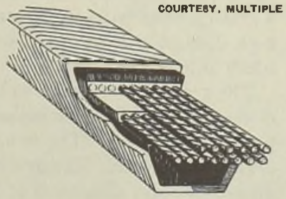
[1] *Chem. Eng. News*, **23**, 2085 (Nov. 25, 1945).

only relatively small loads at slow speed. Through the aid of careful research and experimentation, the modern multiple V-belt, composed of two to twelve individual strands, each strand composed of at least four separate materials, has resulted. It was proved that pressure between the side walls of the belt and grooved pulley, under all conditions of travel around the pulley, must be utilized to the full. Pressure between the bottom of the belt and the flat part of the pulley is less important. There is one exception to this statement. In converting flat belt drives to multiple V-belt drives where a motor pulley of small diameter transmits power to a large, wide pulley several feet in diameter, it has been the custom to use a grooved pulley on the high speed motor but to apply the V-belt surfaces directly to the larger pulley without grooves. This aids in converting from one drive to another. Equalization of tension on the separate belts of the V-drive was obtained by the simple device of permitting the belts to ride in the V-groove at some distance away from the bottom of the slot, entirely through pressure on the side walls. In other words, belts of slightly different lengths would find the proper diameter by riding high or low in the slots, thus equal loads were assumed by each strand of the multiple belt drive.

The modern multiple V-belt is made from a special formula rubber designed to take the wear and friction between the belt and the groove on the pulley. The interior of the belt is backed up with a special resilient rubber for flexibility and durability, without cracking. Strength in the belt has been increased largely by the use of metallic wires molded into the neutral area of the interior. The usual construction is shown in Figure 1.



COURTESY, MULTIPLE V-BELT DRIVE ASSOCIATION

Figure 1. Cross Section Showing Construction Principle of a Modern V-Belt

The multiple V-belt drive has proved so successful that the Multiple V-Belt Drive Association has called it the "dominant drive". There is ample evidence for the suitability of this name. These belts are giving smooth, efficient transmission of power in all types of plants. They have especially demonstrated their efficiency in the drives in textile mills where extreme smoothness of power transmission is essential. In rayon and other textile operations on fine, delicate fibers, a joint in a belt causing jerkiness in the drive has been responsible for the loss of many dollars worth of valuable thread.

The so-called dominant drive has been used for power transmission from a fraction of a horsepower up to several hundred horsepower with over 98% efficiency. Tests have shown that these belts creep less than 0.5%, therefore the friction and wear are minimum. These belts, with centers of 4 feet and less, are transmitting large amounts of power. No reasonable application appears to be too difficult. They run efficiently in the snow and ice under Pullman cars, driving generators which make the interior of the cars more comfortable. They run horizontally, driving 40-inch starch mills on less than 4-foot centers. The combined power of two or more Diesel engines has been transmitted to a common drive shaft by means of three sets of eight multiple V-belts. The power of Diesel engines has been transmitted by this versatile drive to a vertical-shaft deep-well pump. The same engine, through another pulley, drives a horizontal shaft on a booster pump which receives water from the deep-well pump. This complicated arrangement of two pump drives in two directions from a single Diesel engine has been accomplished through the efficiency and versatility of the multiple V-belt means of power transmission.

Acknowledgment

We are indebted to the Multiple V-Belt Drive Association for some of the data presented here and for organizing the industry in a program of cooperative research. This research has resulted in many practical improvements, and has permitted this drive to be used more widely in a shorter time than could possibly have been done without this coordination. The belts of different manufacturers have been standardized. All belts are now capable of a loading for a given size which is also uniform. The belt of any manufacturer will run in the standardized grooves of pulleys of other manufacturers. This association has directed the research which wiped out inconsistencies.

Current Developments in
INSTRUMENTATION

New instruments for emission spectroscopy make increased use of electronics.

Discussed by Ralph H. Munch

THE cornerstone of spectroscopy is the principle that emitted light is characteristic of the atom or molecule that produces it. The development of this principle was a slow process. Newton, in 1666, showed that sunlight is heterogeneous and that a prism separates it into its components. He knew that by the use of a lens he could obtain better separation and a purer spectrum. His apparatus was therefore a nearly modern form of spectroscope. In the next two hundred years many workers nearly grasped this fundamental principle, but none completed the development. It remained for Kirchhoff to state this important generalization. He and Bunsen were the first to make practical use of spectrochemical analysis. Their work on the spectra of the alkali metals led them to the discovery of cesium and rubidium and permitted them to identify some of the elements in the atmosphere of the sun. Qualitative spectrochemistry was firmly established by these achievements.

Quantitative spectrochemical analysis is based on the fact that the intensities of the lines due to a small amount of an element in a matrix decrease as the concentration of the element is decreased. Hartley, in 1882, made the first quantitative spectrochemical analyses. He and other early spectrochemists, such as de Gramont, compared visually the spectra of samples containing unknown amounts of an element with those of a series of similar samples containing known amounts of that element. This method was accurate to about ±25% of the amount present. Since that period, quantitative spectrochemical analysis has so advanced that its accuracy is comparable to that of chemical methods and its speed is much greater.

One of the important factors which have made this advance possible is improved spectrographic equipment. Applied Research Laboratories, Glendale, Calif., and the Harry W. Dietert Company, Detroit 4, Mich., recently announced a large two-meter grating spectrograph. This instrument, shown in Figure 1, was designed to fill a long-felt need for a compact spectrograph of exceptional dispersion, resolution, and versatility. By employing a grating ruled with an unusually large number of lines per inch, high dispersion is achieved without resorting to a bulky instrument of long focal length.

The grating is mounted so that a large portion of the Rowland circle can be used, which makes available a spectrum length of approximately 5 feet. The two gratings available have a ruled area 2.5 × 1.25 inches. The first has 36,600 lines per inch, giving an almost uniform dispersion of 3.4 Å. per mm. in the first order or 1.7 Å. per mm. in the second order. The spectrum available in the first order is from 2100 to 7000 Å. and in the second order, 1850 to 4600 Å. The second grating has 24,400 lines per inch, giving almost uniform dispersion of 5.2 Å. per mm. in the first order and 2.6 Å. per mm. in the second order. The spectrograph can be supplied with either or both of these gratings. When both gratings are supplied, one or the other is brought into use by a small angular shift of the incident beam from one grating to the other.

A 24-inch camera, providing a 20-inch spectrogram on 35-mm. spectrum film, is standard. It is movable on a radius arm which allows positioning along the Rowland circle so that any 20-inch portion of the spectrum may be photographed. With the first grating 1660 Å. can be photographed in the first order or 830 Å. in the second order. For the second grating the corresponding figures are 2500 and 1250 Å. Sixteen spectra suitable for quantitative analytical work can be photographed on a single strip of 35-mm. film. Two 100-foot rolls of film are stored in the camera

(Continued on page 92)

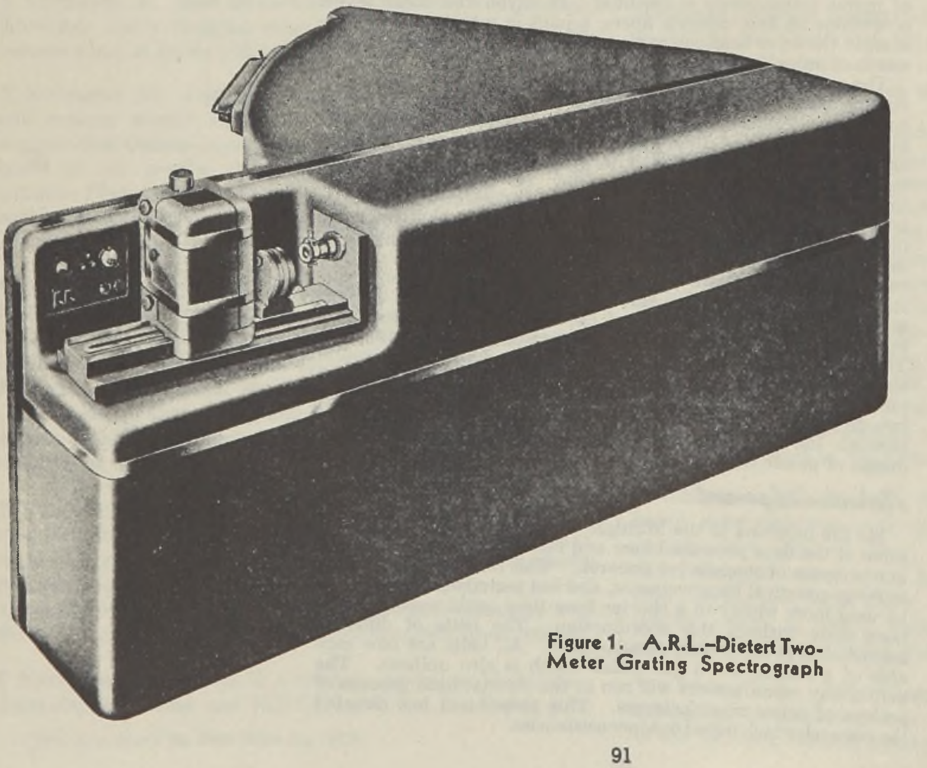


Figure 1. A.R.L.-Dietert Two-Meter Grating Spectrograph

case. Each has a counter to show the number of feet used. Film from either roll can be placed in the camera track without opening the camera. The unused portion of the film is protected from stray light by a mask which also limits the length of the spectrum lines. The camera is racked electrically at the end of an exposure to make the instrument ready for the next spectrum.

The instrument can be supplied either with fixed slits in widths of 15, 30, 60, and 100 microns or with an adjustable bilateral slit calibrated in 2-micron steps. An electromagnetically operated slit shutter within the instrument is controlled by a timer mounted on the control panel of the spectrograph.

The optical bench is fitted with a universal arc-spark stand of rugged design and an intensity control stand and lens holder. All portions of the spectrograph, including the optical bench, are fastened to a massive cast-aluminum base. This is mounted by a three-point suspension in a heavy sheet-metal case. Metal covers which can easily be removed for adjustment or inspection close the top of the base casting. The design of the instrument is such that it can be built into a wall with the camera portion in the dark room and the source-slit portion of the instrument in the lighted part of the laboratory.

Direct-Reading Instruments

Although quantitative spectrochemical analysis using photographic techniques has reached the point where samples of various types can be analyzed for as many as six minor constituents in a total elapsed time of 6 minutes, there are many applications where it would be valuable to decrease the time required. The recent development of electron multiplier-type phototubes has made possible direct-reading spectrochemical apparatus. Two of these instruments were described at the October meeting of the Optical Society of America in New York, one by M. F. Hasler and H. W. Dietert of A.R.L.–Dietert, the other by J. L. Saunderson, V. V. Caldecourt, and E. W. Peterson of Dow Chemical Company. Both instruments consist of grating spectrographs of special design, arranged so that sensitive spectral lines of the constituents to be determined and an internal standard line pass through exit slits and fall on the cathodes of electron multiplier phototubes. Suitable amplifiers and electrical computing circuits are provided to measure the intensities of the unknown lines relative to that of the internal standard line. The Dow instrument is especially designed to control magnesium production by analyzing, in the shortest possible time, samples from the pots before pouring. It supplies a record from which the percentages of seven elements may be read from calibrated scales 55 seconds after the sample electrodes are placed in the instrument. The A.R.L.–Dietert instrument had been used on aluminum alloys and steels in addition to magnesium. Its designers concluded that much quantitative spectrochemical analysis of a routine nature which does not involve spectrographic traces of elements or basic materials possessing complex spectra can be carried out more rapidly and accurately by a direct-reading instrument than by present photographic instruments.

These instruments are a good example of the impact of electronics on instrumentation. Here electronic methods achieve a result unattainable by other means. In addition, there is the possibility of greatly improving these direct-reading spectrochemical instruments by the application of still newer electronic devices. George R. Harrison has suggested that a special iconoscope or television pickup tube might be substituted for the phototubes now used. This would have the advantage that spectral lines too close together for present direct-reading instruments could be resolved, which would greatly increase the utility of direct-reading spectrochemical equipment.

Current Developments in WASTE UTILIZATION

Research in the design of lagoons has been stimulated by developments in the use of chemicals for processing waste.

Discussed by Harold R. Murdock

LAGOONS used by industry in the treatment of waste waters are relatively quiet, shallow bodies of water. A depth of not over 5 feet is considered a practical limit to obtain the optimum advantage of sunlight on the biological life within the lagoon. Industry uses such lagoons to dispose of the effluent from manufacturing processes, which is contaminated with relatively low percentages of soluble residual substances. Usually these shallow basins are constructed near the plant site. When properly designed, they offer possibilities of a complete treatment and, in many cases, at a relatively low cost of operation. New chemicals, combined with improved practice and design, will increase substantially the effectiveness of this method for disposing of dilute waste liquors.

The disposal of vegetable and citrus fruit wash water from canning operations is often accomplished by the use of lagoons. Such operations have been hindered by the nuisance of flies and other insect pests which propagate in the waters. Odors have often prevented the use of lagoons at plants located close to residential properties. However, recent discoveries in the use of effective chemicals, such as DDT, for the control of insect pests herald a broader interest in lagoons. Sodium nitrate, sodium chlorite, and other chemicals have recently been found effective for the control of odors.

Lagoons may be classified into three types. Retention lagoons are the simplest. They are merely storage basins for the untreated waters which are purged into streams at periods of high water freshets. Absorption lagoons are constructed to permit seepage of the residue waters into the ground. They are satisfactory only when porous soil is available, and great care must be taken in their design. Processing lagoons are the most adaptable type for chemical treatment; improved design and new processing methods assure a bright future for this type.

Retention Lagoons

Regardless of the method of disposal, efficient screening of the residual waters from industrial plants through a 20–40 mesh screen is essential. This removes the bulky suspended matter and reduces the load on the lagoon, particularly if the suspended substances have a biochemical oxygen demand. If the suspended material is of fine particle size, it can be settled out in a tank installed ahead of the retention lagoon. A single basin is used by some plants, and when there is high water in the receiving stream, the water in the lagoon is vigorously stirred by the activity of a motor boat before the contents of the lagoon are discharged to the swollen stream. Such crude attempts to solve the problem are to be condemned in the interest of riparian rights.

Absorption Lagoons

A certain large industrial plant located on tidewater was pressed by state authorities to abate the pollution of tidal waters with its high B.O.D. residual water. The plant produced over 15 million gallons of this raw waste each day. A knoll, adjacent to the plant and to a small community, was selected for the construction of a large absorption lagoon. The procedure worked well for about a year, and it appeared that the waste was absorbing into the sandy soil satisfactorily. However, the knoll eventually reached a saturation point, and the raw waste material exuded from the foot of the knoll in many places.

In Iowa a canning plant which was packing peas and corn discharged its waste waters to an irrigation field of about 2 acres. The discharge amounted to about 176 gallons per minute during the hours of work and cleanup time. Furrows, approximately 24 inches wide at the top, 15 inches wide at the bottom, and 9 inches deep, were used to distribute the waste over the field. The ridges were 36 inches wide. This irrigation field has been in use since 1934 and is reported to be satisfactory. The soil of the field is shallow. There is evidence that the waste passing through the soil finds its way through crevices in the underlying limestone formation. The waste has been found to outcrop a fourth of a mile away at a low rate of 5 gallons per minute. No pollution of the stream near by has resulted, but this is another example of the hazards in adopting absorption-type lagoons.

The sandy soil of the citrus belt of Florida is an admirable condition for absorption lagoon installations. At one location the citrus wastes are collected in a large pit which holds the sludge while the supernatant liquor is pumped into lagoons whose bottoms are 10 feet below the surface of the ground but still above the water table. Two lagoons, each about one acre in size, are treated alternately. While one is being treated, the other is allowed to stand for several days. When the lagoon shows signs of clogging, the ground is disked during the resting period to break up the deposit which has formed on the bottom. This is an example of a highly favorable soil condition not available in many locations.

Chemicals are sometimes added to waste waters in absorption lagoons. While lime frequently helps in the flocculation of suspended matter, it is undesirable because it tends to clog the pores in the soil. A dike built across the entrance to the lagoon provides an opportunity for the excess lime and precipitate to settle out. In Wisconsin, a pea packing plant, which produces 3,400,000 gallons of waste water per season, treated its water with 3.4 pounds of sodium hydroxide per 1000 gallons of waste. The pH of the waste remained below 7.2 until the close of the pack. Laboratory studies showed that 5 and 11 pounds of sodium hydroxide per 1000 gallons were needed to keep the pH at 7.2 and 9, respectively.

Processing Lagoons

Last month we discussed how the shallow flats of the Potomac River serve as remarkably efficient processing lagoons for the disposal of sewage and natural organic matter. Nature built this chemical plant; now man must simulate this splendid example. Processing lagoons in the hands of the chemist can be economical and satisfactory methods for the processing of industrial wastes. Chemists have the materials and the ingenuity required to meet the challenge of nature.

The choice of a disposal method, whether it be one of the several types of lagoons, chemical or biological treatment, or disposal at a municipal treatment

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plant, necessitates consideration of the degree of treatment essential in the interest of others, of relative costs, and of availability and topography of potential sites for the disposal plant. Chemical and biological treatments require little land space, but lagoons occupy considerable area. Complete biological treatment is often the most expensive process, but it is most effective when well supervised. Chemical treatments are sufficient in many cases but rarely accomplish a complete stabilization of the waste substances before they are discharged to the river. Lagoon treatments can be the most satisfactory, for they permit both biological and chemical treatments together with sufficient retention time for the waste waters during the processing period.

Specifications for the addition of any material to a stream without creating a nuisance can be stated simply. First, the substance must not be toxic to animal and vegetable life. Second, it must be chemically stable to the environment within the stream. Toxic substances can be removed by chemical treatment or by the use of absorbent solids. Stability can be obtained by oxidation of the substances to more stable materials.

Stability has been obtained already in some industrial waste disposal operations. For instance, sodium nitrate has been added to processing lagoons in the disposal of cannery wastes. The function of sodium nitrate is threefold. First, it makes available the oxygen needed for aerobic bacterial decomposition during the early stages of decomposition of the waste substances. Second, the nitrate stimulates the growth of chlorophyll-containing organisms within the lagoon so that these microscopic bodies can produce additional oxygen by photosynthesis with sunlight. Third, the sodium nitrate maintains a mild alkalinity in the lagoon. In other words, sodium nitrate augments the supply of oxygen obtainable through natural aeration. In the case of cannery waste this chemical has removed odors so that the nuisance is not noticeable 200 feet from the lagoon. The amount of sodium nitrate used is equivalent, in terms of oxygen, to about 20–25% of the 5-day B.O.D. value of the cannery waste.

Recently the Sulphite Pulp Manufacturers Committee on Waste Disposal of Wisconsin released some general information on abating the nuisance of disposing of waste sulfite liquors in the streams of that state. Studies in trickling filters and river reaeration are mentioned. Both of these methods depend upon oxygen stabilization of the waste. The latter is particularly interesting for it is a commendable attempt to supply the deficiency in available oxygen in the stream by diffusing large amounts of air into the river water. In this case the entire river is used as a treating lagoon. Possibly there are good reasons why this waste cannot be treated in such a manner prior to its addition to the stream. The use of treating lagoons should allow more control in such cases. The use of liquid oxygen for such oxidation might be found efficient after an initial aeration in a lagoon. Producers of liquid oxygen as well as other chemical companies, may see opportunities in this experiment.

Sodium chlorite has been used to the extent of 28% of the B.O.D. value of screened pea waste in a northern cannery with outstanding results. Economically the process fails, but with lower costs for this new chemical the process will find increasing use. The treatment of certain wastes with chlorine in lagoons has also passed the experimental stage in some industrial problems. The use of chemicals in solving difficult waste disposal problems is entering a new era. Lagoons will be found useful as reaction basins for this type of treatment.

Current Developments in
PLANT MANAGEMENT

Costs of testing raw materials which are used in the manufacture of chemical products should be kept reasonable.

Discussed by Walter von Pechmann

Rigid control of raw materials expedites determination of the operating conditions needed to create a product of standard quality. However, chemical and physical analyses do not reveal all the facts necessary to guide the production chemist during the manufacturing process. This is especially true in the compounding of certain organic substances or in the incorporation of raw materials in the product in powder and crystal forms which are themselves mixtures of several batches blended together. It is not uncommon for production men to complain that the use of a new container in a shipment has caused trouble in production. The experience of such difficulties is often accompanied by a request to develop new testing methods in the laboratory or to increase the number of samples taken out of each shipment. The acceptance of these recommendations without thorough investigation of existing conditions is likely to result in a expenditure for testing which is out of proportion to other manufacturing costs. Furthermore, the new measures may not bring about the expected improvements. Before an additional burden is put upon existing laboratory facilities, it is recommended that the following investigations be made: (1) Are variations in quality of product really caused by faulty raw materials? (2) What will be the cost of expanding present testing procedures? (3) Is this figure in proportion to the expected advantage? (4) What other measures can be taken to solve this problem at a lower cost?

To make a good product, it is essential to keep the fluctuations in product specifications as low as possible. This applies not only to raw materials but also to working standards. Therefore before it can be concluded why a product has not turned out as expected, it is necessary to investigate job performance and manufacturing facilities as well as the raw materials used. Such factors as poor workmanship, air-bound pipes, split thermometers, and contaminated equipment can produce faults in a product which are likely to be attributed to inferior raw materials. Statistics which show that a raw material used in a product has not entirely met laboratory specifications should not be considered proof that the fault lies in the use of this ingredient. Quality specifications for raw materials are often so strict that suppliers are unable to meet them consistently. This applies especially to color and texture specifications. Quality deviations from such overstated requirements are therefore meaningless. In some cases raw material specifications are too strictly designed by production purposely in order to have an excuse if the product does not turn out as expected.

The importance of using raw materials as directed is not always given sufficient consideration. Department heads frequently accept a raw material at a lower cost with the understanding that the chemical has to be refined (recrystallization, filtering, etc.). Because the difficulties involved in the employment of an additional process have been underrated or because the supplier's request has been forgotten, products are made as before. If trouble in production arises, the "inferior·material" is unjustly blamed.

The amount of money spent in the chemical industry for testing raw materials is frequently underestimated. This applies especially to plants where the material testing is not centralized but is under the supervision of individual manufacturing units. Too often little attention is given to the importance of apportioning correctly the laboratory expenses of a centralized testing unit to the various departments. Mediums of cost distribution, such as direct labor dollars, number of people employed, and number of square feet occupied by each department simplify the work in the accounting department. However, such factors do not put the money where it belongs nor do they allow the various manufacturing units to keep an accurate check on their testing expenses. There is a tendency in the chemical industry today to employ more modern and efficient methods of accounting in laboratories. Some concerns prefer the job cost system, whereas others believe that the process cost system is more suitable. The writer has found that either system works satisfactorily if the head of the laboratory is accounting conscious and supervises the entries to assure that they are more than mere guesses. The contention that work in the laboratory is too complicated and varied to allow accurate time recordings is frequently an excuse for avoiding a small additional assignment. Routine testing procedures do not vary in principle from manufacturing procedures and are often less complicated. The supervisor in the laboratory should know what his men are doing, how long it takes to do the job, and for which department his employees are working. With little effort he should be able to make arrangements for the proper recording of these facts. When a cost system for testing laboratories is developed, consideration should be given to making the proposed measures practical. This may make it necessary to sacrifice accuracy occasionally in order not to interrupt the work in the laboratory or not to increase too much the work in the accounting department. For instance, employees can be asked to record their activities only twice daily. Although this procedure is liable to produce statistics which are not entirely correct, the cost distribution on this basis may nevertheless be sufficiently accurate for proper allocation of the money spent in the laboratory. If the expenses are distributed on an apportioned basis, a medium of apportionment will have to be selected which can be obtained without too much effort. However, this does not mean that laboratory expenses can be apportioned by using the labor dollars spent in the department which receives the service—a method found often even in up-to-date concerns. The writer is not in favor of distributing cost on a predetermined basis even if the apportionment has been established on previous accurate recordings or on a study made by an industrial engineer. Laboratory techniques change frequently, and the number of tests and retests cannot be sufficiently standardized to foretell which portion of the entire work in the laboratory is chargeable to each department. In most instances the overhead expense of a laboratory can be distributed together with the labor. However, where testing methods require the use of special and expensive equipment, or where a large amount of energy or floor space is needed to conduct one type of test, it might be necessary to find another more appropriate means of expense distribution.

Accurate accounting makes it possible to determine more closely the amount of money which will

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Plant Management

have to be spent on testing raw materials. Justification of the increased cost should be judged not on the amount of money which will have to be spent, but on whether the additional expenses are less than the loss which might be expected if the present method of testing were maintained.

It is often believed that materials which go into large batches have to be tested more thoroughly because of the loss which will be suffered when such a batch is spoiled. This is not entirely true. The money lost by the repetitive spoilage of small batches—usually not given much attention—frequently exceed the one time loss of a large batch.

Control Record

The measures usually taken to improve control of raw materials are developing new testing methods, increasing the number of samples which are taken out of each shipment, and compounding small sample batches. Insufficient recognition is given to the fact that intelligent recording enables the production chemist to spot deviations in production before serious damage occurs. This method is not employed more frequently because of the work connected with segregating entries which have no meaning from the deviations which should be analyzed. By stripping a record of all routine entries and recording only the deviations, it is possible to see at a glance all the changes which occurred in production. Applied to the control of raw materials, such a record enables the production chemist to learn without effort in which batch one material was replaced by another, or when a new shipment was made, or even where a new container was used. The technique of developing such a record was described by the writer in detail in an article entitled "Executive Production Control in Chemical Plants" (*Chemical Industries*, October, 1942). In brief, the method works as follows: A control board is made up where the horizontal lines represent chemicals and the vertical lines depict production batches. On the left-hand side of the board exact descriptions of all chemicals used at present are entered in code form. The code numbers contain four digests, one for each of the following: the chemical, its manufacturer, the shipment number, and the container number. For example, material: sodium hydroxide; manufacturer: Merck & Company, Inc.; shipment: No. 135; box: No. 4. The code might be "A — M — a—4"; the key, A = sodium hydroxide, M = Merck & Company, a = first shipment of year (No. 135), and 4 = fourth box in use.

No entries are made on this record until a change takes place in the manufacture of a product. The changes are entered in the squares formed by the vertical and horizontal lines. They are also coded. If, for example, a new barrel is used on the above described chemical, the code number A-M-a-4 changes to A-M-a-5. In order not to clutter the board with unnecessary entries, only the number 5 is recorded. The writer has found it advantageous to color the squares so that the various types of changes stand out more sharply. Changes in shipments, for instance, can be colored yellow, and changes from one manufacturer to another can be indicated by a red marking. This method has the advantage that all changes which occur in an individual batch can be gathered quickly by reading the chart vertically, whereas a complete picture of the changes in the use of one chemical can be analyzed by reading the chart along horizontal lines.

It is recommended that such a control board be given consideration before steps are taken to improve upon the control of raw materials by overloading existing testing facilities.

Last-Minute Flashes

FROM THE EDITOR'S DESK

The surplus problem in benzene and toluene resulting from the sudden cessation of explosives manufacture may be solved. Europe is submitting an active export demand for both as solvents and fuel.

★ A natural rubber price of 16 cents per pound is seen by P. W. Litchfield, Goodyear Tire & Rubber Company chairman. To prevent it from going higher we should produce 200,000 tons of synthetic a year.

★ When Japanese and Chinese menthol return to the market, they will find plenty of competition from Brazilian producers and synthetic manufacturers in this country.

★ Automobiles for 1946 will have no more plastics in their construction than in 1942. Manufacturers are too anxious to get cars off the assembly lines to engage in much research.

★ During the first half of 1945, imports of industrial chemicals rose to $21,000,000, from $15,000,000 in the similar 1944 period.

★ Insecticide users in coming years will want prepared dusts and sprays which require only mixing with water, according to J. J. Davis, Purdue University entomologist.

★ Paper supplies will continue critical for some months to come, warns the Bureau of Foreign and Domestic Commerce. Because of insufficient labor, cutting of domestic pulpwood is still not up to the desired level.

★ Europe's huge nitrogen industry is idle for want of coal, the No. 1 priority problem.

★ The Government is worried over a shortage in castings, which are essential to the automobile and other industries. Gray iron and malleable iron foundries will become serious transition bottlenecks if production is not increased.

★ A survey finds that the average drug wholesaler stocks about 40,000 different items, in some cases as many as 70,000 different products. As a result, labor accounts for over 50% of costs in such establishments.

★ Part of the dismantled German chemical manufacturing equipment in the American occupation zone will be sent here for study.

★ Farm county agents are urged to buy no DDT insecticide preparations unless the label definitely stipulates the percentage of DDT in the container.

★ Out of a dozen categories of plastics, current supplies exceed demand in only two, according to W. S. Landes, head of the Plastic Materials Manufacturers Association.

★ The Navy reveals that one project alone, the radio-operated VT fuse, required each month a total of 1,000,000 pounds of polystyrene, vinyl resins, laminated phenolics, acetate butyrate, and ethylcellulose.

★ Sodium peroxide demands are still not fully satisfied although more sodium metal has been made available for burners. One producer has installed additional burning capacity.

★ The Midwest continues to outstrip the rest of the Nation in increased fertilizer sales. Sales in that area from January to October of 1944 were 199% over the 1935 figure. Sales in the South increased 61%, and seventeen reporting states showed a gain of 73% in fertilizer consumption.