THE INSTITUTE OF PETROLEUM.

CADMAN MEMORIAL LECTURE.

THE Second Cadman Memorial Lecture, organized by the Institute of Petroleum, was delivered by Mr Robert Price Russell in the Lecture Hall of the Royal Institution, London, on June 4, 1947. The Chair was taken by Sir Andrew Agnew, C.B.E., President of the Institute, and a large number of distinguished visitors and members were present.

Introducing the lecturer, Sir Andrew Agnew said : The Cadman Memorial Medal, founded to commemorate the pioneer work of the late Lord Cadman, is awarded by the Institute of Petroleum at appropriate intervals in recognition of outstanding contributions to the petroleum industry.

A year ago the first Medal was presented to Sir William Fraser, and this year the Council of the Institute unanimously approved the recommendation of its Awards Committee that the second Medal be awarded to Mr Robert Price Russell.

Mr Russell is President of the Standard Oil Development Company, which is the central research organization of the Standard Oil Company of New Jersey and one of the world's largest research institutions. Under Mr Russell's guidance, major contributions have been made to development of new chemical processes and in the production of new and improved petroleum products. During the late war Mr Russell rendered signal service to the Allied cause, and was presented by President Truman with the Medal of Merit, the highest civilian award in the United States.

I could recite at length upon the many other services which have been rendered by Mr Russell, but I think that I have said enough to place on record the undoubted fact that whilst the Institute is honouring Mr Russell with the presentation of the second Cadman Medal, the honour is not one-sided, and we now look forward with keen interest to his lecture on "Progress in Petroleum Research."

Mr R. P. Russell then delivered his lecture which was illustrated by numerous lantern slides, a series of cinematograph films, and practical demonstrations. There was also an exhibition illustrating many of the uses of the petroleum derivatives referred to in the lecture.

PROGRESS IN PETROLEUM RESEARCH.

By ROBERT PRICE RUSSELL. (President, Standard Oil Development Company)

THE subject I should like to discuss in this, the Second Cadman Memorial Lecture, is "Progress in Petroleum Research." I am particularly anxious to dwell upon some recent significant developments which provide, I believe, foundation stones for future building.

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In the First Cadman Memorial Lecture, Sir William Fraser, by way of an introduction to future lectures, gave an account of the great personal contribution made by the late Lord Cadman to the development and application of our petroleum resources. The petroleum industry owes its present important position to the whole-hearted application of engineering principles and organized research in oil finding, production, refining, and transportation, with all of which Lord Cadman was associated.

During recent years, oil research scientists have discovered methods for obtaining from petroleum a large range and variety of new products, or products formerly derived from other raw materials. Among them may be mentioned synthetic rubber, many kinds of alcohols, fertilizers, solvents, insecticides, waxes, and numerous chemicals.

The petroleum industry has so completely turned to research for guidance that to-day it is among the leading employers of technically trained personnel. In my own company, for example, research activity began in 1919 with a group of twenty-six people. To-day, our staff includes 2456 technologists, engineers, assistants, and clerical personnel, all working exclusively on research and development problems.

EXPANSION OF WORLD DEMAND FOR LIQUID FUELS.

As we look at the petroleum industry through the eyes of the research scientist, we see certain positive trends which will undoubtedly determine



THE PRINCIPAL SOURCES OF WORLD ENERGY.

These are expressed in B.Th.U. for the period 1925 to 1938. As against a decrease in the energy output of coal, those of petroleum, natural gas, and water power have all increased.

the nature of our activities, at least during the next decade. The increase in the world demand for liquid fuels is, without a doubt, foremost among these trends.

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Fig. 1 shows the distribution of world energy sources through 1938, the last year of normal consumption. The percentage of the total world energy supplied by petroleum and natural gas increased from about 16 per cent in 1925 to about 23 per cent in 1938. To-day we believe it to be close on 30 per cent, and evidences of this vast increase are apparent throughout industry and commerce. In 1914, only 4 per cent of the world's merchant fleet tonnage ran on oil, but by 1945 over 75 per cent was oil burning. The diesel horse-power installed in the United States increased from $5\frac{1}{2}$ million in 1935 to 45 million at the end of 1945. The recent war provided a striking example of the growth in our dependence on oil for energy. A typical division in 1918 had 4000 horse-power behind it, but in 1945 its mechanized counterpart required more than 187,000.



FIG. 2.

GASOLINE QUALITY IN RELATION TO COMPRESSION RATIOS.

The extent to which the octane number of gasoline has increased during recent years, compared with engine compression ratios, is shown.

A decline in coal production in almost every country of the world has coincided with the rise in total energy requirements. Atomic power as a prospective source of energy will probably have little effect on the demand for liquid fuel. My own view is that while atomic energy will probably find important peace-time applications, it will compete for decades to come mainly in the field of large power or heating units now fuelled with coal.

Another major trend bound to influence oil research and development is the increase in octane number of gasoline and the corresponding rise in engine compression ratio. Fig. 2 shows the extent to which the octane number of gasoline has increased in the United States during recent years. By and large, it parallels the increase in compression ratio, which is a measure of the engine's ability to utilize the power of the fuel. During the war, the highest octane gasoline constituents were reserved for military uses, with a consequent decline in war-time gasoline quality, but immediately afterwards an improvement occurred in the quality of motor gasoline and the best premium grades progressed to a point well above pre-war rating. Again, in 1946, there was a slight decline in quality due to a temporary shortage of tetra-ethyl lead, but we know now that the stage is set for a further rise in both octane number and engine compression ratio.

Over the years it has proved necessary for the industry to alter the proportions of the various products made from crude petroleum, and the dominating factor, here, has been the sharp upward trend in gasoline requirements. Fig. 3 shows how the demand for gasoline has been met



FIG. 3.

THE GROWING U.S. DEMAND FOR GASOLINE IS MET BY A LARGER OUTPUT PER BARREL OF CRUDE OIL, ALTHOUGH THIS ENTAILS A PROPORTIONATE REDUCTION IN YIELD OF OTHER OIL PRODUCTS.

through reducing the proportionate production of other oil products. For example, in 1920 the gasoline produced in the United States amounted to only 26 per cent of the crude run. By 1940, however, the gasoline yield had been stepped up to 43 per cent, while the development of oil cracking has made it possible for us to adjust within a wide range the proportion of gasoline and other petroleum products obtainable from a barrel of crude oil.

Still another trend that will have a pronounced effect on oil research is the increasing cost of finding and producing petroleum. This has already imposed on the industry the need for more efficient refining methods and has stimulated investigation into other available sources of liquid fuel.

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A considerable part of the present research and development effort of my own company—nearly one-third of that effort, in fact—is directed to the conversion of natural gas and coal to liquid fuel. The emphasis placed on this field of research and development is not due basically to any fears of future oil shortage. Competent oil geologists have estimated that our proved reserves of crude oil will be greater twenty years hence than they are to-day, and that we shall have plenty of oil for the next 100 years. But the time is already at hand, in some parts of the world, when liquid fuels from gas and coal are becoming competitive with petroleum products.

Chemical developments in the petroleum industry are important to our economy, but the volume of chemicals produced is small in relation to the industry's output as a whole. One half of 1 per cent of the world's annual crude oil production would supply the world's entire rubber needs, while nine-tenths of 1 per cent would take care of the world's alcohol requirements for industrial purposes and even for beverages. The wide range of chemical and synthetic products now being made from oil utilizes only a fraction of 1 per cent of the total world production. As we look at the industry to-day, we see that the principal function of petroleum is that of liquid fuel, and I think it may be assumed that for many years to come petroleum will serve chiefly as a source of energy.

IMPROVEMENTS IN TECHNIQUES OF OIL REFINING.

The developments I propose to discuss are the results of research in petroleum refining, and their chief application is in the production of more abundant and more efficient liquid fuels, although this is by no means the limit of their usefulness. For, as is so often the case in research, each new area of discovery has opened up other interesting and useful fields.

The first of these processes is fluid catalytic cracking, the result of a development brought to the stage of commercial availability not long before Pearl Harbour. The second is hydrocarbon synthesis, an allied process which has opened up real possibilities for utilizing coal and natural gas in the production of liquid fuels and also of a wide variety of chemical products.

Catalytic cracking was first developed as a means of improving motor gasolines. To meet the two-fold demand for increased gasoline yield and also for sharply improved anti-knock characteristics the oil industry turned to the use of catalysts. It was found that by carrying out oil cracking in the presence of catalysts consisting of clay and related solid synthetic materials, the cracking process could be operated at lower pressures and temperatures and with shorter times of reaction than those employed in earlier thermal cracking units. Moreover, the catalytic reactions gave better overall yields in addition to greatly improved product quality.

When catalytic operations were first applied on a large scale in the oil industry, the catalyst was used in stationary beds as lumps or pellets over which the materials to be processed were passed as vapours. This was true of both the high pressure hydrogenation and hydrocatalytic cracking processes developed by my own company on the technical foundation laid down by the I.G. Farbenindustrie in Germany and of the later catalytic cracking process pioneered by Eugene Houdry.

There is no particular difficulty in carrying out fixed bed catalytic

cracking batch-wise on a small scale, but large-scale production gives rise to many practical difficulties. The development of a continuous process seemed desirable in order to avoid complicated valving, heat removal problems, and difficulties in temperature control. These problems finally reached solution in a totally new type of catalytic cracking placed in largescale commercial operation about 5 years ago and known as the fluid catalytic cracking process.

Because of its inherent simplicity and certain unique advantages, the fluid process has a wide variety of potential applications in the oil industry and other fields. Before reviewing some of these applications, it might be as well to explain the basic features of the fluid process.

The term "fluid" is applied to this type of catalytic cracking because the finely divided catalyst actually behaves like a fluid when aerated by a gas or vapour.

Samples of this catalyst, when placed in a bottle, behave just like flour or clay. It is sluggish in movement and travels with difficulty as the bottle is tilted. But when the bottle is shaken vigorously, the whole mass becomes fluid and seeks to find its own level with each movement of the bottle, in a manner similar to water.

In the operation of the fluid catalytic cracking process (Fig. 4), preheated oil vapour produced by flash vaporization enters a reactor, carrying along with it the catalytic material as a suspended powder. Because of the decreased velocity of vapours passing through the reactor, the suspended powder settles out to form a relatively dense, bubbling bed. Cracking proceeds in this bed at a temperature of about 900° F as the rising oil vapours contact the active solid, and is completed in about 20 seconds.

Product vapours then leave the bed, pass through a settling zone to a cyclone separator, carrying with them catalyst still in the form of a suspended powder. Here, a large part of this suspended powder is recovered and returned through a small standpipe to the catalyst bed.

The vapours—substantially catalyst free—proceed to a fractionator where they are separated into gas, high octane gasoline, heating oil, and gas oil fractions. A very small percentage of the catalyst escapes from the cyclone but is recovered as a heavy oil slurry at the bottom of the fractionator, from which it is pumped back into the reactor.

Meanwhile, the catalyst, separated from the cracked oil vapours, is withdrawn from the bottom of the reactor and discharged into an air stream which carries it in suspended form to a regenerator vessel. Because of the decreased velocity of the carrying gas, another violently bubbling bed is formed in this vessel, and the carbon deposited on the catalyst during its passage through the reactor is burned off in the regenerator bed at a temperature of 1100° F. The purified catalyst is separated from the spent air, first in a settling zone above the bed and then in a cyclone separator, after which it is returned through a standpipe and control valve into the stream of hot oil vapour. At this point it begins a new journey into the reactor and a fresh cycle of operation.

The spent air leaving the cyclone passes through an electro-static precipitator where the final traces of catalyst dust are recovered and returned in suspended form to the regenerator bed.

Remarkable results are produced by the violent action in the fluid

catalyst beds. For example, in a plant scale regenerator as much as 200 million B.Th.U. per hour may be liberated, yet the temperature in the regenerator seldom varies more than 5° F from top to bottom. This minor temperature variation, compared with the enormous heat liberation, is realized even though the seething catalyst bed may be 20 feet deep and up to 45 feet in diameter.

Of particular interest is the fact that the complete cycle takes place without the use of a single mechanical moving part. It is the fluid condition of the catalyst which makes this possible. A pressure head is developed by the catalyst in the regenerator standpipe. This pressure is sufficient to cause the catalyst to flow from the regenerator—a zone of relatively low pressure, through the regenerator slide valve into the reactor—a zone of relatively higher pressure.

The average particle of catalyst makes its way around the complete circuit every ten minutes, yet the process runs continuously for months on end.

A large-scale fluid catalytic cracking unit is capable of handling $1\frac{1}{4}$ million tons of feed stock per year, or some 25,000 barrels per day. Such units are about 250 feet high—as lofty as a 20-storey building—and contain more than 24 miles of piping, of which one section may reach 8 feet in diameter. Some 40 tons of catalyst (as much as can be loaded into four railroad cars) are circulated through the unit every minute, yet the catalyst recovery is so complete that only 0.005 per cent of the 60,000 tons circulated daily is lost to the air.

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By virtue of its flexibility, the fluid catalyst cracking process can be used to control almost at will the product distribution and quality obtained from a given refinery. For example, gas oil fractions can be cracked in oncethrough operations with direct gasoline yields of from 45 to 55 volume per These gasoline yields are raised to 55 or even 65 per cent by simple cent. polymerization of low molecular weight unsaturates. Yields such as these may be obtained in once-through operation without the production of any heavy fuel oil whatsoever from the virgin gas oil processed, while by recycling operations it is possible to increase further the yields of gasoline from gas oil. It has even been found possible to crack heavy residue catalytically without the production of tar and obtain high yields of motor gasoline directly comparable in quality with that obtained when processing light gas oil fractions. A comparison of results from thermal and fluid catalytic cracking is made in Table I. The uniformly high octane level of the catalytic gasoline, relative to the thermal product, is particularly worth noting, together with the high yield of gasoline both in single pass and recycle operations and the absence of tar production in most of the catalytic operations.

The fluid catalyst technique was brought to full development just in time, for although it had received large-scale pilot plant demonstration, no commercial plants were yet in operation when we were suddenly confronted with the demand for enormous war-time supplies of aviation gasoline and vast amounts of raw materials for synthetic rubber.

The first commercial fluid catalyst cracker went into successful operation in Baton Rouge, Louisiana, on May 25, 1942. Even before this plant was completed, the process had been chosen by war-planning groups and by

a series and all the	Heavy paraffinic gas oil.				
Operation. Feed stock.	Thermal cracking.	Fluid	catalytic cra	acking.	
Tan State Bride State	Partial recycle.	Single pass.		Recycle.	
Catalyst.	None.	Silica– alumina.	Magnesia.	Silica- alumina.	
Yields :Gasoline + polymer, vol%Excess C_4 , vol%Cycle oil, vol%10° A.P.I. tar, vol%Coke, wt%Dry gas, wt%	38.9 Nil 40-0 20.1 Nil 4.3	57·2 3·3 40·0 Nil 3·5 5·6	63-1 Nil 40-0 Nil 3-5 4-2	75.3 6.5 4.5 7.8 10.6 7.6	
Octane number, gasoline + polymer: A.S.T.M. clear . C.F.R.R. clear . C.F.R.R. + 1.5 cc T.E.L	72-6 82-5 89-0	81·1 95·7 99·3	79·8 93·1 97·3	83·1 95·7 98·5	

Comparison of Results from Thermal and Fluid Catalytic Cracking.

refining organizations of the United States for some thirty plants. These were required to produce the base stock and alkylate raw materials for nearly half of the then projected output of 100-octane aviation gasoline as well as for a considerable portion of the normal butylene and *iso*butylene needed for synthetic rubber. That they did so is now a matter of history, for the Allies were never lacking in vital supplies of 100-octane aviation gasoline.

At the present time, thirty-eight fluid catalytic cracking units are in existence in the refineries of nineteen oil companies and thirteen additional units are under design or construction in the plants of nine companies. The capacity of fluid catalytic cracking plants installed, under construction or on order, has reached the amazing total of nearly 60 million tons/year, or 58.5 per cent of all the installed catalytic cracking capacity in the world outside Russia. The extremely rapid expansion during the war years is a point of interest worth noting.

BENEFITS TO THE MOTORING PUBLIC.

Before proceeding to a discussion of other applications of fluidized technique, it seems desirable to point out what long range benefit to the public will result from these advances in the technique of catalytic cracking. Motor gasolines can be made to-day with existing catalytic cracking equipment and by other fully developed processes to operate in cars with engines of 9.5 to 10 compression ratio as against the present average compression ratio of slightly over 6. From the standpoint of the motorist's pocket-book, these figures have a very real significance. A car giving performance equal to the best obtainable from present-day models, but designed to take full



ROBERT PRICE RUSSELL, CADMAN MEMORIAL LECTURER AND MEDALLIST, 1947.

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R. P. RUSSELL DELIVERING THE CADMAN MEMORIAL LECTURE.



SIR ANDREW AGNEW PRESENTS THE CADMAN MEMORIAL MEDAL TO R. P. RUSSELL.



THREE CATALYTIC CRACKING UNITS AT THE BATON ROUGE, LOUISIANA, REFINERY OF THE STANDARD OIL COMPANY OF NEW JERSEY.



HYDROCARBON SYNTHESIS PILOT PLANT AT THE BATON ROUGE, LOUISIANA, REFINERY OF THE STANDARD OIL COMPANY OF NEW JERSEY.



THE FLUID CATALYTIC CRACKING PROCESS.

By this technique, preheated oil vapour is pumped into the reactor together with a finely divided catalyst agent. There it is "cracked" under heat and pressure into vapours of different molecular structure. In the fractionator these vapours are separated into gas, high octane gasoline, heating oil, and gas oil. The catalyst agent, meanwhile, returns to the regenerator to be cleansed of carbon before it begins a new cycle of operation.



FIG. 5.

THE HYDROCARBON SYNTHESIS PROCESS.

In this technique for the production of synthetic hydrocarbons from natural gas, the pre-heated gas is fed into a generator together with similarly pre-heated oxygen. Here the methane is converted by partial oxidation into carbon monoxide and hydrogen. After cooling, the synthesis gas enters the fluid type reactor and is converted in the presence of an iron catalyst to form synthetic hydrocarbons and water. The synthesis product then passes into a condenser where gases are separated from liquids. The liquid hydrocarbon products are primarily high octane gasoline and disclored by high octane gasoline and disclored by the product include many useful chemicals.



FIG. 6.

EFFECTS OF OIL OXIDATION RESISTANCE.

The Chevrolet piston on the left was run on an oil deficient in oxidation resistance, while that on the right had the benefit of an oil containing an inhibitor offering good resistance to oxidation.



FIG. 7.

PRACTICAL DEMONSTRATION OF VALUE OF OIL DETERGENT.

These two Hercules diesel pistons were photographed after a 120-hour test in which the one on the left had run without an oil detergent. The beneficial effects of the oil detergent are manifestly obvious on the piston on the right.



FIG. 8.

EFFECTS OF AGRICULTURAL WEED-KILLING HORMONE PRODUCED FROM PETROLEUM. Neither the dandelion plant (right) nor the thin-bladed grass shows any immediate ill-effect although both have just been sprayed with weed-killing hormone.



EFFECTS OF AGRICULTURAL WEED-KILLING HORMONE-THE SEQUEL.

A fortnight later: while the grass has grown more luxuriant the dandelion plant is dead. The reason for this is that dandelion, plantain, and other broad-leaf weeds absorb much more of the hormone spray than the thin-bladed grass. Consequently they are killed while the grass is merely stimulated in growth.



AGRICULTURAL EXPERIMENT UTILIZING A WEED-KILLER DERIVED FROM A PETROLEUM DISTILLATE.

This carrot field, overgrown with weeds and abandoned by a farmer for agricultural experiments, is being sprayed with a weed-killer derived from petroleum distillate.



FIG. 11.

SEQUEL TO THE EXPERIMENT ON A WEED-GROWN CARROT FIELD. The same field, later in the season, is scarcely recognizable. The weed-killer has cleared a path between the carrot rows which remain unaffected.

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advantage of these new anti-knock gasolines, would show a substantial gain in miles per gallon. For example, a modern American car with a compression ratio of 6.6 to 1 will cover, let us say, 17 miles per gallon at 40 miles per hour on a level road. A car fully designed for a 9.5 compression ratio engine would achieve 24 miles per gallon. This represents an improvement in mileage of 40 per cent—no small figure.

Assuming that the motorist normally pays 2s. a gallon for gasoline for his 1947 model, with his new model fully designed to take advantage of high octane he could afford to pay two shillings and ninepence per gallon. Now in the normal course of events he will not have to pay any such amount, because the added cost of making the new product, we know, will be far less than its increased value to the motorist.

The motoring public may, therefore, look forward not only to a saving in its annual gasoline bill, but also—according to experts in the automotive industry—to the building of cars with high compression ratio engines at no greater cost than that of present-day cars. Further, from the standpoint of the people and the world as a whole, there is the advantage that would result from a still greater conservation of our petroleum resources.

Catalytic cracking may also contribute towards meeting world requirements of gas turbine fuels, since the process, while converting a large fraction of the raw materials fed to it into high-octane gasoline, simultaneously lifts into the boiling range of kerosines and light gas oils a considerable additional segment of the higher boiling fractions fed to it. These products, either as such, or possibly after saturation-type hydrogenation, may conceivably find application as jet and gas turbine fuels.

HYDROCARBON SYNTHESIS.

The second important process I would like to consider with you is that of hydrocarbon synthesis. Here, the fluid catalyst technique is directed to the conversion of natural gas and coal into liquid fuels.

Synthetic hydrocarbons may be produced either from gas or coal. These basic raw materials, however, must first be converted into synthesis gas (a mixture of carbon monoxide and hydrogen). Once the synthesis gas has been formed and purified, the remainder of the process is similar for both coal and natural gas. The synthesis gas is fed from a generator into a reactor and converted in the presence of a fluidized catalyst into synthesis products, such as gasoline, diesel oil, and chemicals.

At the present time in the United States, synthesis from natural gas is closer to plant-scale application than synthesis from coal. A representative technique for the production of synthetic hydrocarbons from natural gas is illustrated in Fig. 5 where the various steps in this process are shown, from the time the gas enters the generator until the liquid products are ready for final refining.

After pre-heating in a heat exchanger to a temperature of about 930° F, the natural gas, principally methane (CH_4) , is fed into a synthesis gas generator, together with similarly pre-heated, compressed oxygen. The burning zone of the generator is an open chamber lined with refractory insulation, and here the methane is converted by partial oxidation to carbon monoxide and hydrogen. The temperature level in the combustion zone is about 2450° F and the pressure 20 to 30 atmospheres. On leaving the combustion zone, the hot products of combustion are cooled, first in a waste-heat boiler in the generator and then by heat exchange with incoming methane and oxygen. The gas now enters at the base of a fluid-type reactor operating at about 660° F and a pressure of 20 to 30 atmospheres. Here, in the presence of an iron catalyst which, in "fluid" state, is in constant and violent motion, it reacts to form synthetic hydrocarbons and water. The reaction liberates a very large amount of heat, amounting to 14,500,000 B.Th.U. per ton of liquid produced. But high rates of heat transfer through cooling tubes immersed in the fluidized catalyst permit the maintenance of uniform temperature throughout the catalyst. The heat of the reaction is absorbed in the vaporization of water to form high pressure steam which is a source of heat and power throughout the plant.

In the past, the major difficulty in applying the synthesis operation to large-scale production has been the maintenance of an even catalyst temperature despite this large heat evolution, for a relatively deep bed of catalyst is employed in the synthesis reactor. However, this difficulty has been solved as efficiently as in the case of the fluid catalytic cracking process.

The synthesis product leaving the fluid bed in vapour form carries with it a small amount of entrained catalyst. This is recovered in a cyclone and returned through a dip-pipe to the catalyst bed. The vapours leave the reactor to be cooled in a condenser and pass from there into a separator where the liquids are separated from the gases, some of which are recycled for further processing. The liquid products—high octane gasoline, diesel oil and chemicals—then undergo normal finishing treatment.

The gaseous portion of the product is stripped of light hydrocarbon content and the residual tail gas is used to help provide power and heat requirements of the process. Or part of it may be sold as fuel.

In the hydrocarbon synthesis process developed in Germany, using pelleted or granular catalyst in fixed beds, large numbers of closely spaced cooling tubes were required and the capacity of the reactors was limited by the ability to remove heat. In the fluid-type reactor developed in the United States, heat transfer rates are so much higher than was possible with the German tubular type that less than 1 per cent as much cooling surface is required. This naturally means a large reduction in investment, maintenance, and operating cost. Not only are the new iron catalysts used in the fluid process cheap in initial cost, but they also result in production of high octane gasoline instead of the exceedingly poor knock-rating product made by the Germans with their more expensive cobalt-type catalysts.

COSTS-A COMPARISON.

According to our most recent estimates, a hydrocarbon synthesis plant erected in the United States to produce 420,000 tons per year of hydrocarbon liquid products from natural gas will cost about £7,600,000, or roughly £18 per yearly ton. This is over twice the cost of a complete refinery capable of producing the same products from crude oil. Of the 420,000 tons per year of hydrocarbon synthesis liquid products, approximately 380,000 tons per year will be gasoline and 40,000 tons per year gas oil. The gasoline has an A.S.T.M. octane number, unleaded, of 80 and a

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research octane number on the same basis of 93. In addition, a considerable quantity of oxygenated water-soluble products is produced, consisting largely of alcohols. Assuming that the oxygenated products have the same value as gasoline and that natural gas is charged for at 3d. per 100 cubic feet, the cost for gasoline works out at 3.9d. per Imperial gallon. The estimated cost of producing the same quality gasoline in the United States from certain typical crudes is about 5.7d. per Imperial gallon.

Largely because of the additional plant facilities required, the production cost of synthetic gasoline from coal is to-day slightly higher than the cost of gasoline from crude oil. For example, a United States plant capable of producing some 380,000 tons a year of gasoline from coal, together with about 42,000 tons per year of diesel fuel or gas oil and a considerable quantity of oxygenated water-soluble products (mainly alcohols), is estimated to cost about £15,000,000. In addition to the high octane motor gasoline and diesel fuel products, this plant would also yield nearly 40 million cubic feet a day of high heating value gas. Taking into account areas where this gaş could be sold for about 1s. 8d. per thousand cubic feet, and allowing suitable credit for the diesel oil and chemicals produced, the cost of gasoline from such a plant—with good grade coal at 10s. per ton, a figure which can be realized in some parts of the United States comes to approximately 6.5d. per Imperial gallon.

If no market existed for the by-product fuel gas, the cost of gasoline would be about 7.2d. per Imperial gallon. The figure of 6.5d. is not much more than the cost of producing similar quality gasoline from crude oil at present United States crude prices.

The plant investment, however, is more than four times greater, and although the figure of 6.5d. per gallon includes normal depreciation, it does not allow for any return on the added investment. Nevertheless, even with a fair return on the greater investment, motorists could operate their cars on synthetic gasoline from coal at an average additional cost of not more than 6d. a day.

From the investment and operating costs just cited, it is clear that the synthesis operation, based on natural gas, even after all the recent major advances, finds true economic justification in only a few parts of the world. Large-scale application to coal requires additional study, but vigorous investigation is now in progress which will doubtless lead to further significant improvements. The present status is such, however, as to warrant the close interest of anyone interested in the oil industry.

OTHER APPLICATIONS OF THE FLUID TECHNIQUE.

Major new developments of a broad and fundamental nature occur only infrequently. During the twenty years I have been working in the oil industry, for example, less than a dozen such broad advances have appeared. The fluid catalyst principle is without doubt a fundamental advance. It represents something more than a major contribution in the field of catalytic cracking and hydrocarbon synthesis, for it also provides a new chemical engineering medium which appears destined to have numerous important applications in the oil, chemical, and other process industries. Among these, it can be used in making phthalic anhydride for resin manufacture, in lime-burning and coal gasification. In the iron-smelting industry it offers such significant possibilities of lowering costs and reducing metallurgical coke requirements per ton of pig iron produced—perhaps even eliminating the need for metallurgical coke—that the technique is now receiving vigorous study in several quarters.

LUBRICATION IMPROVEMENTS.

In the field of lubricants, the processes of catalytic cracking and hydrocarbon synthesis have also opened up new possibilities for improvements far beyond what was deemed possible a few years ago. The special characteristics essential for satisfactory lubricating oils can be imparted only—or more readily—through the use of additives. Catalytic cracking has uncovered new olefin sources and hydrocarbon synthesis has added still other olefins to our existing raw materials for manufacturing additives.

British scientists have done impressive work in the development of lubricants—on film strength agents in the early twenties and on metallic soaps as sludge dispersers in the early thirties. They were also responsible for the first large-scale use of such detergent additives in aviation oils during the war.

Modern high-speed automobile and aviation engines really give lubricating oil a terrible beating, and it therefore becomes necessary to improve on Nature's product. Small amounts of specially synthesized chemical compounds are added to improve the high temperature stability of the oil, reduced sludge formation and ring sticking, and minimize bearing corrosion.

Fig. 6 shows two pistons from Chevrolet engine tests run under standard conditions and with high oil temperature. One of the oils used was lacking in oxidation resistance, while the other had a small amount of inhibitor added to it and presented good oxidation resistance. The difference in the condition of the two pistons is readily apparent.

The results of tests on a Hercules diesel engine, run for 120 hours under standard conditions, are shown in Fig. 7. The oil used in one test was lacking in detergent properties and unable to keep any sludge in suspension, with the result that there was varnish formation of a serious type. The oil used in the other test contained a small amount of special detergent additive which kept the pistons in exceptionally clean condition.

Much heavy duty commercial equipment to-day is experiencing troublefree performance principally because the proper type of detergent additive is incorporated in the lubricating oils used. During the war, heavy duty oils were called upon to work under the most drastic conditions of military service and one can well imagine what might have happened had these oil additives not been available. The lubricating oil additives used to-day, remarkable as they are, unquestionably will be supplanted by still newer materials uncovered in the course of the intensive research now in progress.

CHEMICAL DERIVATIVES OF PETROLEUM.

I should like to turn now to the field of chemicals produced from oil. Petroleum-chemicals are not important volume outlets for crude oil, since as nearly as we can estimate—*all* the organic chemicals, including rubber and alcohol, needed to meet the entire world's needs for a year, could be made from 10 days' crude oil production. This petroleum-chemical field is nonetheless of extreme importance, for many materials needed all over the world to raise living standards can be made in sufficient volume and at requisite low cost only from intermediate products derived from petroleum. Many of these intermediaries became available in the necessary volume for fullest production only as catalytic cracking reached maturity. Others of these intermediates will make their commercial debuts as hydrocarbon synthesis plants are built.

The first petroleum-chemical product made in volume was *iso*propyl alcohol, and this was followed by the production of various higher alcohols and ethyl alcohol. These are used partly as such and partly for conversion into other important chemicals. They are important industrial solvents and are currently being made on a large scale. For example, the 1946 production of industrial alcohol in the United Kingdom was just under 21 million Imperial gallons, while in 1947 a single synthetic alcohol plant in the United States is expected to produce 16 million Imperial gallons of synthetic grain alcohol and about an equal volume of *iso*propyl alcohol.

The petroleum industry also supplies a wide variety of hydrocarbon solvents, one of the most important of which is toluene. The finding of a more plentiful source of toluene for T.N.T. was one of the major problems inherited by our scientists from the last war. Military estimates placed the toluene requirement for a modern war at 330,000 tons a year, or eleven times the quantity available during the first World War. These estimates proved to be far too low, but the problems attending the production of even 330,000 tons of toluene yearly from its normal source—coal—practically defied solution.

The presence of toluene in petroleum had been known since 1857, following the discovery of benzene in cracked whale oil by Faraday in 1825. Toluene from petroleum was used for the manufacture of T.N.T. in the first World War, but in the recent war the demand was much greater and the required standard of purity far higher.

Success in the synthesis of toluene from petroleum was not, however, attained until the end of 1939, when Poland had fallen and war was about to sweep across Europe. The race against time in our development centres and plants to produce adequate supplies of synthetic toluene was one of the most dramatic in the entire war. The first synthetic toluene-from-oil plant went into operation in September 1941 at Baytown, Texas, and during the war this plant alone turned out more than twice as much toluene as the entire coal industry. By the end of the war, synthetic nitration grade toluene was being produced from petroleum at nearly six times the rate of production from coal-tar. To-day, toluene and related aromatic chemicals synthesized by these new techniques are widely available for pressing peace-time solvent needs, and they already serve as raw materials for a new synthetic chemical industry vital to large-scale plastic production.

The petroleum industry has been engaged for many years in the development of materials to control flies, mosquitoes, and other insects, and during the war enormous quantities of these products were used by the Allied armed forces, particularly in the Pacific. The emphasis is now on more peaceful applications, such as, for example, cattle dips, and petroleum products now find increasing applications in the control of all kinds of insect pests.

PETROLEUM PRODUCTS IN AGRICULTURE.

In the United States alone, tens of thousands of new chemicals are currently being tested for agricultural purposes, and from this maze of products a new substance of some usefulness occasionally emerges. In my own company's agricultural programme, for example, close to a thousand new compounds are being tried yearly for agricultural purposes.

One somewhat remarkable product is a synthetic plant hormone, again based in part on catalytically cracked raw materials. It has proved highly effective for the selective control of broad-leaf weeds and is probably well suited for killing weeds in grass and cereal grain crops. Extensive field tests are now being carried out on various United States crops and in the cultivations of bananas, cocoa, coffee, and sugar-cane.

The principle upon which this weed-killing hormone works is the simple one of stimulation, for it is absorbed through the leaves and literally stimulates the plant to death. Dandelion, plantain, and other broad-leaf weeds absorb much more of a hormone spray than thin-bladed vegetable crops or grass, with the result that they are killed while the thin-bladed plants are merely stimulated in their growth.

The effectiveness of this product as a weed-killer is evident (Fig. 8) from tests made with ordinary grass (*pao pratensis*) and dandelions (*taraxacum officinale*). Both were sprayed uniformly with the same relatively concentrated (550 p.p.m.) water solution of the synthetic hormone. A fortnight later the dandelion was dead while the grass was even more luxuriant than formerly (Fig. 9).

During recent years, several institutions have devised astonishing new techniques in utilizing hydrocarbons for weed control. The most highly developed of these at present is the spraying of carrot fields with petroleum distillates of the white spirits type for the selective killing of weeds and grasses. A newer and equally original technique for the destruction of weed seeds is that of spraying the ground after planting but before sprouting, with the heavier and more toxic hydrocarbons. In this way, weedfree soil can be maintained without cultivation during an entire season. These materials, like the other mentioned previously, are now being tried in connexion with various tropical and semi-tropical agricultural problems.

In one of the large-scale trials made in the United States, the spraying of white spirits to aid the cultivation of carrot crops was carried out on a field so overgrown with weeds that it was impossible to distinguish the rows of carrots. As a matter of fact the farmer had actually abandoned his field and turned it over to us for experimentation (Fig. 10). The petroleum distillate cleared of weeds the space between the carrot rows, as may be seen in Fig. 11. The carrots received only one spraying and no hand weeding, although a cultivator was later on run once between the rows. Without the spraying of white spirits, the rows would never have been found and the crop would certainly have been lost.

This new technique was first tried on a large scale only 4 years ago; yet in 1946 it was applied in the cultivation of 4500 acres on which were raised over 90 per cent of all the carrots grown for market that year in New York State. Approximately 500 additional acres of parsnips, onions, and celery were weeded in the same way.

These and similar developments will undoubtedly have a very significant effect on the economies and living standards of many countries. As industrialization progresses, attracting more and more people from the rural communities, the land must be made to yield the same or more food, but with less and less labour for planting, cultivation, and harvesting. New type synthetic products such as I have mentioned are destined to play an important rôle in the solution of the critical problem posed by the dwindling supply of agricultural labour. This problem of farm labour shortage is becoming acute in the United States, and I believe in Great Britain and Latin America as well. One practical solution to which we may look is the use of synthetic agricultural aids as a step towards greater land production with the expenditure of less man-hours of work.

SYNTHETIC RESINS AND DETERGENTS.

Brand-new type resins can be made by the score from the chemical building blocks available in adequate quantity for the first time as the result of large-scale application of catalytic cracking, or about to become available from hydrocarbon synthesis. Many of these new resins hold important promise for successful application in industry and agriculture. One of them, in particular, is endowed with remarkable moisture-proof qualities. Moisture penetration is less than 1/20th as rapid as with the best of present-day transparent cellulose films, so that fruit wrapped in thin sheets of this material and stored for several months in an uncooled room loses only a small percentage of its moisture content, as against a 40 per cent loss for unwrapped fruit in the same period.

Fruit thus protected tastes just as fresh after 3 months as it did on the day it was wrapped. Resin-wrapped fruit and vegetables can be made available for longer market periods, or shipped and stored without heavy expenditure on refrigeration.

With the new chemical raw materials available in quantity from petroleum as a result of various applications in fluidized catalytic technique, some extremely interesting work has been in progress in the production of textile fibres. Of the hundreds of synthetic resins and plastics synthesized in various research laboratories all over the world, only a small fraction can be converted to fibres. One of the new plastics made largely from petroleum raw materials is extremely tough, strong, and solvent-resistant, and can be drawn into a clear, almost colourless monofilm in a conventional plastics extruder. The extruded fibres have tensile strengths up to 125,000 p.s.i. The chief disadvantage is that there is still some shrinkage in length when the fibre is maintained at elevated temperatures, although significant progress is being made in overcoming this remaining defect.

It is still too early to predict the fields in which this new fibre or some modification of it will be most important, but preliminary tests indicate that bristles, screening, chemically resistant fabrics, upholstery, and even wearing apparel are possible applications.

New types of synthetic emulsifiers, detergents, and soaps are now also being manufactured from petroleum. It is also possible to make them from natural gas. These new products have perfectly remarkable properties, as those of you who have used them well know, and I should not be surprised if within 5 years a significant portion—say, a quarter or more of the world's soap or detergent requirements were to be derived from petroleum sources. Wetting agents recently developed also have a multitude of possible applications, particularly in the dyeing industry and for many household purposes.

SYNTHETIC RUBBER.

One of the latest fields invaded by petroleum chemistry is that of synthetic rubber. Natural rubber, like petroleum, is made up of the elements of carbon and hydrogen, but thus far no one has quite succeeded in duplicating the structural arrangement of the atoms in the natural rubber molecule. A number of synthetic products have, however, been made which can replace rubber successfully for most uses.

Synthetic rubber production in the United States was originally a wartime development, for war in the Pacific deprived us of our main supplies of natural rubber, and the problem was to set up a synthetic rubber industry in time to avoid catastrophe. Fortunately, a process for making one type of synthetic rubber—known as Buna-S—had been developed in Germany and we had sufficient information on this process to apply it, provided raw materials were available. (Ironically enough, the Japanese, by their appropriations, became so rubber-rich that they set up an industry for converting rubber into oil.)

The major raw materials required for the manufacture of synthetic rubber were butadiene and styrene, both synthetic organic chemicals. Of these, butadiene was far more difficult to supply, since it was required in much larger quantities and because no production process existed which was adapted to our national economy.

Our research laboratories took on a problem of staggering proportions and two main processes for producing butadiene were developed with extraordinary speed. One was based on alcohol and the other on petroleum butylene, which could be produced in high yields in fluid catalyst oilcracking operations. Fortunately for the Allied world, both processes worked well. The first Buna-S synthetic rubber manufactured in the United States in commercial quantity was produced at Baton Rouge, Louisiana, on December 20, 1941, 13 days after Pearl Harbour. There, too, the first butadiene-from-butylene plant in the United States went into successful operation on May 21, 1943. War demands for rubber were met in full.

I have mentioned that rubber and petroleum are both made up of carbon and hydrogen. The rubber molecule, however, is enormous in size compared with any compound encountered in petroleum. In rubber, the carbon atoms are strung end to end to form long chains or threads, and these molecular threads are coiled up and snarled together. It is this peculiar structure which gives rubber its elastic properties. The problem of making rubber from petroleum is therefore one of duplicating or imitating the long chain molecular structure. This is done by first making small molecules which possess high chemical reactivity and then coupling these in head-to-tail fashion by polymerization. In the Buna-S synthesis, butadiene and styrene are emulsified with water in the presence of soap and small amounts of various other chemicals used for regulating the reaction. This mixture, which exerts a pressure of several atmospheres, is agitated in 100,000-litre autoclaves at slightly elevated temperatures for 15 to 16 hours. At the end of this time the butadiene and styrene have combined to form finely divided rubber particles.

Buna-S, as it comes from the reactor, closely resembles an oil emulsion, but if a salt solution is added, the particles agglomerate. The further addition of acid produces rubber which comes out much as milk curdles when it turns sour. When this is washed and dried, Buna-S rubber results. Passenger car tyres made of Buna-S are now available. They duplicate in performance tyres made of natural rubber.

If, instead of styrene, we use acrylonitrile with the butadiene, we obtain the rubber called Buna-N or Perbunan. Unlike natural rubber and Buna-S, Perbunan is oil resistant and therefore stands up when oil comes into contact with it. When immersed in oil, Perbunan swells only slightly whereas natural rubber increases in volume several-fold and loses practically all its strength. The main use for such oil-resistant rubber during the war was for bullet-proof or self-sealing oil tanks with which our bombers and fighter planes were equipped, and for the construction of the fuel lines laid across Europe to supply fuel to the advancing Allied forces.

Finally, we come to Butyl rubber, a product made entirely from petroleum *iso*butylene, one of the constituents of refinery gases, with a small amount of diolefin, such as butadiene or isoprene, incorporated to aid vulcanization. Butyl rubber is much more impermeable to air than any other kind of rubber and in the United States is extensively used in the manufacture of inner tubes.

Originally we were highly disappointed to find Butyl apparently lacking in elasticity. It resembled rubber in many respects, but did not bounce. Our chemists regarded this problem of resilience as being in some way related to internal friction, and having had experience with viscosity in oils, they reasoned that temperature should have an effect on rebound. Heat was therefore tried and it was found that a Butyl rubber ball heated to the boiling point of water was almost as lively as one of natural rubber. Conversely, a natural rubber ball chilled to low temperature will bounce no more than one made of Butyl and kept at room temperature.

The process for making Butyl rubber is a unique one in that the polymerization is carried out at -150° F. This in itself presented a great many practical problems, since no one had ever before carried out a chemical reaction on a large scale at such low temperature. There was no experience at all to go by and all equipment had to be specially developed. Moreover, the reaction is extremely rapid and difficult to control in large-size equipment. There were many other difficulties to be overcome, but to-day Butyl rubber is being successfully made at the rate of 300 tons or more a day.

You may feel that in my remarks I have digressed far from the primary business of the petroleum industry, which is, after all, that of supplying liquid fuels and lubricants. I have done so in order to consider with you petroleum as the parent source of countless products now essential to the daily pattern of our lives, and even in so doing I have mentioned but a few.

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As we review the long history of man's development, we see comparative static periods followed by other periods of rapid change. The Greeks knew how to harness steam and actually fashioned a primitive steam engine which, however, was reserved for the æsthetic function of opening the temple doors and was not developed further. For almost 2000 years thereafter, man was content to depend for energy on the wind, water, animals, and his own muscles. Then in a few years came steam, the internal combustion engine, and electricity, with coal and petroleum serving as fuel to generate energy.

Now, during the last few years, we have begun to explore other possibilities of extracting more of the wealth concentrated by Nature in these vital resources. It is encouraging to contemplate that we again stand on the threshold of new and perhaps startling discovery and development. I have no doubt that processes and adaptations will be evolved in the next few years in far greater number and of far wider usefulness than those we know to-day.

Sir Humphry Davy in his "Elements of Chemical Philosophy" stated that one of the aims of chemical philosophy is the application of "natural substances to new uses, for increasing the comforts and enjoyments of man." Towards this end, research and development in our industry have indeed contributed in a substantial and beneficial manner. Given a free and truly competitive system in which to carry on our work, and a political climate in which we can meet in friendship to exchange ideas and enjoy the stimulus of one another's company, I have no doubt that our scientific groups will deal successfully with the many problems which the future unquestionably will bring.

Presentation of Cadman Memorial Medals.

SIR ANDREW AGNEW: It needs no voice of mine to express your great appreciation of the very wonderful address which we have just heard. Mr Russell has covered a lot of ground not only in surveying past progress but also in prophesying the future.

Had he not already found a title for his address he could well have called it "Practical Science." The pictures and demonstrations we have seen have, in fact, covered many aspects of the practice of science.

It is now with very great pleasure that I, as President of the Institute of Petroleum, have to present to Mr Robert Price Russell the Cadman Memorial Medal. The United States was the home of the petroleum industry and has contributed much to the research which has made the industry so successful, although I am happy to say that we in Britain have managed to keep apace with our American friends. It is very fitting, therefore, that the Institute has awarded this second Cadman Medal to an American citizen.

(Sir Andrew then presented the Cadman Medal to Mr R. P. Russell to the accompaniment of prolonged applause.)

MR R. P. RUSSELL: I think you will all understand how affected I feel at the honour which has just been conferred upon me. I also hope you will understand how humbly I accept this honour as a tribute to and on behalf of all who have co-operated in the achievements which I have

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described. All of you who have to do with research are aware that organized research is not an individual effort, but a team effort. It was the team that counted during the war and it is the team to-day. I do, therefore, accept this medal with full humility.

SIR ANDREW AGNEW: I now have two further very pleasant duties to perform in the presentation of Cadman Memorial Medals, one to Lily Lady Cadman, the Widow of the first Lord Cadman, and the other to the Anglo-Iranian Oil Company at Abadan.

It was a condition of the Memorial that two Medals should so be awarded, and this would have been done when the first Award was made last year but for a supply difficulty.

It is unfortunate that Lily Lady Cadman is unable to be here to receive the Medal in person, but I will ask Lord Cadman to accept it on her behalf.

(Lord Cadman accepted the Medal amid applause.)

SIR ANDREW AGNEW : My second duty is to make a similar presentation to Abadan refinery where I am sure it will long be treasured as a memento of the first Lord Cadman. I will ask Sir William Fraser to accept the Medal on behalf of Abadan.

(Sir William Fraser accepted the Medal.)

This terminated the proceedings.

INSTITUTE OF PETROLEUM.

A MEETING of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Wednesday, April 9, 1947, when the Chair was taken by Dr A. E. Dunstan, Past-President.

Introducing the lecturer, the Chairman said : I have very much pleasure indeed in introducing my old friend and colleague, Dr Steiner, particularly because some years ago, after a most distinguished career in the University of Cambridge (Colloid Department), he came to my laboratories, where he stayed for all too short a time. I am certain you will find his paper of the greatest possible interest.

The following paper was then read :

AROMATICS FROM PETROLEUM.

By H. STEINER,* Ph.D.

SUMMARY.

Some general principles governing the formation of aromatics based on thermodynamics and quantum theory are reviewed. The formation of aromatics by dehydrogenation, cyclization, and isomerization is discussed. The hydroforming process makes use of all these reactions to produce toluene, xylenes, and generally high octane spirits. An alternative way of producing aromatics from petroleum is by cracking at high temperatures. The chemical reactions occurring in these processes are outlined, and a process recently developed in this country to produce aromatics together with low molecular weight olefines, such as ethylene and propylene, is described.

AROMATIC hydrocarbons can be obtained from petroleum by extraction of the naturally occurring aromatic compounds contained in it or by a variety of chemical reactions, such as cracking, dehydrogenation, cyclization, and polymerization, which allow one to convert other classes of hydrocarbons, such as paraffins and naphthenes into aromatics. This review will deal with a number of these reactions and the processes based on them, particularly those which have become of importance in the course of the last decade.

Apart from extraction of naturally occurring aromatic compounds, there are, in the main, two distinct classes of processes available which are of importance for the production of aromatics from petroleum. The first class is usually referred to as hydroforming or catalytic reforming, and the second is a development of high temperature cracking, which, with the use of catalysts, has made possible the production of pure aromatics.

The former type of process is based on such chemical reactions as dehydrogenation, cyclization, and isomerization (see Fig. 1) and is characterized by the fact that a given non-aromatic hydrocarbon is converted into the corresponding aromatic compound having the same number of carbon atoms.

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The latter process is based on a much more radical decomposition into olefins and diolefins of low molecular weight, from which, in a second step, aromatic compounds are built up by condensation and polymerization reactions. Since in this process cracking and condensation reactions are involved, there is no rigid correspondence between molecular sizes of charge and product. In general, a wide variety of charging stocks, from natural or cracking gases to high boiling gas-oils, can be used and the products contain the full range of aromatic products from benzene to highly condensed rings.

1. Some General Principles Governing the Formation of Aromatics.

Before dealing in detail with the various reactions leading to aromatics we shall discuss a few general principles which must govern the formation of aromatic compounds which ever process or reaction is used.

An examination of free energy changes involved in the formation of aromatics is by necessity restricted through lack of accurate data. Sufficient data are available only for the reactions leading to one or two of the monocyclic compounds, such as benzene and toluene. These data show that, above a temperature of 400° C, all hydrocarbon equilibria involving these compounds are shifted entirely to the side of the aromatics. From arguments given later it is reasonable to infer that similar conditions hold for the more complicated monocyclic and polycyclic compounds and for aromatics generally.

For the C_6 series of hydrocarbons, for instance, we find the temperatures given in Table I, at which at atmospheric pressure the equilibria indicated are shifted to 99 per cent to the side of the aromatic compound.

Reaction.	Temperature (° C) at which at atmo- spheric pressure reaction proceeds to 99 per cent to right-hand side.
$\begin{array}{c} n\text{-Hexane} \rightleftharpoons \text{Benzene} + 4\text{H}_2 \dots \\ n\text{-Hexene-(1)} \rightleftharpoons \text{Benzene} + 3\text{H}_2 \dots \\ cyclo\text{Hexane} \rightleftharpoons \text{Benzene} + 3\text{H}_2 \dots \\ cyclo\text{Hexane} \rightleftharpoons \text{Benzene} + 2\text{H}_2 \dots \\ n\text{-Hexane} \rightleftharpoons n\text{-Hexene} + \text{H}_2 \dots \\ cyclo\text{Hexane} \rightleftharpoons cyclo\text{Hexene} + \text{H}_2 \dots \end{array}$	370° 120° 230° 310° 870° 720°

820

Q27

1773	T 1
'I'ADT T	1 4
TADTE	

Data from : Thomas, Egloff, and Morrell, Industr. Engng Chem., 1937, 29, 1266; Parks and Huffman, Free Energies of Some Organic Compounds, Chem. Catalogue Co., New York.

Comparison of the first four equilibria with the last two clearly shows the fundamental difference in the transformation of, for instance, a paraffin or cycloparaffin into an olefin or cyclo-olefin having the same number of carbon atoms, and on the other hand into the corresponding aromatic compound. It is seen that a temperature some $400-500^{\circ}$ higher is necessary to let the former reaction go to completion.

Further insight into these conditions is provided by a study of the heat changes associated with these reactions. We find that for the dehydrogenation of a paraffin or naphthene to the olefin or cyclo-olefin, generally an energy of 28-32 kcal/mole is required. Based on these results we would expect for the dehydrogenation of cyclohexane to benzene an endothermicity of 85-95 kcal/mole equivalent to the dehydrogenation of three paraffinic to three olefinic carbon-carbon bonds. Instead, we find the heat of reaction •to be only 48 kcal/mole. The difference is to be attributed to the "Resonance" energy of the benzene ring which, according to the present and similar calculations, is of the order of 37 kcal/mole. We thus find that the energy stabilization due to "resonance" reduces to a remarkable extent the energy requirements necessary to produce aromatic compounds and this is clearly the reason for the peculiar characteristics of the equilibria involving aromatics discussed above.

While this survey is hardly the place to discuss at length resonance phenomena of aromatic compounds, a short discussion of the case of benzene seems useful since the results can easily be extended to aromatic compounds generally, and it can thus be shown that the thermodynamic conditions characteristic of the formation of benzene must hold universally for all aromatic compounds.

If we write down the electronic formulæ for benzene, each bond being represented by an electron pair,



we find for the two Kekulé structures the formulæ given above. It is clear from these formulæ that they are interconvertible by a mere shift of electrons—that is, without requiring a displacement of carbon or hydrogen nuclei. According to quantum theory a tautomeric system of this kind in principle cannot be resolved into its components and closely related to this fact is its greater thermal stability. Such structures are called "resonating" and the stabilizing energy the resonance energy.*

It is easily seen that this principle of structures, interconvertible by a shift of electrons only, can be extended to any cyclic hydrocarbon structure built up of conjugated double bonds and consequently to the most complicated aromatic structures consisting of a number of condensed rings. In fact the energy stabilization increases with the number of conjugated bonds and, therefore, with increasing number of condensed rings.

It is therefore to be expected that the thermodynamic conditions which were shown to apply to monocyclic aromatics, in particular to benzene, hold for aromatic hydrocarbons generally. This conclusion is further supported by general chemical experience which in many instances demonstrates the great thermal stability of highly condensed aromatic rings.

^{*} Further factors contributing appreciably to resonance in aromatic compounds are the possibility of "Dewar" type structures and the fact that all these molecules have a planar configuration.

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While these general principles based on thermodynamics and quantum theory must govern the formation of aromatic compounds, the rate at which the various reactions will proceed is then a question of suitable reaction conditions and particularly of catalysts. We shall proceed, therefore, to discuss in more detail the various reactions involved in aromatization and shall begin with those on which the hydroforming process is based, viz. dehydrogenation, cyclization, and isomerization (see Fig. 1).

Typical examples of—

(a) Dehydrogenation.



n-Heptane.

CH.



Toluene.

 $CH_3 + 3H_2$

(c) Isomerization (combined with dehydrogenation).

$$\begin{array}{c} \mathbf{H}_{2}\mathbf{C} & \mathbf{C}\mathbf{H}_{2} \\ \mathbf{H}_{2}\mathbf{C} & \mathbf{C}\mathbf{H}_{2} \\ \mathbf{C}\mathbf{H}_{2} \\ \mathbf{C}\mathbf{H}_{2} \\ \mathbf{E} \\ \mathbf{t} \\ \mathbf{t$$

Toluene.

2. Aromatization by Dehydrogenation, Cyclization, and Isomerization.

FIG. 1.

The reaction leading to aromatics known for the longest time is the catalytic dehydrogenation of naphthenes. This reaction was discovered by Sabatier and Senderens,² and ever since has been of the greatest importance for organic chemistry. Until recently, however, the industrial applications were limited, since the only catalysts known to bring this reaction about were metals such as nickel, copper, and the elements of the platinum group. All of these are poisoned even by traces of sulphur compounds which inevitably are present in most crudes. However, about fifteen years ago Lazier and Vaughan³ discovered that cyclohexane can be dehydrogenated to benzene over chromium oxide. Their catalyst was only of limited activity, but better catalysts were developed rapidly. These catalysts proved to be entirely sulphur resistant, a fact which removed the main obstacle to a wider application of dehydrogenation reactions in industry. This parallels the somewhat earlier development of hydrogenation, particularly of coal and tars, where large-scale industrial development was greatly helped by the discovery of sulphur resistant catalysts.

Since these oxide catalysts are now of paramount importance, not only

because of their activity for dehydrogenation but also for cyclization and isomerization, the limited information available about their nature and mode of action will be reviewed. Generally, they belong to the class of metallic oxides which can exist in different valency states and are easily convertible from one valency state into another. When functioning as catalysts they are usually in a lower valency state and frequently show paramagnetic properties due to the presence of unpaired electrons in the incomplete electron shell of the metal ion. As will be seen later, this property may be the cause of their catalytic activity. Typical examples are the oxides of chromium, vanadium, and molybdenum. They are widely used on carriers such as aluminium oxide, but magnesium oxide or zirconium oxide have also been employed. In some cases the combination of carrier and metal oxide promoter only is an active catalyst, the carrier or the promoter taken by themselves being entirely inactive. A list of some catalysts mentioned in the literature is given in Table II.

TABLE II.

Catalyst.	Reaction.	- Reference.
CrO ₃	Dehydrogenation	Lazier and Vaughan, J. Amer. Chem.
Cr_2O_3 gel Cr_2O_3 on γ -alumina .	Cyclization, de- hydrogenation —	Turkevich, Fehrer, Taylor, J. Amer. Chem. Soc., 1941, 63, 1129. Archibald and Greensfelder, Industr. Engng Chem., 1945, 37, 356.
Cr_2O_3 on γ -alumina promoted by K, Na, and Ce	Cyclization	
MoS ₂	Cyclization	Moldawski, Kamuscher, and Kobilskaya, J. Gen. Chem. (U.S.S.R.), 1933, 7, 1835.
TiO ₂	_	Moldawski and Kamuscher, Comptes Rend. (U.S.S.R.), 1936, 10, 343.
MoO ₂ on alumina, molybdates with aluminium, thorium, chromium, iron, cobalt, nickel, vanadium	Cyclization, iso- merization	Herington and Rideal, <i>Proc. Roy. Soc.</i> , A, 1945, 184 , 434.

Oxide Catalysts for Dehydrogenation, Cyclization.

The most common catalyst is chromium oxide, which industrially is used on Al_2O_3 as carrier in a concentration of from 5 to 20 per cent. In the laboratory pure chromium oxide, particularly in the form of "chromium oxide gel" as developed by H. S. Taylor and his school,⁴ has been used extensively.

A considerable increase in activity of supported Al_2O_3 - Cr_2O_3 catalysts was obtained by Archibald and Greenfelder.⁵ These authors found that Cr_2O_3 supported on alumina in the γ -form was considerably more active than that supported on the α -form. They further promoted their catalysts with small amounts of potassium, calcium, and also cerium. Such catalysts can cyclize *n*-heptane to toluene to the extent of 80–90 per cent at a temperature of 490° C and at a space velocity of 0.36 vol/vol/hr.

It is a general feature of these catalysts, particularly when used for cyclization, that their activity declines in the course of a few hours due to the accumulation of carbonaceous material on the surface. This can be burned off with air diluted with inert gases, after which treatment and subsequent reduction to the lower oxide the catalyst has regained its initial activity. It was suspected that the poisoning action is due to olefins and diolefins which are strongly adsorbed on the catalyst and polymerize before they have a chance to evaporate again. Eventually these polymers cover the whole surface and thus reduce the activity of the catalyst. That the poisoning of the catalyst is due mainly to olefins is supported by the fact that it is very much slower, in the case of the dehydrogenation of naphthenes, than in a typical cyclization reaction such as that of n-heptane to give toluene. In the case of the naphthene dehydrogenation the concentration of olefins found in the products is very small, whereas in the case of the cyclization it is appreciable.

These qualitative considerations were confirmed quantitatively by Herington and Rideal ⁶ who traced the poisoning mainly to various diolefines, of which the fulvenes are a typical example, and correlated the amount of fulvenes formed in the reaction with the rate of decay of the catalytic activity. On carrier catalysts the decay of the activity is much reduced. These authors were able to show that this is due to the spatial separation from each other of the active metal oxide particles caused by the molecules of the carrier. As a result, the linking up of the olefins on the surface is made more difficult and the catalyst remains active for a longer period.

Very little is known of the actual mode of action of these catalysts, but some pertinent experiments were reported by Herington and Rideal.⁶ It was noted that whereas neither MoO₂ as prepared by reduction of ammonium molybdate is a catalyst for the cyclization of *n*-heptane to toluene, nor is pure Al₂O₃, the combination of 10 per cent MoO₂ on Al₂O₃ on the other hand is an active catalyst. This was correlated with the fact that reduction of the pure molybdate did not stop at the MoO₂ stage but went further to molybdenum metal, which is not an active cyclization catalyst. In the case of the Al₂O₃ promoted catalyst, reduction of MoO₂ to the metal was extremely slow and at temperatures below 500° C practically did not take place. Herington and Rideal concluded that MoO₂ was the active catalyst and attributed its activity to the presence of two unpaired electrons in the metal ion of MoO₂. The unpaired electrons may be able to form links with the hydrocarbon substrate, for instance, with olefins by combining with the electrons forming the double bond (π electrons).

To return to the dehydrogenation of six-ring naphthenes—as far as the detailed mechanism of the reaction is concerned very little work has been done. In general, one obtains the final aromatic molecule in one single step, but this does not necessarily exclude the formation of *cyclo*-olefins and *cyclo*diolefins as intermediate products. Traces of olefins of the order of 1 per cent have been observed frequently in the products,⁵ and it may well be that accurate experiments at short contact time would reveal the intermediate formation of *cyclo*-olefins which subsequently dehydrogenate so rapidly to the corresponding aromatic compound that their concentration cannot build up.

The cyclization and isomerization reactions have been known for a much shorter time than the dehydrogenation of naphthenes, yet they have been studied more extensively and much more is known about their detailed mechanism. The cyclization of *n*-heptane to give toluene was first reported by Moldawski and Kamuscher in 1936,⁷ and at about the same time a patent application covering this process was filed by Morell and Grosse.⁷

The cyclization reaction is not restricted to *n*-heptane or to *n*-paraffins, but, generally, paraffins and also olefins can be converted into the corresponding aromatic compound, having the same number of carbon atoms, by linking together two carbon atoms removed from one another by five bonds. Thus any paraffin of straight or branched chain, but having within its structure a straight chain of at least five successive links, can be converted into the corresponding aromatic compound.



Cyclization of 3-Methyl-heptane.

In many cases alternative products are possible, due to the variety of ways in which a given hydrocarbon chain can link up to form a six-membered ring. For instance, from 3-methyl-heptane we should expect ethylbenzene, mxylene, and p-xylene to be formed, all of which are found (see Fig. 2). Many pure paraffins have been subjected to the cyclization reaction and the products studied. The results, mainly from the work of Hoog, Verhuis, and Ziuderweg,⁸ and from Herington and Rideal,⁹ can be found in Table III. With a few exceptions to be discussed later, the products to be expected according to the simple theory discussed above are formed.

The products from the cyclization of paraffins generally are found to contain considerable proportions of olefins (up to 15 per cent). These olefins were identified as a mixture of those which one can expect by direct dehydrogenation of the corresponding paraffin. It was shown that they are intermediate products which are formed from the paraffins and are then cyclized to the aromatic compounds. This is clearly brought out by experiments at small conversions (Fig. 3) * which show that olefins

* Fig. 3 reproduced from the Trans. Faraday Soc., Vol. 35, page 980 (1939).

TABLE III.

Cyclization of Paraffins.

		Aromatic products formed.	Total conversion into aromatics.*	
			Found.	Calculated.
n-Hexane		Benzene	20	23
n-Heptane		Toluene	36	35
2-Me-hexane		Toluene	31	35
n-Octane	• •	Ethylbenzene (some toluene)		
		o-Xylene p-Xylene	46	42
2 Ma hantana		Tthribon son a	,	and the second second
3-me-neptane	• •	o-Xylene	35	42
2-5-Di-me-hexane		n-Xylene	52	52
3-Ethylhexane		Ethylbenzene	Q.	
n-Nonane .	- :	n-Propyl benzene o-Methyl-ethylbenzene	No comp	arable yields
n-Decane (containing	decene)	Naphthalene (some other compounds)	j given.	

* For standard conditions : 465° C, contact time 18-24 sec. Cr₂O₈ catalyst.



CONVERSION OF *n*-HEPTANE TO TOLUENE.

are built up in the very first stages of the reaction and that the formation of aromatics becomes appreciable only after a certain amount of olefins have been formed.¹⁰ Thus the mechanism of the reaction is as follows :----

paraffin ______, olefin ______ aromatics.

*Cyclo*paraffins or *cyclo*-olefins could not be detected amongst the products and it is assumed, therefore, that these compounds once formed, particularly if still adsorbed on the catalyst, are dehydrogenated so rapidly to the aromatic end-products that they cannot be detected.

The intermediate olefin is strongly adsorbed on the catalyst. This is assumed to take place by a two-point contact by opening of the double bond and formation of links with the atoms of the catalyst. Using this picture, Herington and Rideal were able to account for the relative cyclization rates of the paraffins listed in Table III by consideration of the probabilities for ring closure. The calculated conversions are listed in the last column of Table III and are seen to compare well with those actually found.

When alternative aromatic compounds can be formed, due to different possibilities for ring closure, the state of affairs becomes more complicated. While the sum total of all aromatics formed still agrees with that calculated according to simple probability considerations, the proportion of the various alternative products differs markedly from that predicted. This was found to be due to isomerization reactions, which in some cases also produce compounds which cannot be predicted by the simple cyclization scheme mentioned above. A typical case is that of n-octane.

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Cyclization Products from n-Octane.

Products					Per cent of aromatized product.		
	1100					Observed.	Calculated.
Ethylbenzene						33	66
o-Xylene . m-Xylene .	÷	:	:	-		33 27	33
p-Xylene						7	

According to the cyclization scheme, ethylbenzene and o-xylene should be formed exclusively, but instead m- and p-xylene are formed in addition, mainly at the expense of ethylbenzene. The formation of the two latter compounds is particularly significant, since they cannot be formed without rupture of a carbon-carbon bond and subsequent isomerization. Assuming certain modes of adsorption of the substrate on the catalyst, it can be shown that the isomerizing action is in agreement with the assumption of a twopoint contact on the catalyst.

We are thus led to a third mode of reaction leading to aromatic product namely, *isomerization* with simultaneous cyclization and dehydrogenation. This is particularly important for paraffins of the C_6 range and above, which have a straight chain of less than five links and which cannot cyclize according to the scheme proposed.

After some conflicting evidence in the literature, it was found by Herington and Rideal⁹ that generally two classes of hydrocarbons can be subjected to this isomerizing cyclication reaction, namely :—

(1) Paraffins of the C_6 range and above which have a straight chain of four links, and

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(2) Alkylated cyclopentanes having at least six carbon atoms. (Examples of such reactions can be found in Table V.)

It has to be noted, however, that the reaction temperature at which these isomerizations take place is some eighty degrees higher as compared with cyclizations not requiring simultaneous isomerization.

TABLE V.	T
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Isomerizing Cyclization of Paraffins and Five-Ring Naphthenes.

Substrate.	Product.
2-3-Di-me-pentane 2-2-3-Tri-me-pentane Ethyl-cyclopentane trans-1-2-Di-me-cyclopentane 3-3-Di-me-hexane 2-2-Di-me-hexane	Toluene m-Xylene Toluene Toluene o-m-p-Xylenes m-Xylene

In considering the mechanism it seems significant that the first class of compounds can cyclize to give five-membered rings, and that the second group already contains a five-membered ring within its structure. It is well known that isomerizing reactions of the type



take place readily on catalysts of the oxide type and at temperatures above 450° C, and this is therefore suggested as the mechanism by which isomerization takes place. This is well supported by the fact that paraffins which cannot cyclize to five-membered rings do not give the combined isomerizing cyclization reaction.

Finally, the two hydrocarbons mentioned last in Table V should be noted. These hexanes with geminal methyl groups, in theory, can cyclize to a geminal dimethyl cyclohexane, but not to an aromatic compound. This reaction does not take place. Under conditions of isomerizing cyclization, however, one of the geminal methyl groups could migrate by isomerization, and formation of an aromatic ring should become possible. This is found to be the case.

3. THE HYDRO-FORMING PROCESS.

All of the reactions discussed so far are applied in the hydro-forming process, which is designed to convert paraffins and naphthenes into aromatic compounds. This process was intended at first as a means of raising the octane number of inferior naphthas (Catalytic Reforming). Since the octane numbers of *n*-paraffins or paraffins with only small branches (e.g., methylhexanes) are of the order of 0-50, and those for aromatics between 105-125, even partial conversion into aromatics should raise the octane number considerably. Moreover, in addition to forming aromatics the catalysts discussed are very suitable for eliminating sulphur compounds as hydrogen sulphide and with a slight modification the olefins formed in the process can be hydrogenated by the hydrogen formed in the dehydrogenation reaction. One can thus obtain in one step a sulphur-free fully saturated material of high octane number, which should require none, or very little refining treatment. Nevertheless, in spite of these advantages the process found little application for reforming, possibly because it is too expensive.

Hydroforming was of the greatest importance during the last war, when it became the main process for producing toluene for the manufacture of T.N.T. It thus developed into a key process in the Allied war effort and it is estimated that in 1944 about 250,000 tons of toluene were produced by it. With the end of the war this aspect of the process lost its importance, since the uses for toluene in peace-time are limited and most of it can be supplied from coal-tar. There are, however, interesting peace-time applications which we shall mention later.

In practice the process is carried out under a pressure of 150-300 p.s.i., with a large amount of hydrogen split off during the reaction as recirculation gas (hence the name, hydro-forming).¹¹ The presence of excess hydrogen is of great importance because it helps to keep up the activity of the catalyst for longer periods. It probably acts through a hydrogenating cracking reaction of the surface polymers, which, as mentioned previously, are the main causes for the decay of catalyst activity. These polymers are converted into methane and ethane, and in this form are removed from the catalyst. Otherwise the presence of excess hydrogen does not influence the reaction since, as shown previously, at a reaction temperature of 480-550° C, the dehydrogenation equilibria are displaced to such an extent to the aromatic side that even a considerable partial pressure of hydrogen cannot influence the yield of aromatics.

Some difficulty in carrying out the process is due to its high endothermicity (about 500 k.cal/Kg), coupled with the comparatively low space velocity necessary to achieve complete conversion (about 0.3 vol/vol/hr). One prefers to pass a superheated charge through a thermally insulated catalytic chamber in which the temperature of the charge is allowed to drop due to the heat supplied to the reaction. In this way conversion can proceed only to a limited extent, since with the drop in temperature the reaction will slow up, and more than one, generally two passes through the system are necessary to obtain full conversion into aromatics of all components of the feed which are capable of being cyclized.

In the course of a few hours' run, the activity of the catalyst declines and has to be restored by burning off the carbon deposits. The heat generated is used to raise steam which in turn can drive compressors for recirculating gases, both during the "on stream" and the regeneration period. A number of reactors are used and the charge to be processed is switched from one to another, as regeneration has to be carried out. In this way the process is made continuous.

The choice of the charging stock is of prime importance since it must contain a maximum of components which can be cyclized. For the production of toluene a high content of methyl-cyclohexane is particularly desirable, since it is the C_7 compound which gives best conversion into toluene. Characteristics of a typical charging stock prepared as a narrow cut from a Los Angeles Basin crude are given in Table VI.

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TABLE VI.

Toluene-forming co	Per cent by vol.					
Dimethyl-cyclopentane						11
Methyl- <i>cyclo</i> hexane	•	•	•	•	•	} 25
Foluene (present in charge)						3.5
Total toluene formers						39.5

Charge to Hydroformers for Toluene Production.

By two passes through the hydroformer the compounds listed in Table VI are converted nearly quantitatively into toluene and one obtains about 70 per cent by weight of a product containing 40 per cent toluene. The losses are due to cracking into gases (hydrogen, methane, ethane, propane) and to formation of coke. Further fractionation enriches the toluene in the product to 60 per cent. At this stage special processes are used—such as azeotropic distillation, extractive distillation, or solvent extraction—to separate the toluene further from paraffins and naphthenes of similar boiling points. After a final refining treatment with sulphuric acid, the toluene passes the strictest nitration specification.

With the end of the war many toluene plants became redundant, but an interesting new application for hydroforming has been reported recently.¹² Instead of producing toluene a hydroformer was adapted to produce xylenes from a suitable charging stock. The xylenes so produced contain 20 per cent of the ortho-isomer, which is separated and used as basic material for the production of phthalic anhydride by vapour-phase oxidation according to the formula :—

 $\textcircled{CH}_{CH_3}^{CH_3} + 13O_2 \longrightarrow \fbox{CO}_{CO}^{CO} > 0 + 3H_2O$

In this way orthoxylene replaces naphthalene of which there is a beginning shortage, at least in the U.S.A.

In a similar way a number of other aromatics could be produced, and it may well be that for this purpose the process will become of importance in the future.

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4. AROMATICS FROM VAPOUR-PHASE CRACKING.

It has long been known that aromatics are formed in cracking processes, particularly in vapour-phase processes operating at high temperatures. An early application was the process of Rittman,¹³ which was operated during World War I, for the production of toluene. This process gave bad yields, was cumbersome to operate and great difficulties were experienced due to coking. It was therefore abandoned when the great demand for toluene ceased with the end of the war. During the inter-war period, with the rapid development of cracking and the growing knowledge of such essential factors as heat transfer rates, a number of high temperature vapour-phase processes operating at temperatures around 600° C, which overcame all the troubles of the earlier designs, were established. These processes yielded liquid products containing substantial amounts of aromatics of the order of 30-50 per cent and gave a motor spirit fraction of high octane number, due to the aromatic content. On the other hand, they produced a relatively high proportion of permanent gases and because of the high temperatures corrosion was increased and maintenance costs were high.

In general, such processes were applied to a much smaller extent than the high pressure liquid or mixed-phase cracking system working at lower temperatures.

A process which produces pure aromatics and is based on essentially the same reactions of cracking to olefins and diolefins and subsequent condensation to aromatics as take place in vapour phase cracking is gas pyrolysis. This has been applied on an industrial scale to produce motor fuel containing mainly benzene and some toluene from natural or from refinery gases.¹⁴

A new stage in the development of aromatization was reached when cracking processes with the object of producing a maximum amount of gaseous olefins for chemical synthesis were required. For this purpose cracking at high temperatures where a maximum yield of gases can be obtained is most suitable. At the same time the residual liquid product, which cannot be reduced below a certain level, becomes more and more aromatic in nature. Such high temperature pyrolysis were developed in America during the last few years, particularly in order to supply the ever-increasing amounts of ethylene required for chemical synthesis. The primary object of these processes is to supply low molecular weight hydrocarbons, such as ethylene and propylene; the liquid product is therefore of secondary importance. Since it is only partly aromatized the extraction of pure aromatics would require considerable further processing and, in general, is not carried out.

A development of such processes, which in addition to producing olefinic gases makes the recovery of pure aromatics possible, has been initiated by Ch. Weizmann and E. Bergmann,¹⁵ together with a group connected with Manchester Oil Refinery, Ltd., and led by F. Kind and H. E. Charlton with whom the writer had the good fortune to be associated.* This process uses catalysts to complete the conversion of the liquid product into aromatics. It thus produces a material of very high aromatic content which greatly facilitates the recovery of pure compounds from it. In fact this can be done by simple distillation and crystallization processes.

Before describing these special processes, we shall review the chemistry of high temperature aromatization and try to obtain some insight into the sequence of reaction leading to aromatic products under these conditions.

5. CHEMISTRY OF HIGH-TEMPERATURE AROMATIZATION.

The aromatization of hydrocarbons at high temperatures, starting from various charging stocks ranging from gases up to very high boiling petroleum fractions, such as gas oils and fuel oils, was investigated by a number of

^{*} A considerable number of workers participated in the development of this process (" Catarole " process) particularly Drs. H. S. Boyd-Barrett, K. Michaelis, D. Rowley, M. Sulzbacher, and Messrs. W. E. Huggett, P. Moore, S. Whincup, and E. Zimkin.

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authors, particularly by Groll,¹⁶ Wheeler,¹⁷ and Schneider and Frolich.¹⁸ The sequence of reactions leading to aromatics is obviously a complicated one. There is general agreement that at the temperatures where substantial aromatization is observed, *i.e.*, above 650° C, very rapid decomposition into low molecular weight paraffins and olefins takes place from any charging stock. The principal question then is, How are the aromatic compounds built up again from these low molecular weight intermediates ?

Groll assumed that acetylene in an activated state is the essential intermediate. However, there is hardly any experimental support for this view and it must be abandoned in favour of the mechanism first proposed by Wheeler. According to this mechanism diolefins, which in cracking at these temperatures are formed at appreciable rates, combine with olefins to form *cyclo*-olefinic bodies. The simplest case is that of butadiene which, according to this theory, should combine with ethylene as follows



to give *cyclo*hexene. In a similar manner toluene should be obtained from butadiene and propylene or from isoprene and ethylene. Further, the well-known dimerization of butadiene itself to give vinyl*cyclo*hexene, is a typical reaction of this type, viz.



In a further step, the *cyclo*-olefins formed should be dehydrogenated to the corresponding aromatic compounds. This reaction apparently does not take place in the homogeneous gas phase, particularly when catalytic action is rigorously excluded,¹⁹ but is quite rapid at these temperatures, if catalysts are present. Thus the sequence of reactions outlined gives a satisfactory mechanism for the formation of aromatics in high temperature cracking.

The reaction of ethylene and butadiene to give cyclohexene was first shown to occur by Wheeler and Woods.¹⁶ These authors used sealed glass tubes, that is conditions considerably different from those at which aromatization takes place in practice. It can be shown, however, that even at temperatures of 650° C and probably above, cyclohexene is the primary product of the reaction of butadiene and ethylene.²⁰ Experiments were carried out in a flow apparatus at atmospheric pressure and at temperatures from 550° C to 650° C. The contact time was chosen such that the conversion was restricted to 6–7 per cent. The combined products were distilled in a micro-column and the results are reproduced in the distillation diagram given in Fig. 4.

This distillation diagram shows two distinct flats, the first corresponding in all physical and chemical characteristics to *cyclo*hexene (Bromine number,

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 OsO_4 addition compound), the second one to vinylcyclohexene, which is due to the dimerization of butadiene which occurs simultaneously. The rate of these reactions has been measured and the results confirm that it is high enough to account for at least a good proportion of the aromatics formed in cracking, though, as will be seen later, it is not the only way by which these compounds are generated.





Reactions of this type are typical examples of the well-known class of diene reactions introduced into organic chemistry by Diels and Alder.²¹ Until recently it was thought that polar substituents are necessary, at least on the olefinic partner in the reaction, *e.g.*, the reaction of butadiene and maleic anhydride,



but it has been recognized more and more that pure hydrocarbons readily undergo this reaction, though at somewhat higher temperatures. In fact the reaction of ethylene and butadiene may be considered as the simplest reaction of that class.

It is interesting to note that resonance, as shown previously to be so important in determining the stability of aromatics in general, also influences the

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rate of these diene reactions which, according to our scheme, are the essential step in the formation of aromatics. It was shown by Evans and Warhurst,²² that in the transition complex of the reaction of butadiene and ethylene that is, in the molecular configuration at the moment when reaction takes place—the following resonating structures are possible (again we give the electronic structures, one electron pair corresponding to one bond).



The configuration on the left-hand side corresponds to the initial state of butadiene and ethylene and that on the right-hand side to the final configuration of *cyclo*hexene. It is clear that the two structures are interconvertible by a shift of electron pairs only, which was our previous criterion for resonance. In fact, if we restrict ourselves only to the electron pairs which change their position in the course of the reaction, our picture reduces to



which is a system very similar to that of the two Kekulé structures of benzene discussed initially. In the present case, which corresponds to a reacting configuration, and not to a stable molecule, the effect of the resonance energy is to reduce the activation energy necessary for reaction. According to Evans' and Warhurst calculations, this is lowered from about 40 k.cal/mole to 20-25 k.cal/mole.

Thus we see that considerations very similar to those which explain the exceptional stability of aromatic compounds also explain the facility with which the essential reaction steps leading to their formation are brought about.

If we try to extend the "diene" reaction scheme to the building up of polycyclic aromatic compounds, as it takes place in cracking systems, we meet with difficulties. Thus if one pictures the formation of naphthalene from butadiene and benzene as follows



to give the unknown 1:2:9:10-tetrahydro-naphthalene as intermediate, one finds that such a reaction is energetically impossible. The reason is

the loss of resonance energy caused by the disappearance of the benzene ring system and, on the other hand, a very small corresponding gain due to a much smaller amount of resonance in the products. However, if the condensation of butadiene and benzene takes place with simultaneous dehydrogenation or isomerization to an aromatic structure the reaction becomes possible, viz.



Such a reaction is quite feasible, since the resonance energy lost through disappearance of the benzene structure is regained in tetralin or in naphthalene, both of which are resonating structures.

It is quite possible that this is the correct mechanism for the formation of higher condensed aromatic products, but the evidence we have at present is not yet conclusive.

A similar scheme could be based on the reaction of *cyclo*hexene and butadiene, giving octahydro-naphthalene, viz.



which energetically is quite feasible. However, this scheme would require a high concentration of the intermediate *cyclo*hexene. In fact the *cyclo*hexene concentration in the course of the cracking is quite low and it is therefore unlikely that this reaction plays a considerable part in the building up of higher aromatics.

That the "diene" reaction scheme operates under actual cracking conditions can be seen from the following diagrams (Figs. 5 and 5a), which show the formation of three typical low molecular weight cracking products as a function of the contact time, viz., methane, ethylene, and butadiene. In these experiments a naphthenic naphtha was used as charging stock which was passed at varying contact times through a reactor kept at a temperature of 680° C.

It is seen that in the course of the reaction the amount of methane increases continuously, ethylene is formed rapidly at first but soon its formation comes to a standstill, suggesting a stationary state where as much is formed as disappears due to subsequent reactions. Finally, we note the remarkable behaviour of butadiene which reaches a pronounced maximum in the early stages of the reaction and later on disappears again, thus showing the typical behaviour of an intermediate product.



FIG. 5.

YIELDS OF METHANE AND ETHYLENE AS FUNCTION OF CONTACT TIME.



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The diene reaction scheme, however, is not the only one by which aromatics are formed in high temperature pyrolysis. Apart from other types of condensation reactions, straight dehydrogenation of naphthenes to the corresponding aromatics is of great importance, particularly if catalysts are present. This can be shown by cracking experiments with cycloparaffins, such as cyclohexane and methylcyclohexane, which give relatively high yields of aromatic products. It is further supported by experiments with distillates of identical boiling range but of widely varying chemical composition. Such experiments were carried out with a number of naphthas boiling between 100-200° C and of a composition given in Table XIV.

TABLE	XIV.

Yield of Liquid Products on Cracking Various Charges Boiling Between 100° and 200° C.

		Yield per				
Charge.	Para- ffins.	Ole- fines.	Naph- thenes.	Aroma- tics.	Density.	cent of charge.
Hydrogenated Fischer-Tronsch	93.5	6-2	_		0.719	16
Mixed-base naphtha	47.3	0.5	37.2	14.4	0.771	36
Cracked naphtha .	29.5	41.4	23.6	5.2	0.772	37
naphtha	13.5	0.6	83.8	2.2	0.801	45
$SO_2 \text{ extract}$	11-1	0.8	18.4	70-0	0.819	65
ization oil	. 16	30.9	8.7	44.9	0.820	70

The runs were carried out under such conditions that the liquid products were aromatized to more than 90 per cent. The liquid yield, therefore, is a good measure of the amount of aromatics formed. It is seen from the results of Table XIV that the lowest yield of aromatics is obtained from a charge of straight-chain paraffins such as represented by hydrogenated Fischer-Tropsch product. The yield of aromatics increases with increasing naphthene and naturally with increasing aromatic content. Since the densities of naphthenes and particularly of aromatics are considerably higher than those of paraffins, there should be a relation between yield of aromatics and density. As seen from Fig. 6 this relation is roughly linear.

We can conclude from the results discussed that there are two main reactions by which aromatic compounds are formed in cracking, one by the "diene" reaction scheme, the other by dehydrogenation of naphthenes. In both reaction sequences dehydrogenation reactions take place which should be speeded up considerably by catalysts. Use is made of this factor in the process of aromatization mentioned previously, which shall now be described in more detail.

6. CATALYTIC AROMATIZATION.

(a) General.

The cracking process leading to olefinic gases and at the same time to a practically fully aromatized product, as developed by Weizmann ¹⁵ and

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in Manchester, is carried out in tubes packed with metallic dehydrogenation catalysts. The effect of the catalyst is to reduce the temperature at which full aromatization of the liquid products can be obtained by some $70-80^{\circ}$ C from 750° C to about $650-680^{\circ}$ C. This fact is of importance since in this temperature range even this comparatively moderate reduction in temperature greatly reduces the difficulties due to formation of coke. In addition to the catalytic action, the increase in heat transfer rates due to the packing of the tubes is a further essential factor in reducing excessive temperatures and thus formation of coke.



RELATION BETWEEN DENSITY OF CHARGE AND LIQUID YIELD.

The process is carried out at low pressure and at space velocities of about 0.3-0.4 vol/vol/hr.

An important factor determining plant design is the thermo-chemistry of the process which in the first stages is highly endothermic and in later stages is thermo-neutral, or even slightly exothermic. This is in agreement with the reaction scheme proposed, according to which in the very first stages cracking and dehydrogenation reactions of high endothermicity occur, such as—

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 $\begin{array}{rrrr} \mathrm{C_7H_{14}} & \longrightarrow & \mathrm{C_7H_8} & + & \mathrm{4H_2} & - & \mathrm{49 \ k.cal.} \\ \mathrm{Me}\text{-}\mathit{cyclohexane.} & & \mathrm{Toluene.} \end{array}$

 $C_7H_{16} \longrightarrow C_3H_6 + C_4H_{10} - 30$ k.cal. Heptane. Propylene. Butane. and in later stages condensations such as that of ethylene and butadiene, which are exothermic (40 k.cal/mole) combined with dehydrogenation of the intermediate olefines to aromatics, which are endothermic. As a result the reaction in its later stages is more or less thermo-neutral.

This scheme of consecutive reactions strongly suggests as plant arrangement, the combination of cracking tubes, and a relatively large soaking chamber. The former allow for the large heat input in the first stages of the reaction, the latter for the time factor at a stage where the reaction has become largely thermo-neutral.

The cracking is carried out in cycles of "on stream" periods of some 50-60 hr, after which time regeneration of the catalyst and burning off of coke deposits becomes necessary, which is done in the conventional manner by air diluted with inert gas or steam. After a regeneration period of 10 hr, the plant is put "on stream" again. By combining several cracking furnaces, the process can easily be made continuous, by having one or more furnaces "on stream" while another one is on regeneration.

(b) Charging Stocks and Products.

As has been shown, the chemistry of high temperature cracking to a large part is based on a radical breakdown of the charge and a subsequent resynthesis; one is, therefore, not restricted, as in the case of the hydroforming process, to very specialized charging stocks. Moreover, it is not necessary to concentrate in them a number of critical components, which in the course of the reaction can be transformed into specific aromatic compounds. One obtains always the full range of aromatic products, though the various components may be present in varying proportions. Generally, any charging stock boiling up to 300-350° C can be used and one is only limited by carbonization troubles, which increase with increasing boiling range of the feed. This flexibility in the choice of raw materials also confers to the process a considerable flexibility in the products. It has been already shown that the ratio of liquid to gaseous products, i.e., of olefins to aromatics, depends to a considerable degree on the chemical composition of the charge, and one is thus in a position by proper selection of the charge to vary widely the proportion of gaseous to liquid products. A further variation can be obtained by a change in the boiling range of the charge. In general, the yield of aromatics (liquids) increases with increasing boiling range of the charge. In addition, the distribution of liquid products is shifted toward the higher boiling ones, and it is thus possible by selecting higher boiling charging stocks to produce more of the heavier aromatics.

An analysis of the products from two typical charges is given in Table XV, the one from a napthenic naphtha, the other from a paraffinic kerosine. It is seen that the total yield of aromatics is roughly identical in each case. This is due to the compensation of two effects, the naphthenic nature of the naphtha should tend to increase the yield of aromatics but this is compensated by the higher boiling range of the kerosine which also increases the vield.

On the other hand the distribution of the aromatics is different in the case of the kerosine from that of the naphtha. There is less benzene and toluene in the kerosine product but considerably more alkylbenzenes. If gas oil were used instead of kerosine, a further decrease in the lower boiling products and an increase in such fractions as naphthalene and alkylnaphthalenes would be found.

Boiling range. (Engler) 5- per cent.	-95	Naphtha naphthenic, 110–190° C.	Kerosine paraffinic, 165–268° C.
		• Per cent by we	ight on charge.
Gases.			
Hydrogen		0.5	0.5
Methane		18.3	13.7
Ethylene		7.4	11.6
Ethane		6.5	7.4
Propylene		9-0	10.9
Propane		1.9	1.4
Butylene		4.8	3.9
Butane	• •	1.3	0.5
Total gases .		50	50
Liquids.			
Below benzene		1.1	1 0
Benzene fraction		11.0	7.5
Toluene fraction		11.0	7.5
Xylene fraction		6.0	5.8
Alkylbenzene fraction .		2.6	9.4
Naphthalene fraction .		3.5	3.7
Alkylnaphthalene fraction		4-0	3.8
Anthracene fraction		2.7	$2 \cdot 3$
Chrysene fraction		2.4	1.6
Pitch		6-0	7.5
Total liquids .		50	50

TABLE XV.

Products from High Temperature Cracking.

The discussion of the products will be limited to the liquid part, since in this survey we are concerned with aromatics only. The importance of the gaseous products need hardly be emphasized; from an economic point of view they are, at least at present, even more valuable than the aromatics.

It should be mentioned that it is by no means the first time that polycyclic aromatics such as naphthalene or anthracene have been isolated from cracking products, but we have carried out a fairly full analysis of all products formed, probably fuller than hitherto, and though by no means all, a great many of the components have been identified.

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Boiling below benzene is a small head fraction containing mainly cyclopentadiene, isoprene, cyclopentenes, and pentenes. The benzene fraction itself is usually obtained with a purity of from 92 to 95 per cent, the rest being paraffins and olefines of the benzene boiling range, which can be eliminated, if necessary, by azeotropic distillation. The toluene fraction is still purer than the benzene fraction, generally containing from 95 to 98 per cent of toluene. The xylene fraction is remarkable through its relatively high styrene content of up to 20 per cent. There is also some ethyl benzene present. The styrene can be concentrated by distillation into a narrow cut containing roughly 50 per cent styrene and 50 per cent orthoxylene, which boil only two degrees apart. If further separation is desired, solvent extraction and azeotropic distillation processes must be used. The composition of this fraction is roughly as follows :---

					Per cent by vol.
Ion-aromatic.				 	8
1- and p-Xylene					46
-Xylene .					16
thylbenzene					10
tvrene .					20

TABLE XVI. Composition of Xylene Fraction.

The next fraction boiling between 150° and 200° C contains a variety of alkylbenzenes with a high proportion (up to 50 per cent) of unsaturated aromatics, such as alkenyl benzenes, of which β -methyl styrene is present in large quantities, and indene. By polymerization with acidic catalysts good resins of the indene type can be obtained from this cut.

The fraction boiling between 200° and $230^{\circ}C$ contains mainly naphthalene, which crystallizes and is obtained in good purity by efficient filtration. Apart from naphthalene, tetralene is present giving support to the views expressed previously regarding the mechanism of building up polynuclear aromatics.

The next cut boiling between 230° and 300° C contains a variety of *alkyl* naphthalenes. Those identified are indicated on Table XVII relating to

TABLE XVII.

Polycyclic Aromatics Isolated.

(Above naphthalene-boiling points at atmospheric pressure.)



a-Mono-methyl-naphthalene, b.pt. 244° C.



2-6-Dimethyl-naphthalene, b.pt. 260° C.



Di-phenyl, b.pt. 255° C.

Tri-methyl-naphthalenes 1 : 2 : 5, 1 : 2 : 6, b.pt. 280-290° C.

CH,

 β -Mono-methyl-naphthalene, b.pt. 239° C.

Further identified 1:6-, 1:2-, 1:7di-methyl-naphthalene, b.pt. 260-267° C.



Acenaphthene, b.pt. 278° C.



Fluorene, b.pt. 295° C.

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TABLE XVII (continued).

Anthracene, b.pt. 355° C.

Alkyl anthracenes, 1-methyl, 2-methyl, 2-7 dimethyl, b.pt. 350-365° C.



Chrysene, b.pt. 430-440° C.



Phenanthrene, b.pt. 340° C.

Alkyl phenanthrenes, b.pt. 350-365° C.



Pyrene, b.pt. 380-390° C.



1:2-Benzanthracene.





3:4-Benzpyrene.

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1:2-Benzfluorene.

1:2:7:8-Dibenzchrysene, m.pt. 288° C.



2:3-Benzfluorene.

polynuclear aromatics found in the products. The products indicated are present roughly in the following proportions :---

						Per cent by vol.
Monomethyl naphthalenes Dimethyl naphthalenes . Trimethyl naphthalenes .	:	:	:		•	41 30 18
Acenaphthene	• :	:	:	:		4 4 4

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By further fractionation the cut can be split up into a mono-, di-, and trimethyl naphthalene fraction and 2:6-dimethyl-naphthalene, diphenyl, acenaphthene, and fluorene can all be obtained by crystallization from suitably cut fractions.

The next cut boiling between 300° and 380° C at atmospheric pressure contains a fair proportion of crystallizable bodies, in the first place anthracene and phenanthrene. These are obtained together with some of the monomethyl compounds which, if desired, can be eliminated by further fractionation. Anthracene can easily be obtained pure from these mixtures, in fact the purification is very much easier than in the case of coal-tar anthracene, since the impurity most difficult to separate from the latter, carbazol, is absent. It is more difficult to purify the phenanthrene, and it is impossible by simple crystallization to free it from the last traces of anthracene.

An approximate composition of the crystalline compounds recoverable from this cut is as follows :---

									Per cent by weight of fraction.
Anthracene .									6
Phenanthrene									18
Me-phenanthrenes									8
Me-anthracenes	•	•	-			•	•	•	0.8

The next cut boiling above 380° C at atmospheric pressure contains, as major constituents, chrysene and pyrene, both of which crystallize, the former spontaneously, the latter after refractionation. The crude chrysene is accompanied by a number of impurities which were identified as fluoranthene, 1:2- and 2:3-benzfluorene. Finally, from the very highest boiling portions 3:4-benzpyrene and 1:2:7:8-dibenzchrysene * were isolated.

The residue after removal of the chrysene cut is a hard pitch, which is suitable material to produce electrode coke, since it contains a very small amount of inorganic impurities.

In the present review we hope to have shown that, in the last ten or twenty years, the petroleum industry has made great advances towards producing aromatic hydrocarbons from its own raw materials. It cannot be long until it will be able to supply almost any aromatic hydrocarbon to the chemical industry. In the past, this was necessary only under the abnormal conditions of war-time, when critical shortages such as that of toluene had to be overcome. However, the ever-increasing demand of the organic synthetic industry, stimulated particularly through the production of plastics, may well lead to a shortage of critical aromatics, such as benzene and naphthalene. It seems impossible to increase the supplies of these materials from the traditional source, coal-tar, since the amount of coal carbonized is largely limited by the amount of coke required for

* This compound has not previously been described in the literature. See forthcoming publication by E. Bergmann. metallurgical purposes. The alternative supplies of aromatics from petroleum sources may, therefore, be of great importance in the future.

Petrocarbon, Ltd., Manchester 17.

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DISCUSSION.

THE CHAIRMAN (Dr A. E. Dunstan): Before throwing this important and valuable paper open to discussion, I should like to direct attention to Table XVII, in which are given the multi-nuclear rings isolated from cracked products. I think that is remarkably interesting. Although some of the bodies have been described in the past, this occasion is the first on which I have seen put forward such a series of these multi-nuclear hydrocarbons.

One might supplement Dr Steiner's story by a little chemical history. I can remember talking some years ago with Mr Anfilogoff, who at that time was manager of the refinery of London and Thames Haven Oil Wharves Ltd. He told me that he also had come across the existence of aromatic hydrocarbons in similar crudes, as the result of a very curious mishap. He was going to estimate the amount of unsaturateds in a given gasoline by means of sulphuric acid. Fortunately, or unfortunately, the laboratory boy had mixed up the acids on his bench, and had produced a nitrating mixture. On shaking up the gasoline with that particular acid, Mr Anfilogoff at once noticed the smell of nitro-benzene. That was about 1909 or 1910.

In my own laboratories we did experimental work some years ago, devoted to the production of aromatic hydrocarbons; the earliest that I

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personally can remember occurred about twenty-five years ago, in connexion with the cracking of methane. At that particular time we were associated with the late Professor Wheeler, of Sheffield, who had done for us much work on the pyrolysis of hydrocarbons. Based on his work, we started some rather larger-scale operations in Iran and conducted pyrolysis experiments on Iranian natural gas, containing approximately 85 per cent of methane. Rather surprisingly to us at that particular time, we produced what was in effect a coal-tar. As has been pointed out by Dr Steiner, from a natural gas of that sort can be produced much the same materials as are obtained in the distillation of coal. We were rather impressed by the occurrence of styrene; in the xylene fraction of that particular cracked oil there was styrene in considerable quantity.

I do not know whether Dr Steiner will bear me out when I recall the first views on this matter that were put forward by Professor Wheeler, and possibly by Professor Bone before him—I note the use of the old familiar term "chemical bricks"—that the first phenomenon in the pyrolysis of these lower gaseous hydrocarbons is the formation of radicals; I know that Professor Wheeler thought the CH radical was the most important.

Reference has been made by Dr Steiner to, the early experiments, during the 1914–18 war, by Rittmann, who was producing at that time in the United States a toluol distillate. In Great Britain, too, at Thames Haven, there was a process called the Hall process, in which kerosine or light gas oil was passed through 1-inch tubes at a very high temperature, roughly 750–800° C, and the "toluol distillate," so-called, contained 14 to 15 per cent of actual toluene. That is ancient history.

I think the point we have to bear in mind in reading this paper is that out of petroleum can come every sort of organic chemical we require.

MR H. C. RAMPTON: I would have liked information, not only on the composition of your liquid products in terms of aromatic content, but also concerning the make of individual aromatics, for I notice that in most cases you have certain proportions of aromatics in your liquid products. What proportions of those compounds existed in the charge in the first place? Are you not, in fact, concentrating aromatics to some extent, in addition to the cyclization?

Finally, I would like to know how the actual determination of the amount of styrene was carried out?

DR STEINER: Some of the aromatics found in the cracked products are no doubt present in some of the charges which have been mentioned, for instance in Table XIV. But, to give an example, the naphthenic-base naphtha does not contain more than 2 per cent of aromatic compounds; and yet we get similar fractions as by cracking a charge containing a much greater percentage of aromatic compounds. So that whilst some of the aromatics found in the products may be present already in the charge, I do not think that that alters the picture very much. Most of the aromatics are built up in the way I have indicated from diolefins and olefins after severe cracking or by direct dehydrogenation of naphthenes.

There is a difficulty with regard to the determination of the amount of styrene. If this is done by bromine number, any other olefin present will

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be brominated at the same time, but one can polymerize the styrene and one can isolate also the di-bromo-styrene which crystallizes. Moreover, by combining determinations of bromine numbers and of refractive indices, one can obtain a good indication of the amount of pure styrene present, since the refractive index of styrene is higher than that of any other unsaturated compound which is likely to be present.

THE CHAIRMAN: Can you tell us what is the chance of the *meta* isomers being preponderatingly present in, for example, a cracked spirit? I have found in my experience that there is much more of the *meta*-xylene than the *ortho*- or *para*-, and I think that is so in natural crudes.

It is curious how the *meta*- and *para*- preponderate in the natural crudes. It is probably a time reaction, considering the very great age of the crudes.

DR STEINER: Perhaps I may take up a point you made before on the occurrence of free radical reactions in cracking generally. I purposely did not speak of the reactions occurring in the cracking part of the aromatization itself; I was concerned mainly with the condensations subsequent to the first cracking. I think there is little doubt that cracking is initiated by free radicals which set up reaction chains. But it is interesting to note the distinction between the cracking reactions proper which are free radical reactions and the condensations leading to aromatic compounds which in my opinion are not radical reactions. As can be seen from the results reproduced in Fig. 4, these are well-defined primary products. For instance, in the case of ethylene and butadiene, this is *cyclo*hexene. It is most likely that these reactions are simple associations of diolefins and of olefins, which occur without the intermediate formation of free radicels.

MR E. THORNTON: I was impressed, in the course of a lecture given by Major Cadman at Landarcy, in which reference was made to an American paper on carbon black formation, by the evidence that the carbon black formed in the cracking chamber within the flame does seem to have, not CH radicals, but C radicals. Is there good reason to overlook that possibility in this kind of reaction ?

DR STEINER: So far as I know, there is very little evidence of C radicals being present under cracking conditions in the gas phase. In carbon deposits it has usually been found, by one physical method or another, that one gets a graphite lattice; but that does not mean that the material is graphite. There may be minute and very disordered crystals, but some type of graphite arrangement is usually present.

THE CHAIRMAN : Is it likely that carbon black is probably mainly hydrocarbon with a small hydrogen content.

DR STEINER: I suppose that in carbon black there is some hydrogen present, and probably it may be pictured as condensed aromatic rings which at the boundaries are saturated with hydrogen. If one has a sort of graphite lattice of, say, twelve or twenty rings, then at the boundary there may be hydrogen still present.

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THE CHAIRMAN : I quite agree.

MR. A. J. GOODFELLOW: I would like to ask whether indene has been isolated from these products.

DR STEINER: There is a large amount of indene present in the alkylbenzene fraction.

On the motion of the Chairman, the hearty thanks of the meeting were accorded Dr Steiner for his most illuminating and authoritative paper.

HYDROCARBON SYNTHESIS IN THE PRESENCE OF COBALT CATALYSTS AT MEDIUM PRES-SURES.

By C. C. HALL and S. L. SMITH.

SYNOPSIS.

At the time when the work described in this paper was carried out, the only reliable information concerning the effect of a moderate increase in pressure in the Fischer-Tropsch synthesis was contained in two papers by F. Fischer and H. Pichler of the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim, Ruhr. These workers used a cobalt catalyst of inferior performance at atmospheric pressure to that used by the present authors. Apart, therefore, from the general desirability of obtaining first-hand knowledge of the characteristics of the synthesis at pressures of the order of 10 atm, it was of particular interest to study the performance of the active cobalt-thoria-magnesia catalysts under these conditions. The present paper contains an account of the more important laboratory-scale experiments carried out on these lines at the Fuel Research Station during the war years.

INTRODUCTION.

ALTHOUGH the patent literature prior to 1939 contained many claims concerned with the beneficial effect of a moderate increase in working pressure on the synthesis of hydrocarbons from carbon monoxide and hydrogen, the first authoritative account of the "medium-pressure synthesis" was published by Fischer and Pichler in that year.¹ These workers studied the effect of pressures in the range 1.5 to 50 atm (gauge) on the synthesis, using the type of catalyst (Co : ThO₂ : kieselguhr = 100 : 18 : 100) which they had found most active for the atmospheric-pressure process. They found that in the range 5 to 15 atm the extent of conversion of the carbon monoxide to useful products, the life of the catalyst and the proportion of solid wax in the reaction products all reached a maximum. By increasing the pressure from atmospheric to 5 or 15 atm, the initial yield of products per normal m³ of inert-free gas passed was increased from 120 g to about 150 g, the useful life of the catalyst from about 4 weeks to over 26 weeks, and the proportion of wax from 10 to circa 40 per cent. The optimum temperature range was similar to that used in the atmosphericpressure process, viz., 175 to 200° C and the optimum gas rate (measured at N.T.P.) was also the same, *i.e.*, 1 l/g Co/hr.

Later in the same year (1939) Fischer and Pichler published a further paper ² showing that, by using a low gas rate and two stages of synthesis, yields as high as 89 per cent of the theoretical could be obtained in the medium-pressure process and F. Martin ³ gave a general account of the industrial development of hydrocarbon synthesis from which it was evident that pressures of about 10 atm were in use in full-scale plants.

The object of the experiments summarized in the present paper was to determine the performance under medium-pressure conditions of cobaltthoria-magnesia-kieselguhr catalysts. The activity and life of this type of catalyst at atmospheric pressure has been found ⁴ to be appreciably better than that of the catalyst used in Fischer and Pichler's experiments.

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APPARATUS AND PROCEDURE.

The reaction vessel used was similar in design and dimensions to that employed for experiments at atmospheric pressure ⁴ and consisted of a vertical steel tube 140 cm long and 17 mm internal diameter embedded centrally in an aluminium jacket 6 cm in diameter surrounded by an electric furnace. The temperature at points in the centre of the catalyst bed could be measured by means of a thermocouple in a sheath 5 mm external diameter which passed down from the top of the reaction tube. Gas entered the reaction vessel through a side arm welded to the reaction tube at an angle of about 30° to the vertical. This side arm also served for the



FIG. 1.

FLOW SCHEME FOR MEDIUM-PRESSURE SYNTHESIS.

introduction of the catalyst which rested on a perforated platform situated 26 cm from the lower end of the aluminium jacket. The normal charge of catalyst granules (size 7/14 B.S.S.) was 100 ml and it formed a column 60 cm high. The temperature in the aluminium jacket could be measured by means of a thermocouple in a steel sheath embedded in the wall of the jacket.

The general arrangement of apparatus is shown diagrammatically in Fig. 1. Synthesis gas purified from H_2S and partly purified from organic sulphur compounds is passed through purifiers (A) and (B), which reduce organic sulphur to below $0.2 \text{ g}/100 \text{ m}^3$, is measured in the gas meter (M_1) and compressed by the compressor (C) into the storage vessel (S). The

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THE PRESENCE OF COBALT CATALYSTS AT MEDIUM PRESSURES. 441

gas at the desired pressure, controlled by the "Endurance" regulator (R) then passes via the flow meter (F) to the reaction vessel (D). The needle valve (N) functions as the orifice of the flow meter, and (V_2) is a by-pass valve. (T_1) and (T_2) are thermocouples in the position already described. The oil, wax, and the bulk of the water formed in the reaction collect in the receiver (P₁) which is heated by an electric furnace to 100 to 110° C. A very small amount of water and liquid hydrocarbons collect in the unheated receiver (P₂). The pressure of the exit gases is reduced to atmospheric via the valve (V₃) and after the removal of traces of water in the calcium chloride tube (E) the low-boiling hydrocarbons are removed from the gas in the glass receiver (F) which is cooled to -80° C in crushed solid CO₂. The volume of residual gas is recorded by the meter (M₂). For operation at atmospheric pressure the compressor and storage vessel part of the system is by-passed by means of the valve (V₁).



TEMPERATURE DISTRIBUTIONS IN REACTION VESSEL DURING SYNTHESIS AT 150 P.S.I. GAUGE PRESSURE.

For operation at 10 atm pressure, the storage vessel is charged with gas at 20 atm, the pressure allowed to fall to 12 atm and the vessel then recharged. By starting and stopping a 24-hour or longer test period at the same storage vessel pressure, making due allowance for changes in room temperature, the volume of gas recorded by the meter (M_1) can be taken as the volume of gas passed through the reaction vessel. The variation in the pressure in the reaction vessel as measured by the gauge (G_2) was less than ± 5 p.s.i. (at 150 p.s.i. mean pressure) with variation from 180 to 300 p.s.i. pressure in the storage vessel. During periods when the flow-meter was out of action, it was found that the rate of gas flow into the reaction vessel could be adequately controlled by governing the rate of fall in pressure in the storage vessel as indicated by the calibrated gauge (C_1) .

The weight of liquid and solid hydrocarbons stabilized at room temperature ($ca. 20^{\circ}$ C) obtained during a test period was expressed in g per normal cubic metre of synthesis gas passed.

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The term "gaseous hydrocarbons" used in this paper refers to the

hydrocarbons present in the residual gas leaving the receiver cooled to -80° C; they contained between 60 and 70 per cent of methane.

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Temperature distributions along the central axis of the catalyst bed and in the aluminium jacket during synthesis with an active catalyst are shown in Fig. 2. It will be noted that the temperature recorded by the internal thermocouple was some 2° C higher at the top of the catalyst bed than that existing in the aluminium jacket. The maximum temperature variation throughout the length of the catalyst bed was $\pm 1.5^{\circ}$ C.

ACCOUNT OF THE EXPERIMENTS AND DISCUSSION OF RESULTS.

The work of Fischer and Pichler indicated that the optimum pressure was about 10 atm and all the experiments described in this paper were carried



VARIATION IN YIELD OF PRODUCTS AND REACTION TEMPERATURE WITH TIME. EXPERIMENT 8/3.

out at this pressure. Except where indicated to the contrary, the catalyst used had the composition: cobalt:thoria:magnesia:kieselguhr = 100:6:3:200 and was prepared and reduced by the methods previously described.⁴

Before commencing synthesis under pressure, the activity of the catalyst was tested by a short period of synthesis at normal pressure. The temperature was then reduced to 150° C, the pressure increased to 150 p.s.i. and the temperature raised to 170 to 175° C with a gas rate of 1 l/g Co/hr. (measured at N.T.P.).

The normal synthesis gas used had the average composition : $CO_2: 2.5$ per cent, CO: 31.5 per cent, $H_2: 62.0$ per cent, $N_2: 4.0$ per cent and except

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where otherwise indicated, the yields of product are expressed as g per normal m^3 of gas of this composition.

In preliminary experiments at 150 p.s.i. pressure, although a gas contraction of 80 per cent could be obtained at 180° C, the yield of oil during the first two days was appreciably lower than that obtained at atmospheric pressure and the product was completely fluid at room temperature. After five or six days, however, the yield had built up to a figure of 135 to 140 g/normal m³ and the total product (excluding hydrocarbons below C_5) was a snow-white solid at room temperature. It was found that normal yields are only obtained when the catalyst is saturated with wax and that the preliminary waxing-up process can be carried out more expeditiously and with less risk of causing premature deterioration of the catalyst by using temperatures in the range 170 to 175° C for the first 2 to 4 days of synthesis under pressure.

Catalyst Life Test.

In order to obtain information on the rate of deterioration of the catalyst and to study the effectiveness of the methods of reactivation which had previously ⁴ been found successful in the normal-pressure synthesis, an experiment (No. 8/3) was carried out over a period of about 6 months. The course of this experiment is shown graphically in Fig. 3, and the more important data are summarized in Table I.

The catalyst was reduced in the normal manner at atmospheric pressure and after a period of 10 days occupied partly in synthesis at atmospheric pressure and partly in building-up wax on the catalyst under pressure, yields of 135 to 140 g liquid and solid hydrocarbons were obtained at 185 to 187° C. The temperature had to be raised fairly rapidly at first to maintain the yield at or above the 130 g/normal m³ level, but it was not necessary to raise the temperature so rapidly in the range 189 to 191° C and after attaining 194° C no further increase was required for a period of 27 days. At this latter temperature an average yield of 130 g/normal m³ was maintained.

When the yield began to fall during the last four days of this period the first hydrogen re-activation treatment (A, Table I) was carried out. This treatment caused some revivification and yields of 125 to 130 g/normal m³ were again obtained at a temperature of 190° to 194° C and maintained for* 24 days. A short treatment (B) using a high velocity of hydrogen was then tried, and again, some revivification was effected, but only for a period of 6 days. The former type of treatment was then repeated, but failed to produce any restoration of activity, and the reaction temperature was then raised to maintain activity until, after 20 days, a temperature of 200° C had been reached, when revivification was again attempted. In the earlier hydrogen treatments a relatively small amount (ca 7 g) of wax and oil was removed and no gaseous hydrocarbons were formed. This appeared to indicate a mere physical "sweeping" action by the hydrogen in contrast to the definite chemical reaction occurring in such treatment during atmospheric-pressure synthesis. To test this view, a treatment (D) with nitrogen was carried out in Period 112 (Table I). A small amount of wax (2.5 g) was removed, but the resulting activity was appreciably lower than before the treatment. An exactly analogous treatment (E) with hydrogen removed a similar amount of wax, but only partly restored the activity to

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TABLE I.

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Main Data for Experiment 8/3.

Catalyst : 100 Co; 6 ThO₂; 3 MgO; 200 kieselguhr, 100 ml = 26.7 g = 6.7 g Co. Synthesis gas rate : 1 litre N.T.P./g Co/hr. Gauge pressure : 150 p.s.i.

Test	Time in days	Average	Average yield of liquid and solid	Per ce conve	ent CO ersion
period Nos.	from start of experiment	temperature, ° C	hydrocarbons g/normal m ³ syn. gas	Total	To liquid and solid hcs.
* 1- 4	0- 5	182	121.5		
9-11	11-13	185	134.5		
$\frac{12-13}{14-15}$	14 - 10 17 18	180	139.3	80.9	11
20 - 26	24 - 31	189	131.8		_
35- 38	41-45	191	$125 \cdot 2$	ā	
41-63	48-74	194	130.0	80.2	68
64	Re-activatio	n treatment A	H_2 , 17 hr, 200°	°C, 150 p.s.i.	14 l./hr.
65-66	76-77	185	90.8		
67-72 79 79	78-84	190	125.5		
79- 87	92-102	195	126.0	79.5	64
88	Re-activatio	on treatment H	B (H., 2 hr, 194°	C, 150 p.s.i.,	560 l/hr.)
89-94	104-110	194	129.0	_	
95	Re-activati	on treatment	C (H ₂ , 8 hr, 210°	C, 150 p.s.i.,	14 l/hr.)
96-99	112-117	194	120.5		_
103 - 106	122 - 126	198	121.5	87.5	62
107-111	127-132	200			
112	Re-activati	on treatment.	$D (N_2, 6 hr, 220^\circ)$	C, 150 p.s.i.,	, 14 l/hr.)
113-115	134-137	203	102.0		7470
110	Re-activati	on treatment	$E(H_2, 6 hr, 220^\circ)$	C, 150 p.s.i.,	, 14 1/nr.)
117-118	139-140 Desetimetion	203	113·1		: 14 U/h=
119	followed by	v H., 2 hr. 40	$(H_2, 19 \text{ nr}, 220)$	560 L/hr	1. 14 1/mr.,
123-129	149-154	203	118.3	78-5	63
130-137	155-163	208	114.5	71.0	59
146 - 148	174-176	213	100.2	87.5	53
149	Re-activatio	n treatment G	(500 ml of 170-	240° fraction	at 150° C)
150-151	177-180	212	60.0	59.5	32
152-153	Re-activation 400° C, 150	h treatment H) p.s.i., 14 l/hr	(H ₂ , 16 hr, 230 .)	°C, followed	by 2 hr at
154	184	213	81.6		- 1
155	Re-activation steam, 3	hr, 350-400° C	$(H_2, 2 hr, 400^{\circ} C)$, and then $H_2, 2$, atm press f hr 400° C, a	followed by the press.
156-158	189-192	213	74.5	_	

* At atmospheric pressure.

that preceding the nitrogen treatment. As it was feared that a trace of oxygen in the nitrogen might have damaged the catalyst, re-reduction at 400° C and atmospheric pressure (Period 119, F) was resorted to. The activity of the catalyst for synthesis at atmospheric pressure was tested following this treatment, but was found to be negligible (gas contraction = 25 per cent at 190° C). The activity for medium-pressure synthesis was apparently restored to the level it might be expected to have reached if the

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treatments (D) and (E) had not been carried out—that is to say, that reduction only succeeded in neutralizing the effect of the nitrogen treatment.

It was then found possible to maintain the yield above 110 g/normal m^3 by increasing the temperature up to 208° C, but further increase up to 213° C caused excessive production of gaseous products and the yield of desired products fell below 100 g/normal m^3 . It seemed clear that 210° C was the upper temperature-limit for economic utilization of the synthesis gas.

At this stage, a solvent treatment (G) removed 36 g of hard wax from the catalyst, but unexpectedly caused a sharp fall in activity (from 100 g to 60 g/normal m³) and no subsequent treatments, *i.e.*, hydrogen under pressure at 230° C or at 400° C (H), at atmospheric pressure at 400° C followed by steam treatment at 350 to 400° C and re-reduction in hydrogen (I) did more than effect a very small re-activation.

Although the solvent treatment (G) undoubtedly ruined the catalyst, the relative ineffectiveness of the earlier re-activation treatments gives little grounds for hope that its life could have been usefully extended beyond 180 days.

DISCUSSION OF RESULTS.

It is of interest to compare the results of this experiment with those obtained by Fischer and Pichler¹ for pressures of the same order. The comparable data are set out in Table II. Fischer and Pichler expressed

	Yield o hydrocar	of liquid an bons g/nor	nd solid rmal m ³ *	Reaction temperature, ° C			
Time	Fischer &	k Pichler	Expt. 8/3	Fischer	Expt. 8/3		
	15 atm	5 atm	10 atm	15 atm	5 atm	10 atm	
After 2 weeks . ., 4 ,, . ., 10 ,, .	150 140 130	150 140 132	150 143 139	183 185 193	178 183 190	186 189 194	

TABLE II.

Comparison Between the Results of Experiment 8/3 and those Published by Fischer and Pichler.¹

* Ideal gas, *i.e.*, CO $33.3\% + H_2 66.6\%$.

their yields in terms of "ideal gas," *i.e.*, 100 per cent $(CO + 2H_2)$ and for purposes of comparison the yields obtained in Experiment 8/3 have been calculated to the same basis. As the German workers carried out no reactivation treatments, the comparison has been restricted to the first 10 weeks of the catalyst life.

The figures show that apart from the rather higher temperatures employed initially in Experiment 8/3, the performance was very similar to that reported by Fischer and Pichler.

The figures for CO conversion were similar in the two cases. Thus during the first 4 weeks of Fischer's experiment at 5 atm gauge pressure, 72 per cent of the CO was converted to liquid and solid hydrocarbons and 14.6 per cent to gaseous hydrocarbons; the corresponding figures for the 16th day of Experiment 8/3 are 71 and 15.5 per cent.

Source of data	Expt. 8/3	Fischer & Pichler		
	10 atm	15 atm	5 atm	
Maximum vield, g/normal m ³ (ideal gas)	150	157	157	
Final	119	105	115	
Average	. 135	126	130	
l'ime, davs	163	182	182	
Final temperature, ° C	. 211	201	194	

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Comparison Between Results of Experiment 8/3 and those Published by Fischer and Pichler.¹

In Table III, some figures for the complete period of the experiments are given for comparison, and it would appear that so far from increasing the useful life of the catalyst the attempts at re-activation carried out in Experiment 8/3 may have reduced it.

Comparable data for medium-pressure and atmospheric-pressure synthesis in the absence of re-activation treatments are given in Table IV. The

Source of data	Expt. 8/3	Hall and Smith ⁴	Fischer and Pichler ¹
Gauge pressure, p.s.i	150	0	0
Maximum yield, g/normal m ³ (ideal gas) Final ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,,	150 138 141	134 122 127	130 98 115
Feriod of time, days Final temperature, ° C Rate of fall in yield, g/normal m ³ /day.	$\begin{array}{r} 60\\ 194\\ 0\cdot 2\end{array}$	$40 \\ 197 \\ 0.3$	34 196 0·95

TABLE IV.

Comparison Between Synthesis at Medium Pressure and at Atmospheric Pressure.

Fuel Research Station data are for a catalyst of composition $\text{Co}: \text{ThO}_2$: MgO: kieselguhr = 100: 6:3:200, Fischer's data are for one of composition $\text{Co}: \text{ThO}_2$: kieselguhr = 100: 18:100.

In our experiments, increase in pressure only increased the average yield by 11 per cent and decreased the rate of deterioration by 33 per cent. Fischer's results, however, show an increase of 30 per cent in yield and an 80 per cent decrease in rate of deterioration. Thus, although the performance at medium pressure of the catalyst used in Experiment 8/3 was equal to that of the catalyst in Fischer's experiments, it does not represent anything like the same degree of improvement over the corresponding performance at atmospheric pressure, as that observed by Fischer. It would seem, therefore, that the rate of deterioration of a catalyst at atmospheric pressure may bear little relation to the rate at increased pressure. This is in keeping with the view that the initial life of the catalyst at atmospheric pressure is mainly dependent on the rate of build-up of wax on the catalyst surface and as the catalyst is saturated with wax in the first few days of

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synthesis at medium pressures, it would not be expected that this rate would appreciably affect the life under pressure.

By frequent re-activation with hydrogen it has been shown ⁴ that an average yield of 129 g/normal m³ (ideal gas) can be maintained for 100 days at atmospheric pressure before re-reduction becomes necessary. Fischer and Pichler's results (which are used as being more reliable than those of Experiment 8/3 after the first 70 days) showed that at 5 atm pressure the same average yield (129 g/normal m³ (ideal gas) could be maintained over 182 days, without any re-activation. It appears, therefore, that working to a fixed average yield of products, the "converter" life of the catalyst may be nearly doubled by operation at 5 to 10 atm, but in view of the failure of re-reduction treatment to restore the activity of the medium-pressure catalyst, the "converter" life is also the "total" life. At atmospheric pressure, on the other hand, a total life of over 400 days with an average yield of 123 g/normal m³ (ideal gas) has been obtained ⁴ through the successful application of re-reduction treatments.

The composition of the combined liquid and solid reaction products at selected stages of the experiment is given in Table VI. In the first place, it will be noted that the general change in the nature of the products caused by increase in pressure from atmospheric to 150 p.s.i. is as reported by Fischer and Pichler, *i.e.*, a substantial increase in the proportion of wax with a diminution in the proportion of light spirit and olefins. For the first 70 days a gradual increase in the proportion of wax and a fall in that of the light fractions took place. This is the opposite of the effect observed by Fischer and Pichler, who found that the proportion of wax decreased from 40 to 32 per cent in the first 10 weeks of synthesis at 15 atm, with an increase in reaction temperature from 185° to 193° C.

The products obtained after the first hydrogen treatment (A) showed a sudden increase in wax content which persisted until after treatment (D) when a much bigger change in the reverse direction, together with a 50 per cent fall in olefin content took place. In view of the fact that the main changes in product composition appear to be associated with various reactivation treatments, it is impossible to draw any conclusions concerning the effect of catalyst age and reaction temperature on composition, except over the first 70 days of the experiment.

The sudden, large changes in product composition observed in this experiment, compared with the comparative uniformity of the products obtained over prolonged periods of synthesis at atmospheric pressure,⁴ indicate that product composition in the medium-pressure synthesis is much more dependent on reaction conditions and on the previous history of the catalyst, than in the atmospheric-pressure process.

Further Attempts at Restoring Catalyst Activity.

In Experiment 10A/4, synthesis at 10 atm pressure was studied for a period of 100 days and fresh attempts made to find means for reactivating the catalyst. The catalyst used had the composition :

100 Co: 6 ThO₂: 3 MgO: 250 kieselguhr

and was prepared by the normal method, but in a batch of 3 kg in a semitechnical-scale plant. The kieselguhr used in this batch had the property of increasing the bulk density of the catalyst. Thus, despite the increased proportion of kieselguhr, 100 ml of the unreduced catalyst granules contained 9.4 g cobalt, compared with 6.7 g for the catalyst used in Experiment 8/3.

TABLE V.

Main Data for Experiment 10A/4.

Catalyst : 100 Co ; 6 ThO₂ ; 3 MgO ; 250 kieselguhr, 100 ml = 41.8 g = 9.35 g Co. Gauge pressure : 150 p.s.i.

Test period Nos.	Time in days from start of experiment	Average reaction temp, ° C	Average gas rate l/g Co/hr	Gas contraction, %	Average yield of liquid and solid hydrocarbons, g/normal m ³ syn. gas.
2-4	3_ 0	183	1.0	80	136
5- 8	10-16	185	1.0	-80	140
9-11	17-22	185	1.0	75	- 125
12-18	23-33	188	1.0	78	130
19-20	34-37	191	1.0	79	134
21 - 22	38-40	192	1.4	65	106
23 - 29	41 - 53	192.5	1.0	80	133
30-31	54-58	193	0.5	84	140
32 - 35	57 - 65	194.5	1.0	68	115
36-37	66-69	195	0.5	83	137
38-39	70-74	195	0.1	57	91
40	Reactivation	treatment J	(H ₂ , 8 hr, 205°	C, 450 p.s.i.,	14 l/hr.)
41 - 42	76-78	195	1.0	63	106
43	Reactivation	treatment K	(H ₂ , 16 hr, 20	5° C, atm pres	s, 14 l/hr.)
44-46	81-85	195	1.0	57	81 *
47	Reactivation	treatment L	(H ₂ , 16 hr, 20	5° C, atm pres	s, 14 l/hr.)
48	52	,, M	(H ₂ , 16 hr, 20	5° C, 0.1 atm a	abs 14 l/hr.)
49	89-90	197	1.0	60	71 *
50	- Reactivation	treatment N	(H., 16 hr, 20)	7° C, atm press	s, 14 l/hr.)
51	22	., 0	(500 ml, 150-2	200° C fraction	, 150° C)
52-53	94-97	201	1.0	64	76 *
and the second se					

* These low yields are possibly due to insufficient time having elapsed for the catalyst to become saturated with wax. The gas contraction, in these cases, is the more reliable guide to catalyst activity. 四.四

The more important data for this experiment are recorded in Table V. In the first place, it will be noted that the performance of the catalyst during the first 50 days was very similar to that obtained in Experiment 8/3(Table I), despite the fact that the gas throughput in the present case was 40 per cent higher. As the yield of hydrocarbons per m³ of synthesis gas was the same in both cases it follows that the space-time output of products was also 40 per cent higher in this experiment.

The distribution of carbon in the products, as a percentage of the carbon introduced as carbon monoxide, is given below for Test Period 13.

					Per cent
As unreacted CO					14.8
As gaseous hydroca	rbons				13.0
As liquid and solid	hydrocar	bons		÷ .	70.8
$As CO_2$.					nil
Unaccounted for			÷ .		1.4
					100.0

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In Test Periods 30 and 31, 36 and 37, the gas rate was reduced to onehalf normal and in confirmation of earlier observations (discussed later) the activity of the catalyst fell sharply in each case, when the full gas rate was restored. Thus, after the second gas-rate reduction, the yield obtained was only 70 per cent of that obtained at the same temperature and period in the catalyst's life, in Experiment 8/3.

Advantage was taken of this prematurely-aged state of the catalyst to make a further study of reactivation treatments. The first treatment (J)consisted in passing hydrogen at 205° C at a pressure 20 to 25 atm above the synthesis pressure. This treatment brought about a slight improvement in activity (yield increased from 91 to 106 g/normal m³) but only caused the removal of 2 g of hydrocarbon material, *i.e.*, much less than for a similar treatment ("C", Table I) carried out at the working pressure. A similar treatment (K) carried out at atmospheric pressure removed over 20 g of wax as solid, liquid, and gaseous hydrocarbons, but left the activity of the catalyst unchanged or slightly reduced. A hydrogen treatment at 0.1 atm pressure (M) carried out immediately after an atmospheric-pressuretreatment (L) only removed an additional 1 g of hydrocarbon material and the combined treatments caused no improvement in activity. Extraction of the catalyst with solvent (Treatment O) immediately following an atmospheric-pressure hydrogen treatment (N) showed that some 5 g of wax was left unattacked by the hydrogen. Here again, however, the combined treatment failed to cause any restoration of catalyst activity. The distribution of the products of hydrogen treatment at atmospheric pressure, after medium-pressure synthesis, between solid, liquid, and gaseous hydrocarbons was very similar to that obtained in the hydrogen treatment of catalysts in atmospheric-pressure synthesis.

The effectiveness of hydrogen reactivation treatment in atmosphericpressure synthesis is greatest in the early days of the catalyst's life and becomes progressively less effective as the catalyst ages and the reaction temperature rises. So far, no reactivation had been attempted until after 74 days of synthesis at medium pressure, and it was therefore of interest to determine the effectiveness of hydrogen treatment after a much shorter period.

In Experiment 10A/11, a catalyst similar to that employed in Experiment 8/3 was used for synthesis at 10 atm pressure and at a temperature not exceeding 185° C. After 23 days, hydrogen was passed for 8 hours at 195° C and 10 atm pressure, and after a further period of 12-days synthesis a similar treatment was carried out at atmospheric pressure. The effect of these treatments on the activity of the catalyst, measured in terms of the yield of liquid and solid hydrocarbons is shown graphically in Fig. 4. The first treatment definitely effected a restoration of activity, although much less complete than is obtained under comparable circumstances in the atmospheric-pressure synthesis.⁴

During this treatment $5\frac{1}{2}$ g of wax, oil, and gaseous hydrocarbons were produced. In the second treatment carried out at atmospheric pressure, 33 g of hydrocarbons were collected, but the effect on the catalyst activity was apparently to reduce it to the level it might be expected to have reached if the first treatment had been omitted.

The conclusion to be drawn from all the experiments described is, there-

fore, that for a hydrogen treatment to effect any improvement in catalyst activity it must be carried out at or above the working pressure, but the improvement so obtained is small compared with that obtained by such treatment in the synthesis at atmospheric pressure. Removal of wax by reaction with hydrogen, however, is favoured by reduction in pressure.



VARIATION IN YIELD OF PRODUCTS AND REACTION TEMPERATURE WITH TIME. EXPERIMENT 10A/11.

Effect of Change in Gas Rate.

In an early attempt to determine the life of the catalyst, the gas rate was reduced from the normal 1 l/g Co/hour to one-half this value after 27 days running, and maintained at the lower rate for 16 days. The yield of liquid and solid hydrocarbons at the low rate was 145 g compared with 133 $g/normal m^3$ at the normal rate immediately preceding the change. When the rate was restored to normal again, however, the yield fell to 64 g/normal m³. Although this result strongly suggested that the period of running at low gas rate had caused serious deterioration of the catalyst, such a conclusion could not be substantiated until the same catalyst had been operated for the same total time at normal gas rate. These conditions were fulfilled in Experiment 8/3, which has been described in the preceding pages, and the results are compared with those of the earlier experiment in Table VII. This comparison shows very clearly that operation at half the normal gas rate markedly reduces the activity of the catalyst for subsequent operation at the normal rate.

It has already been noted that in Experiment 10A/4 this effect was still quite marked for shorter periods of running at the low gas rate.

It will be seen from the results given in Table V that in this experiment the effect of an increase in gas rate from 1.0 to 1.4 l/g Co/hr was to reduce the yield of liquid and solid hydrocarbons from 134 to 106 g/normal m³. In this case, however, the higher rate had no adverse effect on the catalyst

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52.6

37-2

37.6 53.6 21.3

25.9 |

19-2

5.2

12.6

	04/16	17-21	12	101	$1 \cdot 0$	l·l		18.2	8.5	21-9		514
	0A/16	9-15	17	100	1.0	1-55		15-9	9.2	23.4		51.5
	A/16 1	5 1-1	15	2	1.0	63		3-0]	0.1	4-9 5		2.0
	A/14 10	16-	13	0	0.1	1-1		2.8 2	18]	24 2		3.0 4
	1/15 10	-16 1	1 09	1	0.	42]) 5 I	1.5 1	3.4 2		6 5
	5 10/	-9		•	-	1		3 2(-	2(4
sure.	10A/1	17-24	195	-	1.0	1.65		20.6	15.4	26.0		38.0
Pres.	10A/15	2, 3	4	-	1.0	67		23.6	14.7	27.5		34.2
10 atm	10A/4	30, 31, 36, 37	9 104	* ^ *	. 0.5	67		19.4	13.1	22.1		48.4
esis at	10A/4 2	26 &	4	-	1.0	61		36-7	14-8	21.2	-	27-3
Synth	10A/4	24 & 29	4	195	1.0	63		24.6	12.8	22.6		40.0
s from	10A/4	22	2 109	-	1.5	67	st.	33.3	14.8	28.8		23.1
roduct	10A/4	(19, 20 & 23	9	195	1.0	67	produc	23.0	13.2	27.2		36-6
olid P	8/3	123- 131	10	-	1.0	57	solid	18.6	6-11	30-8		38.8
and S	8/3	107-	9006	2024	1.0	2	id and	13.2	10-7	24.6		51.5
higuid	8/3	73- 87	104	H D H	1.0	67	nby n	14.9	10-2	23.7		51.2
on of 1	8/3	53- 61	104	FOT	1.0	67	of tote	18-6	10-1	25.1		46-2
npositi	8/3	35-43	11	307	1+0	63	by wt	21.7	12.4	24.5		41.4
Con	8/3	7-16	12	POT	1.0	c1	ns, %	29.0	13.0	22-2		35.8
-	7/49 1	2-3	4	POT	1.0	67	Fractio	40.4	15.5	32.5		11.6
	Experiment No	Test period nos	Period of time, days	THERE MONTH MAINING .	Gas rate, 1/g Co/hr .	H ₂ /CO ratio of syn. gas	Proportion of Main	Spirit up to 150° C .	Fraction 150-200° C.	Middle oil 200-300° C	Wax, residue above	300° C .

TABLE VI.

8

25.4 | 16.0 | 14.0 | 18.0 | 14.0 | 14.0 | In spirit up to 150° C In fraction 150-200° C

Olefins, % by wt :

-

Synthesis at atmospheric pressure. 30 per cent nitrogen added to synthesis gas, gas, gas rate = 1 l. normal synthesis gas/g Co/hr. -

TABLE VII.

Effect of Reduction in Gas Rate.

Gas rate in Expt. $8/3 = 1 \log Co/hr$ throughout. In Expt. 8/2 gas rate the same except over the period 28-42 days, when rate was $0.5 \log Co/hr$.

Time in days from start of experiment		Reaction ture	tempera- o, °C	Yield of liquid and solid hydrocarbons g/normal m ³			
Expt 8/2	Expt 8/3	Expt 8/2	Expt 8/3	Expt 8/2	Expt 8/3		
$ \begin{array}{r} 13-18 \\ 19-23 \\ 27 \\ 43 \\ 45-48 \\ \end{array} $	11-1619-2324-3141-4549-63	185 186 190 191 204	185 188 189 191 194	$140.9 \\ 134.9 \\ 132.6 \\ 64.0 \\ 123.5$	$ \begin{array}{r} 139 \cdot 3 \\ 130 \cdot 6 \\ 131 \cdot 8 \\ 125 \cdot 2 \\ 130 \cdot 0 \end{array} $		

and on returning to normal gas rate the yield again reached 134 g/normal m^3 . This result confirms Fischer and Pichler's conclusions that operations at medium pressures does not permit the use of higher gas rates than those regarded as optimum in the atmospheric-pressure synthesis.

From the data recorded in Table VI, it will be seen that the increase in gas rate caused a marked change in the composition of the products, the proportion of wax falling from 37 to 23 per cent with a compensating increase in the spirit fractions. The decrease in gas rate caused a large decrease in the olefin content but in other respects the product composition was similar to that obtained at the corresponding stage of Experiment 8/3 at normal rate.

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Effect of Dilution of the Synthesis Gas.

There are numerous references in the patent literature to the use of synthesis gas containing over 20 per cent of inert constituents. For a period of 5 days in the course of Experiment 10A/4, the normal synthesis gas containing 6.5 per cent of inert constituents was replaced by one containing an additional 30 per cent of nitrogen; its composition was :

 CO_2 : 3·1 per cent; CO: 20·0 per cent; H_2 : 41·8 per cent; N_2 : 35·1 per cent.

The "ideal gas" rate, *i.e.*, litres of $CO + H_2$ per hour, was kept constant. As will be seen from the following figures, the conversion of $CO + H_2$ to liquid and solid hydrocarbons was reduced by 16 per cent by the dilution.

Time in days from start of experiment	Reaction temp, ° C	% CO+H ₂ in syn. gas	${f Litres} {f CO+H_2/hr}$	Yield of liquid and solid hydrocarbons, gm/normal m ³ CO+H ₂
40-44	192	93·5	9.0	143
45-49	193	61·8	9.2	120
50-51	193	93·5	9.2	142

Dilution of the synthesis gas has been found by the authors to have a similar effect at atmospheric pressure.

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Thus although in practice the use of diluted synthesis gas may have beneficial effects on catalyst life or ease of temperature control it is clear that such advantages can only be obtained at the expense of conversion efficiency.

In view of the fact that Fischer and Pichler found that over the range 5 to 15 atm gauge pressure the yield of liquid and solid hydrocarbons was practically constant for a constant gas rate measured at N.T.P., it would seem that the observed effect of dilution with nitrogen is due to a specific retarding effect on the reaction and not to a decrease in the partial pressure of the carbon monoxide and hydrogen.

It will be seen from Table VI that the addition of nitrogen to the synthesis gas affected the composition of the products in a manner similar to that caused by the 50 per cent increase in gas rate. This effect was not observed in experiments with diluted synthesis gas at atmospheric pressure and is further evidence of the sensitivity of product composition to changes in the reaction conditions in the medium-pressure synthesis.

Effect of Catalyst Density.

In Experiment 10A/4 the use of a catalyst of higher bulk density permitted the use of a higher gas throughput and led to a higher space-time yield than in Experiment 8/3. By suitable selection of the kieselguhr used as support, a catalyst of still higher density (50 g/100 ml) was prepared and was found to give as high a yield and to have as long a life at atmospheric pressure as catalysts of much lower density. In Experiment 10A/14 the performance of this catalyst at 10 atm pressure was determined. The results obtained with the normal synthesis gas are shown in line (i) of Table VIII; the results at atmospheric pressure are shown in line (vi). It will be seen that the yield of liquid and solid hydrocarbons was lower and that of

TABLE VIII.

Effect of Variation in H_2 : CO Ratio of the Synthesis Gas.

(a) Dense Catalyst.

Catalyst : 100 Co; 6 ThO₂; 3 MgO; 200 kieselguhr, 100 ml = 53 g = 13.3 g Co. Gas Rate : 1 l/g Co/hr.

Experiment Test No Nos	Test Period of	H.: CO	Reaction temp, ° O	Gauge	Average hydroc g/norr	Olefins, %		
	period Nos	time, days gas *		pressure, p.s.i.	Liquid and solid hydro- carbons	Gaseous hydro- carbons	fraction <150° C	
ATLADE (1)	5 0	0		104 100	150	195.0	42.0	7.4
(1) IUA/14	9-9	9	2:1	104-109	150	102.9	24.9	7.6
(II) IUA/15	2-3	4	2:1	101	150	120.0	16.7	52.6
(III) 10A/14	11-16	12	1.2:1	196-199	150	120.2	10.7	27.0
(iv) 10A/15	6-16	24	1.42:1	188-194	100	120.0	20.0	01.0
(v) 10A/15	17-24	17	1.65:1	194-196	150	123.0	21.2	20.9
(vi) 9/25	1-6	11	2:1	185	0	130.7	37.1	29.0
(vii) 7/23	7-13	12	1.2:1	185-195	0	104.0	23.0	50-0

* The gas mixture contained, in each case, approximately 93 per cent, $\rm CO + H_a$.

gaseous hydrocarbons higher at 10 atm than at atmospheric pressure—the reverse of the usual effect of pressure on the synthesis. This effect was shown to persist even at lower temperatures (see result for Experiment 10A/15, line (ii), Table VIII). The design and dimensions of the reaction. tube employed in the tests at the two pressures were identical. The above result is therefore strong evidence that heat dissipation is more critical under medium-pressure conditions than in the atmospheric-pressure process.

Effect of H_2 : CO Ratio.

In the hope of reducing the formation of gaseous hydrocarbons by reducing the proportion of hydrogen in the ingoing gas, the normal synthesis gas (H₂: CO = 2:1) used in the first 9 days of experiment 10A/14 was replaced by water-gas (H₂: CO = 1.2:1). The device was strikingly successful; the gas production was reduced by 60 per cent while the production of liquid and solid hydrocarbons was only reduced by 4 per cent (Table VIII, line (iii)). As the reaction still utilized hydrogen and CO in the proportion of 2 to 1, 92 per cent of the hydrogen in the water-gas was consumed, but only 50 per cent of the carbon monoxide. In contrast to the behaviour of this catalyst with normal synthesis gas, the effect of increase in pressure from atmospheric to 150 p.s.i. was a marked increase in yield of liquid and solid hydrocarbons, and a decrease in yield of gas (compare lines (iii) and (vii), Table VIII).

With the normal gas, $H_2/CO = 2$, increase in pressure caused a fall in the olefin content of the spirit fraction, but, as can be seen from Table VIII, decrease in the H_2 : CO ratio more than compensated for this effect and when using water-gas the olefin content was slightly greater at 150 p.s.i. pressure than at atmospheric pressure.

In view of these results, it was reasonable to suppose that an optimum ratio between $H_2/CO = 2$ and $H_2/CO = 1$ would be found to give maximum yields of liquid and solid hydrocarbons with a reasonably low yield of gaseous hydrocarbons. The ratios $H_2/CO = 1.4$ and 1.7 were tried, but, as will be seen from Table VIII, although a maximum yield of liquid and solid hydrocarbons was obtained for this catalyst at ratio 1.4, with a satisfactory low gas production this maximum (126 g/normal m³) was considerably below the yields obtainable with the less dense catalysts when using synthesis gas, $H_2/CO = 2$, in Experiments 8/3 and 10A/4.

In Experiment 10A/16 the effect of variation in H_2 : CO ratio was examined using a catalyst of only half the density of that used in the foregoing experiments (*i.e.*, similar to that used in Experiment 8/3). The results are shown in Table IX. They show that a definite optimum ratio of H_2 : CO exists in the region of 1.5 H_2 : 1 CO, giving a slightly higher yield of liquid and solid hydrocarbons and an appreciably lower yield of gaseous hydrocarbons than the normal ratio of 2 H_2 : 1 CO. It will be observed that whereas with this optimum ratio the yield of liquid and solid hydrocarbons is higher by 15 g/normal m³ for the light catalyst as compared with the dense one used in the preceding experiments, the yield with watergas is only higher by 4 g/normal m³.

This striking effect of low H_2 : CO ratio, in "correcting" the gas-forming tendency of the dense catalyst suggests that if water-gas is used as raw material, reaction vessels with a lower ratio of cooling surface to catalyst volume than is necessary for normal synthesis gas might be employed. The use of water-gas is attractive by reason of the high olefin content of the

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TABLE IX.

Effect of Variation in H_2 : CO Ratio of the Synthesis Gas. (b) Light Catalyst.

Catalyst : 100 Co; 6 ThO2; 3 MgO; 200 kieselguhr, 100 ml = 26.6 g = 6.7 g Co. Gas rate : 1 l/g Co/hr.

Experi- ment No	Test period Nos	Period of time, days	H _s : CO ratio of synthesis gas	Reaction tempera- ture, ° C	Gauge pressure, p.s.i.	Average yield of hydrocarbons, g/normal m ³		Olefins, % by wt in fraction
						solid hydro- carbons	Gaseous hydro- carbons	<150° O
10A/16 10A/16 10A/16 7/49	2-7 11-15 17-21 2-7	13 12 12 13	2:11.55:11.2:12:1	177–180 188–192 196–198 185	$150 \\ 150 \\ 150 \\ 0 \\ 0$	138·0 141·0 124·3 131·0	$ \begin{array}{r} 29 \cdot 0 \\ 21 \cdot 5 \\ 15 \cdot 0 \\ 32 \cdot 5 \end{array} $	$\begin{array}{r} 21 \cdot 3 \\ 37 \cdot 2 \\ 52 \cdot 6 \\ 25 \cdot 4 \end{array}$

products, combined with a moderately good yield. From the data for product composition given in Table VI it will be seen that, in addition to the effect on olefin content, decrease in H_2 : CO ratio markedly increases the proportion of wax.

Although a complete life test has not yet been carried out using synthesis gas with the optimum ratio $H_2: CO = 1.5: I$, evidence has been obtained which suggests that the catalyst life will be at least as long under these conditions as with gas of normal ratio $H_2: CO = 2: I$.

The results of Experiment 10A/18 in which a catalyst of intermediate density was used for synthesis at 10 atm pressure using synthesis gas $H_2: CO = 1.5: 1$ are summarized in Table X.

TABLE X.

Main Data for Experiment 10A/18.

Catalyst : 100 Co; 6 ThO₂; 3 MgO; 200 kieselguhr, 100 ml = 38.9 g = 9.2 g/Co. Gauge pressure : 150 p.s.i. Synthesis gas : H₂: CO = 1.5:1.

Test	Time in days from	Average reaction	Gas rate,	Average yield of hydro- carbons g/normal m ³ syn. gas		
period Nos	experiment	° C	i/g co/nr	Liquid and solid	Gaseous	
4- 6	8- 14	186	1.0	136.2	26.8	
7-11	15- 25	190	1.0	138.0	32.4	
12-23	26 - 55	192	1.0	132.4	25.0	
24 - 26	56 - 62	192	0.5	145.3	26.6	
27 - 29	63- 68	192	1.0	113.8	28.0	
33	16 hr H ₂ at 202° C, 1 hr at 250° C, 14 l/hr then 2 hr H ₂ at 400° C, 560 l/hr.					
35-36	- 77- 80	187	1.0	92.0	-	
37 - 41	81-91	192	1 0	130.0	23.5	
42	16 hr H ₂ at $1/hr$.	202° C, 14 l/hr,	up to 400° C i	in 4 hr, 2 hr a	400° C, 560	
44-46	95-101	188	10	105.2		
47-52	102-115	192	1 0	130-2	20.2	

II

It will be seen that after an initial, rapid deterioration indicated by a rise in reaction temperature from 185° to 192° C in 25 days the activity remained substantially constant for 30 days. At the end of this period a reduction in the gas rate to half normal for a period of 6 days brought about a reduction in activity similar to that previously observed. It was then found that a high-tenperature hydrogen treatment ("re-reduction") carried out following a wax-removal treatment at low temperature, restored the activity to the level existing before the reduction in gas rate, but not to the initial level. A repetition of this treatment carried out some twenty days after the first one caused no further change in the catalyst activity.

The activity of the catalyst on the 115th day of the experiment was almost as high as on the 27th day, and as the only effect of the hydrogen treatment was to neutralize the deleterious effect of the change in gas rate, it is reasonable to suppose that this constant level of activity would have been observed in the absence of any such treatments provided the gas rate had been maintained constant throughout.

PROPERTIES OF THE WAXES.

The residue obtained by the routine distillation of the total liquid and solid product leaving the reaction vessel and the wax obtained by extraction of the used catalyst with benzene, were fractionated at 2 mm pressure and the molecular weights of the fractions and residues determined by the ebullioscopic method. The results of this examination are recorded in Table XI together with similar data for the analogous products obtained by

Gauge pressure used in synthesis, p.s.i.	150				. 0			
Source of wax	Total reaction product		Catalyst		Total reaction product		Catalyst	
Boiling range of fraction, ° C (corr. to 760 mm)	% by wt of total	Mol. wt.	% by wt of total	Mol. wt.	% by wt of total	Mol. wt.	% by wt of total	Mol. wt.
330-350 350-375 375-400 400-425 425-450 Residue at 450 450-585 Residue at 585 Loss	$\begin{array}{r} 7 \cdot 0 \\ 12 \cdot 4 \\ 9 \cdot 0 \\ 10 \cdot 0 \\ 12 \cdot 0 \\ (49 \cdot 2) \\ 33 \cdot 0 \\ 16 \cdot 2 \\ 0 \cdot 4 \end{array}$	258 288 315 342 370 548 485 680	$ \begin{array}{r} 7 \cdot 1 \\ 10 \cdot 5 \\ 11 \cdot 4 \\ 11 \cdot 2 \\ 15 \cdot 4 \\ 44 \cdot 0 \\ \\ 0 \cdot 4 \end{array} $	279 295 326 351 517 —	22·4 29·9 25·5 16·3 4·6 0·7 — 0·6	258 276 308 337 361 	2·2 2·4 7·6 8·2 18·6 60·6 — 0·4	 326 367 399 510
Total	100-0		100.0	-	100.0	- 1	100.0	-

TABLE XI. Composition of Waxes.

synthesis at atmospheric pressure using the same type of catalyst. The boiling ranges have been calculated to a uniform initial boiling point and the temperatures corrected to 760 mm. In all cases, the fractions with boiling range above 375° C were completely solid at 20° C, but none of the fractions possessed a definite melting point. The congealing point (IP76/44T) ⁵ of the residues above 450° C was about 91° C in all cases.

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Of the residue above 450° C obtained from the medium-pressure reaction product, $25 \cdot 2$ per cent remained insoluble after 60 hours' continuous extraction with boiling ethyl ether. This insoluble residue formed a white amorphous powder, m. p. 102° to 112° C.

The data given in Table XI show that the wax retained by the catalyst at medium pressures is of similar constitution to that present in the total product, and, in a general way, similar to that present on the catalyst at atmospheric pressure. The wax fraction of the atmospheric pressure products, however, is of much lower boiling range and molecular weight, and contains virtually no hydrocarbons distilling above 450° C, whereas the other waxes contain 45 to 60 per cent of such hydrocarbons.

At the start of medium-pressure synthesis only liquid products collect in the receivers and in the course of the first 3 or 4 days, the products become richer in wax until the normal product is obtained. It seems, therefore, that the catalyst preferentially retains the higher hydrocarbons and as, at atmospheric pressure, the activity of the catalyst is seriously inhibited before saturation takes place, none of the higher hydrocarbons appear in the collected products. At 10 atm pressure, however, saturation takes place in the first few days owing to the greater production of the higher-molecular-weight hydrocarbons, and thereafter, the entire products of the reaction collect in the receivers.

THE CAUSES OF CATALYST DETERIORATION.

Fischer and Pichler¹ concluded that, in view of the fact that the catalyst had a longer life at medium pressures, despite the predominance of wax as a product, the former conception of wax as a prime cause of catalyst deterioration must be erroneous. They considered it more probable that deterioration was due to the formation of more complex bodies which, under the conditions of higher pressure, were more readily hydrogenated to harmless products.

Although the precise cause of the initial deterioration of the catalyst at atmospheric pressure may not be the presence of hydrocarbons readily extractable from the catalyst with solvent, it is an undoubted fact in the authors' experience that the rate of deterioration of the catalyst can be closely correlated with the rate of deposition on the catalyst of such hydrocarbons. Furthermore, the characteristics of the synthesis at medium pressure can be interpreted as an indication that the presence of wax on the catalyst exerts a serious retarding effect on the reaction rate. Thus, despite the ten-fold increase in time of contact obtained by raising the pressure to 10 atm at a constant gas rate measured at N.T.P., the extent of conversion is only increased by 5 to 10 per cent. It would appear that when the catalyst is completely saturated with molten wax, the higher partial pressure of reactants and longer time of contact are necessary to achieve the same order of conversion as that obtained at atmospheric pressure where the catalyst is relatively free from wax.

As the catalyst at medium pressures is always saturated with wax, Fischer and Pichler are clearly right in concluding that production of this wax is not a cause of catalyst deterioration *under medium-pressure conditions*, and the ineffectiveness of hydrogen and solvent de-waxing procedures is not surprising, if removal of this wax is their only function. The fact that hydrogen treatment at the working pressure (a relatively inefficient process for removing wax) produced a greater degree of reactivation than the treatment at atmospheric pressure can be taken as some support for Fischer and Pichler's "complex-body" theory of deterioration.

The comparative ineffectiveness of all hydrogen reactivation treatments including re-reduction at a temperature of 400° C in the medium-pressure synthesis suggests, however, that the complex bodies formed under these conditions are more resistant to hydrogenation than those formed at atmospheric pressure. A possible explanation of the extremely deleterious effect of reduction in the gas rate observed in the above experiments is that this condition particularly favours the formation of such bodies. If this is so, an increase in catalyst life might be obtained by operation at a gas rate higher than the normal.

The observation, made on several occasions, that a catalyst which has been used for synthesis at 10 atm pressure is of low activity for synthesis at atmospheric pressure, even after hydrogen treatment at 400° C, is evidence that conditions of operation under pressure produce a more permanent poisoning of the catalyst than any which has been experienced during synthesis at atmospheric pressure.

SUMMARY.

The synthesis of hydrocarbons from carbon monoxide and hydrogen at a gauge pressure of 150 p.s.i. has been studied using cobalt-thoria-magnesia-kieselguhr catalysts.

With synthesis gas $(H_2: CO = 2:1)$, conversion to liquid and solid hydrocarbons is about 10 per cent greater and the rate of catalyst deterioration 30 to 50 per cent less than under otherwise comparable conditions at atmospheric pressure. The performance of the catalyst and the nature of the products obtained at 150 p.s.i. pressure is very similar to that reported by Fischer and Pichler,¹ but represents a much smaller degree of improvement over the performance at atmospheric pressure than that observed by the German workers for a cobalt-thoria-kieselguhr catalyst.

Hydrogen treatment at temperatures in the synthesis range and hightemperature hydrogen re-reduction treatments are ineffective in prolonging catalyst life under medium-pressure conditions. The total life of the catalyst at 150 p.s.i. pressure when working in one stage to an average yield of 129 g of non-gaseous hydrocarbons/normal m³ inert-free gas is of the order of 6 months. Operation at half the normal gas rate of 1 l/g Co/hour causes a serious deterioration of the catalyst activity for subsequent operation at the normal gas rate, which can only be restored by re-reduction in hydrogen at 400° C.

Catalysts with a high cobalt content per unit volume which operate satisfactorily at atmospheric pressure give excessive production of gaseous hydrocarbons at 150 p.s.i. Use of water-gas ($H_2: CO = 1 \cdot 2: 1$) in place of synthesis gas ($H_2: CO = 2: 1$) completely suppresses this tendency, reducing the yield of gaseous hydrocarbons from 45 to 17 g/normal m³ inert-free gas while only reducing the yield of non-gaseous hydrocarbons from 134 to 130 g/normal m³. At the same time the olefin content of the

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spirit fraction (30 to 150° C) is increased from 8 to 53 per cent. Use of water-gas gives similar results with catalysts of normal cobalt content.

The most efficient conversion to liquid and solid hydrocarbons is obtained using gas of H_2 : CO ratio ca 1.5:1. The yield in the first few weeks of the catalyst's life is 145 to 150 g non-gaseous hydrocarbons per normal m³ inert-free gas which represents 85 per cent of the carbon monoxide and hydrogen converted. There is reason to believe that the life of the catalyst will be at least as long under these conditions as when using the normal synthesis gas $(H_2: CO = 2: 1)$.

Since the completion of the above work British and American investigators have obtained fairly complete information concerning the operation and development of the Fischer-Tropsch process in Germany. As a result of this it is now known that four commercial plants were operating the process at 10 atm pressure using a cobalt-thoria-magnesia-kieselguhr catalyst. The process was usually operated in three stages using synthesis gas of H_2 : CO ratio 1.5-1.8: 1 with a yield of 150 g C₃ and higher hydrocarbons per normal m³ inert-free gas and with a catalyst life of 6 to 8 months. The use of water-gas as raw material was studied on a pilot-plot scale at 10 atm pressure with the object of producing olefins for further synthesis.

The effect of variation in gas rate on the activity of the catalyst and the effectiveness or otherwise of re-reduction treatment in restoring the activity of catalysts in the medium-pressure synthesis do not appear to have been investigated.

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OBITUARY.

SIR THOMAS HENRY HOLLAND.

SIR THOMAS HOLLAND, K.C.S.I., K.C.I.E., HON.LL.D., F.R.S., D.Sc., and the recipient of many academic honours, died on May 15, 1947. He was a Founder Member and Past-President of the Institute.

Thomas Henry Holland was the son of John Holland, of Springfield, Manitoba, and was born at Helston, Cornwall, on November 22, 1868. He was a youth of marked character and independence and, at the early age of sixteen, he won in open competition a National Scholarship, tenable at the Royal College of Science; a truly remarkable and characteristic achievement. At the College he won the Murchison Medal and Prize, obtained a first-class diploma in the subject of geology, and was appointed assistant in the department. In 1889, he was awarded a Berkeley Fellowship of Owen's College, Manchester, and in 1880, at the early age of twentyone, he was appointed Assistant Superintendent of the Geological Survey of India.

Holland travelled to India via the United States, Canada, Japan, and China, and on arrival in Calcutta took up his new duties with characteristic energy. In 1894, he gained much publicity and credit in connexion with the Gohna landslip. Two large landslips formed a huge dam across a river, and there was much public apprehension that the very large lake that was forming would break down the dam, and cause much destruction and loss of life. Holland inspected the site, proved that the dam would hold back the lake permanently, and predicted that about the middle of August, 1894, the lake would fill, and the water flow quietly over the dam and resume its normal course down the valley. There was still much public disquiet, and a marked reluctance to rely on the findings of a young geologist of twentyfive, but, of course, everything happened as Holland had predicted.

Holland made numerous and notable contributions to the Records and Memoirs of the Geological Survey, mainly on mineralogical and petrological subjects. His most notable contribution to petrology was his description of a distinctive, holocrystalline, hypersthene-bearing granitoid rock, which he named Charnockite, as the tombstone of Job Charnock, the founder of Calcutta, consists of this rock. He later extended the term to the Charnockite Series to include intermediate, basic, and other special varieties of the original Charnockite. He also took a great interest in the broad general classification of the rock formations of India. He relegated the Dharwars to the Archaean Group; regarded the unfossiliferous Cuddapah and Vindhyan Systems as Pre-Cambrian, and named them the Purana Group; placed all formations from Basal Cambrian to Carboniferous inclusive in his Dravidian Group; and everything from the Permian to the Pleistocene inclusive in his Anyan Group. This classification was soundly based on important and widespread unconformities, which are the most definite and striking relics of the pulsations of our slightly variable planet. He also wrote on the subject of the origin of laterite and, in collaboration



SIR THOMAS HENRY HOLLAND, K.C.S.I., K.C.I.E., Hon.LL.D., F.R.S., D.Sc. 1868-1947.

with the late Dr. Christie, proved that the salinity of the Sambhar lake, and of other salt-lakes in Rajputana, is due to wind-borne salt. Unfortunately, space does not permit of reference to his many other contributions to our knowledge of the geology of India.

Holland made rapid progress as a Survey Officer and, in 1903, at the early age of thirty-four years, he was appointed Director over the heads of several of his senior colleagues. Until then the Survey had been scientific, academic, and even esoteric. However, in addition to being a first-class scientist, Holland was a robust extrovert, and his practical genius developed the applications of geology to the mining and industrial life of India, at a time when they were most needed and could be most effective. This task did not exhaust his energies; in 1906–1907 he was President of the Mining and Geological Institute of India; in 1909, President of the Royal Asiatic Society of Bengal; he was also the first Professor of Geology at Calcutta University, and in 1909 was the Dean of the Faculty of Science. In that year he resigned the directorship of the Survey on accepting the Chair of Geology and Mineralogy at Manchester University. By that time he was impressed with the interrelation and interdependence of industries, and was perfectly equipped for his future work in India.

Holland retained the Chair of Geology and Mineralogy at Manchester until 1918. In 1910 he was President of the Royal College of Science Association; member of the Advisory Committee of the Imperial Institute from 1910 to 1916; President, Manchester Geological and Mining Society in 1913; President of the Geological Section of the British Association in 1914, and President of the Institution of Mining Engineers in 1915–1916.

In April 1916 Holland returned to India as President of the Indian Industrial Commission, and various departments of Government were quickly impressed by his wide range of exact knowledge. In 1917, he became President of the Board of Munitions, and rendered valuable service to the war effort. In 1920, he was appointed to the Viceroy's Executive Council as Member for Commerce and Industry.

Holland's career in India was cut short in 1921 in connexion with the Calcutta munitions case. Continuation of the case, whatever the verdict, would have had serious political and industrial consequences. Moreover, Counsel's opinion was that a conviction before a jury was very doubtful in view of the complicated character of the case. Holland, after consulting two of his colleagues on the Viceroy's Executive Council, stopped the case, which normally would and should have passed into oblivion. Unfortunately, the Advocate-General of Bengal stated in open Court his opinion that the case against the accused could be proved, but that he did not intend to offer any evidence. The Viceroy, a former Lord Chief Justice of England, strongly and rightly resented this statement. He was on less firm ground in objecting to the political implications of failure to consult him before the case was withdrawn, as the administration of India was an undertaking so vast that it could not have been carried on had it been necessary to consult him on all matters of importance. The Viceroy and the Secretary of State for India did not see eve to eve in the matter, and at one stage the former contemplated resignation. The matter ended with Holland's resignation, and both the Viceroy and the Secretary of State bore public testimony to his complete integrity, and to the great services he had rendered to India.

He felt this first and temporary check to his long career of brilliant and uninterrupted success, but had the satisfaction of knowing that he had rendered invaluable services to the war effort in the manufacture of munitions and other essential requisites, and had done more than any other man for the mineral and industrial development of India.

Holland returned to England in the autumn of 1921, and in 1922 was appointed Rector of the Imperial College of Science and Technology. He made considerable progress in the development of the corporate and social life of the College. For some years there had been considerable and growing agitation for the College to be reconstituted as a separate University, but an influential deputation rightly failed to convince the first Lord Balfour, then Lord President of the Council, of the desirability of acceding to their request. Later, Holland inadvertently came across a letter from Balfour, in which the latter suggested affiliation with London University as the solution of the difficulty and, thanks mainly to Holland's influence and efforts, this suggestion was gradually carried into effect. In 1925, an agreement was reached with the University of London whereby the final examinations for the various Associateships became also the final examinations for the B.Sc. degrees in the several subjects, for such students as had matriculated at that University. In 1929, the new statutes of the University came into force, and the Rector of the Imperial College became, ex officio, a member of the University Senate and of the Collegiate Council; while, in 1930, the Professors of the Imperial College became Professors of the University. These changes, effected mainly by Holland, represented a landmark in the history of the College, and long before they came to pass. Balfour had, characteristically, completely forgotten that he had written the letter which stimulated Holland to action.

In 1929, Holland was appointed Principal and Vice-Chancellor of Edinburgh University, and for fifteen years he held this position with distinction, the University benefiting financially and otherwise through his tenure of the office. During this period he became a DeputyLieutenant of the County of Edinburgh; Hon. President of the Royal Scottish Society of Arts and of the Mining Institute of Scotland; and he achieved the unique distinction of having conferred upon him the Hon. LL.D. of all four Scottish Universities. He intended to retire in 1940, but owing to the war his retirement was deferred until 1944, when at the age of seventy-five he returned to London with full vigour of mind and body unimpaired.

Holland had a long and close connexion with petroleum. In 1891, he published a paper "On Mineral Oil from the Suleiman Hills," and also an account of a careful examination of eight samples of oil from shallow wells in the Yenangyaung field. He also wrote on the subject of petroleum in his many reviews of the mineral production of India. In 1908, he was President of the Burma Oilfields Committee, whose report led to the appointment of a Warden of the Oilfields, assisted by an Advisory Board drawn from the staffs of the oil companies. From 1911 to 1913 he was a member of the Royal Commission on Oil Fuel and Engines, and during this period he discussed with Sir Boverton Redwood the formation of the Institution of Petroleum Technologists. In his own words "The idea of forming an Institution of Petroleum Technologists was a by-product of the conclusions which were impressed on certain members of the Royal Commission that investigated, under the late Lord Fisher, the problem of utilizing oilfuel for the Navy." He was a Founder Member of the Institution, an original Member of Council, and was elected a Vice-President in 1915. Early in 1916, the Council elected him President, but before he could take office at the Annual General Meeting he was called to India as President of the Indian Industrial Commission. He was President of the Institution from 1925 to 1927, and thereafter as a Past-President he was a Member of Council until his death. His paper on "Some Geometrical Features of the Anticline" was the first scientific contribution to the *Journal*, and presented the results of the first serious attempt to evolve a method of constructing cross sections of asymmetrical anticlines from surface dip evidence, a matter of great importance in the location of wells. Other publications in the *Journal* include his Presidential Address, a paper on "Conditions affecting the Petroleum Prospects of the Empire," and contributions to discussions of early geological papers.

On the first of April, 1911, Holland was appointed Consulting Geologist to the Burmah Oil Co. Ltd. and retained this post until his death. For the greater part of the same period he was also a Geological Adviser to the Anglo-Iranian Oil Co. Ltd. For some years prior to 1921 he was Geological Adviser to the Assam Oil Co. Ltd.

Holland wished to retire from India when he came to England on leave in 1920, but the Viceroy, Lord Chelmsford, extracted a promise from him to return. This undertaking prevented him from accepting a post in the petroleum industry, which would probably have occupied him for the remainder of his career. In 1928, he visited Trinidad to advise Government on the subject of Petroleum Regulations, notably in respect of royalties and other conditions governing the grant of mining leases and prospecting licences.

Holland was in great demand as a lecturer. In 1929, he was Trueman Wood Lecturer of the Royal Society of Arts; in 1930, Ludwig Mond Lecturer, Manchester University; in 1937, Huxley Memorial Lecturer, Imperial College of Science; in 1938, Fison Memorial Lecturer, Guy's Hospital; and in 1941, Bruce-Preller Lecturer, Royal Society of Edinburgh. In addition, he gave many Presidential Addresses.

He was elected a Fellow of the Royal Society in 1904 and was a Vice-President from 1924 to 1945. His personality and abilities were so outstanding that he became President or Chairman of every other Society and Institution to which he belonged. He became President of the Royal Asiatic Society of Bengal, the Mining and Geological Institute of India, the Institution of Mining Engineers, the Institution of Mining and Metallurgy, the Geological Society of London, the British Association, the Mineralogical Society of London, and the Geographical Association. He was also Chairman of Council, Royal Society of Arts, and of the Empire Council of Mining and Metallurgical Institutions. He was Foreign Secretary of the Geological Society from 1943 until his death, and was President Elect of the International Geological Congress, to be held in London in 1948.

Holland rendered valuable services on a number of Government Commissions. He was President of the Burma Oilfields Committee, member of the Royal Commission on Oil Fuel and Engines, President of the Indian Industrial Commission, President of the Board of Munitions, India, and Chairman of the Departmental Committee on Qualifications of Colliery Officials.

He was the recipient of many honours. Created K.C.I.E. in 1908, and K.C.S.I. in 1918, he was also Knight Commander, Polonia Restituta; a Deputy Lieutenant, County of Edinburgh; Hon. LL.D. of Manchester, Glasgow, St. Andrews, Edinburgh and Aberdeen; Hon. D.Sc. of Calcutta and Melbourne and Hon. D.Sc. (Eng.) Witwatersrand; Bigsby Medallist, Geological Society; Gold Medallist, Institution of Mining and Metallurgy; and Albert Medallist, Royal Society of Arts.

In 1896, Holland married Frances Maud, daughter of the late Charles Chapman, Deputy Commissioner of Oudh. There was one son and one daughter of the marriage. The first Lady Holland died in 1942, and, in 1946, he married Miss Helen Verral.

Holland enjoyed robust health throughout his life, and had little experience of even minor and common ailments. Within a few weeks of his death he was active as ever and immersed in his numerous interests. Although he complained of feeling a little unwell, there was no sign that he was on the verge of serious illness. Perhaps the very cold spell in February and March sought out some weak spot and undermined his health. His illness was of brief duration, and perhaps it was fortunate that the curtain fell swiftly, for his active mind and body and his zealous spirit seemed illsuited to the life of an invalid. However, he was indomitable and resourceful, and might have overcome any handicap. In 1935, he had an attack of laryngitis, and was order by his medical adviser not to speak for a month. Since he could not speak, he settled down to write, and when the sentence of silence expired he had completed his book on "The Mineral Sanction as an Aid to International Security."

Holland's robust health was the source of his high spirits and abounding energy and vigour. He was a great raconteur, with a keen wit and a slightly malicious sense of humour. Of tough fibre, and with a streak of hardness, his sympathy was reserved for the really serious hardships and sufferings of others. And it was noteworthy how considerate he could be in time of danger, or as a companion in the restricted conditions of the jungle and the desert.

It is unfortunate that Holland did not publish his autobiography for, however voluminous the records he has left behind, a biography could not display the brilliance and pungency of his own style.

Holland's wit and infectious humour, and the ease and gaiety with which he carried his many honours, tended to conceal his more basic qualities. He inherited a sound constitution and a keen and active brain and, during the formative years when his mind and character were still plastic, he was a student of the great Thomas H. Huxley, and was subjected to his rigorous and logical methods of teaching and training. The result was that his mind and character became set, fixed, and crystallized in the rigid Huxley mould. It was therefore fortunate that Huxley aimed at producing men, rather than specialists. As Huxley wrote :—

"That man, I think, has had a liberal education, who has been so trained in youth that his body is the ready servant of his will, and does with

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ease and pleasure all the work that as a mechanism it is capable of ; whose intellect is a clear, cold logic engine, with all its parts of equal strength, and in smooth, working order ; ready, like a steam engine, to be turned to any kind of work, and spin the gossamers as well as forge the anchors of the mind ; whose mind is stored with a knowledge of the great and fundamental truths of nature and of the laws of her operations ; one who, no stunted ascetic, is full of life and fire, but whose passions are trained to come to heel by a vigorous will, the servant of a tender conscience ; who has learned to love all beauty, whether of nature or of art, to hate all vileness, and to respect others as himself.

"Such an one and no other, I conceive, has had a liberal education, for he is as completely as a man can be, in harmony with nature He will make the best of her, and she of him. They will get on together rarely; she as his ever beneficent mother; he as her mouthpiece, her conscious self, her minister and interpreter."

Thomas Henry Huxley was the godfather of Thomas Henry Holland.

With Holland's death a brilliant career has been brought to a close, and a robust, vigorous, vivid, and unique personality has passed away. Behind the success and the achievements, and beneath the load of honours and the trappings of office, was a man with a constitution of steel, a mind like a diamond, and a tongue and a pen like a sword. He was inflexibly honest, and a glittering and deadly foe of falsehood and error. And his honesty was the outward expression of an inner love of truth. He loved and admired seekers after truth, and his hero was Charles Darwin. Truth to him was a religion, and he was a worshipper so devout that he became a priest in one of the courts of her temple.

T. DEWHURST.

