# THE EFFECT OF SULPHUR AND PHOSPHORUS ON AVIATION FUEL PERFORMANCE. 

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#### Abstract

Summary. The effect of small quantities of sulphur and phosphorus and their compounds on the performance of fuels is discussed both for octane (motor method) ratings and rich mixture performance (3-C) ratings. It is shown that the adverse effect of sulphur on engine performance of leaded fuels is very much greater by rich mixture rating than by motor method rating, but that phosphorus shows the reverse effect, having for very low concentrations a slight positive effect on rich mixture rating. The effect on fuel performance of different classes of compounds containing these elements is discussed.




## Introduction.

The effect of sulphur compounds on motor fuel has been very fully studied, and some of the earliest refining processes were directed to modification or removal of these compounds. This refining was, however, directed to prevention of corrosion and odour, and it is only more recently that the effect of sulphur compounds on the performance of a motor fuel has been systematically studied. In 1942, J. G. Ryan published his results ${ }^{1}$ on "The Influence of Sulphur Compounds on Octane Number and Lead Susceptibility of Gasolines." He was able to show that there was a reduction of octane number of clear fuels and also a reduction of lead susceptibility. The reduction of octane number for a given sulphur content in clear fuel was dependent both on the type and molecular size of the sulphur compound, whereas the effect on lead susceptibility was shown to be dependent almost entirely on the type of compound. Further results on the effect of sulphur compounds and also of organic chlorine compounds on octane number have recently been published. ${ }^{4}$

In an aviation fuel a property of major significance is its performance under maximum power in a supercharged engine-and this is normally measured experimentally as the "rich mixture performance number." Preliminary experiments showed that sulphur compounds in a fuel had a very marked effect on rich mixture performance rating. It was therefore decided to study this effect for a number of sulphur compounds. As the high performance required of aviation fuels can normally only be obtained by the addition of tetraethyl lead, $\dagger$ the effect of sulphur compounds on the rich mixture performance rating of a clear fuel was not determined. A typical leaded fuel was therefore selected and rich mixture performance numbers determined by the oxygen method reported elsewhere. ${ }^{2}$

The effect of phosphorus on the performance of aviation fuels was studied in this laboratory in 1940 in connexion with the development of methods for sabotaging fuel storage. A great reduction of the octane number of leaded fuels by very small additions of phosphorus was noted. Although

[^0]this method of sabotage was not used in practice, it was recently decided to make a fow tests on the rich mixture performance of aviation fuels containing small additions of phosphorus. The unexpected nature of the results has prompted publication here in the hope that they may eventually contribute to a consistent explanation of the behaviour of fuels containing small additions of compounds containing sulphur, phosphorus, or nitrogen.

## Experimental.

Sulphur Compounds.
Approximately 1 per cent solutions of the various sulphur compounds were prepared and the sulphur content checked by the lamp method. These were then added in the required amounts to the clear fuel and the tetraethyl lead added just prior to test.

## Fuel.

The fuels used for test were blends of straight-run components and alkylate with rich mixture performances of 98.0 to 99.0 per cent of the Air Ministry 100 -octane reference fuel (B.A.M. 100) when leaded at 4.8 M.T.I.G.

The rich mixture performance numbers of the series of fuels are shown in Tables I and II.

Table I.
Effect of Sulphur Compounds on Rich Mixture Performance.
Fuel Composition: $36 \%$ alkylate.
$64 \%$ straight-run component. $0.005 \%$ S.
4.8 M.T.I.G.

| Compound added. | \% by wt of added sulphur. | Rich mixture performance (\% B.A.M. 100). | Depression of R.M.P. | Equivalent drop in lead content, M.T.I.G. | $\begin{gathered} \mathrm{Pb} / \mathrm{S} \text { mol } \\ \text { ratio } \\ \text { reacted. } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| - | - | 98.0 | 0 | - | - |
| Ethyl mercaptan | 0.0003 | $97 \cdot 5$ | $0 \cdot 5$ | - | - |
|  | 0.0031 | $95 \cdot 1$ | $2 \cdot 9$ | 0.8 | $1 \cdot 3$ |
|  | 0.0124 | $87 \cdot 0$ | 11.0 | 1.9 | . 8 |
| Di-ethyl disulphide | 0.0015 | 97.4 | $0 \cdot 6$ | - | - |
|  | 0.0034 | $96 \cdot 0$ | $2 \cdot 0$ | $0 \cdot 6$ | 0.9 |
|  | 0.0066 | $92 \cdot 7$ | $5 \cdot 3$ | $1 \cdot 0$ | 0.8 |
|  | 0.0072 | $90 \cdot 7$ | $7 \cdot 3$ | $1 \cdot 4$ | - 1.0 |
|  | 0.0145 | $84 \cdot 6$ | $13 \cdot 4$ | $2 \cdot 2$ | $0 \cdot 8$ |
| Elementary sulphur | 0.0004 | 97.7 | $0 \cdot 3$ | - | - |
|  | 0.0035 | 95.5 | $2 \cdot 2$ | 0.7 | 1.0 |
|  | 0.0140 | 89.5 | $8 \cdot 2$ | $1 \cdot 6$ | $0 \cdot 6$ |
| Thiophen | 0.0124 | 97.4 | $0 \cdot 6$ | - |  |
|  | 0.0248 | $96 \cdot 1$ | $1 \cdot 3$ | $0 \cdot 6$ | 0.01 |
|  | 0.0496 | 91.2 | $6 \cdot 2$ | $1 \cdot 3$ | 0.01 |
| Carbon disulphide | 0.0124 | $97 \cdot 0$ | $1 \cdot 0$ | $0 \cdot 2$ | 0.008 |
|  | 0.0248 | 96.7 | $1 \cdot 3$ | 0.3 0.8 | $0.006$ |
|  | 0.0496 | $94 \cdot 3$ | $3 \cdot 7$ | 0.8 | $0 \cdot 008$ |

Table II.
Lead Response of Fuel used in Sulphur Addition Tests.

| M.T.I.G. | R.M.P. |
| :---: | :---: |
| 4.8 | (\%.A.M. 100). |
| 4.0 | 98.0 |
| 3.0 | $95 \cdot 0$ |

## Phosphorus and Phosphorus Compounds.

White phosphorus was weighed into the clear fuel at $0 \cdot 1$ per cent wt concentrations and dissolved after several hours' shaking. This solution was used to prepare the required blends, which were leaded just prior to engine test. Master solutions were also prepared by weighing the esters into the clear fuel.

## Engine Tests.

The rich mixture performance ratings were determined by the oxygen injection method reported elsewhere ${ }^{2}$ for the sulphur compound additions and by the standard 3-C method for the phosphorus additions. The excellent correlation of results obtained by the two methods for different types of fuel makes it highly probable that their direct comparison is permissible.

The octane ratings were made under " motor method" conditions in the C.F.R. engine.

## The Effect of Added Compounds on Rich Mixture Performance of Leaded Fuels.

(a) Sulphur Compounds.

One obvious explanation for the effect of sulphur compounds on lead susceptibility would be an assumed reaction of the lead with the sulphur, possibly (as suggested by J. G. Ryan) in the form of $\mathrm{H}_{2} \mathrm{~S}$. If this were so, then the performance number should be lowered the same amount by the removal of the chemically equivalent quantity of tetraethyl lead as by the addition of a sulphur compound. If it be assumed that one atom of lead is chemically equivalent to one atom of sulphur in these reactionsfor example, with an end product of $\mathrm{PbSO}_{4}$-then in the fuel used, $4 \cdot 8$ M.T.I.G. is chemically equivalent to 0.0241 per cent by wt sulphur. The rich mixture performance number of the fuel with varying amounts of lead is shown in Table II.

If the results of Table I and Table II are considered together, it will be noted that for the reactive types of sulphur compound (mercaptan, disulphide, elementary sulphur) the rich mixture performance is lowered approximately nine numbers for an addition of 0.01 per cent $S$. On the assumption that the depression of rich mixture performance from addition of sulphur is due to reaction of the sulphur with the lead, the lead/sulphur mol ratio reacted is shown in the last column of Table I.

The results are also shown graphically in Fig. 1 to illustrate this point by showing the response to sulphur additions and to lead subtractions on chemically equivalent scales.

The results also support the view put by J. G. Ryan that ease of pyrolysis of the sulphur compounds is related to their effect on engine performance, as carbon disulphide and thiophen have only about one-twelfth the effect of the other compounds studied.
J. G. Ryan's interpretation of his results has been developed recently ${ }^{5}$ by A. Adirovich, who has shown that the relation between decrease in


Fig. 1.
THE DFFECT OF SULPHUR ADDITIONS ON RICF MIXTURE. THE SCALE FOR LEAD ADDITIONS IS DRAWN ON A CHEMICALLY EQUIVALENT SCALE ON THE ASSUMPTION THAT ONE ATOM OF LEAD REACTS WITH ONE ATOM OF SULPHUR. THE SULPHUR ADDITIONS ARE EACH MADE TO A FUEL CONTAINING $4 \cdot 8$ M.T.I.G
lead susceptibility and sulphur content can be derived from kinetic considerations.
In order to compare the effect of the addition of sulphur compounds on the rich mixture performance and motor method octane ratings of leaded fuels, some of the results presented by J. G. Ryan ${ }^{1}$ have been recalculated (Table III) to show the decreases in octane number resulting from sulphur compound additions as the corresponding decreases in lead content. From this rearrangement of the results it can be seen that if the major effect of the sulphur is to remove lead as an effective anti-knock agent, then only less than 40 per cent of the chemical equivalent of the sulphur present is

Table III.
The figures in this table are calculated from the results presented by J. G. Ryan ${ }^{1}$ (Table III, p. 827). Reformed gasoline leaded at $3.0 \mathrm{cc} / \mathrm{U} . \mathrm{S} . \mathrm{gal}$.

| Sulphur compound added. | \% Wt | A.S.T.M. octane no. depression. | * Equivalent drop in lead content |  | $\begin{aligned} & \mathrm{Pb} / \mathrm{S} \mathrm{~mol} \\ & \text { ratio } \\ & \text { reacted. } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | ce/U.S. gal. | \% wt Pb. |  |
| Thiophen | 0.053 | 1.2 | 0.6 1.75 |  | 0.06 |
|  | 0.292 0.053 | 3.8 | ${ }_{0}^{1.75}$ |  | 0.03 0.09 |
| n-Propyl sulphide | 0.053 0.103 0 | 1.5 2.1 | $1 \cdot 9$ $1 \cdot 15$ | 0.3 0.41 | 0.06 |
| n-Propyl mercaptan | 0.053 | 3.7 | 1.7 | $0 \cdot 61$ | $0 \cdot 18$ |
| n-Propyl disulphide | 0.053 | 3.7 | 1.7 | 0.61 | 0.18 |
|  | 0.103 | 4.7 | $2 \cdot 0$ | 0.72 | 0.11 |
| Tert-butyl tetrasulphide | 0.033 | ${ }^{5} 5$ | $2 \cdot 25$ | $0 \cdot 81$ | $0 \cdot 38$ |

* These figures are taken from a lead susceptibility graph for the fuel drawn to J. G. Ryan's figures.
removed, even for the most active compounds. J. G. Ryan's results for disulphide additions have been confirmed in this laboratory.

Comparable figures are also obtained by calculations made on the results presented by H. Bottomley ${ }^{3}$ for the reduction of octane number by known sulphur compound additions.

If the two sets of results for rich mixture performance, and for octane ratings, be compared, it is clear that sulphur compounds have the same general effect on leaded blends, but that in the rich mixture tests this effect is very much greater. The major differences in engine conditions are in the increased speed, mixture strength, and inlet pressure for the rich mixture test. The overall effect would be a higher temperature in the mixture just before combustion, and this supports the view that the reaction of the sulphur with the lead is increased with temperature, but that the reaction is of the same type in both tests and is not affected appreciably by the greatly increased mixture strength in the rich mixture test.

## (b) Phosphorus.

The general effect of white phosphorus on octane number and on rich mixture performance is evident frem Figs. 2 and 3 respectively. These results can be considered in the same manner as those for the effect of sulphur compounds by expressing the depression of rating number in terms of the equivalent reduction of lead. These equivalents are shown in Tables VI and VII, and from these it can be seen that the maximum $\mathrm{Pb} / \mathbf{P}$ mol ratio observed is for low concentrations ( 0.005 per cent wt) of phosphorus, either as white phosphorus or as tributyl phosphate, and that it agrees with the equivalent ratio for formation of $\mathrm{Pb}_{3}\left(\mathrm{PO}_{4}\right)_{2}(\mathrm{~Pb} / \mathrm{P}=$ 1.5).

The results for the rich mixture performance of leaded fuels containing small amounts of phosphorus indicate a very much smaller reduction in rating than for the octane rating of a corresponding blend. White phos-
phorus also shows a small increase in performance when added in amounts up to 0.006 per cent wt. This unexpected result is supported by five separate ratings by the $3-\mathrm{C}$ method, so that there seems little doubt that it is a real effect. The addition of phosphorus as an ester does not show this increase in performance and the effect is not shown in the clear blend with white phosphorus.

Calculation of the $\mathrm{Pb} / \mathrm{P}$ ratio shown in Table VII indicates that at concentrations below 0.01 per cent $\mathbf{P}$ the reaction of phosphorus with the lead cannot be more than 30 per cent complete at most, and it thus contrasts sharply with octane ratings of corresponding blends, where the reaction is apparently almost complete.


No rigid conclusions can be drawn from this consideration of the effects of sulphur and phosphorus on the engine performance of fuels under different test conditions, but certain general tendencies are clear.

It appears highly probable that under appropriate conditions either sulphur or phosphorus compounds will react in the combustion chamber with lead at ratios approaching the theoretical $\mathrm{PbSO}_{4}$ and $(\mathrm{Pb})_{3}\left(\mathrm{PO}_{4}\right)_{2}$ respectively. The reaction between sulphur and lead is greatly accelerated when going from weak to rich test conditions, but the phosphorus-lead reaction is retarded when going from weak to rich test conditions. Phosphorus itself can act as an anti-knock agent within a narrow range of concentration, and under rich mixture test conditions.


Fig. 3.
Table IV.
Effect of Phosphorus on Octane Number (Motor Method).

Fuel.
Fuel.

| Aviation blend |
| :---: |
| with $60 \%$ aro- |
| matics |

Aviation blend-
isoparaffins +
straight-run com.
ponents

Table V.
Effect of Phosphorus on Rich Mixture Performance (\% B.A.M. 100).

| Fuel. | Lead addition, M.T.I.G. | \% Phosphorus by wt. | Phosphorus compound added. | $\begin{gathered} \text { R.M.P } \\ (\% \text { B.A.M. } \\ 100) . \end{gathered}$ | Depression of R.M.P. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Aviation blendisoparaffin + straight-run components | $4 \cdot 8$ | 0.001 | Elementary (white) | 99.0 | $-2.0$ |
|  | 4.8 | 0.0015 | Elomontay (white) | 99.0 | $-2.0$ |
|  | 4.8 | 0.002 | ", ", | 98.9 | $-1.9$ |
|  | 4.8 | 0.005 | ", " | 97.5 | -0.5 |
|  | 4.8 | 0.01 | ", ", | $95 \cdot 8$ | 1-2 |
|  | $4 \cdot 8$ | 0.015 | ", ", | 82.9 | $14 \cdot 1$ |
|  | $4 \cdot 8$ | 0.001 | Tributyl phosphate | 97.0 | Nil |
|  | 4.8 | 0.0015 |  | $96 \cdot 1$ | 0.9 |
|  | $4 \cdot 8$ | 0.006 | ," ", | $94 \cdot 2$ | $2 \cdot 8$ |
|  | $4 \cdot 8$ | 0.015 | " | $91 \cdot 1$ | $5 \cdot 9$ |
|  | $4 \cdot 8$ | Nil | - | 97.0, 96.9 | Nil |
|  | $3 \cdot 0$ | " | - | 86.6 | 10.4 |
|  | 1.5 | , |  | $75 \cdot 5$ | 21.5 |
| Blend 2 | $4 \cdot 8$ | $\xrightarrow{\stackrel{\mathrm{Nil}}{0.0025}}$ | Elementary (white) | $99 \cdot 3$ $100 \cdot 2$ | $\overline{-0.9}$ |
| S4 reference fuel | Clear | Nil |  | 83.0 |  |
|  | ," | 0.002 | Elementary (white) | 82.5 | 0.5 |
|  | " | 0.01 | " " | 81.1 | 1.9 |

Table VI.
Lead reacted with Phosphorus in Octane Ratings (Motor Method) (Calculated from Table IV).

| Added <br> compound. | \% <br> Phosphorus <br> in blend. | M.T.I.G. <br> equivalent <br> to octane no. <br> depression. | Pb/P <br> mol ratio <br> reacted. |
| :---: | :---: | :---: | :---: |
| Elementary (white) | 0.005 | $1 \cdot 6$ | $1 \cdot 6$ |
|  | 0.01 | 2.3 | 1.1 |
| Tributyl phosphate | 0.02 | 4.8 | 1.2 |
|  | 0.005 | 1.6 | 1.6 |
|  | 0.01 | 2.7 | 1.3 |

Table VII.
Lead reacted with Phosphorus in R.M.P. (\% B.A.M. 100 Ratings)
(Calculated from Table V).

| Added <br> compound. | $\%$ <br> Phosphorus <br> in blend. | M.T.I.G. <br> equivalent <br> to R.M.P. <br> depression. | $\mathrm{Pb} / \mathrm{P}$ <br> mol ratio <br> reacted. |
| :---: | :---: | :---: | :---: |
| Elementary (white) | 0.01 | 0.4 | 0.2 |
|  | 0.015 | 2.3 | 0.8 |
| Tributyl phosphate | 0.0015 | 0.2 | 0.6 |
|  | 0.006 | 0.5 | 0.4 |
|  | 0.015 | 1.0 | 0.3 |

## Acknowledgments.

The authors wish to thank the Directors of Trinidad Leaseholds Ltd. for permission to publish this report of experimental work carried out in the Central Laboratory, King's Langley.

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# AUTOMATIC CONTROL OF REFINERY OPERATIONS. 

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Synopsis.


#### Abstract

Instruments for the automatic control of refinery operations are considered from the viewpoint of the user. Their design or how they operate is not considered, but stress is laid on the capabilties of the instruments and the means by which they can be made to give the best results.


For the best to be got out of any instrumentation it is desirable that there should be very close co-operation between the instrument engineer and all levels of operating personnel. Although it is essential to avoid any unskilled interference on the part of the operating personnel with control instruments, it is equally essential, if they are to co-operate intelligently with the instrument department, for them to have a certain minimum knowledge of the theory of automatic control. This paper attempts to review this necessary minimum of theory, and also considers certain examples of instrumentation which are common to many refinery plants, treating them from the viewpoint of the plant operator rather than the instrument engineer.

The extensive use of automatic control is essentially a result of the development of continuous processes in petroleum refining, as compared with the batch processes originally employed. It is perfectly possible to control a batch still with the assistance of only two or three thermometers and to produce materials meeting close specifications. Modern continuous units, however, present problems in control which are essentially dynamic rather than static, and can only be solved by advanced types of automatic control instruments. It is no exaggeration to say that the modern large continuous unit could not have been developed without the parallel development of the present control instruments.

Before proceeding further, it is necessary to define certain variables inherent in the design and settings of all control instruments, and which directly affect their performance.

Load.
The load on a controller may be defined as the quantity of material which has to pass through the control valve in order to maintain the system at the required control point. This definition of load should be understood as independent of the type of controller, flow, temperature, liquid level, etc, which is concerned.

## Throttling Range.

May be defined generally as the proportional change in control valve position corresponding to a given proportional deviation of the controlled variable from the required control point. Applying this to air-operated controllers, with which type alone this paper deals, throttling range may be defined as the change in air pressure to the control valve corresponding
to a given departure of the indicating or recording pen from the control point. To simplify discussion, the pen connected to the measuring device, whether for flow, temperature, or pressure, etc., will be referred to throughout as the recording pen, irrespective of whether the instrument is of the recording or merely indicating type; and the pen attached to the mechanism by which the control point is set, as the index pen.
Throttling tange is frequently expressed as a percentage of the full-scale reading of the instrument. This is illustrated in Fig. 1, for pressurecontrollers set to 10 per cent and 50 per cent throttling ranges.


## Droop.

The term droop will be used to describe the permanent departure from the control point brought about by a change in load, when using instruments of the simple throttling type (Fig. 2). It will be evident that the degree of droop will be dependent on the extent of the load change, and also on the throttling range to which the instrument is set. The recording pen can


Fig. 2.
be brought back to the original control point, and the load change compensated, by manual resetting of the index pen, but this will not prevent a further departure from the control point if a fresh change in load occurs. In certain processes load changes are infrequent, and it is therefore possible to use simple throttling controllers and reset them by hand as necessary. In the petroleum industry, however, departures from the control point calling for manual resetting of the instrument cannot generally be tolerated, and it is necessary to provide controllers with automatic reset.

## Automatic Reset.

For the present purpose this can be regarded simply as an automatic means of doing what the operator does when he resets the index pen of a
controller after a load change. There is no need to consider the mechanism by which this resetting is effected. It should, however, be understood that it is capable of re-adjusting the air pressure to the control valve to the limit in either direction in order to restore the recording pen to the control point. The rate at which this re-adjustment is effected can be modified by altering the setting of the reset mechanism.

## Automatic Controllers.

Automatic controllers can be divided into three main groups, in so far as their operation is concerned. The first of these is on-off controllers.

## On-off Controllers.

In this group there are only two possible positions for the control valve, fully open or fully shut, dependent on whether the variable under control is above or below the control point, or vice versa. Controllers of this type can only be applied successfully when there is considerable storage capacity for the variable under control, and find virtually no applications in continuous refining processes, where in most cases storage capacity is very small.

The second group is throttling controllers, with variable throttling range.

## Throttling Controllers.

Instruments of this group are so designed that the control valve is held in a position intermediate between fully open and completely shut, the exact position being dependent on the position of the recording pen relative to the index pen. They can be used successfully in applications where appreciable permanent departure from the original control point with change in load can be tolerated. Such applications are, however, comparatively rare in petroleum refining, and most of the instruments used in modern plant fall into the third group, throttling controllers with automatic reset.

## Throttling Controllers with Automatic Reset.

These instruments combine throttling control, having the width of throttling range adjustable over wide limits, with automatic compensation for load changes through the automatic reset mechanism. In their standard form they are capable of dealing with all normal process lags, and are the type invariably chosen for any critical control service.

## Instrumentation in Practice.

Having outlined such theory of automatic controllers as concerns the plant operator, and divided the range of instruments available into three main groups, we will now consider how the actual user of such instruments, the plant operator, can assist the instrument engineer. He can do so materially both at the design stage of a new plant, and also during its subsequent operation. The determination from the flow-sheet of those portions of the plant which are inherently stable will avoid the installation of instruments which subsequently prove to be unnecessary. The instrumentation scheme should be studied for possible unfavaurable reactions
of one instrument upon another, or upon another part of the plant. Such reactions will probably have been anticipated by the instrument engineer, but the plant operator should carefully check the proposed instrumentation from his own viewpoint. Special attention should be paid to the action chosen for each instrument on air failure, not only as regards the immediate effect on the variable controlled by the particular instrument, but also as regards the effect on the plant as a whole. Control valves will have been sized by the instrument engineer in accordance with the quantities shown on the design flow-sheet for normal operation. Normally the operating range of the modern control valve is sufficient to take care of the variations in load that will be encountered, and leave adequate margin for unavoidable errors in the initial sizing. The plant operator can, however, materially assist the instrument engineer by drawing his attention to any valves in which under-sizing, or alternatively over-sizing, will prove particularly troublesome.

Modern practice is to group the majority of the control instruments in a central control room, and this arrangement has many obvious advantages. However, in the case of flow and pressure control and measuring instruments, it entails the use of long instrument lines from the orifice or pressure tapping point. This not only makes for sluggish response of the instruments, but also increases the risk of fire in the control room in case of leakage from instrument lines which may be under high pressure. Both these disadvantages can be avoided by the use of remote recording instruments using electric or pneumatic transmission from the measuring elements located out on the plant. Such instruments are necessarily more expensive than the normal type, but against the increased cost should be offsett the saving in not having to run long instrument lines, the better response obtained in the case of flow instruments, and the fact that the control room need no longer be regarded as a hazardous area. It would appear that the remote recording type of instrument might be more widely employed than it is at present. With the foregoing in mind, the plant operator can materially assist the instrument engineer by indicating those instruments which must be located in the control room, and those which can equally conveniently be placed out on the plant with a considerable saving in cost.

As regards plants which are in operation, the user of control instrumentsthat is, the plant opera'rir-can greatly assist the instrument department in their work by informed co-operation at all levels. To this end, it seems desirable that all plant-operating personnel down to the status of chargehand should have some instruction in the elementary theory and practice of automatic control. Too often reports of faults are very laconic, and there is an impression amongst the operating personnel that they can make no useful contribution to the work of the instrument department. The report of a fault should include at least a precise statement of the symptoms, exactly when the trouble occurred, and whether its onset coincided with any known change in operating procedure or the material being processed. Any steps taken to overcome the trouble should be given in detail. The plant charge-hand and the instrument mechanic sent to rectify the fault must collaborate closely if the fault is to be rectified with minimum delay, and the instrument put back into operation with the least disturbance to the plant. The plant charge-hand will be considerably assisted in this if
he has sufficient theoretical knowledge to understand the steps that the instrument mechanic is taking, at any rate in principle.

As far as recording instruments are concerned, and most important control instruments in a refinery plant are of this type, certain common faults can be readily diagnosed from a study of the trace produced on the chart. It may be of interest to consider these in some detail.

## Hunting.

True hunting must be cyclic (Fig. 3), with a regular periodicity. It may, however, start at a considerable amplitude and then gradually reduce its amplitude to zero, after which satisfactory control is obtained until some fresh disturbance to the system restarts the hunting. In general, hunting is due to process lags, and the remedy is the use of a wider throttling range. In itself a wider throttling range will increase the tendency

$$
\begin{aligned}
& \text { Hurn }
\end{aligned}
$$

Fig. 3.
for droop, or departure from the control point, on changes in load. Normally, the droop will be corrected by the automatic reset mechanism, but in order to reduce the amount of work which the latter has to do, it is undesirable to employ a throttling range much wider than is strictly necessary to cope with the process lags. If alteration to the throttling range fails to make any appreciable impression on the hunting, it is almost certain that it is a reflection of hunting in some other instrument, and the cure must be looked for in locating and resetting the instrument concerned. For example, apparent hunting of the pressure controller on a distillation column may actually be due to hunting of the top temperature controller, which is causing a cyclic variation in the amount of reflux.

## Droop.

This has been described already as characteristic of throttling controllers not provided with automatic reset. Assuming that the instrument concerned is provided with automatic reset, and that the case is not one of the


Fig. 4.
incorrect application of a simple throttling controller, this fault can only be due to the automatic reset mechanism becoming inoperative (Fig. 4).

## Wandering.

As will be seen (Fig. 5) this consists of a somewhat irregular departure from the control point for an appreciable period, followed by a gradual
return to it, with possible overshooting and further wandering on the other side of the control point. This fault is normally only met with in applications involving considerable process lags, and is due to the use of too wide a throttling range setting, or too slow operation of the automatic reset.


Fig. 5.
The remedy consists in narrowing the throttling range, or in speeding up the operation of the automatic reset mechanism by cutting out some of the pneumatic resistance.

## Sticking of Control Valve.

This fault may be immediately recognized by the characteristic "stepped" trace on the chart (Fig. 6), and the remedy is to reduce the friction in the control valve. In some cases, such as high pressure and high temperature


Fig. 6.
operation where there is bound to be appreciable friction in the valve gland, it may be essential to employ a valve positioner. The manner in which this is connected is shown diagrammatically in Fig. 7. The device consists essentially of a pressure relay supplied with air at the standard working


Fig. 7.
pressure, usually 17 p.s.i., from an independent source. Its operation can best be illustrated by an example. Supposing the controller increases the air pressure on the output side from 8 p.s.i. to 9 p.s.i. The control valve should then take up a position appropriate to 9 p.s.i. If, however, there is appreciable friction in the valve system, the valve may only move to a position appropriate to $8 \frac{1}{2}$ p.s.i. The linkage between the valve spindle and the positioner mechanism will indicate to the latter that the spindle has not moved the correct amount, whereupon the positioner will apply an increasing air pressure to the diaphragm of the valve until the latter does eventually move. If, as is probable, the valve overshoots the correct
position, the positioner will automatically reduce the diaphragm pressure, until by a series of successive overshootings the valve spindle is brought to rest in the correct position. To obtain the best performance from any controller, the use of valve positioners is desirable in all cases where there is the possibility of considerable friction in the valve gland, also where the distance between the control instrument and the control valve is great.

The contribution which the operating personnel can make to the improved operation of the control instruments of any plant will largely consist of the correct and careful reporting of faults, carried to its ultimate conclusion, so that eventually no fault remain to be eliminated. For this to be acheived they must not only have a high standard of performance to aim at but must also realize the limitations of their control instruments, as well as having a clear idea of what irregularities in the various factors under measurement or control can justifiably be laid at the door of the control instruments, and what are inherent in the operation of the process and the design of the plant. For example, where the top temperature of a distillation column is controlled by varying the quantity of reflux returned, and at the same time a flow-recorder is provided to measure the quantity of reflux, the plant operator may reasonably expect a smooth trace on the chart from the temperature controller, but cannot at the same time expect a smooth chart from the reflux flow-recorder.

A point which may easily be overlooked when a plant has been in operation for a considerable period is the correctness of control valve sizes. It is quite frequently found necessary to operate with the by-pass round a control valve cracked open; alternatively it may be necessary to throttle one of the isolating valves on one side of a control valve to limit the maximum quantity passed by the latter. In neither of these cases, in general, can the controller give its best performance, and the attention of the instrument department should be drawn to the fact, so that the control valve may be exchanged for one of the correct size. The only case in which it may be necessary to retain the partially cracked by-pass is one in which the variations in load are too great to be taken care of by the range of the normal control valve. Even in such a case, the preferable course is to install two control valves in parallel, of different sizes which between them will cover the load range required, and to select the control valve appropriate in size to the operating conditions at the time.

To illustrate the principles dealt with in the foregoing, the instrumentation of a simple distillation unit will be considered. A simplified flow-sheet is shown in Fig. 8, and it is assumed that the unit charges a reduced crude and produces gas oil as overhead, lubricating oil distillates from two side streams, and bitumen as bottoms. In this case the column will operate under vacuum, and it will be necessary to pump away all products. For the sake of simplicity all heat exchangers and product coolers have been omitted from the flow-sheet, since they will have no bearing on the instrumentation.

The feed to the plant will be controlled by the recording flow-controller F.R.C.1. We have assumed that the feed pump will be of the rotary positive-displacement type, consequently the control valve has been placed in a by-pass between the delivery and suction of the pump. For smooth operation of the plant it will be essential that the rate of feed be kept
constant, independent of load changes brought about by changes in temperature or viscosity of the feed. Consequently, controller F.R.C. 1 must be a full-throttling controller equipped with automatic reset.
The furnace outlet temperature will be a critical factor in the operation

- of the plant, since the penetration of the bitumen produced will largely depend on this temperature. There will be a considerable process lag in the passage of the feed through the furnace, and there may also be appreciable load changes. The outlet temperature controller must therefore be of the full-throttling, automatic reset type. It has been assumed that the heater is oil fired, using pressure-atomizing burners. Disregarding for the present the special relay shown between the temperature controller


Fig. 8.
and the pressure controller, the temperature controller is arranged to reset pneumatically the control point of the indicating pressure-controller I.P.C.1. This pressure-controller in its turn regulates the control valve in the return fuel oil line from the burners to maintain the required control pressure at the burners. With this type of burner the quantity of fuel passed, and consequently the heat input to the furnace, is proportional to the fuel oil pressure at the burners. The object of using a pneumatically reset pressure-controller instead of connecting the output side of the tem-perature-controller directly to the control valve, is to enable incidental variations in the temperature or viscosity of the fuel oil, or in the output of the fuel pump, which would affect the burner pressure, to be immediately corrected by the pressure controller before they have had time to affect the outlet temperature. The pneumatic setting device on the pressure-
controller, which shold not be confused with the normal automatic reset mechanism, consists simply of a bellows connected to the output side of the temperature controller and linked to the normal setting arrangement of the pressure-controller so that the control point of the latter can be set over the required range by variations in the output pressure from the temperature controller. With rise in temperature the control point of the pressure-controller is lowered, and vice versa.

With most refinery heaters the process lags are such that even the most advanced type of temperature controller cannot deal with them without occasional departures from the control point for a longer period than can be tolerated. In such cases it is necessary to employ a special relay between the temperature-controller and its controlled valve, or in this case between the temperature-controller and the pressure-controller. This special relay has the power of analysing the rate at which the temperature is departing from the control point before any serious departure has taken place. It then passes on to the control valve, or in this case to the pressure-controller, a greater change in air pressure than the change which has been fed into it, the degree of magnification being proportional to the rate of change. This magnification, which can be adjusted by varying the settings of the relay mechanism, applies a drastic correction for rapid rates of change, and effectively overcomes the process lags.

The top temperature of the column will require careful control, and this has been arranged by recording temperature-controller R.T.C.2, which should preferably be of the potentiometer type, and must in any case be equipped with full throttling range adjustment and automatic reset. The use of the potentiometer type in preference to the thermometer type is advisable both to give a quicker response and also to avoid the use of long and vulnerable capilliary connexions between the temperature point in the vapour line and the instrument, which will be located in the control room. Since the control valve will probably be located some considerable distance from the instrument, it will be advisable to equip it with a valve positioner.

Part of the gas oil overhead product will be returned to the column as reflux, under the control of R.T.C. 2 as already mentioned, and part will have to be diverted to storage. The latter quantity is controlled by liquid level controller L.L.C.1, of the external float-cage type, which regulates the control valve shown on the line to storage, Although this level controller must be of the full-throttling type, variations in the exact level held in the accumulator tank with variations in load will not matter, and the instrument need not be equipped with automatic reset. For the correct functioning of R.T.C. 2 and L.L.C. 1 it is evident that the pressure upstream of their respective control valves must be held as constant as possible. This is achieved by the direct-acting pressure controller P.C.1, which regulates the steam supply to the gas oil pump.

As regards sidestream control, the simplest and generally the most satisfactory arrangement is to withdraw the sidestream at a constant rate, which is re-adjusted only when a change in the specification of the sidestream is required. Usually there is a constant head between the draw-off tray level and the sidestream stripper, and all that is required is the provision of a remote operated valve, as shown, which can be manually
set from the control room. It will be seen from the flow-sheet that remote operated valve R.O.1 regulates the first sidestream, and R.0. 2 the second sidestream. The corresponding flow recorders, F.R. 1 and F.R.2, will be located in the control room, with their orifices installed in the lines to storage.

Liquid level controllers L.L.C. 2 and L.L.C. 3 regulate the bottom level in the two sidestream strippers by control of the steam supply to the corresponding pumps. Usually variation in level in the strippers over the range of the normal outside float-cage level controller, which is the type that will most probably be employed, can be tolerated consequent on changes in load. If, however, the design of the stripper is such that the level must be held very closely to the same control point, irrespective of changes in load, then full-throttling controllers fitted with automatic reset must be used for this service. In order to obtain a readable chart on flow-recorders F.R.1 and F.R. 2 it is essential that there should be no hunting of level controllers L.L.C. 2 and L.L.C.3. Since the width of throttling range that can be employed in any instrument without automatic reset is limited, it is preferable that these level controllers should in any case be provided with automatic reset.

The bottom level in the main column has been shown as controlled by liquid level controller L.L.C.4, of internal float type, regulating a control valve in a by-pass between the delivery and suction of the positive displacement rotary bottoms pump. To reduce to the minimum variations in the bottom level, with variations in load, which may be considerable, L.L.C. 4 should be fitted with automatic reset mechanism. Since the control valve will be handling bitumen, with the strong probability of the valve sticking on occasions, it should be equipped with a valve positioner.

Even with the simple example of refinery plant which has been chosen as an example there are several alterative instrumentations which could be put foreward as workable propositions. The one illustrated should not be regarded as the only one, or necessarily the best, but merely as a typical example.

# THE FLUID SOLIDS TECHNIQUE: APPLICATIONS IN THE PETROLEUM INDUSTRY.* 

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A NEW chemical engineering technique involving the use of finely-divided solids is receiving widespread application in the petroleum industry, and its use in other industrial fields, such as the chemical, coal processing, and metallurgical, is under active consideration. This technique, an outgrowth of the Standard Oil Development Company's work in developing the widely accepted fluid catalytic cracking process, potentially has application to any process in which large quantities of heat are transferred, or in which very intimate contact between gases and solids is desired. The petroleum industry has already applied the fluid solids technique on either a commercial or semi-commercial scale to both catalytic and non-catalytic fuel production processes. It is the object of this paper to explain the basic elements of the Fluid Solids Technique, and to describe three specific applications of this development in the petroleum field, namely, the catalytic processing of gas oils, the extraction of liquid fuels from shales, and the synthesis of the higher hydrocarbon homologues from natural gas.

## Basic Elements of the Fluid Solids Technique.

Fundamentally, the fluid solids technique represents a useful application of two basic properties or characteristics of finely-divided solids. These properties may be described simply as follows:
(1) Properly sized solids, when mixed with a gas, will form a homogeneous solids-gas mixture or " fluid," this "fluid" having flow properties similar to ordinary liquids but its density being subject to variation through simple manipulation of either the solids to gas ratio or the flowing conditions.
(2) A powdered solid, when suspended in a gas stream flowing upwards at relatively low velocities, will form, contrary to Stokes' law, a continuous dense phase which in many aspects resembles a boiling liquid and which assumes a relatively well defined level.

The first of these properties makes possible the circulation of vast quantities of solids without benefit of mechanical devices, such as pumps, elevators, etc, and it also allows the use of more or less conventionally designed equipment, such as pipes, valves, and exchangers, to handle and to control the solids. The second property provides means for carrying out such functions as heat transfer under excellent conditions, and also for providing process reaction time requirements in reasonably sized equipment.

[^1]The fluid solids technique as applied to manufacturing processes consists essentially of either one or both of two basic elements, namely, a circulating system and a zone in which a concentrated or "dense phase" of solid is built up or maintained for the basic purpose of carrying out a desired reaction. An illustration of a simple combination of these two elements is given in Fig. 1.

## Circulation of Solids.

The circulation system consists of a standpipe in which the static head of the flowing solid itself builds up the pressure requisite for its circulation, and a carrier line which contains a gas-flowing stream into which the solids


Fig. 1.
BASIC ELEMENTS OF THE FLUID SOLIDS TECHNIQUE.
are dispersed and are carried to a reaction zone. The fluid solids in the standpipe are maintained in a relatively high density state in order that reasonable build-up of static pressure per unit length of standpipe will be obtained. However, the solids mixture, being compressible, can attain excessively high densities such that the mixture loses its "fluid " characteristics; gas is accordingly added to the solids mixture at points along the length of the standpipe to maintain its density in a " fluid " range. - Control of catalyst flow in the standpipe is maintained by means of a modified gate type valve located at the base of the standpipe. Pressure having been built up in this manner, the solids mixture can then be injected into a suitable gas stream for conveyance to any desired point, normally a reaction zone. The density of the solids-gas mixture in the carrier line is maintained low in order to facilitate circulation of the solids. Low density mixture is obtained simply by operating at relatively high gas velocities and maintaining a low solids/gas ratio.

## The Fluid Dense Bed.

A zone or bed of high solids concentration can be established and maintained simply by controlling the velocity of a solids-gas mixture at a relatively low level, e.g., 1 to $3 \mathrm{ft} / \mathrm{sec}$, at which conditions the solids tend to settle out and disengage from the gas. The bed formed as a result of this phenomenon is of more or less uniform density, but is in a continuous state of violent agitation-a fact which results in extremely efficient contacting of gas with solids and also in uniform temperature maintenance. A fluid bed of this type can be maintained with or without circulation of solids from it. In cases where circulation is carried out, solids can be charged to the bed either directly from a stand-pipe in a dense state, or in a dilute phase by means of the fluidizing gas as is shown in Fig. 1. Similarly, removal of the solids from the bed can be accomplished by direct withdrawal through standpipes, or by entrainment overhead with the effluent gases. The former method, illustrated in Fig. 1, results in simpler equipment to separate the solids from the gas.

## Versatility of Application.

The specific arrangement and combination of the basic elements of the fluid solids technique described is obviously subject to wide variation depending on the particular application. For example, functions such as heat removal or exchange can be readily carried out by either immersing coils directly in a dense phase bed, or by recycling solids through a standpipe and heat exchanger located in the dilute phase carrier line. The fluid technique is obviously versatile in its application, and the American petroleum industry alone has developed applications of the technique to a variety of fuel production processesp which involve both catalytic and non-catalytic reactions and which may or may not require the circulation of solids.

## The Fluid Catalyst Cracking Process.

The most extensive industrial application of the fluid solids technique at present is in the catalytic cracking of petroleum fractions, an application which involves the use of catalytic solids and the circulation of the solids between a reaction and regeneration zone. The use of the fluid technique in a regenerative catalytic process of this type has resulted in substantial simplification in design, construction, and operations over fixed-bed type plants, and has imparted to the fluid catalyst process a degree of flexibility as regards choice of feed stocks and operating variables that has not been heretofore possible with either the fixed or the moving bed-type catalytic processes. The adoption of the fluid catalyst process by the petroleum industry has as a result been rapid and widespread; developed in the extremely short period of three years preceding the entrance of the United States into World War II, it assumed a vital position in the war-time economy of the United States, supplying a major share of the raw materials needed for the production of 100 -octane number aviation gasoline and synthetic rubber.

## Description of Process.

A fluid catalyst cracking plant is composed of essentially three sections : cracking, regeneration, and oil product fractionation. The cracking reaction takes place continuously in one reactor, the spent catalyst being removed and replaced continuously for simultaneous regeneration in a separate vessel. Continuity of flow of catalyst, as well as of oil, is thus accomplished with the result that the characteristic features of fixed-bed designs involving the intermittent shifting of reactors through cracking, purging, and regeneration cycles are eliminated. The flow through a typical plant is as shown diagrammatically in Fig. 2.


Fig. 2.
THE FLUID CATALYST CRACKING PROCESS,
Regenerated catalyst is withdrawn from the regenerator and flows by gravity down a standpipe wherein a sufficiently high pressure head is built up on the catalyst to allow its injection into the fresh liquid oil stream. The resulting mixture of oil and catalyst flows into the reaction vessel in which gas velocity is intentionally low so that a high concentration of catalyst will result. The cracking which takes place results in carbon deposition on the catalyst, thereby making necessary regeneration of the catalyst. The cracked product oil vapours are withdrawn from the top of the reactor after passing through cyclone separators to free them of any entrained catalyst particles, while the spent catalyst is withdrawn from the bottom of the reactor and is injected into a stream of undiluted air which carries the catalyst into the regeneration vessel. The products of combustion resulting from the regeneration of the catalyst leave the top of this vessel and pass through a series of catalyst recovery equipment which consists of cyclone separators and a Cottrell precipitator. The regenerated catalyst is withdrawn from the bottom of the vessel to complete its cycle.

## Operating Range.

The flexibility of the fluid catalyst process permits choice of cracking operations over wide ranges of temperatures, conversion levels, feed stocks, and catalyst. Each of these factors affects profoundly the results that will be obtained. Cracking at low temperatures produces gasolines characteristically low in olefin content, while gasolines produced at high tempera: ture levels are high in both unsaturate and aromatic components. Depth of cracking and feed-stock type similarly affect product yields and qualities. In the application of fluid eatalytic cracking to refinery operations, therefore, the type of operations are determined primarily by the economics and demands of the refiner, rather than by narrow process limitations.

## War Products Operation.

To satisfy war-time demands and aviation fuel specifications, singlepass, high-temperature operation of the fluid plants was generally found to be optimum, resulting in a high yield of butylenes which could be used for


Fig. 3.
aviation gasoline production by fluid catalyst crácring wartime ECONOMY OPERATION.
either rubber production of alkylate manufacture, and in reasonable yields of high anti-knock quality naphtha fractions which, upon suitable treatment, were extremely desirable components for 100 -octane number aviation fuel. Fig. 3 illustrates a typical application of the fluid process in a refinery scheme of operations to produce Grade 100/130 aviation fuel; based on gas oil charged to the fluid cracking plant, roughly 78 brls of finished 100 -octane number aviation fuel containing 4 ce of $\mathrm{TEL} / \mathrm{gallon}$ could be produced from 100 brl of gas oil charge.

Other war-time operations of the fluid process included low-temperature single-pass operations, as well as two-stage operations in which the charge to the second stage was the naphtha produced from first stage cracking the original gas oil feed. A tabulation of the characteristics of the aviation gasolines produced from each type of operation is given in Table I. Operations such as these result in high octane number quality base stock primarily,
with relatively little production of the butylenes which were in such great demand as raw material for alkylate and synthetic rubber production.

Table I.
The Fluid Catalyst Cracking Process Typical Product Quality of Aviation Base Stocks.

| Type operation : | Single-stage. |  |  | 2-Stage. |
| :---: | :---: | :---: | :---: | :---: |
| Cracking temperature Feed-stock type * : | $\begin{aligned} & \text { High } \\ & \text { P. } \end{aligned}$ | $\begin{aligned} & \text { Low } \\ & \text { P. } \end{aligned}$ | $\begin{aligned} & \text { Low } \\ & \text { N. } \end{aligned}$ | $\begin{aligned} & \text { High } \\ & \text { P. } \end{aligned}$ |
| Gravity, ${ }^{\circ}$ API | $60 \cdot 2$ | 67.7 | 57.6 | 56.6 |
| Vapour pressure, RVP | 7 | 7 | 7 | 7 |
| Aniline point, ${ }^{\circ} \mathrm{F}$. | 66 | 122 | 85 | 64 |
| Sulphur, Wt.-\% | 0.03 | 0.01 | 0.01 | 0.03 |
| Bromine No. | 63 | 20 | 10 | 13 |
| Acid heat, ${ }^{\circ} \mathrm{F}$ A.S.T.M. Distillation : | 135 | 39 | 24 | 27 |
| I.B.P., ${ }^{\circ} \mathrm{F}$. | 121 | 114 | 114 | 108 |
| $10 \%$ at, ${ }^{\circ} \mathrm{F}$ | 141 | 141 | 140 | 139 |
| $50 \%$ at, ${ }^{\circ} \mathrm{F}$ | 190 | 189 | 203 | 210 |
| $90 \%$ at, ${ }^{\circ} \mathrm{F}$ | 292 | 294 | 273 | 293 |
| F.B.P., ${ }^{\circ} \mathrm{F}$ | 338 | 316 | 300 | 324 |
| Octane Number Rating: |  |  |  |  |
| A.S.T.M., Clear . | 80.5 | 77.9 | $81 \cdot 6$ | $83 \cdot 1$ |
| A.F.D. -1C, 4 ec TEL/G | $90 \cdot 6 \dagger$ | $93 \cdot 3$ | 96.0 | $97 \cdot 0$ |

* "P" designates a paraffinic base type gas oil, and "N" a naphthenic type stock.
$\dagger$ The anti-knock quality can be increased to 96 A.F.D-1C with 4 ce TEL/gal. by hydrogenating the fraction boiling below $225^{\circ} \mathrm{F}$.


## Peacetime Economy Operations.

Peace-time operations of the fluid cracking plants has been carried out at somewhat lower cracking severities, but at moderately high temperatures, in order that a high anti-knock quality product might be obtained. Typical results from a commercial plant operating at such conditions is given in Table II. Based on gas oil charged, a 40 per cent yield of 10 lb RVP motor gasoline having a clear C.F.R.-R octane number of 95 is readily obtained when cracking a paraffinic type gas oil. If the butylenes and propylenes produced are considered as potential motor gasoline components, they would, when polymerized, increase the yield to 50 per cent on feed and the clear C.F.R.-R quality to 96.1 octane number. Commercial cracking operations on naphthenic type feed stocks have produced motor gasolines having anti-knock qualities as high as 98 C.F.R.-R clear, and 100 C.F.R.-R with 1.5 ce TEL. In general, the motor gasoline produced from fluid operations is quite stable, and no finishing treatment is normally required aside from a light caustic or soda wash and the addition of an inhibitor.

## Extent of Application.

The performance of thirty-four commercial plants during the war period established the fluid process as an advanced means of converting the heavier petroleum fractions with maximum efficiency and economy into premium aviation and motor fuels. Since the end of the war the bulk of

Table II.
The Fluid Catalyst Cracking Process. Typical Results-Peace-Time Economy Operations.

new catalytic cracking installations, installed and projected, are the fluid type. World-wide fluid catalytic cracking capacity in operation or under construction to-day amounts to more than $1,000,000 \mathrm{brl} /$ day, or somewhat ovar 60 per cent of the total catalytic cracking capacity in the industry.

## The Fluid Shale Oil Retorting Process.

The fluid solids technique has been applied to extracting oil from oilbearing shales, an application which basically involves supplying a solid raw material to a retorting zone and maintaining that zone in an operable condition and at a uniform temperature. This process, while not in use at present on a commercial scale, has been developed satisfactorily through the pilot plant stage by the Standard Oil Development Company. Commercial scale application of this process is contingent on the general economics involved in obtaining oil from shale deposits.

Description of Process.
The processing of shale to recover its oil involves simply heating the raw material and maintaining it at temperatures of 700 to $1000^{\circ} \mathrm{F}$ for a period
of 8 to 20 minutes, at which conditions the oil evolves quite readily as vapour. The process in essence, therefore, consists of a retorting vessel in which the shale is decomposed, a burner vessel which supplies the process heat requirements, and a solids circulating system for transferring heat and for conveying raw and spent solid material to and from the processing zone proper. A diagram showing the principal features of a projected commercial scale plant is given in Fig. 4 and is described below :

Shale rock, ground to a suitable size, is charged to a feed hopper from which it is fed by means of a standpipe into a hot spent shale stream which circulates from the burner vessel to the retort. The combined fresh and spent shale stream, now at retorting temperature, is carried by steam into the retort vessel in which a dense phase of solids is maintained by operating at gas velocities of 1.0 to $1.5 \mathrm{ft} / \mathrm{sec}$. The retorting vessel is sized to provide


Fig. 4.
THE FLUID SHALE OIL RETORTING PROCESS.
the time necessary for converting the kerogen content of the shale to hydrocarbon vapours. The volatilized products from the retort pass overhead to a product recovery and treating system.

Spent shale is withdrawn from the retort, is stripped of residual hydrocarbon vapours by steam, and is injected into an air stream which carries it into a burner vessel where a sufficient amount of the residual carbon and hydrogen in the spent shale is burned to supply the heat requirements of the process. A portion of the burned spent shale is recycled as a heat carrier to the retort, while the remainder is withdrawn from the dense phase through a cooler to recover waste heat prior to its disposal as waste. Waste heat is also recovered from the flue gas which disengages from the solids in the burner vessel.

A processing scheme involving the use of a single vessel to carry out the retorting and combustion can also be used. In such a scheme, combustion air is introduced directly into the retorting zone and a portion of the shale
oils is burned to supply the heat required for the decomposition of the shale which is occurring simultaneously. While such a scheme simplifies the retorting section, recovery of products is made far more difficult due to the dilution of the hydrocarbons with the products of combustion.

## Experimental Operation.

Development of the fluid shale process was carried out on a pilot plant scale using as raw material a relatively rich Australian shale which contained by weight 63 per cent carbon, 8 per cent hydrogen, and 0.7 per cent sulphur. Preliminary assay work on the material in a fixed-bed apparatus bed indicated that the shale assumed a semi-plastic state at about $825^{\circ} \mathrm{F}$, with the result that agglomeration of the spent shale occurred. In the pilot plant, however, non-clinkering " fluid" beds of shale were readily maintained by virtue of the fact that the fluid type operation made it possible to heat instantaneously the cold shale feed to retorting temperature by mixing with the fluid mass of spent shale and to maintain an extremely uniform temperature throughout the retorting zone-two factors which are requisite for a non-clinkering operation. Retorting was carried out at temperatures ranging from $850^{\circ} \mathrm{F}$ to $1000^{\circ} \mathrm{F}$.

Shales that are leaner in oil content than the Australian have also been satisfactorily processed. The product yields obtained were lower, but were consistent with assays of the raw material.

## Process Results.

The extent of removal of hydrocarbons from a given shale is principally a function of retorting temperature. Results obtained from the pilot plant work on Australian shale, shown in Fig. 5, indicate that when retorting at $1000^{\circ} \mathrm{F}$ about 85 per cent of the carbon and hydrogen in the shale was


Fia. 5.
retorting australian oil shale.
Shale assay: 63 per cent $C$; 8 per cent $H ; 0 \cdot 7$ per cent $S$.
recovered as hydrocarbon product, whereas recovery was but 65 per cent when retorting was carried out at $850^{\circ} \mathrm{F}$. Variations in residence time in the 8 - to 20 -minute range indicated no significant effect of this variable on rate of removal of hydrocarbon or on results obtained.

Retorting of the Australian shale yielded a relatively high boiling oil,

15 to 25 per cent of which was in the gasoline boiling range and 40 to 45 per cent boiling above $800^{\circ} \mathrm{F}$. The gravity of the oil ranged from 20 to $25^{\circ}$ A.P.I., and its sulphur content was 0.5 to 0.7 wt per cent. The distribution of hydrocarbons in the total product varied markedly with retorting temperatures, the gas yields increasing from 4.5 wt per cent on shale at $850^{\circ} \mathrm{F}$ operations to $15 \cdot 2 \mathrm{wt}$ per cent at $1000^{\circ} \mathrm{F}$.

The oil product as obtained is unsuitable for use without further treatment because of the nitrogenous and sulphurous compounds present. The further processing that is required depends on the use made of the products. The spent shale from the retorting operations is relatively rich in carbonaceous matter, 35 to 45 wt per cent, and its heating value of roughly $8000 \mathrm{~B} . \mathrm{Th} . \mathrm{U} / \mathrm{lb}$ qualifies it for consideration as a powdered solid fuel. Typical results obtained from the pilot plant at two different temperature levels are given in Table III.

## Table III.

Fluid Retorting of Australian Shale.
Shale Asssy : 63 wt per cent carbon, 8 wt por cent hydrogen.

| Retort temperature ${ }^{\circ} \mathrm{F}$. | 896. | 1004. |
| :---: | :---: | :---: |
| Process yields * |  |  |
| Wet gas, wt \% | $5 \cdot 4$ | 17.1 |
| Crude oil, wt \% . | $43 \cdot 1$ | $38 \cdot 1$ |
| Spent shale, wt \% | 48.8 | $40 \cdot 3$ |
| Carbon burned, wt \% | 1.6 | $4 \cdot 0$ |
| Hydrogen burned, wt \% | 0.8 | 0.5 |
| Crude Oil Quality: |  |  |
| Gravity, A.P.I. | $25 \cdot 1$ | 20.5 |
| Sulphur, wt \% | $0 \cdot 53$ | $0 \cdot 64$ |
| A.S.T.M. distillation : |  |  |
| $5 \% \mathrm{at},{ }^{\circ} \mathrm{F}$ | 269 | 270 |
| $10 \%$ at, ${ }^{\circ} \mathrm{F}$ | 375 | 311 |
| $30 \%$ at, ${ }^{\circ} \mathrm{F}$ | 586 | 508 |
| 50\% at, ${ }^{\circ} \mathrm{F}$ | 835 | 695 |

* Based on shale charged.


## Application.

Retorting of shale on a commercial scale to produce oil in competition with oil from other sources is contingent primarily on richness of the shale, the cost of obtaining the raw shale rock, and the location of the shale beds. With petroleum costs at present levels, the processing of shale in the U.S.A. is not competitive with refining of naturally occurring crude oils. A process for extracting the oil from the shale rock, however, is available for application to a commercial scale whenever the economics become favourable or whenever necessity demands.

## The Fluid Hydrocarbon Synthesis Process.

Application of the fluid solids technique has been made to the synthesis of hydrocarbons from carbon monoxide and hydrogen, a non-regenerative catalytic reaction which evolves extremely large quantities of heat. In this
instance, the fluid solids technique is attractive primarily because of the high rate of heat transfer than can be obtained from its application. The effect of this factor alone has resulted in outstanding simplifications in plant design and consequently in reduction in plant investment since cooling surface, a major cost item in a fixed-bed type design, is but 1 per cent of that needed in a fixed-bed plant. The development of the process by the American petroleum industry has reached an advanced scale, and its application to commercial production is being made.

## Description of Process.

The synthesis of liquid hydrocarbons involves simply the production of a suitable mixture of hydrogen and carbon monoxide, and the reaction of the mixture in the presence of a catalyst; regeneration of the catalyst is not required. The synthesis gas can be produced either from coal or from


Fig. 6.
THE FLUID HYDROCARBON SYNTHESIS PROCESS. -
naturally occurring gas, but American development has been largely based on the use of the latter. A simplified diagram showing the basic features of a hydrocarbon synthesis plant incorporating the fluid solids technique is given in Fig. 6.

Natural gas containing roughly 90 per cent methane is partially burned with oxygen in a generator to form a mixture of carbon monoxide, hydrogen, and water. Water is removed from this mixture in a conventional scrubbing tower, and the resultant synthesis gas is charged in admixture with process recycle gas to a reactor which contains the solid catalyst in a fluidized state. The effluent gas from the fluid catalyst bed passes overhead through recovery equipment which removes any entrained catalyst and returns it to the catalyst bed. Heat removal from the reaction zone is accomplished by means of cooling tubes inserted in the catalyst bed itself, and the heat of reaction is absorbed by water to produce steam.

The reactor effluent gas is cooled and condensed. A water layer containing water soluble alcohols and acids produced in the process is separated
from the oil layer, a portion of the gas separated is recycled back to the reaction zone for further conversion. The liquid hydrocarbons are then recovered, stabilized, and treated to improve stability characteristics and anti-knock quality.

## Process Conditions.

Experimental work on the hydrocarbon synthesis process using the fluid technique has been carried on for several years on a semi-commercial scale by the Standard Oil Development Company. The synthesis reaction is normally carried out at a pressure of $250-450$ p.s.i.g. at temperatures ranging between $560^{\circ}$ and $750^{\circ} \mathrm{F}$. The catalyst used is generally iron, but work has been carried out using a cobalt catalyst.

## Product Distribution.

In a typical operation using an iron catalyst, roughly 90 per cent of the reactants fed are converted, yielding per cubic metre of gas fed 215 to 225 cc of hydrocarbons boiling higher than ethane. An additional quantity of water soluble alcohols and acids amounting to perhaps $25 \mathrm{cc} / \mathrm{cu} . \mathrm{m}$ of gas fed is also obtained. In terms of commercial scale production, 10,000 $\mathrm{brl} /$ day of oil can be produced from $120,000,000 \mathrm{ct} . \mathrm{ft} /$ day of natural gas; of this total oil, roughly 92 per cent is gasoline and the balance is diesel oil.
The hydrocarbons produced in the synthesis step contain appreciable quantities of oxygenated compounds which are undesirable from a product quality standpoint. The oxygenated compounds in this hydrocarbon phase may be recovered as such, or the entire mixture may be subjected to a treating step which will remove this material to yield a stable gasoline of improved anti-knock quality. The light hydrocarbons produced can be polymerized to increase the overall yield of liquid hydrocarbons. The overall gasoline pool produced from such integrated operations is high in antiknock quality, rating approximately 79 A.S.T.M. and 93 C.F.R.-R octane number; upon addition of 2 cc of lead tetraethyl per gallon of gasoline, the anti-knock quality is increased to 84 A.S.T.M. and 98 C.F.R.-R.
The oxygenated compounds in the aqueous phase consist largely of ethyl and propyl alcohols with smaller amounts of acids, aldehydes, ketones, and esters. Most of these compounds can be separated economically in a reasonable degree of purity.

## Application.

The hydrocarbon synthesis process using the fluid solids technique has been developed to a point where the manufacture of gasoline from natural gas is competitive economically in the United States to gasoline produced conventionally from crude oil. A commercial plant is now being constructed in the state of Texas, and construction of a second plant in Kansas is soon to follow.

## Applications in Other Industrial Fields.

Applications of the fluid solids technique to fuel production processes other than those described are under active development by the petroleum
industry. Among these are the coking of residual fuel oils, and the carbonization and gasification of coal. Industries other than the petroleum are also active in adapting the fluid solids technique : in the chemical industry, phthalic anhydride is being manufactured using a fluid solid catalyst, while in the metallurgical field, there are interesting possibilities for reduction of iron ore and for other purposes. It is evident that the fluid solids technique has aroused extensive interest throughout the industrial world, and its application to many types of industrial operations is visualized.

## REFINING SOUTH AMERICAN CRUDES.*

By Davis Read $\dagger$ and Gustav Egloff $\dagger$ (Fellow).

Virtually all modern refining methods have been applied to the processing of South American crudes. By far the greatest amount of work, both in the laboratory and in commercial operations, has been carried out on crudes produced in Venezuela. This is not surprising in view of the fact that in 1946 Venezuelan crude production comprised approximately 85 per cent of the total crude produced in South America.

## South American Production-1946.

Barrels (estimated).


The variation in the quality, i.e., the gasoline and sulphur contents, of these crudes covers nearly the same range as those produced in Central and North America, so that the refining of these oils presents no unusual problems.

With the present emphasis on the development both of oil resources and refining capacity, the volume of oil from all producing countries of South America is expected to increase during the next few years. As an aid to the oil technologist, this study presents a summary of information now available on the properties of a number of South American crudes and illustrates the application of several processes to the refining of these oils.

## Properties of Crudes.

The quality of South American crudes varies considerably and in many cases the variation in the properties of crude from a given field is quite large. The information contained in Tables I and II shows the properties of one sample from each of the fields studied.

In addition to the gravity and distillation characteristics, which determine in general the yields of refined products obtainable, the sulphur and salt contents of a given crude are important factors in determining the refining procedure required to produce marketable finished products. Both sulphur and salt cause corrosion in refining equipment and in order to meet

[^2]Table I.
Properties of Venezuelan Crude Oils.

| Field: | Lagunillas. | La Rosa. | Temblador. | Oficina. | Colon. | Jusepin. | " Western." * | Cumarebo. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Crude Oil :- |  |  |  |  |  |  |  |  |
| Gravity, ${ }^{\circ}$ A.P.I. | 16.9 | $23 \cdot 3$ | $32 \cdot 0$ | $22 \cdot 3$ | 31.4 | $33 \cdot 4$ | $38 \cdot 7$ | $47 \cdot 5$ |
| Sp. gr. at $60^{\circ} \mathrm{F}$. | $0 \cdot 9535$ | 0.9141 | 0.8654 | 0.9200 | 0.8686 | 0.858 | 0.8314 | $0 \cdot 7905$ |
| \% total sulphur | $2 \cdot 37$ | $1 \cdot 70$ | 1.0 | 0.90 | 0.89 | 0.55 | $0 \cdot 23$ | $0 \cdot 11$ |
| B.S. \& W., \% . | $0 \cdot 4$ | $0 \cdot 1$ | - | $0 \cdot 1$ | $0 \cdot 4$ | 0.4 | Trace | $0 \cdot 2$ |
| Salt as sodium chloride, $\mathrm{lb} / 1000 \mathrm{brl}$. | None | - | 5 |  | - |  |  | - |
| Cold test, ${ }^{\circ} \mathrm{F}$. . | Below 0 | Below 0 | 10 | Below 0 | Below 0 | Below 0 | Below 0 | 30 |
|  |  |  |  |  |  | ( 500 ml |  |  |
| 100 ml distillation : |  |  |  |  |  | distillation) |  |  |
| I.B.P., ${ }^{\circ} \mathrm{F}$. | 215 | ¢ 166 | 120 | 210 | 150 | 77 | 110 | 122 |
| $5 \%$. | 350 | 274 | 200 | 333 | 222 | 200 | 160 | 164 |
| 10\% . | 445 | 336 | 255 | 401 | 282 | 255 | 184 | 198 |
| 20\% | 572 | 466 | 320 | 493 | 382 | 350 | 234 | 242 |
| 30\% . | 646 | 572 | 390 | 558 | 484 | 447 | 280 | 288 |
| $40 \%$. | 675 | 648 | 490 | 622 | 572 | 535 | 348 | 350 |
| $50 \%$. | 692 | 684 | 580 | 670 | 654 | - | 444 512 | 406 483 |
| 60\% | 700 | 703 | - | 697 | 688 | - | 586 | 538 |
| $80 \%$. | - | - | - | 707 | 704 | - | 670 | 610 |
| 80\% . | - | - | - | 718 | 712 | - | 730 | 698 |
| \% over . | 89.5 | 92.0 | - | 724 | 93.5 | - | 98.5 | $97 \cdot 5$ |
| \% bottoms . | 83 | - | - | - | - | - | - | 1.4 |
| \% loss. |  |  | - | - | - | - | - | $1 \cdot 1$ |
| \% coke by weight | $10 \cdot 7$ | $8 \cdot 0$ | - | $7 \cdot 4$ | $6 \cdot 5$ | - | $1 \cdot 3$ | - |

* Exact field or fields not known.
Properties of Crudes from Argentina, Colombia, Peru, Ecuador, Bolivia, Brazil and Chile.


[^3](c) Crude distillation temperatures obtained under 10 mm vacuum and converted to atmospheric pressure.
sulphor specifications on the finished products it is necessary in some cases to install extensive treating facilities.

In specifying the refining scheme for a given crude many factors must be considered in determining whether the crude should be desalted and the equipment protected from corrosion by the use of alloys. In general, for high on-stream efficiency in a refinery having average thermal cracking capacity, desalting is recommended when the salt content of the charge exceeds about 15 to $25 \mathrm{lb} / 1000 \mathrm{brl}$. Similarly, extensive corrosion protection with alloys is usually needed when the sulphur content of the cracking unit charge exceeds 0.7 to 0.8 per cent. There are, of course, many exceptions to these general rules and the economics of each situation must be studied in working out the proper refining scheme.

The eight Venezuelan crudes listed in Table I vary in A.P.I. gravity from 16.9 to 47.5 with corresponding $400^{\circ}$ F E.P. gasoline contents of 5.7 to 50.9 per cent. The Lagunillas crude is typical of the relatively high sulphur, asphaltic or naphthenic type of crude, while the Cumarebo crude is more paraffinic and contains a relatively small amount of sulphur. Note that the crudes are listed in this table in the order of decreasing sulphur content.

The properties of crudes from one or more fields of all of the other oilproducing countries of South America are listed in Table II. With the exception of the Colombian and the El Sosneado, Argentina, crudes, these ails are quite low in sulphur content. The extremely high cold tests of the Itaparica and Candeais, Brazilian, crudes indicate their unusually high paraffin content. While the data available on the salt contents of these oils are somewhat limited, the Itaparica, Brazilian crude is the only one of the samples tested which contained an excessive amount of salt.

## Crude Distillation.

Tables III and IV show the yields and properties of the fractions obtained in laboratory distillation of samples of the various crudes. Most of the samples were fractionated to produce $400^{\circ} \mathrm{F}$ end point gasoline, kerosine, gas oil and reduced crude in 800 ml Hempel distillations, although in some cases only the gasoline was removed in the distillation. In the past the usual commercial practice has been to produce a $400^{\circ} \mathrm{F}$ end point straightrun gasoline which after treatment was sold directly, or blended with cracked gasoline for sale as motor fuel. With the recent trends towards higher octane ratings of finished motor fuel much information has been obtained on the effect of " under cutting," or decreasing the gasoline end point, on its octane number. Fig. 2 shows the effect of undercutting on the F-2 or motor method octane numbers of gasoline from twelve South American crudes. Similar data on three crudes are plotted on Fig. 2 to show the relationship between the end point and the $\mathrm{F}-2$ octane rating of the gasolines after the addition of 3 ce per gallon of tetraethyl lead. The corresponding yields expressed as volume per cent of the crude are plotted versus gasoline end point on Fig. 3.


Fig. 1.
F-2 (MOTOR METHOD) OCTANE NUMBER-END POINT FELATIONSHIP OF VARIOUS SOUTH AMERICAN STRAIGHT-RUN GASOLINES.


Fig. 2.
F-2 (MOTOR METHOD) OCTANE NUMBER-END POINT RELATIONSHTP OF STRAIGHTRUN GASOLINES (PLUS 3 CO T.E.L./GAL).
Table III．
Composition of Venezuelan Crudes．

| Field： | Lagunillas． | La Rosa． | Temblador． | Ofcina． | Colon． | Jusepin． | ＂Western．＇ | Cumarebo． |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Straight Run Gasoline ：－ |  |  |  |  |  |  |  |  |
| Vol \％of crude | 5.7 | ${ }^{16.0}$ | 12.1 | ${ }^{31.0}$ | 22.2 58.8 | 24.0 58.9 | $49 \cdot 1$ |  |
| Gravity，A．P．I． Sp．gr，at $60^{\circ} \mathrm{F}$ | $55 \cdot 2$ 0.758 | ${ }^{56 \cdot 9} 0$ | ${ }_{0}^{52 \cdot 2}$ | 50.7527 | 58.8 0.7436 | 58.9 0.743 | 5.0 0.7507 | ${ }_{0} 0.7286$ |
| \％total sulphur | Below 0－1 | Below $0 \cdot 1$ | $0 \cdot 03$ | 0.02 | 0.03 |  | $0 \cdot 02$ | $0 \cdot 02$ |
| \％mercaptan sulphur | － | － | $<0.0003$ | $<0.0003$ | $<0.0003$ | $<0.0003$ | $<0.0003$ | $<0.0003$ |
| Reid vapour pressure， lb | － | － | $4 \cdot 7$ | － | － | － |  |  |
| Octane numbers ： $\mathrm{F}-2$（motor）clear | － | 55 | $65 \cdot 5$ | 57 | 46 | 60 | 68 | 54 |
| F－2＋ 3 ce T．E．L．／U．S．gal．． |  |  |  | 78 |  |  |  |  |
| 100 ml distillation： |  |  |  |  |  |  |  |  |
| I．B．P．，${ }^{\circ} \mathrm{F}$ ． | 140 | 118 | 116 | 105 | 134 | 108 | 110 | 104 |
| 10\％ | － | 190 | 195 | 173 | 190 | 171 | 152 | 150 |
| 30\％． | 二 | 230 | 249 | 226 | 242 | 226 | 195 | 210 |
| $50 \%$ | － | 272 | 286 | 266 | 280 | 271 | 238 | 246 290 |
| 70\％ |  | 310 346 | 320 364 | 305 353 | 294 <br> 354 | 305 359 | 280 344 | 290 |
| ${ }_{\text {E．}} \mathrm{P}^{9}$ ．，${ }^{\circ} \mathrm{F}$ | 380 | 402 | 400 | 400 | 398 | 3.95 | 400 | 394 |
| Kerosine ：－ |  |  |  |  |  |  |  |  |
| Vol \％of crude | － | － | 17.7 | － | 13.6 | $10 \cdot 0$ | － |  |
| Gravity，${ }^{\circ}$ A．P．I． | － | － | 33.8 | － | 41.9 | 41.0 | － | － |
| Sp．gr．at $60^{\circ} \mathrm{F}$ | － | － | 0.8560 | － | 0.8160 | $0 \cdot 8205$ | － |  |
| \％total sulphur | － | － | $0 \cdot 18$ | 二 | 0．15 | － | － |  |
| Smoke point，mrn ． | － | 二 | － | 二 | $\xrightarrow{23}$ | 24 | 二 |  |
| Flash point Tag closed cup，${ }^{\circ} \mathrm{F}$ ． Viscosity S．S．U．at $100^{\circ} \mathrm{F}$ | － | 二 | $34 \cdot 5$ | 二 | 100 |  | 二 | － |
| 100 ml distillation ： |  |  |  |  |  |  |  |  |
| I．B．P．，${ }^{\circ} \mathrm{F}$ ． | － | － | 410 | － | 310 | 364 |  | － |
| 10\％ | － | － | 441 | － | 387 | 397 | － | － |
| 50\％． | － | － | 475 | － | 456 | 431 | － | － |
| E．P．，${ }^{\circ} \mathrm{F}$ | － | － | 567 | － | 542 | 517 | － | － |


| Gas Oil:- |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Vol \% of crude | 14-7 | - | - | - | $\begin{aligned} & 21 \cdot 9 \\ & 32 \cdot 8 \end{aligned}$ | $21 \cdot 5$ | - | - |
| Gravity, ${ }^{\circ}$ A.P.I. | $33 \cdot 0$ | - | - | - |  | $33 \cdot 1$ | - | - |
| Sp. gr. at $60^{\circ} \mathrm{F}$ | 0.860 | - | - | - | 0.8612 | 0.8595 | - | - |
| \% sulphur . | 0.60 | - | - | - | 0.75 | $0 \cdot 19$ | - | - |
| Cetane number, delay method. | - | - | - | - | 60 * | - | - | - - |
| Cold test, ${ }^{\circ} \mathrm{F}$. | - | - | - | - | 35 | 20 | - | - |
| Viscosity S.S.U. at $100^{\circ} \mathrm{F}$ | - | - | - | - | 55 | - | - | - |
| Characterization factor . | - | - | - | - | $12 \cdot 0$ | - | - | - |
| 100 ml distillation: | 40 |  |  |  |  |  |  |  |
| I.B.P., ${ }^{\circ} \mathrm{F}$. | 406 | - | - | - | 524 | 453 | - | - |
| 10\% . . . | - | - | - | - | 560 | 495 | - | $\cdots$ |
| $30 \%$. . | - | - | - | - | 598 | 522 | - | - |
| $50 \%$. . | - | - | - | - | 624 | 552 | - | - |
| $70 \%$. . | - | - | - | - | 670 | 592 | - | - |
| $90 \%$. . | - | - | - | - | 732 | 660 | - | - |
| E.P., ${ }^{\circ} \mathrm{F}$. . | - | - | - | - | 750 | - | - | - |
| Topxed or Reduced Crude :- |  |  |  |  |  |  |  |  |
| Vol \% of crude . . | $79 \cdot 6$ | $83 \cdot 8$ | $70 \cdot 0$ | $69 \cdot 0$ | $42 \cdot 1$ | 44-5 | $52 \cdot 1$ | $48 \cdot 9$ |
| Gravity, ${ }^{\circ}$ A.P.I. | $11 \cdot 9$ | $18 \cdot 3$ | $15 \cdot 8$ | $23 \cdot 0$ | $18 \cdot 7$ | 19.3 | $24 \cdot 1$ | $35 \cdot 4$ |
| Sp. gr, at $60^{\circ} \mathrm{F}$ | 0.987 | $0 \cdot 9446$ | 0.9606 | 0.9159 | 0.9421 | 0.938 | 0.9094 | 0.8478 |
| $\%$ sulphus . | $2 \cdot 8$ | 1.9 | 1.21 | 1.4 | 1.57 | $1 \cdot 18$ | $0 \cdot 35$ | $0 \cdot 15$ |
| Cold test, ${ }^{\circ} \mathrm{F}$ | - | - | 10 |  | 45 | 90 | 30 | 65 |
| Viscosity S.S.F. at $122^{\circ} \mathrm{F}$ | 1050 | - | 134 | 20 | 230 | 120 | 11. | - |
| Characterization factor | 11.45 | - | $11 \cdot 53$ | $11 \cdot 7$ | 11.8 | 11.8 | $11 \cdot 5$ | 11.8 |

Table IV.
Composition of Crudes from Argentina, Colombia, Peru, Ecuador, Bolivia, Brazil and Chile.



[^4]

Fig. 3.
END POINT OF STRAIGHT-RUN GASOLINE VERSUS YIELD ON CRUDE.

## Preparation of Feed Stock for Cracking.

## Thermal Cracking.

No special feed preparation steps are required for thermal cracking, other than salt removal in some cases. Any of the heavier fractions of the crudes, such as the kerosine, gas oil or the reduced or topped crude, listed in Tables III and IV, can be thermally cracked to increase the overall gasoline yield from crude.

When asphalt or lubricating oils are to be produced, the refinery scheme is usually arranged to include vacuum flashing of the reduced crude from the crude distillation unit. The vacuum unit produces overhead gas oil fractions for use in lubricating oil manufacture and crude residue which may be blended with other fractions to produce asphalt of the required specifications. The lighter fractions from the crude distillation unit and the excess heavy vacuum gas oil which is not used in lubricating oil manufacture can then be thermally cracked.

## Fluid Catalytic Cracking.

Kerosines, gas oils and some types of topped crudes can be charged as liquids to a fluid catalytic cracking unit. The stocks should be free of salts
which poison the catalyst and should preferably be relatively low in Conradson carbon content. The latter requirement eliminates the consideration of most topped or reduced crudes as charging stock for catalytic cracking since the coke-forming tendencies of these residual oils are usually quite high and the regeneration requirements for the catalyst are excessive. Topped crudes having Conradson carbon contents of 1 to 2 per cent have been successfully processed in commercial fluid catalytic cracking units, but these are unusually clean-topped crudes. There are four well-known methods which may be employed for the preparation of feed stocks for catalytic cracking from reduced or topped crudes :
(1) Vacuum flashing;
(2) Viscosity breaking;
(3) Propane deasphalting;
(4) Thermal coking.

It appears at present that vacuum flashing has the greatest application as a means of preparing feed stock for fluid catalytic cracking in the average smaller refinery. The installation and operating costs for viscosity breaking are competitive with vacuum flashing, but it is, of course, not possible to produce straight-run asphalts and the heavier lubricating oils when the reduced crude is subjected to viscosity breaking temperatures.

Propane deasphalting may be advantageous in some cases where maximum gasoline and minimum overall heavy fuel oil yields are required, but the installation and operating costs per barrel of charge stock are somewhat higher than the corresponding costs for vacuum flashing. Propane deasphalting may also have the advantage, however, of permitting the production of superior lubricating oils which could not be produced by vacuum flashing. Certain types of reduced crudes are cracked slightly even at the relatively low temperatures employed in vacuum flashing, and the overhead products from such an operation are usually unsuitable for lubricating oil manufacture.
The thermal coking of reduced crude to produce coke distillate which is subsequently cracked in a fluid catalytic unit is now being carried out commercially. This operation is again more expensive than vacuum flashing, but in areas where there is a good market for coke and little demand for heavy fuel oils, consideration must be given to this method of feed preparation.

As an example of one of the methods of feed preparation the results of a pilot plant continuous vacuum flash distillation of Lagunillas, Venezuela, reduced crude are given in Tables V and VI. The $12.7^{\circ}$ A.P.I. gravityreduced crude was flashed at an oil pressure of approximately 35 mm Hg in three separate tests at the successively higher flash tower top temperatures of $590^{\circ} \mathrm{F}, 630^{\circ} \mathrm{F}$, and $675^{\circ} \mathrm{F}$. Note that the sulphur content of the overhead gas oil increased from 1.53 to 1.94 per cent and its Conradson carbon content increased from 0.08 to 0.46 per cent as the depth of flashing was increased.

## U.O.P. Fluid Catalytic Cracking.

A flow diagram of the U.O.P. fluid catalytic cracking process is shown on Fig. 6. This process can be operated to produce high octane number motor

## Table V.

## Vacuum Flash Distillation of Lagunillas, Venezuela, Reduced Crude. Properties of charge stock.



## Table VI.

Vacuum Flash Distillation of Lagunillas, Venezuela, Reduced Crude.
Yields and properties of fractions.

| Test no. : | 1. | 2. | 3. |
| :---: | :---: | :---: | :---: |
| Overhead Fractions :- |  |  |  |
| Yield, volume \% of reduced crude | 38.0 | 44-8 | 55-4 |
| Gravity, ${ }^{\text {a A.P.I. . . }}$ | $23 \cdot 3$ | 21.9 | $20 \cdot 9$ |
| $\mathrm{Sp}_{\text {che }} \mathrm{gr}$. at $60^{\circ} \mathrm{F}$ | 0.9141 | 0.9224 | 0.9285 |
| Sulphur, wt \%. | 1.53 | $1 \cdot 60$ | 1.94 |
| Pour point, ${ }^{\circ} \mathrm{F}$ | -25 | -20 | -30 |
| Cold test, ${ }^{\circ} \mathrm{F}$. ${ }^{\text {Pensky Martens flash point, }{ }^{\circ} \mathrm{F}}$ | $\begin{array}{r}-30 \\ \hline 205\end{array}$ | $\begin{array}{r}-25 \\ \hline 20\end{array}$ | $\begin{array}{r}-35 \\ \hline 145\end{array}$ |
| Conradson carbon, wt \% . | 0.08 | $0 \cdot 17$ | ${ }^{145} 0.46$ |
| Universal viscosity at $100^{\circ} \mathrm{F}$, sec | 83 | 122 | 171 |
| Characterization factor | 11.41 | 11.41 | $11 \cdot 42$ |
| 100 ml distillation * :- |  |  |  |
| I.B.P., ${ }^{\circ} \mathrm{F}$ | 410 | 436 | 410 |
| 5\% | 483 | 500 | 498 |
| 10\% | 523 | 550 | 565 |
| 30\% | 625 | 658 | 680 |
| $50 \%$ $70 \%$ | 687 748 | 725 785 | 759 |
| 90\% | 825 | 860 | 818 903 |
| 95\% | 859 | 900 | 952 |
| \% recovery | 98.0 | 95.0 | 97.0 |
| \% bottoms and coke | $2 \cdot 0$ | $5 \cdot 0$ | $3 \cdot 0$ |
| Bottoms Fractions :- |  |  |  |
| Yield, volume \% of reduced crude | 62.0 | 55.2 | 44.6 |
| Gravity, ${ }^{\circ}$ A.P.I. | $7 \cdot 6$ | $5 \cdot 7$ | $1 \cdot 3$ |
| Sp. gr. at $60^{\circ} \mathrm{F}$ | 1.0172 | I. 0313 | 1.0655 |
| Softening point, ball and ring, ${ }^{\circ} \mathrm{F}$ | 97 | 114 | 138 |
| Road oil viscosity at $210^{\circ} \mathrm{F}$, sec | 83 | 195 | 840 |
| Sulphur, wt \%. . . | 3.07 | 2.99 | 3.27 |

[^5]fuel, aviation gasoline components, and raw materials for the production of synthetic rubber. The conditions of operation for the manufacture of motor fuel are somewhat different from those required for the production of aviation gasoline components. In general, it is desired to minimize the olefinic hydrocarbon content of aviation gasoline, while mono-olefins are a desirable constituent of motor fuels.
During the war aviation gasoline was composed largely of base stock, which was produced in a catalytic cracking unit, alkylate and isopentane. The olefin content of the base stock was minimized by operation of the catalytic cracking unit at relatively low temperatures using synthetic cracking catalysts in the single-stage units, and by retreating or passing the first-stage gasoline through a second reaction zone in the two-stage units.

At present the fluid catalytic cracking units are being operated, in some cases, at somewhat higher temperatures using acid-treated clays or synthetic catalysts to produce more olefinic motor fuels. The aviation gasoline produced contains little or no olefins since it is composed largely of low end point straight-run gasoline, alkylate, and isopentane.

The results obtained by fluid catalytic cracking the $20.9^{\circ}$ A.P.I. gravity heary Lagunillas, Venezuela, gas oil, which was described in Table VI, are given in the first columns of Tables VI and VIII. The Lagunillas gas oil was catalytically cracked in once-through operation at an intermediate conversion level of 56.4 per cent ( 100 vol charge minus recycle stock) and produced 44.6 per cent of $80.6 \mathrm{~F}-2$ octane number debutanized motor fuel. The butylenes and propylene produced can be polymerized to increase the motor fuel yield or utilized to alkylate isobutane in the production of aviation or motor gasoline as described later.

Note that even though the charge stock contained 1.9 per cent sulphur, the gasoline was low in mercaptan sulphur and contained 0.19 per cent total sulphur. The olefin content of the gasoline was 40 per cent by weight, which accounts for its high sensitivity, or spread between the motor and research method octane ratings, of 11.4 numbers. In some areas the research method octane rating is becoming more important than the motor method since it correlates more satisfactorily with road performance of passenger cars, particularly under conditions of low-speed knocking, than the motor method. The catalytic cracking process is well adapted to the production of fuels with high research method ratings as the data illustrate.

Of considerable importance in evaluating the fluid catalytic cracking process is the fact that it is possible to upgrade heavy distillate oils, which can be sold only as bunker fuels, into lower boiling fractions which can be blended for sale as light distillate fuels. This is illustrated by the data in Table VIII which show that in addition to high octane number motor fuel, 43.6 per cent of the Lagunillas heavy gas oil, which has a 50 per cent distillation point of $759^{\circ} \mathrm{F}$, was converted to cycle stock having a 50 per cent point of only $549^{\circ} \mathrm{F}$. In other words, about 70 per cent of the cycle stock produced in this operation will meet the No. 2 fuel oil distillation specifications.

Since pilot plant data on the eatalytic cracking of other South American oils are somewhat limited, typical results on both a low sulphur Midcontinent gas oil and a high sulphur West Texas gas oil are also included in Tables VII and VIII. These operations were each carried out at high

## Table VII. <br> U.O.P. Fluid Catalytic Cracking Various Gas Oils. <br> Properties of charge stocks and yields.

|  |  |  |  |
| :--- | :---: | :---: | :---: | :---: |

conversion by recycling a portion of the cycle stock in order to increase the gasoline yield.

The $29.4^{\circ}$ A.P.I. gravity Midcontinent gas oil produced 66.5 per cent of debutanized gasoline having a motor method octane rating of 78.3 at a conversion level of 79.8 per cent. The West Texas gas oil produced 54.9 per cent of debutanized gasoline having a similar octane rating at a conversion of 72.9 per cent.

These data illustrate the flexibility of the process, in that it is possible to recycle the fractions boiling above the gasoline range when the production of distillate fuels is not advantageous. The cost of operating at high conversion is greater than that at low conversion, however, so that the conversion level at which a given unit is operated is dictated by economic considerations.

Table VIII.
U.O.P. Fluid Catalytic Cracking Various Gas Oils.

Properties of products.

| Source of charge stack : | Laguníllas, Venezuela. | Mid. <br> Continent, United States. | West <br> Texas, <br> United <br> States |
| :---: | :---: | :---: | :---: |
| Propertites of Products. Composition of Ethane and Lighter Hydrocarbons, Mol \% : - |  |  |  |
| Hydrogen . . . . . | 50 | 46 | 40 |
| Methane | 22 | 32 | 34 |
| Ethylene | 6 | $\stackrel{7}{15}$ | ${ }^{7} 9$ |
| Ethane | $\stackrel{22}{100}$ | 15 | 19 |
| Total . | 100 | 100 | 100 |
| Debutanized $400^{\circ} F \quad E . P$. Gasoline (Untreated) :- |  |  |  |
| Sp. gr. at $60^{\circ} \mathrm{F}$ | 0.7653 | 0.7483 | 0.7587 |
| Total sulphur, wt \% . | $0 \cdot 19$ | 0.05 | $0 \cdot 19$ |
| Mercaptan sulphur, \%. | 0.002 | 0.004 | 0.003 |
| Reid vapour pressure, lb | $5 \cdot 1$ | $5 \cdot 5$ | $5 \cdot 5$ |
| Octane numbers: |  |  |  |
|  |  |  |  |
| $\mathrm{F}-2+3.0$ ce T.E.L./gal | 84.2 | 83.5 | $82 \cdot 7$ |
| F-1 (research method) clear | $92 \cdot 0$ | 88.7 | $89 \cdot 4$ |
| $\mathrm{F}-1+3.0$ ce T.E.L./gal ${ }^{\text {a }}$. | $95 \cdot 3$ | $95 \cdot 8$ | $94 \cdot 0$ |
| Composition, wt \% (P.O.N.A. analysis) : |  |  |  |
| Paraffins and naphthenes . . | 32 | 33 | 34 |
| Olefins | 40 | 52 | 43 |
| Aromatics | 28 | 15 | 23 |
| 100 ml distillation : |  |  |  |
| I.B.P., ${ }^{\circ} \mathrm{F}$ F | 125 | 110 | 110 153 |
| 10\% | 155 | 146 245 | 153 249 |
| 90\% | 368 | 360 | 364 |
| E.P., ${ }^{\circ} \mathrm{F}$ | 405 | 400 | 398 |
| Cycle Stock:- |  |  |  |
| Gravity, ${ }^{\circ}$ A.P.I. | - 16.9 | $25 \cdot 1$ | $24 \cdot 3$ |
| Sp.gr. at $60^{\circ} \mathrm{F}$ | 0.9535 | 0.9036 | $0 \cdot 9082$ |
| Cold test, ${ }^{\circ} \mathrm{F}$ | Below -30 | 20 | 10 |
| Universal visc, at $100^{\circ} \mathrm{F}$, sec | $\begin{array}{r}40.4 \\ \text { Approx } \\ \hline\end{array}$ | $34 \cdot 0$ 0.46 | 35.4 1.54 |
| Sulphur, wt \% 100 ml distillation : | Approx. $1 \cdot 9$ | $0 \cdot 46$ | 1.54 |
| 100 ml distillation: | 435 | 445 | 437 |
| 5\% | 466 | 466 | 450 |
| 10\% | 480 | 476 | 456 |
| 30\% | 512 | 502 | 477 |
| 50\% | 549 | 533 | 503 |
| 70\% | 600 | 574 | 540 |
| 90\% | 691 | 639 | 622 |

## U.o.P. Thermal Cracking.

Although a considerable amount of information has been published on the thermal cracking of South American stocks, typical results obtainable by the use of this process are given in Tables IX and X in order to complete the present discussions.

Table IX.
U.O.P. Two-Coil Thermal Cracking High and Low Sulphur Reduced Crudes.

Properties of charge stocks and yields.


* Obtained in commercial distillation equipment.

The U.O.P. thermal cracking process has been used extensively for many years to convert heavy*residual oils into gasoline and bunker fuels. It is simple and economical to operate, but the quality of the gasoline produced by this process is not as high as that obtained by catalytic cracking. Unfortunately, comparable data on the thermal and catalytic cracking of the same South American oils are not available, but, in general, tests on other stocks have shown that the motor method octane rating of catalytic gasoline is 8 to 10 points higher than the octane number of thermal gasoline produced from the same gas oil charge.

The data presented in Tables IX and X show that the $16.5^{\circ}$ A.P.I. gravity Temblador, Venezuela, reduced crude produced 31.3 per cent of 74 octane number gasoline and 65.5 per cent of bunker fuel having a Furol viscosity of 224 seconds at $112^{\circ} \mathrm{F}$. Similar tests on the $24 \cdot 6^{\circ}$ A.P.I. gravity Sanandita, Bolivia, reduced crude produced 52.4 per cent of 65 octane number gasoline and 40.2 per cent of 303 S.S.F. at $122^{\circ} \mathrm{F}$ bunker fuel. The Temblador reduced crude is quite naphthenic as indicated by its relatively low characterization factor and hence it produces a gasoline having a considerably higher octane number than the more paraffinic Sanandita reduced crude.


Table X.

U.O.P. Two-Coil Thermal Cracking High and Low Sulphur Reduced Crudes. Properties of products.


The effect of varying the residuum quality on the yields in the thermal cracking operation is illustrated in Fig. 4. The data obtained in these tests on the Sanandita reduced crude are plotted versus the A.P.I. gravity of the residuum on this graph. As the residuum gravity is decreased the gasoline yield increases and the residuum yield decreases. The cold test and viscosity of the residuum increase with decreasing residuum gravity as would be expected.

## U.O.P. Thermal Reforming.

The U.O.P. thermal reforming process has been used extensively in all parts of the world to convert low-grade naphtha and gasolines into motor fuel. Since the catalytic cracking catalysts which are used for heavy oil cracking are not suitable for fluid catalytic reforming, it appears that even in refineries where catalytic cracking is installed the thermal reforming process will still have utility. This is particularly true when crudes containing low octane number naphthas are being processed.
An example of the reforming of a low octane number Argentina 250 to $385^{\circ} \mathrm{F}$ straight-run naphtha is given in Tables XI and XII. The tabular Y Y


Fig. 4.
EFFECT OF RESIDUUM QUALITY ON YIELDS, U.O.P. TWO-COIL CRACKING OF. SANANDITA, BOLIVIA, REDUCED CRUDE.
data show that the 38 motor method octane number naphtha was reformed to produce a yield of 85 per cent of 66 octane number 10 lb Reid vapour pressure gasoline which contained a small amount of mercaptan sulphur and only 0.01 per cent total sulphur. Note that the spread between motor and research method octane ratings is six points or approximately one-half that obtained by catalytic cracking as previously mentioned.

Fig. 5 shows the effect of varying the severity of the reforming conditions on the yields and octane number of the gasoline produced from this naphtha.

## U.O.P. Catalytic Polymerization.

The U.O.P. catalytic polymerization process is one of the first of the many types of catalytic processes now being employed in the refining industry. The propylene and butylenes produced in fluid catalytic cracking, thermal cracking, and thermal reforming, which might otherwise be burned as fuel gas or sold as liquid petroleum gas, can be converted to high octane number liquid polymer and thus increase the overall motor fuel yield and octane number.
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Table XI.
U.O.P. Thermal Reforming Argentina Straight-Run Naphtha.
Properties of charge stock and yields.
Properties of Charge Stock :-
Gravity, ${ }^{\circ}$ A.P.I. ..... $54 \cdot 4$
Sp. gr. at $60^{\circ} \mathrm{F}$. ..... 0.7612
Sulphur, wt \% ..... 0.03
F-2 octane number (motor method) ..... 38
Characterization factor ..... 11.95
100 ml distillation
I.B.P., ${ }^{\circ} \mathrm{F}$ ..... 248
10\% ..... 265
30\% ..... 275
$50 \%$ ..... 285
70\% ..... 297
$90 \%$ ..... 327
E.P., ${ }^{\circ}{ }^{\mathbf{F}}$ ..... 386
Yields \% of Naphtha Charge * :-
Ethane and lighter hydrocarbons, cu.ft/brl ..... 240
Propylene, liquid vol \% ..... 5•I
Propane, ..... $5 \cdot 8$
Butylenes, ..... $5 \cdot 7$
isoButane, ..... 1.3
$n$-Butane, ..... $2 \cdot 1$
$400^{\circ}$ F E.P. gasoline, vol \%:
Debutanized basis ..... $78 \cdot 5$
10 lb Reid vapour pressure basis ..... $85 \cdot 0$
Residuum, vol \% ..... 1.5

* The proportion of light gases produced was estimated from correlations.
Table XII
U.O.P. Thermal Reforming Argentina Straight-Run Naphtha.
Properties of products.
Composition of Ethane and Lighter Hydrocarbons,* Mol \% :-
Hydrogen ..... 6
Methane ..... 42
Ethylene ..... 12
Ethane ..... 40
Total ..... 100
Properties of Untreated Gasoline :-
Gravity, ${ }^{\circ}$ A.P.I. ..... 55.5
Sp. gr. at $60^{\circ} \mathrm{F}$ ..... 0.7567
Total sulphur, wt \% ..... 0.01
Mercaptan sulphur, wt \% ..... $<0.0001$
Reid vapour pressure, Ib ..... $10 \cdot 7$
F-2 octane number (motor method) ..... 66
F-1 octane number (research method) ..... 72
100 ml distillation :
I.B.P., ${ }^{\circ} \mathrm{F}$ ..... 90
5\% ..... 139
$10 \%$ ..... 165
20\% ..... 216
50\% ..... 273
$90 \%$ ..... 356
E.P., ${ }^{\circ} \mathrm{F}$ ..... 403
\% over ..... 95.0
bottoms ..... $1 \cdot 0$
loss ..... $4 \cdot 0$* Estimated from correlations.

The propylene and butylenes can be polymerized either separately or together, depending upon the type of product desired. When the butylenes are polymerized selectively in the absence of other olefins the product can be hydrogenated to produce a 90 to 95 motor method octane number saturated liquid suitable for use as a component of high-grade aviation gasoline.


Fig. 5.
E.O.P. THERMAL REFORMING OF ARGESTISA STRAIGFT-RCS SAPHTHA.

Table XIII lists the yields of non-selective polymer which can be obtained by polymerizing the propylene and butylenes produced in the fluid catalytic cracking, thermal cracking, and thermal reforming operations described in Tables VII to XII. These yields are based on a recovery of 75 per cent of the propylene and 95 per cent of the butylenes in a gas concentration unit. When using the reactor type of polymerization unit it is possible to realize a

Table XIII.
Non-Selective Polymerization of Gases from Fluid Catalytic Cracking, Thermal Cracking and Thermal Reforming.

conversion of 90 per cent of both the propylene and the butylenes to polymer gasoline.

The overall polymer yields given in Table XIII are, of course, dependent upon the quantity of olefins produced in the cracking or reforming operation and the olefin yields in turn depend upon the type of charging stock and operating conditions employed in the cracking or reforming steps. It is interesting to note that in all three of the fluid catalytic cracking tests there is an excess of butanes produced over that required for pressuring the cracked gasoline and the propylene-butylene polymer to $10-\mathrm{lb}$ R.V.P. There was a slight deficiency of butanes when producing 3 to 4 per cent polymer from the gases formed in thermal cracking. In the thermal reforming test it would be necessary to use outside butanes for vapour pressure amounting to 3.5 per cent of the reforming unit charging stock when producing 7.3 per cent of $10-\mathrm{lb}$ R.V.P. polymer from the propylenes and butylenes.

The properties of a typical non-selective polymer are also given in Table XIII. The unsaturated character of this material is illustrated by its high research method octane ratings and the bromine number.

U.O.P. Paraffin Alkylation.

As previously mentioned, extensive use was made of the U.O.P. alkylation process during the war for the production of aviation gasoline components. In this process isobutane is normally alkylated with propylene, butylenes, or amylenes. Either sulphuric acid or hydrofluoric acid may be used as the catalyst. The alkylate produced is a mixture of saturated, stable, liquid, isoparaffinic hydrocarbons boiling in the gasoline range
and having a motor method octane rating of 88 to 95 depending upon the conditions of operation and the quality of the charging stock.
The alkylate produced may be used either as motor fuel or aviation gasoline. At present it would appear that the process will have a greater application for the manufacture of aviation gasoline than for motor fuel. The alkylation process is best suited to operate in conjunction with a catalytic cracking unit, since a greater yield of isobutane is produced in fluid catalytic cracking than in thermal cracking or reforming.

The yields and properties of alkylate given in Table XIV are based on the alkylation of the recoverable isobutane with butylenes in each case to produce a depentanized $350^{\circ} \mathrm{F}$ end point alkylate. A normal recovery of 95 per cent of the $\mathrm{C}_{4}$ hydrocarbons has been assumed in these calculations. The yield of depentanized butylene alkylate amounts to approximately 1.6 volume per volume of butylene converted and for each volume of alkylate produced about 1.25 volumes of isobutane are required. The yields shown in Table XIV are all based on the charge to the catalytic cracking unit and have been calculated for two cases :

Case I-Assuming that no outside isobutane is available and that the $n$-butane available is not isomerized;

Case II-Assuming that sufficient outside isobutane is available to alkylate all of the butylenes.

In this case the $n$-butane available is also isomerized for use in the alkylation step.

It is apparent that the maximum alkylate yields are obtained in Case II, but there is a deficiency of isobutane in all of the tests. In the operation of the catalytic cracking unit specifically for the production of aviation gasoline it is possible to adjust the cracking conditions to produce a balanced alkylation unit feed stock so that there will be no excess or deficiency of butylenes or isobutane.

As shown at the bottom of Table XIV the butylene alkylate has an unleaded motor method octane rating of $93 \cdot 2$. The $\mathrm{F}-3$ and $\mathrm{F}-4$ aviation gasoline octane determinations were each made with the addition of 4 cc of tetraethyl lead per gallon of the alkylate. The F-3, or lean mixture rating, is indicative of the performance of the fuel under airplane cruising conditions and is equivalent to iso-octane plus 1.2 ce tetraethyl lead per gallon. The F-4, or rich mixture rating, predicts the performance of the fuel under take-off conditions and is equivalent to the reference fuel S plus 2.9 cc of tetraethyl lead per gallon.

## Treating and Inhibiting.

Dyed rather than water white gasolines are marketed almost exclusively in the United States, with a resultant saving in treating costs and a reduction of gasoline losses. If it were necessary to produce a water-white finished gasoline in all cases, much more extensive treating facilities would be required in the average refinery. With the use of dyes and the addition of inhibitors to motor fuels to prevent deterioration in storage, the problem of treating gasolines is primarily one of sulphur reduction to meet odour or arbitrary sulphur specifications.

Table XIV.
U.O.P. Alkylation of isoButane with Butylenes from Fluid Catalytic Cracking.

| Charge stock to cracking : | Lagunillas, gas oil. | MidContinent, gas oil. | West Texas, gas oil. |
| :---: | :---: | :---: | :---: |
| Reference : table nos. : | VII-VIII. | VII-VIII. | VII-VIII. |
| Yields, Vol \% of Charge Stock to Cracking Unit :- |  |  |  |
| Butylenes . . . | $4 \cdot 3$ | 6.9 | $5 \cdot 7$ |
| isoButane | $3 \cdot 6$ | $4 \cdot 2$ | $3 \cdot 0$ |
| $n$-Butane | $1 \cdot 0$ | $2 \cdot 3$ |  |
| Case I.-isoButane limiting, no isomerization. |  |  |  |
| Depent. $350^{\circ} \mathrm{F}$. E.P. alkylate . . | $4 \cdot 3$ | 5-0 | $3 \cdot 6$ |
| Excess butylenes after alkylation | $1 \cdot 4$ | $3 \cdot 5$ | 3.1 |
| Case II.-Alkylation of all butylenes, including isomerization. |  |  | - |
| Depent. $350^{\circ}$ F E.P. alkylate . . | $6 \cdot 6$ | $10 \cdot 6$ | $8 \cdot 6$ |
| isoButane deficiency | 1.0 | 2.5 |  |
| Properties of Butylene Alkylate * :- |  |  |  |
|  |  | $70 \cdot 2$ 0.7015 |  |
| Sp. gr. at $60^{\circ} \mathrm{F}$ <br> Reid vapour pressure, lb |  | 0.7015 2.8 |  |
| Octane ratings : |  |  |  |
| F-2 (motor method) |  | 93.2 . |  |
| F-3 (1-C method + 4 ce T.E.L/gal). | isooct | $+1.2 \mathrm{cc}$ | /gal |
| F-4 (3-C method + 4 ce T.E.L/gal). 100 ml distillation : |  | ce T.E.L |  |
| I.B.P., ${ }^{\circ} \mathrm{F}$. |  | 140 |  |
| 10\% |  | 191 |  |
| 30\% |  | 211 |  |
| 50\% |  | 219 |  |
| 70\% |  | 225 |  |
| ${ }_{\text {E.P. }}{ }^{\text {E }}$ 。 F |  | 242 350 |  |
| E.P., 1 |  |  |  |

* From butylenes produced by catalytic cracking.

The U.S. Federal Government specification for the total sulphur content of motor fuel is now 0.25 per cent maximum, which is followed by most states. One pipeline company specifies $0 \cdot 1$ per cent maximum sulphur on the gasoline transported in its lines. It has been firmly demonstrated, however, that motors are not harmed by operation on ordinary fuels containing as much as 0.25 per cent total sulphur and in some areas motor fuel containing 0.4 per cent total sulphur or higher have been marketed without difficulty.

Fortunately a large number of the South American crudes are quite low in sulphur content as shown by the data given in Tables I and II. With an increasing demand for petroleum and its products, however, the trend may be towards the use of crudes with higher sulphur contents. If it becomes necessary for South American refiners to process a greater proportion of these crudes to produce motor fuels of unduly low sulphur content, the treating of the gasoline will be costly.

Table XV has been prepared to illustrate, largely with estimated results based on experience with the treatment of other gasolines, the treating steps
Treatment of Gasolines from Fluid Catalytic Cracking, Thermal Cracking aud Thermal Reforming.


[^6]which would be recommended to produce finished gasolines from the cracked and reformed products described in earlier sections of this paper. The following paragraphs discuss the treatment of the gasolines produced in these operations.

## Fluid Catalytically Cracked Gasoline.

Untreated catalytically cracked gasolines are usually characterized by long induction periods and relatively high copper dish gums, as indicated in the first column of Table XV. These properties are generally attributed to the presence of cresols in the raw gasoline. The addition of synthetic inhibitor to the gasoline will not reduce the gum in most cases, and it is only after the cresols have been removed and a synthetic inhibitor added that the gum test is normally satisfactory.

A relatively strong 30 to $35^{\circ}$ Bé caustic wash is used to remove cresols prior to inhibiting. It is estimated that if the Lagunillas catalytically cracked gasoline described in Table XV were caustic washed and inhibited with 0.005 per cent U.O.P. No. 4 inhibitor, a product of satisfactory storage stability having a copper dish gum lower than 25 mg and an induction period of about 400 minutes would be obtained. Caustic washing does not usually completely sweeten the gasoline, but in many cases the product is sweet after a few days' storage, and, in any case, will be of good odour. Either doctor or copper sweetening could, of course, be employed to obtain a sweet product before storage.

## Thermally Cracked Gasoline.

The cracked gasoline produced from the Temblador reduced crude, as described in Tables IX and X, contained 0.11 per cent mercaptan sulphur and 0.37 per cent total sulphur. This gasoline was acid-treated in two separate treats using both 6 and 10 lb of acid per barrel of gasoline in order to determine the amount of acid required for sulphur reduction. In view of the rather high mercaptan content of the gasoline a " split " caustic type of treatment was used. This treatment consists of washing with caustic before acid treatment and also before doctor sweetening in order to remove the lighter mercaptans by solution rather than converting these mercaptans to other sulphur compounds which might remain in the gasoline. The data show that a loss of nearly 10 per cent of the gasoline was incurred while producing a product containing 0.13 per cent total sulphur in the 10 lb acid treat.

If total sulphur specifications will permit, the Unisol mercaptan extraction process is a much simpler and more economical method of producing a finished fuel from the Temblador cracked gasoline. In this process the mercaptans are extracted with a caustic methanol solution continuously and removed from the system. As shown in Table XV it is estimated that the Unisol treated Temblador gasoline would still be very slightly sour to the doctor test, but would contain no trace of odour. Normally this degree of sulphur reduction by the removal of mercaptans from this type of gasoline will result in an improvement of approximately two points in the leaded motor method octane rating.

The thermally cracked gasoline produced from the low sulphur Sanandita
reduced crude would merely be batch caustic washed, sweetened and inhibited to produce a finished product. A relatively strong caustic wash ( 30 to $35^{\circ}$ Bé) would be used to remove cresols, the presence of which are indicated by the high induction period of the raw gasoline.

## Thermally Reformed Gasoline.

The treatment of the reformed Argentina gasoline listed in Table XV is simple since it is low in mercaptan and total sulphur content and has a satisfactory response to inhibitor before treatment. A dilute batch caustic wash followed by inhibiting is all that should be required since it would be expected that the small amount of mercaptan present would be oxidized in storage.
The preceding discussion of treating methods has been based on the assumption that dyed gasolines can be marketed. If it is necessary to produce a water-white fuel, either clay treating or acid treating usually must be employed. The choice of the type of clay treating or the decision to use acid treating depends upon the type of gasoline to be treated and many other factors. For example, since the catalytic cracking unit fractionator operates at relatively low pressure it is not feasible to consider vapour phase clay treating the gasoline from this process. In order to produce a waterwhite catalytically cracked gasoline, low temperature liquid phase clay treating would probably be used. Vapour phase clay treating installed in the fractionator vapour line on thermal cracking and reforming units is a satisfactory method of improving colour. A clay life of 1000 to 3000 barrels of gasoline per ton of clay can usually be obtained in this operation. The treated product requires re-running in order to remove the polymers formed, which normally amount to 3 to 4 per cent of the gasoline charge.

## OBITUARY.

## ARTHUR HAMILTON.

Arthur Hamilton never sought the limelight. His name did not appear on the front cover of the Journal as a Member of Council or as an Honorary Officer of the Institute. Nevertheless, throughout some twentyfive years of membership, he took a keen interest in the Institute's affairs and always encouraged the members of his staff to do the same.
For forty-five years he served the Anglo-American Oil Co., Ltd., and was manager of the Technical Department at the time of his retirement in 1941. He was one of the first to realize the importance of the technician in the industry, and many of the young technical men whom Arthur Hamilton engaged now hold responsible positions in the company. Nothing gave him greater pleasure than to see them make rapid progress.

After he retired in 1941, almost every week he was to be seen at the laboratory keeping in touch with his "boys." Everyone who knew him respected him and regarded him with real affection. His wide circle of friends, both in his company and in the industry generally, will always remember his keen sense of humour-for many years the Hamiltonian puns were a byword-which remained with him to the end, in spite of serious illness.

In the passing of Arthur Hamilton, on July 30, 1947, at the age of sixty-seven, the Institute has lost a firm adherent, and many of us have lost a friend and wise counsellor.

> C. C.


[^0]:    * Trinidad Leaseholds Ltd., Central Laboratory, King's Langley, Herts.
    $\dagger$ Additions of tetraethyl lead to a fuel will here be expressed as M.T.I.G.-millilitres tetraethyl lead per Imperial gallon.

[^1]:    * Paper read before 11th International Congress of Pure and Applied Chemistry, London, July 17-24, 1947.
    $\dagger$ Standard Oil Development Company.

[^2]:    * Paper read before XIth International Congress of Pure and Applied Chemistry, London, July 17-24, 1947.
    $\dagger$ Universal Oil Products Company.

[^3]:    (a) Sample believed to have been obtained from the La Cira Field.
    (b) Data supplied by Foster Wheeler Corpn.

[^4]:    (a) Softening point, ring and ball, ${ }^{\circ} \mathrm{F}$.
    (b) Data supplied by Foster Wheeler Corp

[^5]:    * By vacuum distillation at $2-3 \mathrm{~mm} \mathrm{Hg}$ converted to atmospheric temperature.

[^6]:    $\pm$ Before final caustic wash and doctor sweetening. Values may be slightly low due to oxidation in handling laboratory samples.

