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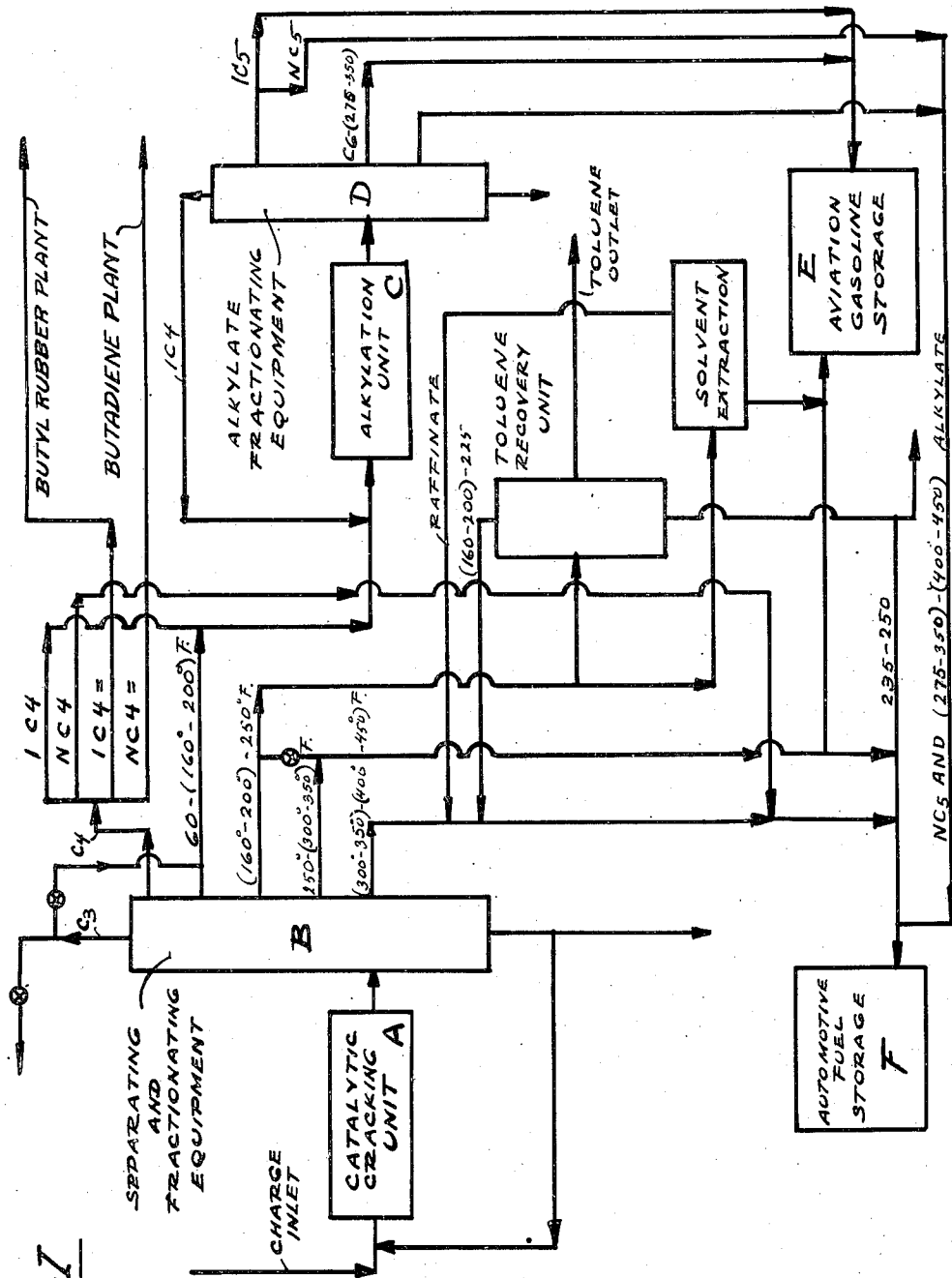
W. J. SWEENEY

2,387,309

CONVERSION OF HYDROCARBON OILS

Filed June 20, 1942

6 Sheets-Sheet 1



William J. Sweeney Inventor
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Oct. 23, 1945.

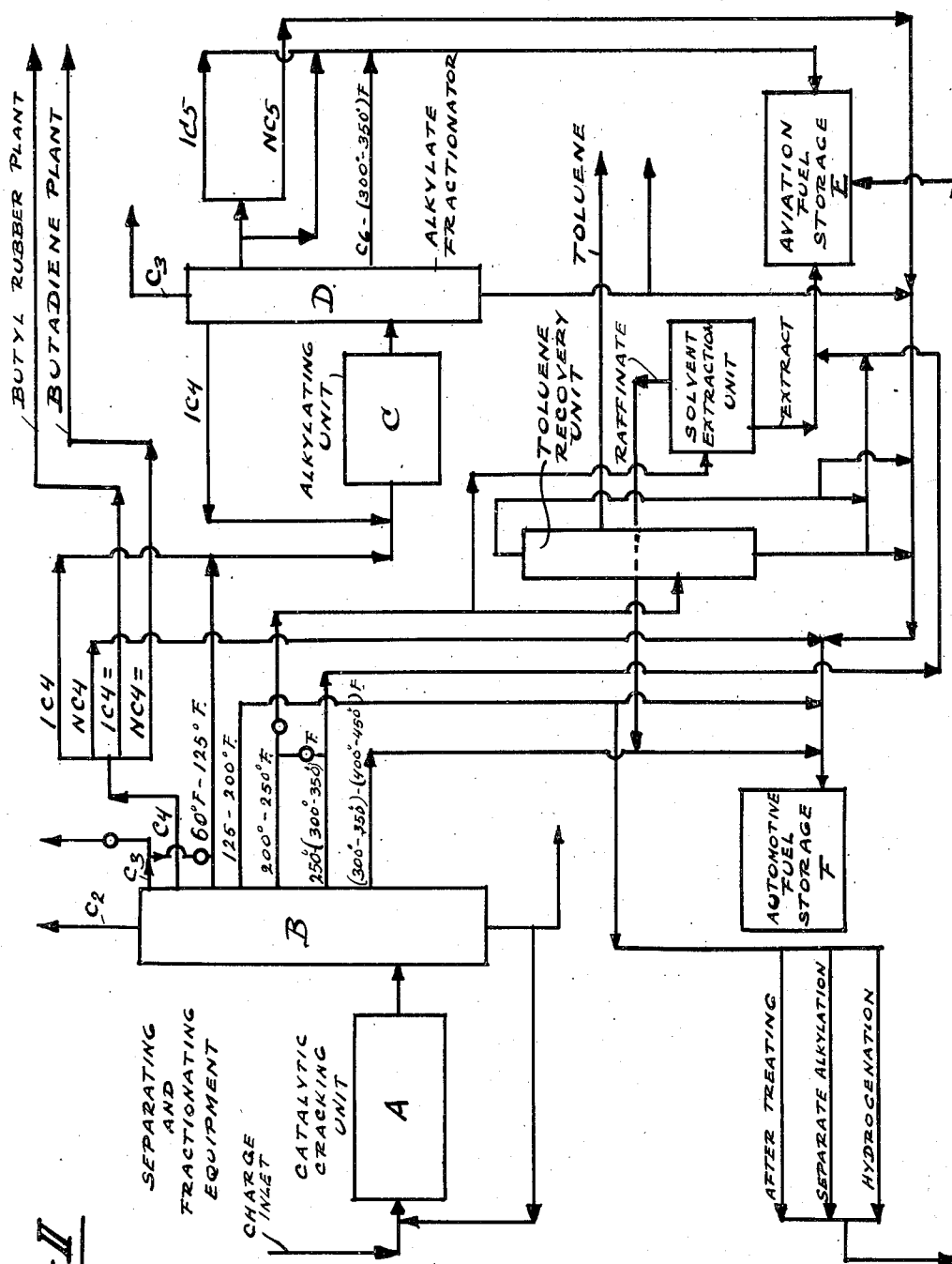
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CONVERSION OF HYDROCARBON OILS

Filed June 20, 1942

6 Sheets-Sheet 2



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CONVERSION OF HYDROCARBON OILS

Filed June 20, 1942

6 Sheets-Sheet 3

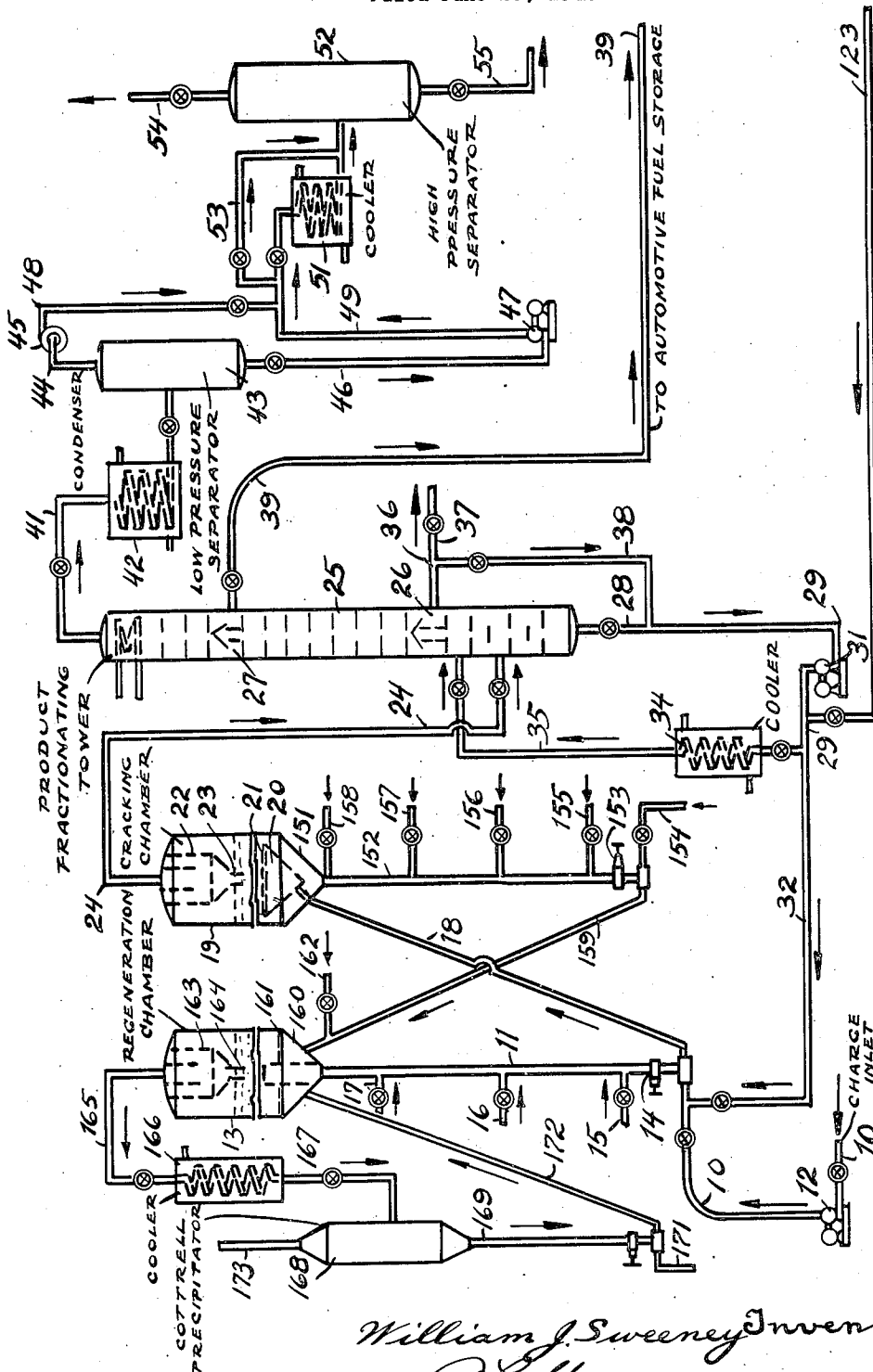


FIG. - III

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CONVERSION OF HYDROCARBON OILS

Filed June 20, 1942

6 Sheets-Sheet 4

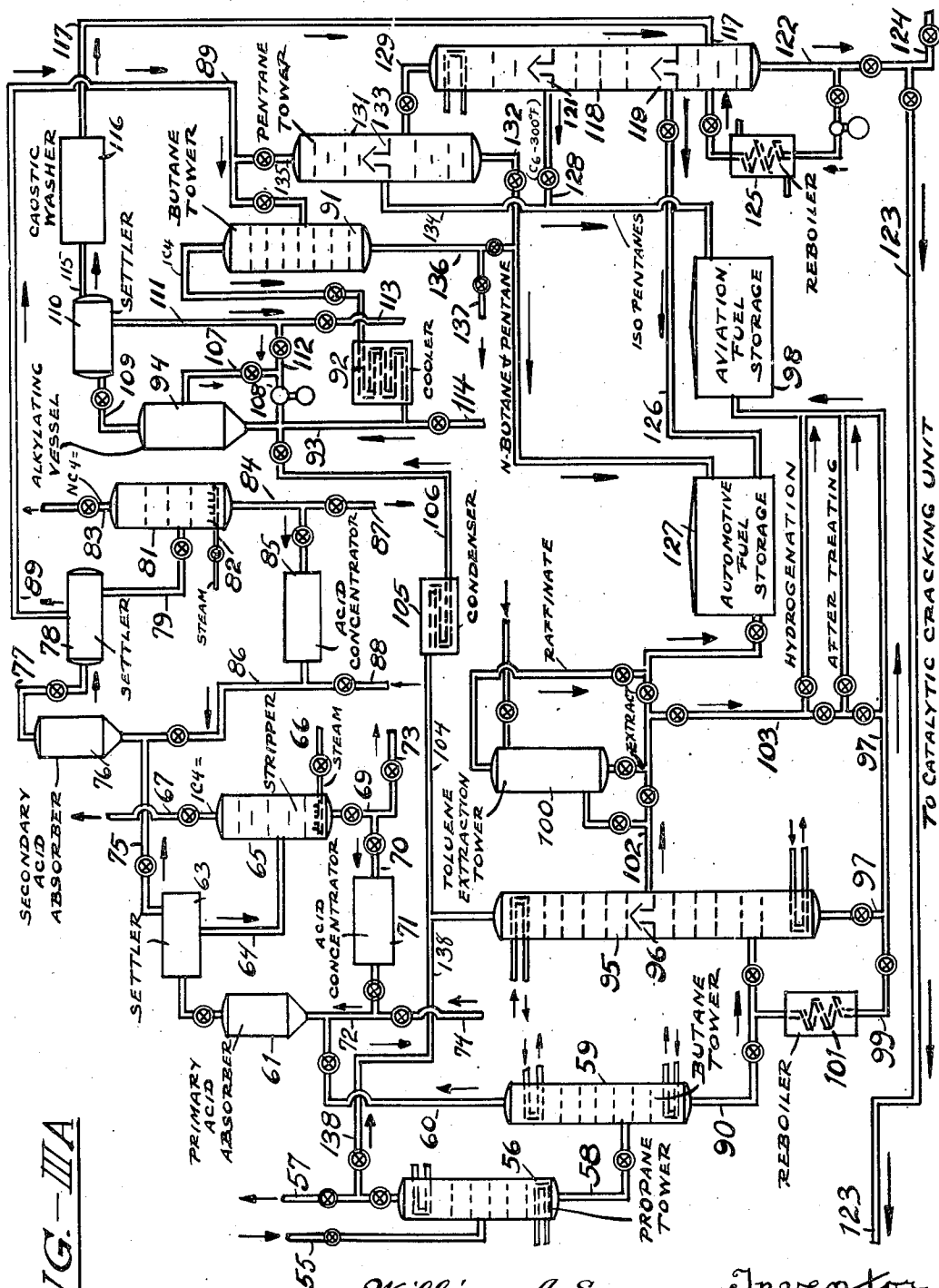


FIG.-III

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2,387,309

CONVERSION OF HYDROCARBON OILS

Filed June 20, 1942

6 Sheets-Sheet 5

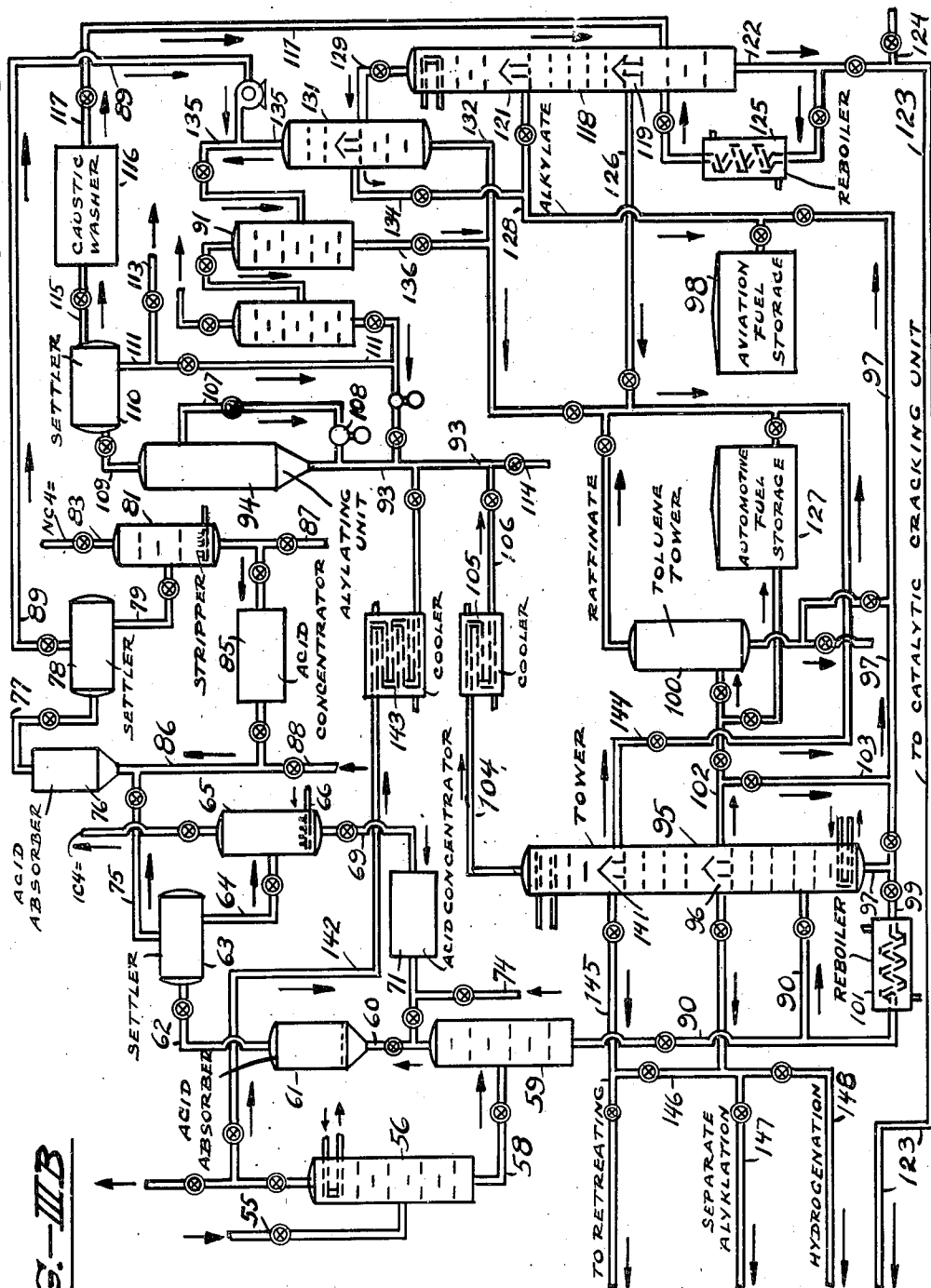


FIG. III B

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CONVERSION OF HYDROCARBON OILS

Filed June 20, 1942

6 Sheets-Sheet 6

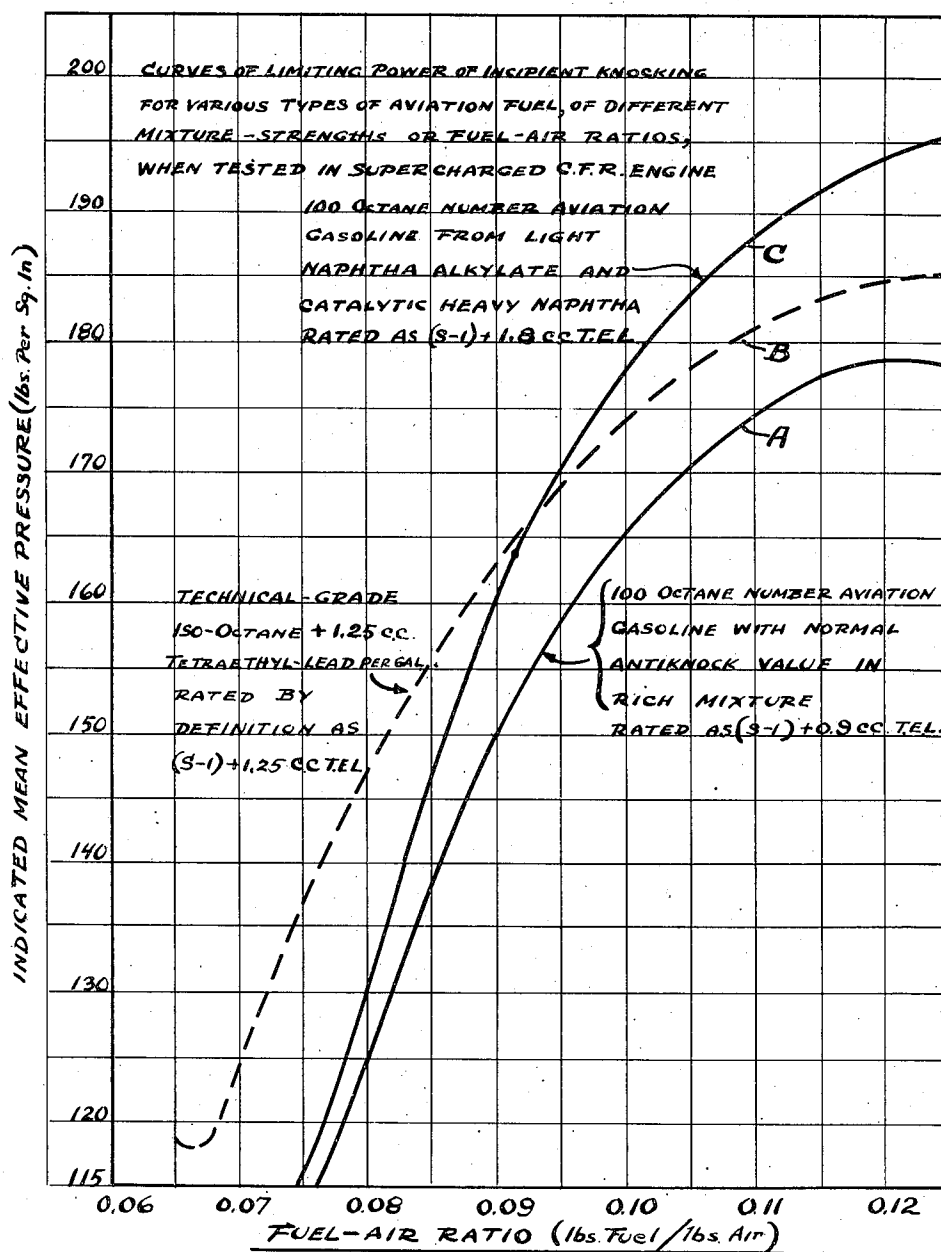


FIG. - IV

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UNITED STATES PATENT OFFICE

2,387,309

CONVERSION OF HYDROCARBON OILS

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Application June 20, 1942, Serial No. 447,787

8 Claims. (Cl. 196—12)

This invention relates to the conversion of hydrocarbon oils and forms a continuation-in-part of the invention described in application Serial No. 301,769, filed October 28, 1939, now U. S. Patent 2,310,327.

In the earlier filed application, I have described a process in which a gas oil or other similar petroleum stock is first cracked in the presence of an active catalyst. The gasoline resulting from the cracking step is then separated into a light naphtha substantially free of aromatics and a heavy naphtha fraction. The light naphtha fraction, including the butane constituents, together with the propene constituents, if desired, is then treated with an isoparaffin such as isobutane under alkylating conditions wherein the olefins contained in the light naphtha are alkylated. The alkylate, or a selected cut therefrom, is then blended back with the heavy naphtha from the catalytic cracking step to form a gasoline. The resulting gasoline has an extremely low acid heat coupled with a high octane number and lead susceptibility which makes it of particular value for aviation service.

I have now found that by modifying the process described in the above application I can obtain all of the advantages above described and at the same time produce a high yield of butenes and isobutylene which may be utilized for the production of synthetic rubber or which may be further alkylated to increase the yield of aviation gasoline produced.

One of the primary objects of the present invention is to provide a process for the conversion of petroleum oil which will not only produce a high yield of more valuable hydrocarbons but which will utilize the valuable hydrocarbon constituents to a better advantage.

In accordance with the broader phases of the present invention, a relatively heavy petroleum oil, such as a gas oil, reduced crude or the like, is first subjected to cracking in the presence of a highly active catalyst, such as an artificial adsorptive material containing silica and alumina, at relatively high temperatures of the order of from 850° F. to 1000° F. or more and for a period sufficient to obtain extremely high conversion, such as from 50% to 80% or more, as measured by the amount of fresh feed disappearing during the cracking operation.

Under the above-named conditions, the amount of butanes and butenes formed may range from 15% to 30%, motor fuel from 30% to 50%, and the balance may be in the form of normally gaseous products and coke.

Analytical determinations have shown that under the above-mentioned conditions the lower molecular weight hydrocarbon fraction boiling below about 200° F. obtained from the cracking process will comprise essentially isoparaffins and olefins, with only a relatively small percentage of normal paraffins and benzene. The relative amounts of isoparaffins and olefins contained in the lower boiling fraction may be varied within certain limits by the conditions under which the oil is cracked.

The high concentration of olefins in lower boiling fractions makes this material unsuitable for aviation fuel without further treatment.

One of the more specific objects of the invention is to provide a method of treating this fraction which will convert it into a high-grade aviation gasoline and which will at the same time make available large quantities of isobutylene and normal butenes which may be used for the production of synthetic rubber or diverted to other valuable uses.

It has also been found that the heavy naphtha fraction boiling above about 200° F. consists predominantly of aromatic hydrocarbons with only a relatively small percentage of olefins or normal paraffins. This fraction is particularly suitable for aviation gasoline, since it materially improves the rich mixture performance of aviation motors.

Further in accordance with the present invention, the butane-butene fraction obtained from the catalytic cracking process is segregated into butenes and isobutane. The butenes are then removed from the process as one of the products thereof and may be utilized in the production of synthetic rubber. The isobutane segregated from this fraction is then caused to react with olefins other than butenes formed during the cracking operation.

According to one of the modifications of the present invention, the isobutane obtained from the cracking operation is caused to react with the light naphtha fraction boiling, for example, up to from 160° F. to 200° F. The product obtained by reacting the isobutane with the light naphtha may then be blended with the heavy aromatic naphtha formed by the cracking operation for producing the aviation gasoline.

According to another modification of the present invention, a narrower fraction consisting essentially of pentanes and pentenes may be segregated from the light naphtha fraction which may be reacted with the isobutane to form a pentene-isobutane alkylate and this alkylate blended with the aromatic heavy naphtha to form aviation

gasoline. When operating in this manner, the remaining light naphtha fraction boiling between the pentane fraction and 200° F. may be diverted to automotive gasoline, or it may be further treated to remove the olefins therefrom. Such treatment may, for example, include separate alkylation of this fraction, hydrogenation, or aftertreating under conditions to remove olefins therefrom.

The term "aftertreating" used in this specification refers to the low temperature catalytic cracking of a naphtha fraction to transform olefins to isoolefins of the same boiling range, i. e., low temperature reforming.

In such operation, the amount of isobutane formed may be more than that required to alkylate the pentenes. In this case, the excess isobutane may be used to alkylate the propene and thereby increase the total yield of aviation gasoline. Also, if desired, the propene may be alkylated with isobutane from an extraneous source to increase further the yield of aviation alkylate.

It has also been found that the aromatic heavy naphtha fraction boiling above 200° F. is relatively rich in toluene, whereas only a relatively small amount of benzene is found in the cracked products. The invention further contemplates segregation of the toluene from the heavy naphtha. The toluene so separated may be nitrated to form trinitrotoluene and the remainder employed for aviation fuel.

With the above nature and objects in view, the invention will be better understood by reference to the accompanying drawings wherein—

Fig. I is a flow plan of the process forming one embodiment of the invention in which the different steps are shown symbolically;

Fig. II is a similar flow plan showing a modification;

Fig. III is a diagrammatic view showing a part of the apparatus suitable for carrying the invention into effect in greater detail;

Fig. III—A is a continuation of Fig. III showing the remainder of the apparatus for carrying out one modification of the invention;

Fig. III—B is a continuation of Fig. III showing another modification; and

Fig. IV is a graph showing rich-mixture performance characteristics of aviation fuel prepared according to the present invention as compared with 100-octane fuels now commonly employed.

Referring to the broader phases of the present invention shown by the flow plan forming Fig. I, a petroleum oil, such as a gas oil or a topped or reduced crude, is first charged to a catalytic cracking unit in which it is cracked in the presence of a highly active cracking catalyst. For this purpose, artificial adsorptive materials comprising silica and alumina have been found more suitable than natural materials, such as activated clays. Other types of highly active synthetic gel catalysts, such as silica-zirconia, boric oxide-alumina and the like, may be employed.

A particularly suitable catalyst may be prepared from natural clays of the bentonite type by first subjecting the clays to drastic acid treatment sufficient to remove all natural impurities together with a large portion of the alumina. Additional alumina may then be reprecipitated on the clay.

The temperature of the cracking operation is preferably maintained at from 850° F. to 1000° F. or more, preferably between 900° F. and 1000° F., so as to produce a high yield of isobutylene and butenes. The time of contact between the oil and the catalyst is controlled to obtain conver-

sions of the order of from 50% to 80%, preferably between 60% and 70%, as measured by the amount of feed oil disappearing during the process. Under such conditions, the butane-butene fraction produced by the cracking operation may amount to from 15% to 30% of the feed, the amount of naphtha from 30% to 50%, and the remainder of the cracked products will consist of normally gaseous hydrocarbons and coke.

In carrying out the cracking operation, it is preferred to employ a fluid catalyst type of cracking equipment in which the catalyst in finely divided form is caused to flow through cracking and regenerating zones in a continuous manner. This type of operation permits more flexible control of the cracking operation and makes it possible to regulate better the yield and type of various products produced.

The cracked products issuing from the catalytic cracking unit A shown in Fig. I are then subjected to suitable separation and fractionation to divide them into a plurality of relatively narrow fractions. The normally gaseous fraction comprising propane, propene and lower boiling constituents may be rejected from the system, or the propene may be segregated and alkylated with extraneous isobutane to increase the amount of aviation gasoline formed from the process.

For convenience, the type of fractions segregated from the cracked products will be referred to in many cases by the number of carbon atoms contained in the molecules. For example, the butane-butene fraction will be referred to as the C₄ fraction, with the understanding that this fraction includes all of the hydrocarbons containing 4 carbon atoms to the molecule.

As illustrated, the cracked products are segregated in suitable separating and fractionating equipment to separate C₄ fraction which is, in turn, further segregated into its various components, such as olefins and paraffins. The olefins may be further treated to separate the isobutylene from the butenes. The isobutylene may then be utilized in the production of butyl rubber and the butenes may be dehydrogenated into butadiene for conversion into synthetic rubber. The isobutane, with or without first separating the normal butane therefrom, is then combined with a fraction containing C₅ hydrocarbons and other hydrocarbons boiling below 200° F., and in some cases below 160° F. In case this fraction includes constituents boiling up to 200° F., a small amount of benzene will be included in this fraction. However, since the amount of benzene formed during the cracking operation is normally low, the fraction between C₅ and 200° F. may be combined with the isobutane passing to the alkylation unit. The mixture of isobutane and the fraction containing the C₅ and higher boiling constituents up to from 160° F. to 200° F. passes to the alkylation unit C in which the isobutane is reacted with the olefins contained in the C₅—160–200° F. fraction to form a saturated alkylate.

Products from the alkylation unit are then further fractionated in fractionating equipment D to separate an aviation alkylate containing the C₅ hydrocarbons and higher boiling hydrocarbons boiling up to the end point of the aviation specifications, such as from 275° F. to 350° F. This fraction is passed to the aviation storage tank E. The unreacted pentane contained in the alkylate removed from the alkylating unit C may be segregated into isopentane, which is passed to the aviation gasoline storage tank D, and into normal pentane, which may be passed to the

automotive storage tank F. The unreacted isobutane is returned to the alkylation unit. The alkylate fraction boiling above the end point of aviation fuel and below the end point of motor fuel may be segregated as a separate fraction from the alkylation tower and passed to the automotive fuel storage tank F. The alkylate fraction boiling above the end point of automotive fuel may be removed from the alkylation tower and used for special purposes or returned to the catalytic cracking unit for further processing.

Returning to the separating and fractionating equipment B, a fraction of the cracked products boiling between 160-200° F. and 250° F. will contain a high percentage of toluene. This fraction, if desired, may be passed to a toluene recovery plant for the separation of toluene therefrom for nitration into trinitrotoluene. In this case, the raffinate from the toluene recovery plant may be passed to the automotive fuel storage tank F. The heavy naphtha fraction boiling between 250° F. and 300-350° F. from the fractionating equipment B is passed directly to the aviation gasoline storage tank E. In cases where it is not desired to segregate the toluene from the cracked products, a fraction of the cracked products boiling between 160-200° F. and 275-350° F., and preferably between 200° F. and 295° to 350° F., may be passed to the aviation gasoline storage. The heavy naphtha fraction boiling above the end point of the aviation gasoline, such as a fraction boiling between 300-350° F. and 400-450° F., is passed to the automotive fuel storage tank F. The cracked constituents boiling above the end point of automotive fuel may be recycled to the cracking unit or they may be withdrawn from the system as a heating oil, or employed for other purposes. When operating the cracking unit to obtain a high conversion of petroleum oil, the amount of cycle stock boiling above motor fuel will be relatively small.

Fig. II shows a further modification in which the isobutane is alkylated with a C₅ fraction rather than the C₅-160-200° F. fraction. In this case, the 125-200° F. fraction containing the C₆ and C₇ hydrocarbons may be diverted to automotive fuel, or it may be subjected to alkylation or hydrogenation to convert it into aviation gasoline. As a further alternative, the 100-200° F. fraction may be aftertreated in a different catalytic cracking unit, as described in my earlier application Serial No. 428,995, filed January 31, 1942. In this case, a part or all of the propylene formed in the process may be combined with the ptenenes passing to the alkylation unit.

In other words, the modification shown in Fig. II differs from Fig. I in that the hydrocarbons boiling between 100° F. and 200° F. are not alkylated along with the C₅ fraction, but a portion of the C₅ fraction may be alkylated in its place.

In both of the modifications shown in Figs. I and II, an intermediate naphtha fraction having a boiling range within 160° F. and 250° F. may be segregated and subjected to solvent extraction or otherwise treated to remove the toluene and/or benzene formed therein and the aromatic extract passed to the aviation fuel, whereas the paraffin-olefin raffinate may be passed to the automotive fuel storage tank.

Referring more particularly to Fig. III, which illustrates a type of equipment for carrying out

the initial steps of the present invention in greater detail, the reference character 10 designates a charge line through which the oil is introduced into the system. As previously mentioned, this charging oil may be a clean condensate stock, such as gas oil, or it may comprise a residual oil, such as a topped or reduced crude.

The oil introduced into the process through line 10 is placed under a pressure by means of pump 12 at least sufficient to overcome the pressure drop through the cracking and fractionating equipment. In general, it is preferred to carry out the cracking operation at substantially atmospheric pressure. However, the operation can be conducted at moderately elevated pressures, if desired. The oil introduced into the process through line 10 may be preheated by heat exchange with products from the process or by other suitable means (not shown) prior to the introduction of a catalyst therein. In practical operations, however, it is preferred to supply the bulk of the heat requirements for the process by the sensible heat of the hot catalytic material discharging into the oil through conduit 11. The catalyst passing through conduit 11 may be heated, for example, during its passage through the regenerating chamber 13 by burning of carbonaceous deposits contained on the catalyst as a result of the cracking treatment.

As previously described, the catalytic material introduced into the oil stream may comprise, for example, an adsorptive contact material containing silica and alumina. This gel may be formed by first preparing a purified silica hydrogel by reacting sodium silicate with an acid under conditions to form a clear hydrosol which subsequently sets into a silica hydrogel containing from 85% to 95% moisture. This gel is then washed free of alkaline impurities and then impregnated with an aluminum salt, such as aluminum sulfate, which is subsequently decomposed by means of ammonia to form the silica-alumina composite. This product is then dried and activated to form the catalyst. Another active catalyst of this type may be prepared by employing natural clays as a base for the production of the silica. To this end, a bentonite clay may be first treated with an acid in an amount sufficient to remove substantially all of the alkaline impurities contained therein. This will require from 0.5 to 1 pound or more of acid per pound of clay. Under such conditions, the acid treatment will effect the removal of a large portion of the alumina originally present in the clay. This alumina can be replaced by impregnating the acid-treated clay with an aluminum salt solution and then precipitating the aluminum salt, as previously described. Both of these methods have been found to produce a catalyst which is particularly desirable for carrying out the present invention.

Other highly active cracking catalysts, such as silica-magnesia, silica-zirconia, boric oxide-alumina, or combinations thereof, may be used in place of the silica-alumina catalysts.

The catalytic material introduced into the oil stream should be in finely divided form, having a particle size ranging, for example, from 1 to 100 microns in diameter. As a typical example, the catalytic material may be ground to a fineness such that from 60% to 80% is capable of passing a 400-mesh screen.

The amount of catalytic material introduced from conduit 11 into the oil stream 10 may be regulated by a suitable valve 14 positioned in the conduit. The amount of catalytic material intro-

duced into the oil stream will depend upon whether or not the heat for the cracking operation is obtained from the sensible heat from the hot catalytic material. For example, if the bulk of the heat required for the cracking operation is supplied by hot catalytic material from conduit 11, it will be necessary to introduce larger quantities of such material than would be the case in which the oil has been initially preheated to the desired reaction temperature before contacting with the oil. In general, the amount of catalytic material introduced into the oil stream may range from 2 to 20 parts or more of catalytic material per part of oil.

In cases where large amounts of material are introduced into the oil stream, it may be desirable in some cases to dilute the catalytic material with a solid diluent which may serve as a heat carrier for supplying heat to the oil without affecting the nature of the cracking operation. Such diluent material may, for example, comprise finely divided sand, diatomaceous earth, kieselguhr, silica gel and other solid, relatively inert materials. In some cases, the active catalytic material may be deposited on the inert carriers.

In order to prevent the possibility of the oil passing through line 10 from escaping upwardly through the catalyst conduit 11 into the regenerating chamber 13 and to insure flow of catalytic material from conduit 11 into the oil stream, it is necessary to maintain the catalytic material passing through the feed valve 14 under a pressure slightly greater than the pressure on the oil stream passing through line 10. The pressure on the catalytic material necessary to feed it into the oil stream may be developed by making the conduit 11 of a height sufficient to develop a hydrostatic pressure at the base thereof greater than the pressure on the oil. In order to develop a hydrostatic pressure at the base of the column 11, it is essential that the catalytic material contained in conduit 11 be in a freely flowing fluidized state. This state may be maintained by introducing a small amount of a fluidizing gas in admixture with the catalytic material during its passage through the conduit. To this end, the fluidizing gas may be introduced at one or more points along the conduit 11 through lines 15, 16 and 17. This fluidizing gas may comprise any suitable gas which does not adversely affect the catalyst or oil. In some cases, it has been found that both steam and carbon dioxide have an adverse effect on the activity of the catalyst. In such cases, a hydrocarbon gas, such as a residual gas from the cracking operation comprising hydrogen, methane and ethane, may be utilized as the fluidizing medium in the conduit 11. The oil upon mixing with the hot catalytic material discharging through conduit 11 is heated to the desired reaction temperature which should be above 850° F., and preferably from 900° F. to 1000° F. or more. When using gas oil as the charging stock, all of the charging oil will be vaporized at these temperatures. When using heavy residual oils as the charging stock, the amount of catalytic material introduced into the oil stream should be sufficient to absorb completely any unvaporized constituents of the oil so as to prevent the formation of any viscous, tacky mixture of oil in the catalytic material. Under such conditions, the resulting mixture will comprise essentially oil vapors and catalytic material. This suspension of catalytic material and oil vapors then continues through line 18 into a cracking chamber 19 through a nozzle 20. The nozzle 20 is preferably

provided with a perforated grid plate 21 for distributing the mixture within the main cracking chamber 19. The nozzle 20 is preferably spaced from the outer walls of the cracking chamber 19 to form an annular passage through which catalytic material continuously passes into the bottom section of the cracking chamber and from which it may be withdrawn and passed to the regenerating chamber 13, as later described.

The velocity of the oil vapors passing upwardly through the cracking chamber 19 is preferably controlled to permit the settling of the finely divided catalytic material into a relatively dense mass which is maintained in a highly turbulent state by the passage of the oil vapors there-through.

The cracking chamber 19 should be of sufficient height above the nozzle 20 to provide a disengaging space above the dense turbulent mass so as to reduce the amount of entrained catalytic material in the cracked products being removed from the cracking zone, as later described. The depth of the dense turbulent mass above the inlet nozzle 20 may be controlled by regulating the amount of catalytic material being removed from the cracking chamber, as later described. The depth of the dense turbulent mass of catalytic material above the nozzle 20 should be sufficient to obtain the required contact time between the oil vapors and the catalyst to obtain the desired conversion under the obtaining temperature conditions. The extent of conversion should, as before mentioned, amount to from 50% to 80% or more, as determined by the amount of feed oil disappearing during the process. The actual contact time for accomplishing these conversions may range from 5 seconds to 1 minute or more, depending upon the temperature, activity of the catalyst, and other factors.

The cracked products after passing through the dense turbulent catalytic mass contained in the cracking chamber 19 may then pass to a cyclone separator 22 positioned in the top portion of the cracking chamber 19 above the dense catalytic mass. Entrained catalytic material separated from the cracked products in the separator 22 may be returned to the cracking chamber through conduit 23.

The cracked products after passing through the cyclone separator 22 may continue through line 24 to the product fractionator 25 in which they are subjected to fractionation to condense the higher boiling constituents thereof.

The fractionating tower 25 may be provided with trap-out trays 26 and 27 which segregate condensate formed in the tower into separate fractions.

The initial condensate formed in the bottom section of the fractionating tower 25 below the trap-out tray 26 will contain residual catalytic material remaining entrained in the cracked products after passing through the cyclone separator 22. This initial condensate is withdrawn from the bottom of the fractionating tower 25 through line 28 and is returned to the cracking chamber through line 29, pump 31 and line 32 which merges with feed line 10. A portion of the condensate withdrawn from the bottom section of the tower 25 through line 28 may be pumped through line 29, pump 31 and line 33 to a cooler 34 and then returned through line 35 to the tower 25 below the trap-out tray 26. The oil recirculated through cooler 34 and line 35 to the tower 25 serves to cool the entering cracked products to the dew point and to scrub entrained catalytic

material contained therein. To this end, the amount of oil and the temperature of the oil being circulated should be sufficient to cool the cracked products from their reaction temperature down to condensation temperature.

The temperature of the intermediate section of the tower 25 between the trap-out trays 26 and 27 may be controlled to condense substantially all of the constituents boiling above the end point of motor fuel. This liquid condensate formed in the intermediate section of the tower 25 will collect in trap-out tray 26 and may be withdrawn through line 36. This cycle oil, amounting to from 10% to 30% of the fresh feed, may be removed from the system through line 37 as a product of the process, or it may be passed through line 38 and combined with the condensate from the bottom of the tower passing through line 29 and be returned to the cracking chamber, as previously described.

The temperature of the top section of the tower 25 above the trap-out tray 27 may be controlled by means of suitable cooling elements and by a reflux medium to condense a heavy naphtha fraction boiling between the end point of aviation gasoline and the end point of automotive fuel. This fraction may, for example, consist of a fraction boiling between 300° F. and 400° F., or between 350° F. and 450° F. This condensate formed in the top section of the tower 25 will collect in trap-out tray 27 and is removed therefrom through line 39 and passed to automotive fuel storage shown in Figs. III—A and III—B.

Vapors remaining uncondensed in the fractionating tower 25 and comprising the aviation gasoline constituents together with lower boiling components pass overhead from the fractionating tower through line 41 to a condenser 42 in which normally liquid constituents are condensed. The products from the condenser 42 may then pass into a low-pressure separator 43 in which the liquid distillate formed in the condenser 42 separates from the uncondensed gases.

Under the relatively low pressure conditions at which the cracking operation is normally carried out, the gaseous constituents will contain the C₄ and lower boiling hydrocarbons. In order to recover the C₄ hydrocarbons from these gases, together with the C₃ hydrocarbons, in case it is desired to utilize the latter, the overhead products from the separator 43 may be passed through line 44 to a compressor 45 and placed under a pressure of from 100 to 500 pounds per square inch. The liquid distillate separated in the separator 43 is withdrawn through line 46 and may be placed under a similar pressure by means of pump 47. The compressed gases from compressor 45 are then passed through line 48 which merges with line 49 on the pressure side of pump 47. The resulting mixture may be then subjected to further cooling, if desired, in cooler 51 and later transferred to a high-pressure separator 52.

In many cases, the gases may be subjected to cooling during compression at least sufficient to remove the heat of compression. In such cases, it is not always necessary to provide a cooler 51 in the line leading to the high-pressure separator 52 and in such cases the products may be bypassed around the cooler 51 through line 53.

The temperature and pressure conditions within the high-pressure separator 52 may be controlled by means of the compressor and cooler to liquefy a substantial portion of the propane-propene constituents along with the C₄ and other higher boiling hydrocarbons. Gases remaining

uncondensed in the high-pressure separator 52 and comprising hydrogen, methane, ethane, ethene, and some propane and propene are removed from the high-pressure separator through line 54.

The liquid distillate separated in the high-pressure separator 52 is withdrawn through line 55. This fraction may contain a substantial amount of propane-propene constituents, together with higher boiling hydrocarbons, including aviation constituents boiling up to from 300° F. to 350° F.

In cases where the propylene is not further utilized in the process, the temperature and pressure conditions in the high-pressure separator 52 may be controlled to reject the bulk of the propane-propene constituents in the gases removed overhead through line 54.

Referring to Fig. III—A, the liquid distillate removed from the high-pressure separator 52 passes through line 55 into a propane tower 56 in which the temperature or pressure, or both, is modified to liberate the C₃ constituents from the liquid distillate. This may be accomplished by raising the temperature of the distillate passing into the tower 56 or by reducing the pressure, or by a combination of both. The C₃ fraction liberated in the tower 56 is removed overhead through line 57 and may be removed from the system or treated as hereinafter described. The liquid distillate after passing through the propane tower 56 may then continue through line 58 to a butane tower 59 in which the temperature and pressure are modified to vaporize the C₄ constituents.

To this end, the temperature may be increased or the pressure reduced. As previously pointed out in describing the cracking operation, the amount of C₄ hydrocarbons formed during the cracking operation will be relatively high, amounting to from 15 to 30 volume per cent or more of the amount of oil cracked. This fraction, furthermore, will contain C₄ olefins and isobutane with only a small percentage of normal butane.

In accordance with the present invention, the C₄ hydrocarbons are treated to separate the isobutane from the C₄ olefins. This separation may be accomplished by various ways well known in the art, involving distillation and solvent or chemical extraction. The isobutylene may also be separated from the butenes and both utilized for producing synthetic rubber. In some cases, it may be alkylated with isoparaffins to provide additional alkylate for aviation gasoline, as described in the earlier application Serial No. 301,769, now U. S. Patent 2,310,327.

For illustrative purposes, the separation of the C₄ hydrocarbons will be carried out by a combination of distillation and acid extraction, it being understood that the separation may be accomplished by other means, as mentioned above.

When employing acid extraction and distillation for separation, the C₄ hydrocarbons removed overhead from the butane tower 59 are passed through line 60 leading to a primary acid absorber tower 61 in which the fraction is contacted with a relatively dilute sulfuric acid solution, having a strength ranging from 60% to 70%. The conditions maintained in the acid absorber 61 are controlled to absorb selectively the isobutylene constituents in the charge. The particular conditions for accomplishing this end are generally known and need not be discussed in detail. The mixture of hydrocarbons and acid after passing through the acid absorber 61 con-

tinues through line 62 to a settling chamber 63 in which the acid extract containing the isobutylene separates from the unreacted hydrocarbon vapors. The acid extract is withdrawn from the settling chamber 63 through line 64 and may be passed to a stripping tower 65, in which the acid is diluted by the introduction of steam through line 66 or by other suitable means to regenerate the acid and liberate the isobutylene absorbed therein. The isobutylene liberated in stripping tower 65 is removed overhead through line 67 as a product of the process. This material may be further purified and utilized for the production of butyl rubber or for other purposes outside the purview of the present invention.

The regenerated acid is removed from the stripping tower 65 through line 69 and may be passed through line 70 to a suitable acid concentrator 71 and thereafter returned to the acid absorber 61 through line 72.

A portion of the acid from the stripping tower 65 may be continuously withdrawn through line 73 and fresh makeup acid may be introduced through line 74.

Referring again to the settling chamber 63, vapors remaining unreacted with the acid are removed from the settling chamber 63 through line 75 and passed to a secondary acid absorber 76 in which they are contacted with a more highly concentrated sulfuric acid solution, having a strength ranging, for example, between 85% and 95%. This acid absorber is maintained under conditions to absorb the usual butene constituents contained in this vapor fraction. Here again the particular conditions of temperature, acid concentration and other factors for obtaining these ends are well known in the art and need not be discussed in detail.

The mixture of hydrocarbon vapors and acid after passing through the acid absorber 76 continues through line 77 to a second settling chamber 78 in which the acid extract containing normal butene constituents separates from the unreacted normal butane and isobutane.

The acid extract is removed from settling chamber 78 and passed to a stripping tower 81 in which the acid is diluted by means of steam introduced through line 82 or by other suitable means to regenerate the acid and liberate the normal butenes therefrom. The normal butenes recovered from the acid in the stripping tower 81 are removed overhead through line 83. The butenes so liberated may be passed to a dehydrogenation plant (not shown) for conversion into butadiene and utilized as a raw material in the production of synthetic rubber.

The regenerated acid is removed from the stripping tower 81 through line 84 and may be passed to an acid concentrator 85 and then returned through line 86 to the acid absorber 76. Spent acid may be removed from this cycle through line 87 and makeup acid may be introduced through line 88.

The butane fraction consisting largely of isobutane and only a relatively small amount of normal butane is removed overhead from the settling chamber 78 through line 89. This fraction may be treated with a caustic in suitable equipment (not shown) to neutralize the acid entrained therein and then passed into a butane tower 91 in which it is subjected to fractionation to separate the isobutane from the normal butane.

The isobutane removed overhead from the butane tower 91 may be passed to a condenser 92 wherein it is liquefied and then passed through

line 93 to an alkylating vessel 94 wherein it is caused to react with another fraction from the catalytic cracking unit, as later described.

Returning to the initial butane tower 59, the unvaporized fraction is removed therefrom through line 90 and passed to a fractionating tower 95 wherein it is subjected to further fractionation to segregate it into a plurality of separate fractions. For example, the fractionating tower 95 may be provided with a trap-out tray 96. The temperature below the trap-out tray 96 may be controlled to retain in liquid form the hydrocarbons boiling between about 250° F. and the end point of aviation gasoline, which may be from 275° F. to 350° F.

As previously mentioned, this fraction will consist principally of aromatic constituents in the aviation gasoline boiling range and can be utilized directly for aviation fuel without further processing to improve the octane number thereof. In accordance with the present invention, this fraction is removed from the bottom of fractionating tower 95 through line 97 and passed to an aviation fuel storage tank 98. If desired, a portion of this fraction may be passed through line 99 and reboiler 101 and then returned to the bottom of the fractionating tower to supply the necessary heat to accomplish the distillation and fractionation within the tower 95.

The temperature of the fractionating tower 95 above the trap-out tray 96 may be controlled to condense constituents boiling between 160–200° F. and 250° F. In cases where the initial temperature of this fraction is 200° F. rather than 160° F., it will consist largely of toluene. Condensate formed in the top section of the tower 95 is collected in trap-out tray 96 and may be removed therefrom through line 102. In cases where it is desired to recover toluene as a separate product of the process, this fraction may be passed to a toluene extraction tower 100 wherein it is subjected to further extraction and distillation to segregate toluene therefrom.

In cases where the top temperature of the tower 95 is controlled to obtain a fraction boiling between 160° F. and 250° F., the tower 100 may be used to recover both benzene and toluene. The benzene and toluene extract may be passed to aviation fuel or further treated to separate the benzene from the toluene. The raffinate formed in the treatment of this intermediate fraction may be used for motor fuel.

In cases where it is not desired to segregate toluene as a product of the process, this intermediate fraction boiling between 200° F. and 250° F. may be passed to the aviation fuel storage tank 98 through line 103.

In lieu of subjecting the intermediate fraction boiling between 160–200° F. and 250° F. to solvent extraction for recovery of toluene or utilizing it directly as aviation fuel, this fraction may be subjected to hydrogenation or aftertreating before being used as aviation fuel.

The top temperature of the tower 95 is controlled to take overhead the lower boiling constituents containing the C₅ hydrocarbons and hydrocarbons boiling up to 160–200° F.

In accordance with the modification of the invention illustrated in Fig. III—A, this overhead fraction is alkylated with the isobutane previously referred to to form aviation alkylate. To this end, the overhead products are removed from the tower 95 through line 104 to a condenser 105. Liquid from the condenser 105 is then passed through line 106 to the alkylating tower

94 in which it is intermixed with isobutane recovered from the C₄ fraction, as previously described.

The alkylating reaction between the olefins contained in the C₃—(160–200)° F. fraction and the isobutane is carried out in the alkylating tower 94 in the presence of a suitable alkylating catalyst, such as sulfuric acid, fluorosulfonic acid, aqueous and anhydrous boron fluoride, anhydrous hydrofluoric acid, chlorosulfonic acid, etc. For example, with concentrated sulfuric acid having a concentration ranging from 75% to 110%, the temperature of the alkylation tower 94 may range from 10° F. to 125° F. To obtain a satisfactory yield, it is important to maintain a substantial excess of isobutane in the alkylating vessel. For example, the molar ratio of isobutane to olefins contained in the reactor should be in excess of about 5 parts of isobutane to 1 part of olefins. It is also desirable to maintain the reaction mixture within the vessel 94 in a highly turbulent state. To this end, a portion of the reaction mixture may be withdrawn from the reaction vessel 94 through line 107 and recycled by means of pump 108 into the bottom section of the vessel 94.

The stream of acid and reactants is also preferably injected into the reaction chamber through a plurality of jet nozzles or other suitable mixing devices. The particular details in bringing about the reaction between the isoparaffins and olefins contained in the reactor are generally well known in the art and need not be further described. A portion of the reaction mixture may be continuously withdrawn from the top of the alkylating vessel 94 through line 109 to a settling chamber 110 in which the acid extract separates from the hydrocarbon fraction. The acid extract may be withdrawn from the settler 110 through line 111 and recycled through line 112 and pump 108 to the reaction chamber. A portion of this acid extract may be withdrawn from the system through line 113 and fresh acid may be introduced through line 114.

The hydrocarbon fraction separated from the acid extract in the settler 110 is removed therefrom through line 115 and is passed to suitable caustic washer indicated symbolically by the rectangle 116 for removing acid absorbed or dissolved in the hydrocarbon fraction. The hydrocarbon fraction is removed from the caustic washer 116 through line 117 and passed to an alkylate fractionating tower 118 in which it is subjected to fractionation and separation to segregate a plurality of separate fractions. For example, the fractionating tower 118 may be provided with trap-out trays 119 and 121 for separately collecting different fractions, as later described. The temperature of the fractionating tower 118 below trap-out tray 119 may be controlled to vaporize all constituents boiling below the end point of motor fuel, such as those boiling below 400° F.—450° F. The alkylate boiling above the end point of the motor fuel constituents is removed from the bottom of the tower 118 through line 122 and may be passed to the catalytic cracking unit through line 123 as indicated, or it may be removed from the system through line 124. A portion of the alkylate withdrawn from the bottom of the tower 118 may be passed through a reboiler 125 and then returned to the tower 118 to supply the required amount of heat for effecting the distillation and fractionation of the products contained therein.

The temperature of the intermediate section

of the fractionating tower 118 may be controlled to segregate the fraction boiling between the end point of aviation gasoline and the end point of motor fuel. The boiling range of this fraction may, for example, be between (275–350)° F. and (400–450)° F. This alkylate product may be diverted through line 126 to an automotive fuel storage tank 127.

The top temperature of the fractionating tower 118 may be controlled by suitable cooling elements and by the use of reflux to condense constituents boiling above the C₅ constituents. For example, this fraction may have a boiling range between 100° F. and (275–350)° F. This alkylate is withdrawn from the fractionating tower 118 through line 128 and is passed to the aviation fuel storage tank 98 as blending agent for the aviation gasoline contained therein.

Vapors remaining uncondensed in the fractionating tower 118 and comprising chiefly C₄ and C₅ constituents pass overhead through line 129 to a pentane tower 131 wherein the vapors are fractionated to segregate the normal pentane from the isopentane. The normal pentane may be withdrawn from the bottom of the pentane tower 131 through line 132 and passed to the automotive fuel storage tank 127. The isopentane may be collected in trap-out tray 133 positioned in tower 131 and withdrawn therefrom through line 134 and passed to the aviation fuel storage tank 98. Vapors remaining uncondensed in the pentane tower 131 and comprising principally isobutane are removed overhead through line 135 which merges with line 89 and are therein mixed with the butane fraction passing to the butane tower 91. This mixture is then passed to the butane tower 91 in which the temperature conditions are controlled to segregate the normal butane from the isobutane, as previously described. The normal butane is removed from the butane tower 91 through line 136 and may be passed together with the normal pentane to the automotive fuel storage tank 127, or the normal butane may be removed from the system through line 137.

If desired, a part or all of the propylene fraction from the propane tower 56 may be passed through line 138 and combined with light naphtha passing through line 104 to the alkylation tower 94. When utilizing propylene in the alkylation treatment, additional means (not shown) for converting the propylene into liquid may be provided.

The modification shown in Fig. III—B differs from that shown in Fig. III—A in that the 125° F.—200° F. fraction is segregated from the C₃ fraction. The C₃ fraction, either with or without the addition of propylene, is then passed to the alkylating vessel 94 for alkylation with isobutane. The 125° F.—200° F. fraction, on the other hand, is subjected to further treatment, as later described.

Referring particularly to Fig. III—B, the liquid distillate removed from the high-pressure separator 52 (see Fig. III) is passed into the propane tower 56, as described with reference to Fig. III—A. The separation of the propane and butane constituents is the same as that illustrated in Fig. III—A and corresponding parts are indicated by the same reference characters.

The bottoms from the propane tower 56 pass to the butane tower 59 in which the butane is distilled, as described with reference to Fig. III—A. The bottoms from the butane tower 59 then pass into fractionating tower 96 which, in this case, is provided with an additional trap-

out tray 141 for segregating a fraction boiling between about 125° F. and 200° F. and consisting principally of C₆ and C₇ hydrocarbons. In this case, the top temperature of the tower 96 is maintained to condense these constituents in the top of the fractionating tower. The overhead vapors from the fractionating tower 96, which, in this case, consist essentially of C₆ hydrocarbons, pass through line 104 and condenser 105 to the alkylating vessel 94, as previously described.

If desired, a part or all of the C₃ fraction removed overhead from the initial propane tower 56 may be passed through line 142 to a cooler 143 wherein it is subjected to a temperature and pressure which will convert it into a liquid phase. The liquid is thereafter mixed with the fraction passing through line 106 to the alkylating tower 94.

The 125° F.-200° F. fraction segregated in trap-out tray 141 from the fractionating tower 96 will contain a relatively high concentration of olefins which are not particularly suitable for alkylation of isobutane under conditions favorable for the alkylation of the pentenes. This fraction may be removed from trap-out tray 141 through line 144 and passed to the automotive fuel storage tank 127.

Instead of diverting this fraction to the automotive fuel storage tank 127, it may be separately treated to remove the olefins therefrom and subsequently utilized in aviation fuel. For example, a part or all of this fraction may be removed from the trap-out tray 141 through line 145. This fraction may be passed through lines 146 and 147 to a separate alkylating unit (not shown) in which it is alkylated with isobutane or other isoparaffins under conditions which are more amenable to the alkylation of these higher boiling olefins. The alkylate formed by this separate alkylation boiling in the aviation boiling range may then be passed to the aviation fuel storage tank. Instead of subjecting this fraction to separate alkylation, it may be passed through line 148 to a hydrogenation unit (not shown) in which the olefins are hydrogenated into paraffins and the hydrogenated product may then be utilized as aviation fuel.

In lieu of subjecting this fraction either to separate alkylation or to hydrogenation, it may be separately subjected to further catalytic cracking treatment in the same or different unit than that employed in cracking the initial feed stock, as described in my earlier application, Serial No. 428,995, filed January 31, 1942.

The intermediate fraction boiling between 200° F. and 250° F. removed from fractionating tower 95 through line 96 may be treated in any of the various ways previously described in connection with Figure III—A.

Referring again to the cracking chamber 19 shown in Fig. III, catalytic material after being retained in the main body of the reactor for a substantial period discharges through the annular passage formed between the nozzle 20 and the outer shell of the reactor 19 into the bottom section 151 of the reactor 19 from which it is continuously withdrawn through conduit 152 and discharges through feed valve 153 into a stream of air passing through line 154.

If desired, an aerating and stripping gas may be introduced at one or more points in the bottom section 151 of the chamber 19 to maintain the material in a fluidized condition and to remove

absorbed hydrocarbon vapors contained therein. Any inert stripping medium may be utilized for this purpose. In many cases, such as, for example, in the case of silica-alumina gels, the use of steam tends to deactivate the catalyst. In such cases, a spent refinery gas comprising mixtures of hydrogen, methane, ethane and the like may be introduced into the bottom section of the reaction chamber as a stripping medium for the catalytic material.

If desired, additional stripping and fluidizing gas may be introduced at spaced points along the conduit 152 through lines 155, 156, 157 and 158. The conduit 152 may also serve as a standpipe for developing pressure on the catalyst being circulated through the system. For example, the conduit 152 should be of a height sufficient to develop a pressure at the bottom thereof slightly greater than the pressure in the air in line 154, which, in turn, must be sufficient to overcome the pressure drop through the regenerating chamber 13 and auxiliary equipment.

The mixture of air and catalytic material formed by the introduction of the catalytic material into the line 154 is transferred through line 159 to the bottom of the regenerator 13. The bottom section of the regenerator may be in the form of an inverted cone, as shown, having a grid plate 161 through which the mixture discharges into the main body of the regenerating chamber 13.

The velocity of the air passing upwardly through the regenerator 13 is preferably controlled in the same manner as the oil vapors passing through the cracking chamber 19 to maintain a relatively dense fluidized mixture of catalytic material within the regenerator 13.

The air passing through the catalytic material in the regenerator 13 burns combustible deposits formed on the catalyst as a result of the cracking operation. The burning of these combustible deposits results in the evolution of heat. As a result, the catalytic material is heated within the regenerator 13 to a temperature above that within the reaction chamber 19.

According to the preferred mode of operation, the catalytic material is heated in the regenerator 13 to a temperature materially above the reaction chamber so that the sensible heat of the catalyst developed during regeneration is sufficient to supply the bulk of the heat required for the cracking operation. In cases where the amount of combustible deposits laid down by the catalytic material during the cracking operation is insufficient to supply the necessary heat for the cracking operation, additional fuel may be charged into the regenerator through line 162 to supply additional heat thereto. The catalytic material after being subjected to regenerative treatment in regenerator 13 discharges through conduit 11 back into the oil stream passing through line 10, as previously described. The temperature of this catalytic material introduced into the oil stream may, for example, be from 1050° F. to 1200° F., depending upon the nature of the catalyst. For example, many types of catalysts are adversely affected by extremely high temperatures and it is necessary to restrict the temperature attained during regeneration to avoid deactivation of the catalyst.

Spent regenerating gas after passing through the catalytic material in the regenerator 13 passes into a cyclone separator 163 located in the top portion of the regenerator. Entrained catalytic material separated from the spent regenerating

gas in the cyclone separator 163 is returned to the regeneration chamber through conduit 164.

The spent combustion gases after passing through the cyclone separator 163 continue through line 165 to a cooler 166 in which they are cooled from the regeneration temperature down to a temperature of the order of from 400° F. to 600° F., after which they are discharged through line 167 into a Cottrell precipitator 168 in which additional fines entrained in the spent regenerating gas are recovered. The catalytic material so recovered passes from the Cottrell precipitator 168 through line 169 into a stream of air passing through line 171 and is returned through line 172 to the regenerating chamber 13.

The spent regenerating gas after passing through the Cottrell precipitator 168, being substantially free of catalytic material, may be vented to the atmosphere through line 173.

The rate of flow of the catalytic material through the regenerator and cracking chamber may be regulated by valve 14 in conduit 11 and valve 153 in conduit 152. For example, the time of residence of the catalytic material within the reaction chamber 19 may be regulated by means of the feed valves 14 and 153 to maintain the catalyst at the desired level of activity. This provides an additional means of controlling the composition of the cracked products issuing from the cracking chamber. For example, by reducing the residence time of the catalytic material within the reaction chamber 19, the activity of the catalyst may be maintained at a higher level, since the formation of carbonaceous deposits during the cracking operation tends to reduce its activity. Conversely, by increasing the residence time of the catalytic material in the reaction chamber 19, the activity of the catalyst may be reduced by increasing the amount of carbonaceous deposits contained on the catalytic material being withdrawn from the reaction chamber. As a further example, the time of residence of the catalytic material in the reaction chamber 19 may be regulated by the feed valves 14 and 153 to deposit a predetermined amount of combustible deposits on the catalyst.

From the above description, it should be evident that the present invention provides a process capable of converting heavy oils into aviation gasoline and at the same time make available large quantities of butenes and isobutylene which may be utilized for the production of synthetic rubber.

These objectives are accomplished according to the broader phases of the invention by first cracking the heavy oils in the presence of an active catalyst under conditions controlled to produce high yields of isoparaffins and olefins which are distributed in the light naphtha and C₄ fractions and a high concentration of aromatic hydrocarbons in the heavy naphtha fraction. The cracked products are then fractionated to segregate a heavy aromatic naphtha fraction which is utilized directly in aviation fuel and is of particular value in improving the rich-mixture performance of aviation gasoline. The light naphtha fraction, or a selected cut therefrom, is then alkylated with isoparaffins formed in the process to form an aviation alkylate which is then blended with the heavy aromatic naphtha in the necessary proportion to form an aviation fuel capable of meeting aviation specifications for 100-octane gasoline with the addition of 4 cc. of tetraethyl lead.

The relatively high concentration of aromatics

in the heavy ends of the gasoline makes the resulting fuel of outstanding advantage under rich-mixture conditions present during take-off and maneuvers.

This is exemplified in the curves shown in Fig. IV, in which incipient knocking pressure in pounds per square inch is plotted against the air-fuel ratio in pounds of fuel per pound of air. Curve A of the graph shows the effect of air-fuel ratio on the knocking pressure of a typical 100-octane aviation gasoline now commonly in use. Curve B shows the same effect of fuel composed of technical-grade isooctane containing 1.25 cc. of tetraethyl lead, and Curve C is a characteristic curve of a fuel prepared from a blend of light naphtha alkylate and aromatic heavy naphtha obtained from catalytic cracking.

It is evident from these curves that the fuel prepared according to the present invention is superior to the 100-octane gasoline now commonly used over the entire range of fuel-air ratios shown on the graph and is particularly outstanding in the richer mixtures. This fuel, for example, is equivalent to technical isooctane containing 1.8 cc. of tetraethyl lead.

The following example may serve to illustrate the results obtainable by the present invention, it being understood that the values and conditions given therein are illustrative rather than

limitative. A gas oil derived from Tinsley crude, having an A. P. I. gravity of 31.5°, was charged to a cracking unit of the general type illustrated in Fig. III. The temperature of the cracking operation was maintained at about 975° F. The catalyst employed was an artificial silica-alumina gel formed by first preparing a purified silica hydrogel which was then impregnated with alumina by soaking the silica hydrogel with an aluminum sulfate solution and then decomposing the aluminum sulfate with ammonia. The amount of alumina contained in the catalyst amounted to from 12% to 15% by weight of the catalyst.

The amount of catalyst introduced into the oil was about 10 parts of catalyst per part of oil by weight and about 3 parts of oil were treated per hour for each part of catalyst contained in the reactor. The oil was maintained under these conditions for a period sufficient to effect a total conversion of about 65% of the feed. The conversion products comprised about 42 volume per cent of gasoline having a Reid vapor pressure of 10 pounds, 23% of heating oil, 12% of a gas oil, 20.5% C₄ hydrocarbons in excess of those in the gasoline, 11 weight per cent gas and 3% coke deposit. The C₄ fraction contained about 16% isobutylene, 36.3% normal butenes, 41% isobutane, and about 7% of normal butane.

The gasoline had an A. S. T. M. octane number of 85 and a research octane number of 99. The amount of amylene contained in the C₅ fraction amounted to about 43%.

The gasoline formed was segregated to a light naphtha fraction boiling between 60° F. and 200° F. and substantially free of butanes and butenes, and a heavy naphtha fraction boiling between 200° F. and 350° F. The 60° F.-200° F. light naphtha fraction was then alkylated with isobutane at a temperature of 45° F., using sulfuric acid having a titratable acidity of 85%. The ratio of isobutane to olefins in the reaction zone was maintained at about 6 to 1.

Under the above conditions, the total yield of alkylate formed amounted to 125 volume per cent based on the light naphtha charged. The avia-

tion fraction, having a 90% point of 290° F., amounted to about 109 volume per cent based on the light naphtha charged.

The aviation alkylate fraction had a clear A. S. T. M. octane number of 86.5 which, with the addition of 4 cc. of tetraethyl lead, was equivalent to technical isooctane to which 0.16 cc. of tetraethyl lead had been added, as determined by the A. S. T. M. aviation method.

The heavy naphtha from the catalytic cracking operation boiling between 225° F. and 332° F. contained about 85% aromatics and had a clear octane number of 93.7, which was increased to 100 by the addition of 4 cc. of tetraethyl lead, as determined by the A. S. T. M. aviation method.

An aviation blend containing about 73% of aviation alkylate prepared as described above and 28% of the heavy aromatic naphtha from catalytic cracking had a clear octane number of about 85.5 and about 100 with the addition of 4 cc. of tetraethyl lead.

The following is a typical example of results attainable from combined catalytic cracking and alkylation unit of the type shown in the accompanying drawings, having a daily capacity of 42,000 barrels of gas oil.

The oil may be charged through line 10 into which about 10 parts of hot, finely divided catalyst per part of oil are introduced through conduit 11. The resulting mixture may pass into the cracking chamber 19 which is maintained at a temperature of from 900° F. to 1000° F. by the sensible heat of the mixture passing therethrough. The oil vapors may then pass upwardly through the reactor 19 at a velocity of about 1.5 to 2 feet per second. The oil vapors may be maintained in contact with the catalyst for a period of from 5 to 30 seconds, sufficient to obtain about 65% conversion into products outside the boiling range of the feed.

The cracked products may then be passed through line 24 to the fractionating tower 25.

When charging 42,000 barrels a day of gas oil derived from Tinsley crude of 31.5° A. P. I. gravity, as above described, and operating at 65% conversion, about 5100 barrels of cycle oil of 22° A. P. I. gravity may be removed from the bottom of the tower through line 28, about 9600 barrels of heating oil of 27° A. P. I. gravity may be withdrawn as a side stream through line 36, and about 2140 barrels of heavy automotive naphtha boiling between 350° F. and 400° F. may be withdrawn from trap-out tray 27 through line 39.

From the overhead products from the fractionating tower 25, about 3000 barrels of propylene, 3580 barrels of isobutane, 1400 barrels of isobutylene, 3135 barrels of normal butylene, 600 barrels of normal butane, 9190 barrels of 60° F. to 200° F. fraction, 1490 barrels of 200° F. to 250° F. fraction, 4180 barrels of 250° F. to 350° F. fraction, and 2140 barrels of 350° F. to 400° F. fraction may be recovered.

The 60° F.-200° F. fraction will contain about 6040 barrels of C₅ hydrocarbons, of which about 43% will be olefins.

By alkylating the 60° F. to 200° F. fraction with the isobutane formed in the operation, about 9800 barrels of aviation alkylate may be formed, together with 1380 barrels of heavier bottoms. In addition, there is an excess of isobutane sufficient to alkylate 495 barrels of butylene to form about 800 barrels of C₄ alkylate.

By combining the C₄ alkylate and 60° F.-200° F. aviation alkylate with the 4180 barrels of the aromatic 250° F.-350° F. fraction, 14,780 barrels

of aviation blend may be produced from the process, to which 1000 barrels of 75 octane virgin naphtha may be added to form 15,780 barrels of aviation gasoline having a 90% point at 293° F. and an aviation octane number of 100 with the addition of 4 cc. of tetraethyl lead.

In addition to the aviation gasoline, there will be available, after alkylating 495 barrels of butene with the excess of isobutane, 2640 barrels of normal butylene, equivalent to 70,000 short tons of butadiene per year for rubber.

Furthermore, there will also be available 1400 barrels of isobutylene, equivalent to 40,000 long tons of butyl rubber per year.

The 1490 barrels of the 200° F.-250° F. fraction may be treated to extract 566 barrels of nitration-grade toluene.

By combining the 2140 barrels of 350°-400° F. fraction from catalytic cracking with the 1490 barrels of 200° F.-250° F. fraction and the 1380 barrels of heavy alkylate bottoms, 5010 barrels of heavy automotive naphtha having a research octane of 97 may be recovered, to which may be added 600 barrels of normal butane and 200 barrels of the available isobutylene to form 5810 barrels of automotive fuel.

When alkylating only the C₅ fraction, as distinguished from the 60° F.-200° F. fraction, passing the 125° F.-200° F. fraction to motor fuel and utilizing excess isobutane to alkylate butenes, about 12,653 barrels of aviation base may be made from the combined C₄ and C₅ aviation alkylate and the aromatic heavy aviation naphtha from catalytic cracking. To this may be added 4000 barrels of 75 octane natural aviation base fuel to form 16,653 barrels of aviation gasoline having a 90% point at 293° F. and an aviation octane number of 100 with the addition of 4 cc. of tetraethyl lead.

When operating in this manner, the other products will comprise 2640 barrels of butene, 1200 barrels of isobutylene, and 7910 barrels of automotive gasoline, together with the same amount of heating oil, cycle oil, dry gas and excess propylene as previously described.

In cases where the toluene is extracted from the 200° F. to 250° F. fraction, the amount of automotive gasoline formed will be reduced by the amount of toluene extracted from this fraction by passing the raffinate from toluene extraction to motor fuel.

The above are typical illustrations of results generally obtainable by two embodiments of the invention and are not indicative of results obtained in all cases.

In the above description I have described the different boiling range fractions to the nearest 10 degrees. It will be understood that the invention is not limited to the exact fractions so disclosed. For example, the 60° F. to 200° F. fraction or the 125° F. to 200° F. fraction is intended to exclude any substantial amounts of toluene, which boils at 230.9° F. By sharp fractionation, it is possible to increase the end point of this fraction up to 220° or 225° F. and still exclude the toluene. Likewise, the 60° F. to 125° F. fraction is intended to exclude any substantial amount of C₅ olefins, although it may include C₅ branch-chain paraffins. The other fractions may also be modified, depending on the boiling and volatility of the desired products.

I have also shown the olefin fraction to be alkylated as passing directly from the distillation tower to the alkylating chamber. In some cases,

the acid consumed may be reduced and other advantages realized by subjecting the olefin fraction to preliminary acid washing. For example, the olefin fraction passing to alkylation may be washed with sulfuric acid of about 65% strength at temperatures of from 80° F. to 120° F. before passing to the alkylation zone.

The term "artificial gels" as employed herein is intended to mean synthetic gels or natural adsorptive materials which have been drastically treated to change materially the character of the material. This last-named product, for example, may comprise a bentonite clay which has first been drastically treated with an acid to remove the impurities together with a large amount of the alumina and the alumina then added back to the treated clay by precipitation or other means.

Having described the preferred embodiment of the invention, it will be understood that it embraces such other variations and modifications as come within the spirit and scope thereof.

What is desired to be protected by Letters Patent is:

1. A process for producing gasoline which comprises passing a hydrocarbon oil boiling above gasoline through a cracking zone, contacting said oil within said cracking zone with a cracking catalyst while at active cracking temperature above 850° F., maintaining said oil in contact with said catalyst within said cracking zone to convert at least 50% of said oil into other constituents comprising gasoline, butane and butene constituents and lower boiling hydrocarbons, the amount of butane-butene constituents contained in said cracked products being at least 15 volume per cent of said oil being cracked, thereafter fractionating the cracked products to segregate a heavy naphtha fraction having a boiling range within 160° F. and the end point of said gasoline consisting principally of aromatic constituents, a light naphtha fraction having a boiling range within 50° F. and 200° F. containing substantial amounts of olefinic constituents, a butane fraction consisting principally of isobutane and a butene fraction, combining the light naphtha fraction with said isobutane fraction, the amount of said isobutane fraction being in excess of the amount of olefinic constituents contained in said light naphtha fraction, causing said mixture of isobutane and light naphtha to react to alkylate the olefinic constituents contained in said light naphtha fraction and form a substantially saturated alkylate product, and thereafter combining the alkylate product so produced with a heavier aromatic fraction to form gasoline.

2. A process for producing gasoline which comprises passing a hydrocarbon oil boiling above gasoline through a cracking zone, contacting said oil within said cracking zone with a cracking catalyst comprising an artificial adsorptive product containing silica and alumina while at active cracking temperature above 850° F., maintaining said oil in contact with said catalyst for a period sufficient to convert at least 50% of said oil into other constituents comprising gasoline constituents, butane and butene constituents and lower boiling hydrocarbons, the amount of butane-butene constituents formed being at least 15% by volume of the amount of oil cracked, thereafter fractionating the cracked products to segregate a heavy naphtha fraction having a boiling range within 160° F. and the end point of gasoline consisting principally of aromatic constituents, a lighter naphtha fraction having a boiling range

above the butane-butene constituents and below about 200° F., said light naphtha fraction containing substantial quantities of olefinic constituents, separating isobutane from the remainder of the butane-butene constituents, passing said light naphtha fraction and said isobutane so segregated through an alkylating zone, the amount of isobutane contained in said zone being in excess of the olefinic constituents contained in said light naphtha fraction, regulating the conditions within said alkylating zone to react said isobutane with the olefins contained in said light naphtha to form a substantially saturated alkylate product and combining said alkylate product with said heavy aromatic naphtha fraction to form gasoline.

3. A process for producing gasoline which comprises passing a hydrocarbon oil boiling above gasoline in vapor form upwardly through a cracking zone, introducing a finely divided cracking catalyst into said cracking zone in direct contact with the oil passing therethrough, regulating the velocity of the oil vapors passing upwardly through said cracking zone to maintain a dense turbulent mass of catalytic material within said cracking zone, maintaining said oil while in contact with said catalyst within said cracking zone at a temperature above 850° F., keeping said oil within said cracking zone for a period sufficient to convert at least 50% of said oil into other constituents comprising gasoline components, butane-butene constituents, and lower boiling constituents, separating cracked products from said finely divided catalytic material, fractionating the cracked products to segregate a heavy naphtha fraction having a boiling range within 160° F. and the end point of the gasoline to be produced consisting principally of aromatic constituents, a light naphtha fraction containing a relatively high concentration of olefinic constituents and substantially free of aromatic constituents, separating the butane-butene fraction formed during the cracking operation into a paraffinic fraction consisting principally of isobutane, and an olefinic fraction, passing said isobutane fraction so separated and said light naphtha fraction containing said olefinic constituents through an alkylating zone, reacting said isobutane with olefinic constituents in said light naphtha fraction in the presence of an excess of isoparaffins within said alkylating zone to form an alkylate product, and combining alkylate so formed with said heavy aromatic naphtha to form gasoline.

4. A process for producing gasoline which comprises passing a hydrocarbon oil boiling above gasoline through a cracking zone containing finely divided cracking catalyst, maintaining said oil during contact with said catalyst within said cracking zone at a temperature above 850° F., keeping said oil within said cracking zone for a period sufficient to convert at least 50% thereof into other constituents comprising gasoline components, butane-butene constituents, and lower boiling constituents, separating cracked products from said catalytic material, fractionating the cracked products to segregate a heavy naphtha fraction having a boiling range within 160° F. and the end point of aviation gasoline consisting principally of aromatic constituents, a lighter naphtha fraction containing a relatively high concentration of olefinic constituents and substantially free of aromatic constituents, and a butane-butene fraction, separating the butane-butene fraction into a paraffinic fraction consisting principally of isobutane and an olefinic fraction, re-

moving said olefinic fraction from the process as a final product thereof, passing said isobutane fraction so separated together with said light naphtha through an alkylating zone, reacting said isobutane with the olefinic constituents of said light naphtha in the presence of an excess of isoparaffins within said alkylating zone to form an alkylate, and combining alkylate so formed with said heavy aromatic naphtha fraction to form gasoline.

5. A process for producing gasoline which comprises passing a hydrocarbon oil boiling above gasoline while in vapor form upwardly through a cracking zone, introducing a finely divided cracking catalyst into the stream of oil passing through said cracking zone, controlling the velocity of the oil vapors passing upwardly through said cracking zone to maintain a dense turbulent mass of catalytic material within said cracking zone, maintaining said cracking zone at a temperature above 850° F., maintaining said oil vapors in contact with said catalyst within said cracking zone for a period sufficient to convert at least 50% of said oil into other constituents comprising gasoline components, butane-butene constituents, and lower boiling constituents, thereafter separating the cracked products from the finely divided catalytic material, fractionating the cracked products to segregate a heavy naphtha fraction having a boiling range within 160° F. and 350° F. consisting principally of aromatic constituents, a lighter naphtha fraction containing a relatively high concentration of olefinic constituents and substantially free of aromatic constituents, and a butane-butene fraction, separating said butane-butene fraction into a paraffinic fraction consisting principally of isobutane and a butene fraction, removing the butene fraction from the process as a product thereof, passing the paraffinic fraction containing said isobutane and said light naphtha fraction containing said olefinic constituents through an alkylating zone, reacting said isobutane with the olefinic constituents in said light naphtha in the presence of an excess of isoparaffins within said alkylating zone to form an alkylate product, and combining alkylate product boiling below 350° F. with said heavy aromatic naphtha to form an aviation gasoline.

6. A process for producing gasoline which comprises passing a hydrocarbon oil boiling above gasoline while in vapor form upwardly through an enlarged cracking chamber, introducing a finely divided cracking catalyst comprising an artificial adsorptive material containing silica and alumina, regulating the velocity of the oil vapors passing upwardly through said cracking zone to maintain a dense turbulent mass of catalytic material within said cracking zone, keeping said oil while in contact with said catalyst within said cracking zone at a temperature above 850° F., maintaining said oil in contact with said catalyst within the cracking zone for a period sufficient to convert at least 50% of said oil into other constituents comprising gasoline components, butane-butene constituents, and lower boiling constituents, thereafter separating the cracked products from the catalytic material, fractionating the cracked products to segregate a heavy naphtha fraction having a boiling range within 160° F. and the end point of said gasoline consisting principally of aromatic constituents, a lighter naphtha fraction containing a relatively high concentration of olefinic constituents and substantially free of aromatic constituents, segregating

an isobutane fraction and a butene fraction from the cracked products, removing the butene fraction as a product of the process, passing the isobutane fraction and said light naphtha fraction through an alkylating zone, reacting said isobutane with the olefinic constituents contained in said light naphtha within said alkylating zone in the presence of an excess of isoparaffins to form an alkylate, combining alkylate so formed with said heavy aromatic naphtha to form gasoline, passing catalytic material separated from the cracked products and containing combustible deposits into a regenerating zone, burning said combustible deposits within said regenerating zone, heating said catalytic material during said regeneration to a temperature materially above the temperature within said cracking zone, and thereafter passing said regenerated catalytic material while at said higher temperature in contact with said oil passing through said zone to supply heat to said cracking zone.

7. A process for producing aviation gasoline which comprises passing an oil boiling above aviation gasoline in vapor form upwardly through a cracking zone, contacting the oil vapors passing through said cracking zone with a finely divided cracking catalyst comprising an artificial adsorptive material containing silica and alumina, controlling the velocity of the oil vapors passing upwardly through said cracking zone to maintain a dense turbulent mass of catalytic material therein, keeping said cracking zone at a temperature above 850° F., maintaining the oil in contact with the catalyst for a period sufficient to convert at least 50% thereof into other constituents comprising gasoline components, butane-butene constituents, and lower boiling constituents, separating the cracked products from the catalytic material, fractionating the cracked products to segregate a heavy naphtha fraction having a boiling range within 200° F. and 350° F., an intermediate fraction boiling between 100° F. and 250° F., a light naphtha fraction having a boiling range between 50° F. and said intermediate naphtha fraction, separating isobutane from the cracked products, passing the isobutane and said light naphtha fraction to an alkylating zone, reacting said isobutane with olefinic constituents contained in said light naphtha fraction within said alkylating zone to form an alkylate product, separating said intermediate fraction into a paraffinic fraction and an aromatic fraction, and combining alkylate obtained from said light naphtha and isobutane and the aromatic fraction of said intermediate naphtha with said heavy naphtha fraction to form a gasoline within the aviation boiling range.

8. A process for producing gasoline which comprises passing a hydrocarbon oil boiling above gasoline through a cracking zone, contacting said oil within said cracking zone with an active cracking catalyst while at a temperature above 850° F., maintaining said oil in said cracking zone for a period sufficient to convert a substantial portion of said oil into gasoline constituents, fractionating the cracked products to segregate a heavy naphtha fraction having a boiling range above 160° F. and below the end point of gasoline, an intermediate fraction having a boiling range above 100° F. and below said heavy naphtha fraction, a light naphtha fraction boiling above 50° F. and below said intermediate naphtha fraction containing substantial quantities of olefinic constituents and being substantially free of aromatic constituents, passing said light naphtha fraction to

an alkylating zone, introducing isoparaffinic hydrocarbons into said alkylating zone in an amount in excess of the olefinic content of said light naphtha fraction, controlling conditions within said alkylating zone to react said isoparaffins with the olefins contained in said light naphtha fraction to form a substantially saturated alkylate

5 product, treating said intermediate naphtha fraction to remove olefins therefrom, and thereafter combining said intermediate fraction substantially free of said olefins with said heavy naphtha fraction and with the alkylate product to form gasoline.

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