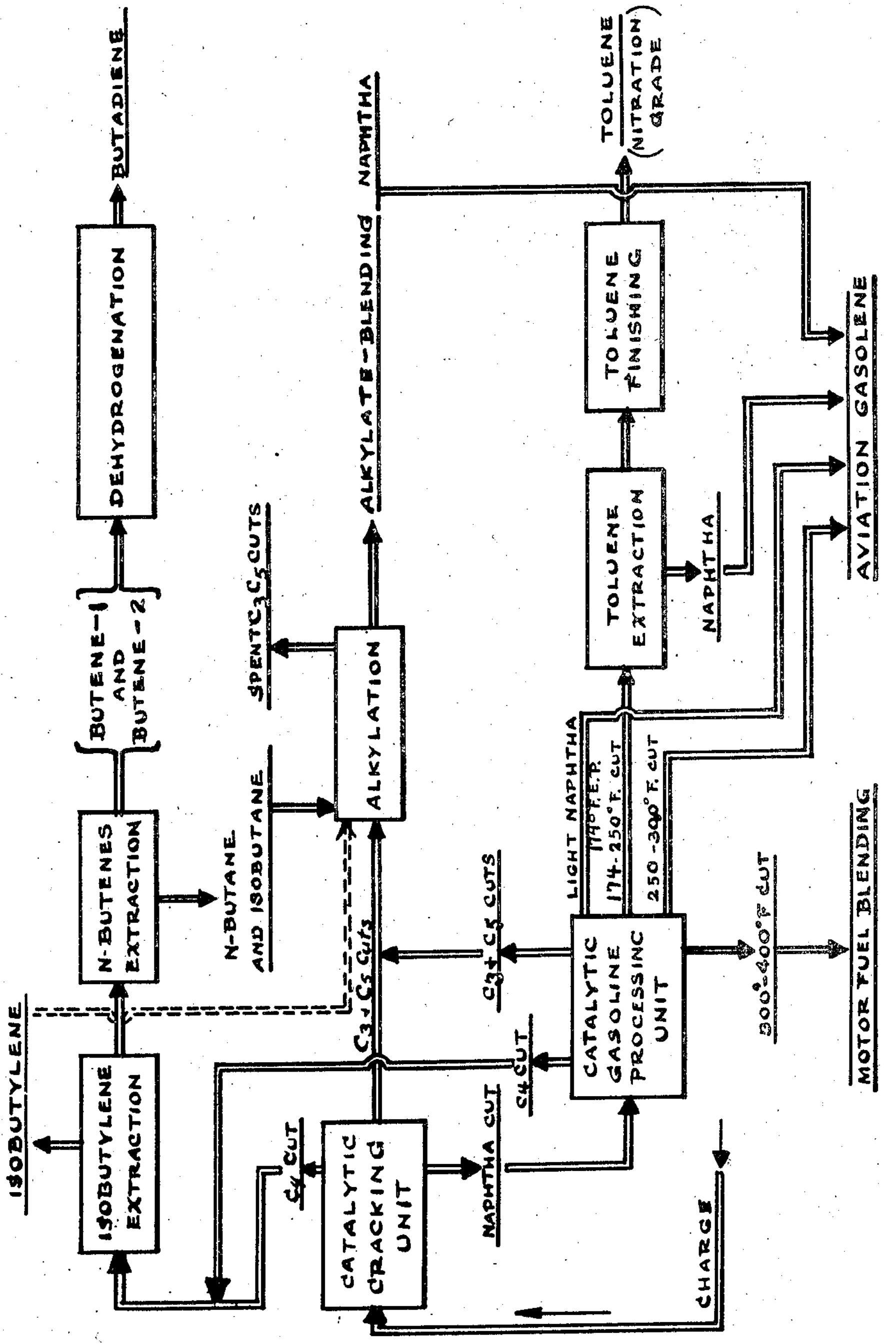
March 23, 1948. R. P. RUSSELL ET AL 2,438,456

HYDROCARBON CONVERSION

Filed Aug. 21, 1942 5 Sheets-Sheet 1

FIG-1



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HYDROCARBON CONVERSION

Filed Aug. 21, 1942 5 Sheets-Sheet 2

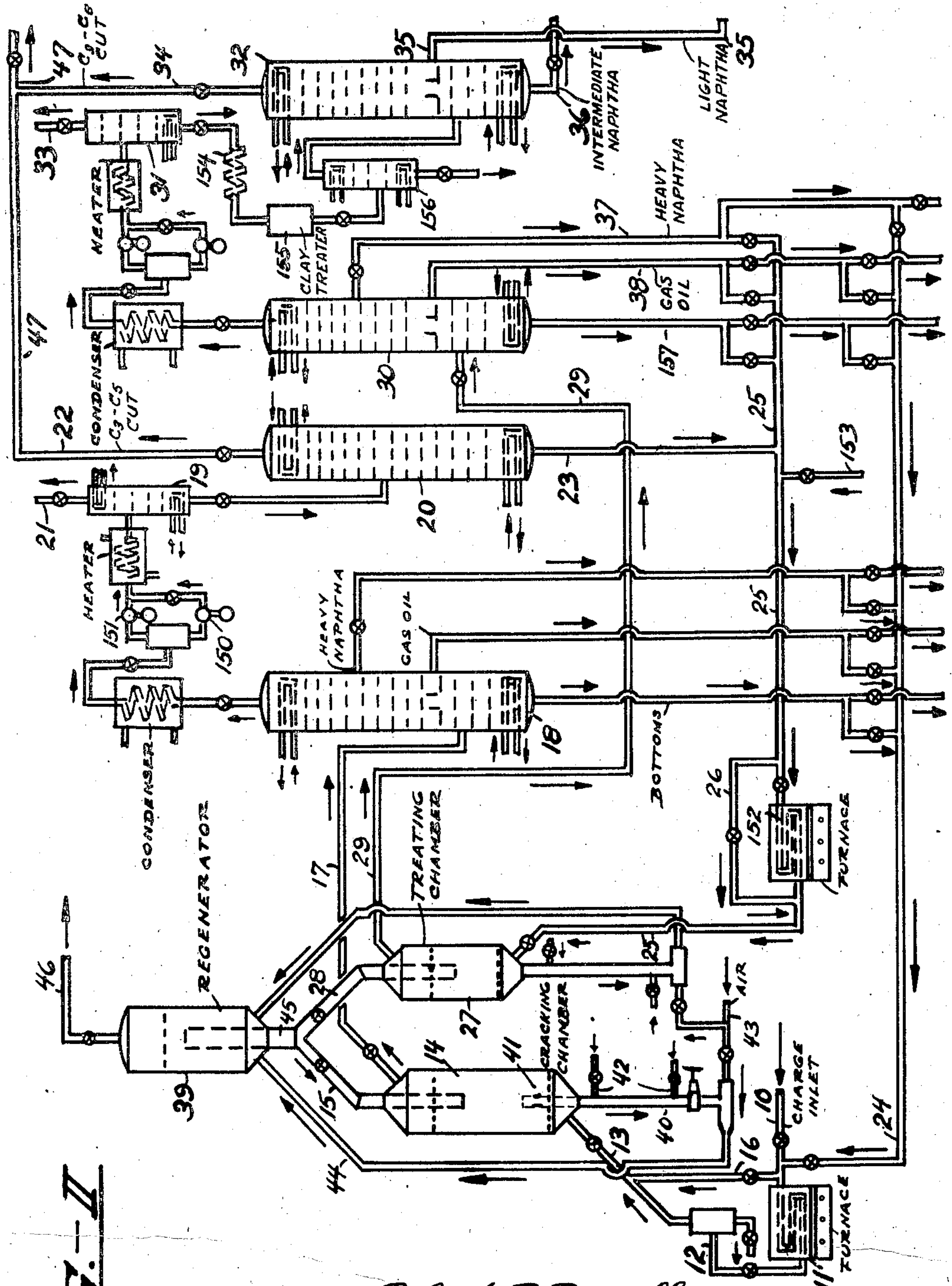

FIG.-II

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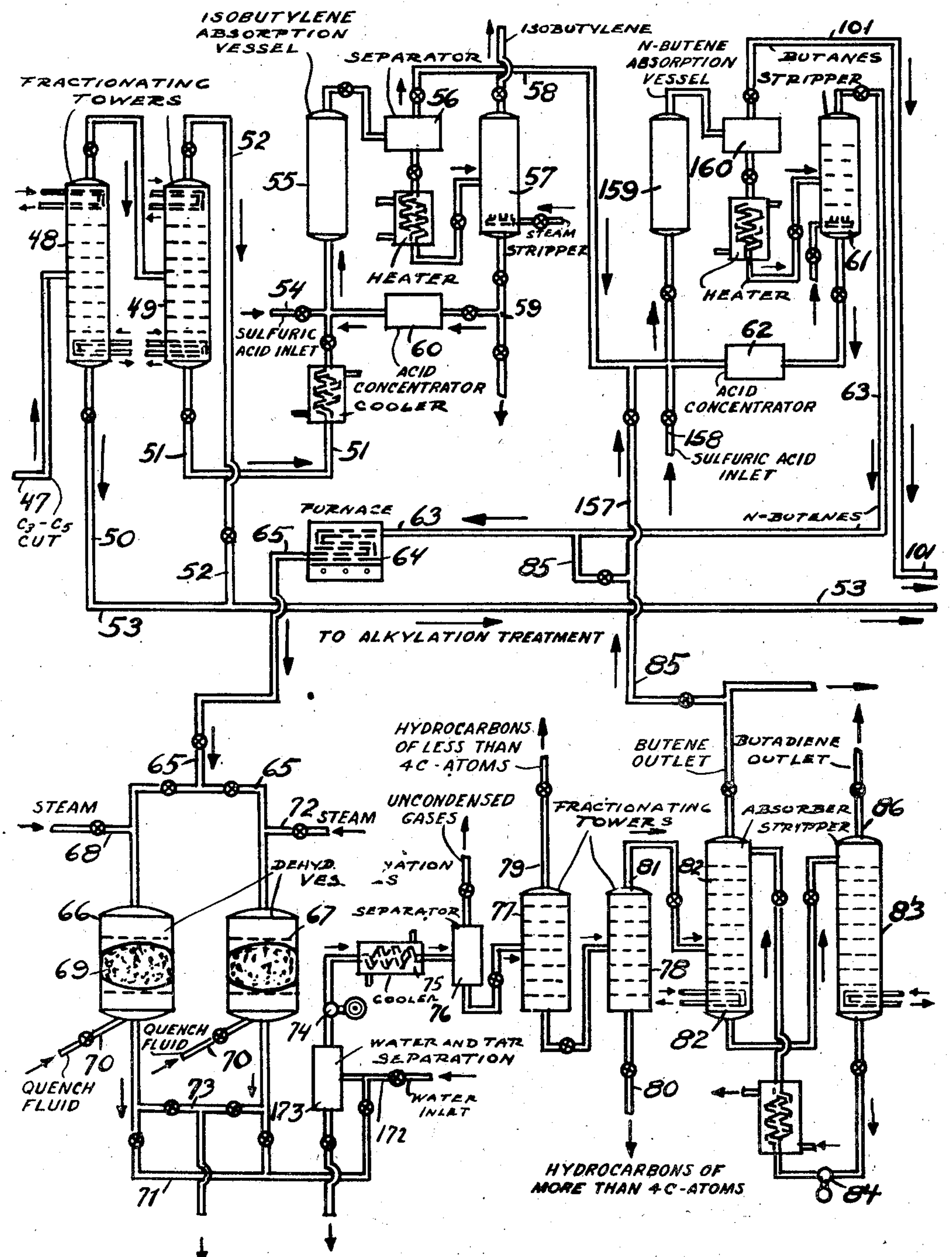

FIG.-IIA

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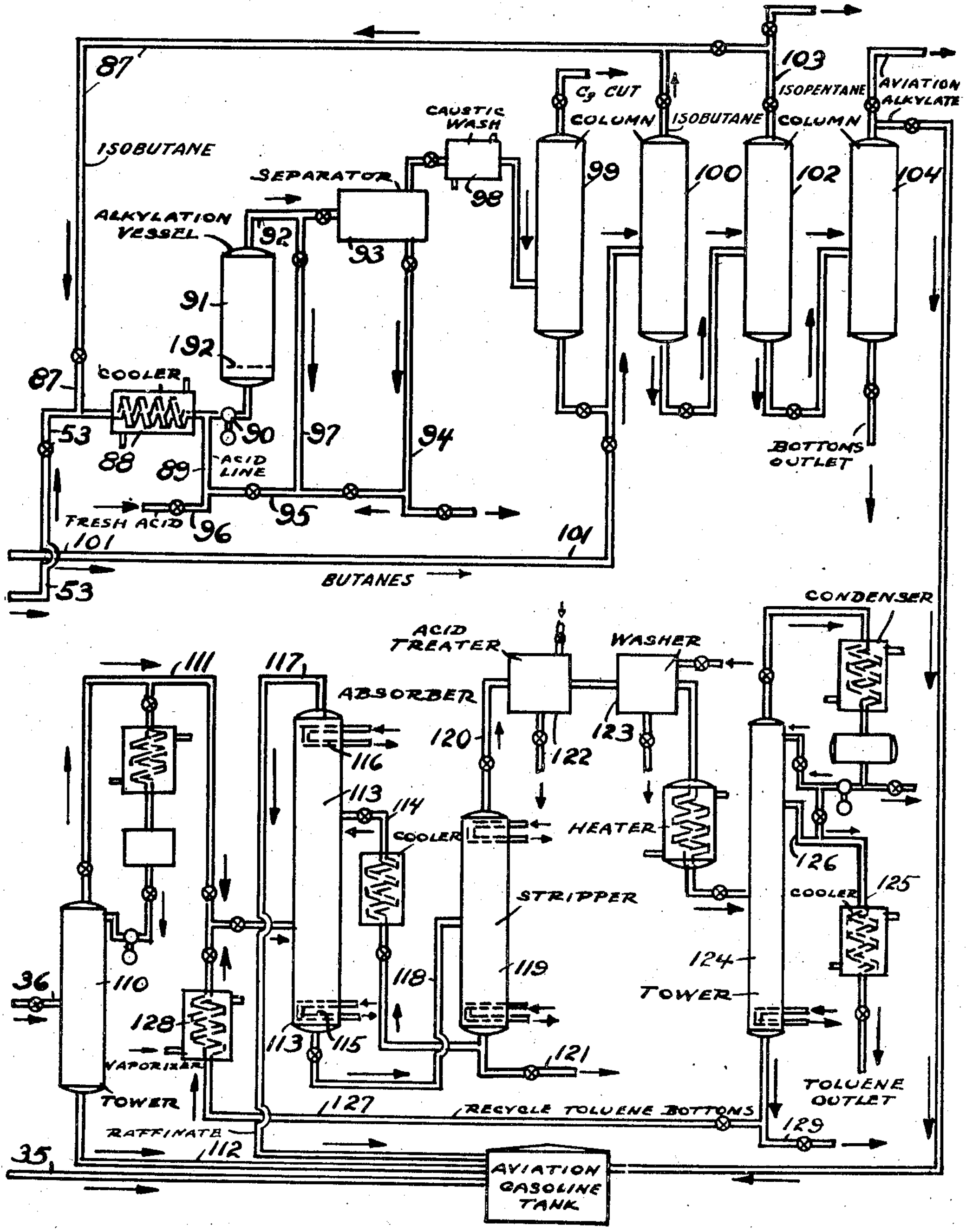

FIG.-IIB

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HYDROCARBON CONVERSION

Filed Aug. 21, 1942 5 Sheets-Sheet 5

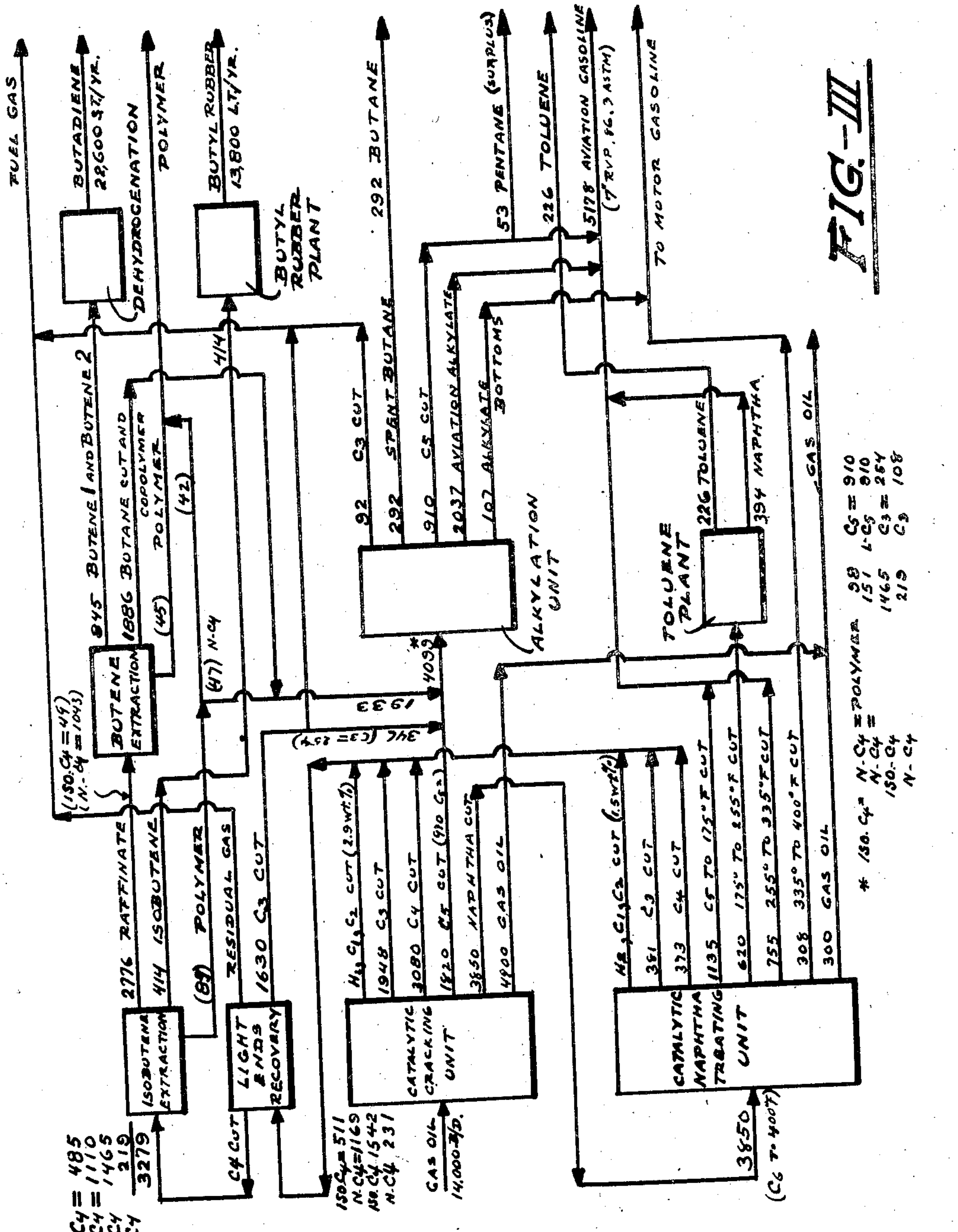

FIG.-III

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UNITED STATES PATENT OFFICE

2,438,456

HYDROCARBON CONVERSION

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Application August 21, 1942, Serial No. 455,574

6 Claims. (Cl. 260—683.4)

This invention relates to the conversion of hydrocarbon oils and involves an improved process for the production of high quality aviation gasoline and of aviation base naphtha and alkylate blending stocks. The process of this invention is especially designed for the utilization of byproducts to produce also pure toluene and low molecular weight olefins and diolefins, specifically isobutylene and butadiene.

One object of this invention is to provide an integrated process adapted for the catalytic conversion of hydrocarbon oils to aviation base stock of required low acid heat, high aviation octane number and high lead response. A further object of this invention is to augment the yield of such aviation base stocks by an improved alkylation process in which selected portions of the low molecular weight and normally gaseous hydrocarbon products of 3 to 5 carbon atoms per molecule are converted to additional high quality aviation base stocks. A further object of this invention is to provide a process in which the butenes are separated from the low molecular weight hydrocarbon conversion products prior to this alkylation reaction and in which the isobutylene and the n-butenes are thus separately made available as valuable by-products which are suitable for the preparation of polymers and co-polymers including motor fuels and high molecular weight synthetic rubber-like products, as well as for conversion to materials also useful in the preparation of such products; for example, the n-butenes may be dehydrogenated to produce butadiene. It is a still further object of this invention to provide a process in which toluene of nitration grade (suitable for the preparation of explosives) is separated from catalytically converted aviation base stock.

Other objects and advantages of the invention will be apparent from the following description, the drawings and the claims.

Referring to the drawings, Figure I presents a diagrammatic flow plan of the process of this invention and indicates the flow of materials between the various reaction and treating units involved. Figures II, II*a* and II*b* present a more detailed illustration of suitable types of reaction and treating units which may be used in an apparatus for carrying out the process of this invention. Figure III is a detailed flow sheet indicating quantities and distribution of the various streams in an example of the invention.

Referring to Figure II, the reference character **10** designates a charge line through which the oil to be processed is introduced into the system.

While this oil is preferably a clean condensate stock, such as a gas oil, it is also possible to employ virgin gasolines, kerosene or crudes or topped or reduced crudes containing unvaporizable material as the charging material. The charge passes through a preheating and vaporizing furnace **11** wherein the oil is heated to a temperature sufficient to vaporize a substantial portion thereof. The products from the heating furnace may be passed into a separator **12** in which unvaporized materials are separated from the vapors, these being removed overhead by line **13** and passed into a cracking chamber **14** into which an active cracking catalyst of the type later to be described may be introduced through line **15**.

In many cases, the preheating furnace **11** and separator **12** may be omitted and the oil may be passed in relatively cold condition through lines **10**, **16** and **13** directly into the reactor **14**. In this case, the heat necessary for carrying out the cracking operation may be supplied entirely by the hot catalyst introduced into the cracking chamber through line **15**.

While this catalyst may comprise any suitable material for the catalytic cracking of hydrocarbon oils, such as activated clays and the like, the catalyst used is preferably a synthetic gel having as its principal constituents silica and alumina. Such synthetic gel catalysts may contain from about 5% to 30% alumina, preferably between 10 and 20%, and may be prepared by adding alumina or a solution of an aluminum salt which may be subsequently converted to alumina, to a hydrous silica or to a solution from which the hydrous silica is formed. The resulting catalyst may be activated by maintaining it at a temperature from 800 to 1000° F. for a period of several hours. Other highly active synthetic gel catalysts may also be used, and may comprise silica-zircona, boria-alumina, tungsten oxide-alumina, beryllia-silica, beryllia-alumina, silica-magnesia, and the like. All such catalysts are preferably free from alkali metals, especially sodium, in order to permit repeated regeneration without loss in activity. Three-component catalysts may be employed containing silica, alumina and zircona or silica, alumina and thoria or silica, alumina and magnesia. Other catalysts may be activated clays on which alumina, boria, thoria, magnesia and the like may be added by impregnation.

While the catalytic cracking and treating processes to be described may be conducted with any suitable type of equipment in which the catalyst is maintained in a stationary bed in the reaction chamber and is used alternately for cracking oil passed therethrough and then subjected to regeneration, the preferred process utilizes the catalyst in a finely divided powdered state, having a particle size such that the bulk of the material may pass through a 200 mesh standard screen, this catalyst being at least partially suspended in a highly mobile state in the oil vapors undergoing cracking. The catalyst may also be in a granular state and moved through the reactor by gravity and transported between vessels by mechanical conveyors.

As illustrated, the cracking chamber **14** is in the form of a vertical upright vessel having an inverted conical base in which the oil to be treated is discharged. A perforated grid is preferably provided in the lower portion of the reaction chamber **14** forming a distributing plate to insure more uniform distribution of the oil vapors throughout the catalyst mass. The velocity of the oil vapors passing upwardly through the cracking chamber **14** should be adjusted to maintain a relatively dense, turbulent fluidized mass of oil vapors and catalysts therein, and may range, for example, between 0.5 to 5 feet per second to maintain a density of about 5 to 40 pounds per cubic foot in the lower portion of the cracking chamber. The velocity of the vapors is preferably not so high as to cause entrainment of any substantial proportion of catalyst in the vapors reaching the top of the cracking chamber. The amount of catalyst introduced into the cracking chamber may range from 0.5 to 25 or more parts by weight per part of oil supplied thereto, depending upon whether it is desired to supply all the heat of the cracking operation by the hot catalyst introduced. The time of residence of the oil vapors in the cracking zone in contact with the catalyst should be sufficient to obtain a conversion of between 40% and 80% of the feed oil to other constituents and may be, for example, between about 5 seconds and 1 minute or more, depending upon the activity of the catalyst. While the pressure is ordinarily about atmospheric in the cracking chamber, mild superatmospheric pressures of about 2 to 10 atmospheres may be employed.

It will be understood that in accordance with the present invention the cracking conditions in the cracking chamber **14** are preferably controlled to obtain a maximum yield of olefinic, isoparaffinic and aromatic hydrocarbons. The temperature in the cracking chamber **14** may be maintained between about 750° F. and 1100° F., and preferably between about 875° F. and 1000° F., with the synthetic gel catalyst described above.

The cracked products are withdrawn through line **17** and passed to suitable fractionating equipment, such as towers **18**, **19** and **20**, operated to produce an uncondensed gas fraction containing mainly hydrogen and hydrocarbons of the methane and ethane series which is withdrawn by line **21**, a fraction containing hydrocarbons of 3 to 5 carbon atoms per molecule withdrawn by line **22**, and a naphtha fraction withdrawn by line **23**. Towers **19** and **20** are preferably operated at pressures substantially above that of cracking chamber **14** in order to avoid refrigeration in the reflux condensers. This is secured by pump **150** and compressor **151**, operating respectively on the liquid and gaseous portions of the tower **18** distillate. The heavier materials may also be separated in tower **18** into a residual fraction and gas oil and heavy naphtha fractions, either or all of which may be withdrawn from the system or recycled to the cracking chamber **14** by line **24**.

In accordance with the preferred embodiment of the invention, the naphtha in line **23** constitutes the initial feed for the production of aviation base fuel by a further catalytic treatment later to be described. This naphtha may be a 400° F. or higher end point motor fuel fraction, a 300° F., or a 325° F. or 335° F. end point aviation gasoline fraction, or it may be a light naphtha boiling up to 200 or 225° F. It has been found, for example, that the fraction of the cracked product boiling between 200 and 300° F. is rich in aromatics and isoparaffins and contains only a relatively small amount of olefins. Hence it may be withdrawn and used directly as a motor fuel or aviation gasoline blending stock, or subjected to extraction to recover aromatics such as toluene contained therein.

A naphtha produced by a single stage cracking treatment of heavier oils is relatively low in octane number and lead response as compared to the naphtha obtained by subjecting this product to a second stage catalytic reforming treatment. This second stage treatment not only increases the yield and availability of pure toluene in the product but also so increases the octane number and lead response of this product (with or without toluene extraction) that the catalytically reformed naphtha is a valuable blending stock for the preparation of 100 octane number aviation gasoline. It is thus preferable in the process of this invention to remove in line **23** a naphtha boiling up to about 300 to 400° F. and to subject this naphtha to further catalytic treatment.

As will be discussed later the second treating step saturates the olefins. Consequently, C_5 hydrocarbons may be included in the feed in line **23** in accordance with the requirements for isopentane for the aviation gasoline vapor pressure. In general it is preferable to exclude the C_5 cut to the second stage because it is more advantageously converted to alkylate in subsequent alkylation than to aviation base stock in the second stage treating step.

This naphtha is passed by line **25** through preheater **152** or by-pass **26** into a second catalytic treating chamber **27**, which is suitably of the same design as the cracking chamber **14**, and is supplied with a similar powdered catalyst by line **28**. Chamber **27** is also operated similarly to chamber **14** in that the velocity of the oil vapors passing upwardly through the treating chamber is preferably controlled to maintain a dense, agitated, fluid mass of catalyst and oil vapors within the main body of the treating chamber and to avoid carrying overhead with the vapors any substantial amounts of the catalyst. This catalyst is preferably of the same general type as that used in the cracking chamber **14**, as this catalyst has been found to be particularly suitable for producing aviation gasoline of low acid heat, high aviation octane number and lead response. Because of the large quantity of alkylate raw materials normally produced in the cracking step, additional aviation base stock for blending therewith may be produced by adding thermally cracked naphthas, thermally reformed naphthas and other olefinic gasolines or virgin gasolines, kerosenes and light gas oils to the feed to reactor **27** through line **153**.

The treating conditions, such as temperature, catalyst ratio, time of contact, etc. maintained in chamber **27** are adjusted to produce an aviation gasoline blending stock of high aviation octane number and lead response and of low unsaturates and acid heat, one of the principal functions of this second treatment being to reduce the unsaturates content and the acid heat and to increase the octane number of the aviation fraction of the naphtha feed. In the case of high sulfur distillates, this further treatment materially reduces the sulfur content of the finished product. The temperature maintained in the treating chamber **27** should be between about 600 and 1000° F., and is preferably between about 750 and 900° F. The time of contact and the catalyst-oil ratio in chamber **27** may be substantially the same or less than in chamber **14**.

While both reactors **14** and **27** are shown to be fed from a common catalyst source, separate catalyst streams from separate regenerators of the same or different catalysts may be used.

The treated naphtha products are withdrawn by line **29** and passed to suitable fractionating equipment, such as towers **30**, **31** and **32**, which are operated to produce an uncondensed gas fraction containing mainly hydrogen and hydrocarbons of the methane and ethane series which is withdrawn in line **33**, and a fraction containing hydrocarbons of 3 to 5 carbon atoms per molecule which is withdrawn by line **34**. The distillate from tower **30** is also preferably compressed before fractionation, by the same method used to compress the distillate from tower **18**. It is also desirable to subject this distillate, or the naphtha fraction thereof, to clay treating or other suitable treatment to remove any diolefins, peroxides or other unstable materials which may be present. This improves the octance number of the gasoline, and also the operation of the phenol extraction process, as it removes materials which would degrade the phenol and cause troublesome deposits. The feed to tower **32**, for example, may be vaporized in heater **154** and passed at approximately the temperature of its dew point, downwardly over activated clay in vessel **155**, then through fractionating tower **156** from which high boiling polymers are removed as bottoms and the distillate is passed into tower **32** for further fractionation. A light naphtha fraction boiling up to about 175 to 200° F. is withdrawn by line **35** and is suitable for use as an aviation gasoline blending stock. An intermediate naphtha fraction boiling up to about 300° F. is withdrawn by line **36**. This fraction contains a high proportion of toluene and very little unsaturates. It provides an especially desirable source of pure toluene which may be extracted by a process to be later described. A heavier fraction boiling between about 300 and 400° F. may be withdrawn by line **37** and used as a motor fuel blending stock. This may also be recycled to either catalytic treating unit in order to increase the total yield of toluene. A gas oil and a residual fraction consisting mainly of polymers and entrained catalysts are withdrawn by lines **38** and **157** and either may be recycled to the treating chamber **27** by line **25** or to chamber **14** by line **24**.

When an aviation gasoline of 90% at 293° F. is to be produced as a final product, it is advantageous to include hydrocarbons boiling in the 300–335° boiling range in the treated aviation base, as indicated in Figure III. Then, the low boiling alkylate will give sufficient volatility to the final blend. By doing so the overall octane number and yield will be increased by the inclusion of this high octane number (100–110 with 4 cc. TEL) cut.

Considering further the treating chambers **14** and **27**, the catalysts contained therein gradually accumulate carbonaceous deposits which reduce their activity. As a result, it is necessary to regenerate these catalysts. This may be done most conveniently by continuously withdrawing catalyst from the reaction chambers, regenerating it by treatment with an oxidizing gas to remove the carbonaceous material, and then returning the regenerated catalyst to the reaction chambers. Where different catalysts are used in the two chambers **14** and **27**, such regenerative treatment must of course be conducted in separate units. In the preferred case illustrated, the same catalyst is used in both chambers and is passed through a common regenerator **39**, which may suitably be of the same construction as the reaction vessels **14** and **27** as regards the middle and lower portions.

The catalyst is withdrawn from chamber **14** through a conduit **40**, which preferably has an extended portion **41** projecting upwardly into the reactor. A stripping and fluidizing gas may be introduced into the conduit **40** at one or more spaced points by means of lines **42**. This is the preferred method used in transferring the powdered catalyst in order to maintain it in a mobile or readily flowing state, and it is to be understood that suitable fluidizing gases (preferably inert or not reactive with the medium in contact with the catalyst at the particular point of supply) are supplied continuously to all vessels and conduits in which the catalysts may collect. The catalyst from conduit **40** discharges into a stream of air entering through line **43** and is suspended therein and passed upwardly through line **44** into the regenerating chamber **39**. A large amount of heat is liberated in this regeneration and it is desirable to control the temperature of the regenerator **39** below a predetermined point which would tend to impair permanently the activity of the catalyst. This control may be accomplished by the amount of catalyst circulated through the reaction chambers or by the temperature, the amount or the oxygen content of the regenerating gases. A recirculating cooler for vessel **39** may be added to give more flexibility to controlling the regeneration temperature.

The catalyst after undergoing the desired degree of regeneration in chamber **39** is withdrawn through conduit **45** which connects with lines **15** and **28** and is then returned to the reaction chambers **14** and **27**. The spent regenerating gas is withdrawn through line **46** and may be subjected to any suitable treatment for recovery and return of catalyst powder entrained therein.

Returning to the cracked products, the fraction containing hydrocarbons of 3 to 5 carbon atoms in lines **22** and **34** contains large proportions of olefins and isoparaffins, thus making it extremely valuable to combine this catalytic cracking process with processes for the recovery and use of these materials. It has been found especially advantageous to separate the isobutylene and normal butenes from this fraction and to subject the remainder to an alkylation treatment to produce increased yields of aviation gasoline. Of course, where either the isobutylene or the normal butenes are not desired for other purposes, they may be also subjected to the alkylation treatment.

The fractions in lines **22** and **34** (described conveniently as the C_3—C_5 cuts) are combined in line **47** and passed through fractionating towers **48** and 49, see Figure IIA from which the fraction containing hydrocarbons of 5 or more carbon atoms per molecule (the C_5 cut) is withdrawn by line 50, the C_4 fraction by line 51, and the C_3 fraction by line 52. The C_3 and C_5 fractions are combined in line 53 and passed to an alkylation treatment to be later described.

The C_4 fraction is then treated to separate the isobutylene and the normal butenes from the butanes by any suitable method. The preferred, illustrated method is to absorb the isobutylene by mixing with cold, concentrated sulfuric acid supplied by line 54, the mixture of sulfuric acid and C_4 cut being passed through one or more absorption vessels 55 in which it is maintained for a time sufficient to permit substantially complete absorption of the isobutylene. The sulfuric acid is preferably supplied at a concentration of about 65% and the absorption temperature is maintained throughout at about 60° F. to 65° F. in order to absorb the isobutylene selectively without substantial absorption of the normal butenes, the pressure being sufficiently high to maintain the C_4 cut in liquid phase. After the acid and C_4 cut are passed through one or more absorption vessels 55 (either concurrently or countercurrently), a separation of layers is effected in separator 56 and the heavier acid extract layer is heated and stripped with steam in a tower 57 to liberate the isobutylene. This tower is suitably supplied with open steam (which may come from subsequent reconcentration of the acid) and may be maintained at a temperature of about 240° F. at the bottom and about 170° F. at the top. The distillate from this tower is further fractionated to separate isobutylene from aqueous alcohol and small amounts of polymer. The aqueous alcohol may be mixed with the acid extract and thus recycled continuously to the stripper wherein it is converted largely to isobutylene. The acid leaving the bottom of the stripper by line 59 will have an acid concentration of about 40 to 55%. It may be passed through an acid concentrator 60 wherein it is concentrated to the desired strength of about 65% for recycling to the absorber.

Since it is necessary to separate isobutylene from the butenes before their recovery, the isobutylene extraction is necessary whether or not the isobutylenes are to be used as a purified product as in production of Butyl rubber. Where it is not used separately, the isobutylene is fed in line 53 with the C_3 and C_5 olefins. Also, the bottom acid layer from 56 may be heated to 225-275° F. and cooled so as to form the dimer and trimer of isobutylene which may be fed to alkylation through line 53. For alkylation, this separation from acid is preferred.

The upper layer of unextracted C_4 cut in separator 56 is withdrawn by line 58 and may be passed directly to the alkylation treatment, or, if desired, it may be treated with a more concentrated sulfuric acid suitably of 80 to 85% strength, supplied by line 158, to absorb the normal butenes. This absorption system may be substantially similar to that just described and may contain one or more absorption vessels 159, a separator 160, a stripping tower 61 and a concentrator 62 for recycled acid. The absorption is suitably also conducted with the C_4 cut in liquid phase at about the same temperature of 60° F. although somewhat higher temperatures up to about 100° F. may be used. The stripping tower 61 is supplied at the bottom with open steam and is operated to maintain a bottom temperature of about 290° F. and a top temperature of about 190° F. The distillate therefrom will also contain aqueous alcohol and polymer, which are separated from the n-butenes, the alcohol being returned to the feed line to the stripper 61.

The n-butenes, after washing with aqueous alkali and water to remove traces of acid, are then ready for conversion to butadiene. This may be accomplished by thermal or catalytic dehydrogenation, preferably conducted at a low partial pressure of butene of about 40 to 100 mm. mercury absolute pressure which may be provided by operation under suitable vacuum or by the use of diluent, inert gases or steam, depending upon the type of catalyst employed. The catalytic dehydrogenation may be conducted with a finely powdered catalyst suspended in the reacting gases, using, for example, apparatus similar to that described above for the catalytic cracking operation, or the catalyst may be held stationarily in a reaction vessel and the reagents passed therethrough. The catalyst usually becomes contaminated with carbonaceous materials and may be periodically regenerated by treatment with oxidizing gases, such as air or steam. When using stationary catalyst beds, it is preferred to maintain two or more reaction vessels in parallel to permit alternate on-stream and regeneration treatments in each vessel without interrupting the continuous supply of butadiene. This process is illustrated in the drawings. In all types of reaction, it is desired to subject the n-butenes to the dehydrogenation temperature for a very short time of about one-tenth to one second. Where the nature of the catalyst permits, it is desirable to heat the n-butenes only to a temperature at which thermal decomposition is not pronounced, say 1100° F., and to mix the heated butenes with highly superheated steam or other gas, which is separately preheated to a temperature sufficiently high, say about 1400 to 2000° F., to bring the mixture up to the desired reaction temperature of about 1150 to 1300° F. This involves the use, for example, of about 7 to 12 mols. of steam per mol of hydrocarbon under the temperature conditions just described. It is also desirable to cool the products leaving the dehydrogenation zone to below a temperature causing degradation of the products, say below about 1000° F. as quickly as possible, for example, by introducing a spray of water or cooled reaction products into the hot products as they leave the reaction zone.

Referring to the drawings, the normal butenes are passed by line 63 through a furnace 64 wherein they are heated to a temperature just below that at which thermal decomposition becomes appreciable, for example, about 1100 to 1200° F., and are passed through line 65 to dehydrogenation vessels 66 or 67. Highly superheated steam is supplied by line 68 and the resulting mixture at reaction temperature is passed through a bed of a suitable catalyst 69. A spray of water is introduced just below the catalyst bed by line 70 to quench the reaction products which are removed by line 71 and passed to suitable fractionation equipment to separate a butadiene product and unconverted butenes, which may be recycled, from lighter and heavier products.

The catalyst 69 may be any suitable dehydrogenation catalyst that permits the use of steam in the reaction vessel and is preferably a catalyst having both dehydrogenating and water gas activity, in order to promote the steam-carbon reaction. Such catalysts, for example, may contain a major proportion of magnesium oxide, say about 50 to 90%, lesser proportions of manganese dioxide, chromium oxide or iron oxide up to about 40% to 49%, and small amounts, between about 0.5% and 20% and generally below 5 or 10% of alkali or alkaline earth oxides, such as the oxides of sodium and potassium. Similar small amounts of stabilizers may also be included to prolong the life of the catalyst, such as the oxides of metals of the righthand side (transition series) of groups 1, 2 and 3 of the periodic system, particularly the oxides of copper, silver, and also the oxides of cerium, barium, aluminum, lead and titanium. Other dehydrogenation catalysts, such as chromia (about 10% by weight) supported on activated alumina, or molybdena supported on alumina may be used. These, however, undergo loss in activity on contact with steam, and hence any substantial amount of water vapor should be avoided when they are used. They may be regenerated by treatment with air, while steam is preferably used for regeneration of the previously described catalysts. Such regeneration may be carried out, for example, in dehydrogenation vessel **67** by supplying steam or air alone, heated to the reaction temperature, through line **72**. When air is used, the vent gases are separately removed through line **73**.

The dehydrogenated product in line **71** may be cooled to about atmospheric temperature with water supplied through line **172**, and passed into a water and tar separator **173**. The gases may then be compressed by compressor **74** and passed through cooler **75** into separator **76** wherein uncondensed gases containing mainly hydrogen and hydrocarbons of less than 4 carbon atoms per molecule are separated from the liquid hydrocarbons. These uncondensed gases may be further treated by oil scrubbing or other suitable methods to recover any C_4 hydrocarbons which may be passed with the liquid from separator **76** to fractionating towers **77** and **78**, hydrocarbons of less than 4 carbon atoms being withdrawn through line **79** and hydrocarbons of 5 or more carbon atoms being withdrawn through line **80**. The hydrocarbons of 4 carbon atoms per molecule are passed by line **81** to suitable absorption equipment for separating butadiene from butenes, illustrated diagrammatically by a butadiene absorber **82** and stripper **83** through which a suitable solvent, such as a copper salt solution, is circulated by pump **84**. Butenes may be recycled to the dehydrogenation treatment by line **85**. A portion of the recycled butenes may be passed to the butene extraction treatment by line **157**, in order to prevent build-up of isobutene or butanes in the recycle stream. Concentrated butadiene is withdrawn through line **86**. It may be scrubbed with water to remove solvent materials, such as ammonia, and subjected to any further purification that may be desired; generally water scrubbing alone is sufficient to provide a concentrated butadiene product of sufficiently high purity (98% or more) for use in the preparation of synthetic rubber, such as the "Buna" type rubbers prepared by emulsion polymerization with styrene or acrylonitrile, or the "Butyl" type of rubber prepared by low temperature copolymerization with isobutylene.

While any suitable solvent having selective properties and capable of separating butadiene from mono-olefins may be used in the absorber **82**, it is generally preferred to use an aqueous solution of a copper salt, such as copper chloride or copper acetate and a nitrogen base, such as ammonia or pyridine.

As indicated above, the C_3 and C_5 fractions are subjected to alkylation, preferably in admixture with the isobutane fraction of the C_4 cut. This alkylation treatment is designed to cause reaction of the isoparaffins with olefins to form saturated branched chain hydrocarbons boiling in the motor fuel range. This occurs when one molecule of an isoparaffin, such as isobutane and the isopentanes, combines with one molecule of an olefin, such as propene, the normal butenes, isobutene, the pentenes and isopentenes. The alkylation products are of high anti-knock value and lead response and provide a valuable aviation gasoline blending stock. They may also be used in motor fuels. The alkylation reaction conditions are adjusted so as to substantially avoid reactions between olefins to form unsaturated polymers. This is accomplished by suitable adjustment of the reaction conditions and catalyst activity and especially by the use of a very large excess of isoparaffins to olefins in the reaction zone, ratios of total isoparaffin to total olefin in the reaction zone ranging from about 100/1 to about 400/1 being illustrative. Suitable catalysts for promoting the alkylation reaction include sulfuric acid, fluorsulfonic acid, chlorsulfonic acid, boron fluoride-water, boron fluoride-phosphoric acid, aluminum chloride-hydrogen chloride, sodium chloride-aluminum chloride and similar complexes of aluminum chloride with other salts, also activated clays and the like. The reaction may be conducted in vapor or liquid phase, the latter being generally used, in which event the pressure on the reaction zone should be sufficiently high to maintain the hydrocarbons undergoing treatment substantially completely in the liquid phase, i. e., the pressure on the reaction vessel should be at least equal to the vapor pressure at the reaction temperature of the mixture of hydrocarbons in the reaction zone.

The reaction will be described, with reference to the drawing, with strong sulfuric acid as the alkylation catalyst, although it is to be understood that the other catalysts mentioned above may also be used with appropriate changes in the reaction conditions as may be necessary for optimum results with each catalyst.

Turning to the drawings, C_3 and C_5 hydrocarbons (containing both olefins, paraffins and isoparaffins) are supplied by line **53**, see Figure IIA, and are mixed with a large excess of isobutane from line **87**, for example, in sufficient amount to provide a total isoparaffin/total olefin ratio in the mixture of about 200/1. This mixture is passed through cooler **88** and cooled to a temperature between about 35 and 65° F., preferably sufficiently low to maintain a temperature in the reaction zone of about 50° F. Strong sulfuric acid, having a concentration of preferably about 97 to 98% and at least above about 92%, supplied by line **89**, is mixed with the cooled feed stock and the mixture is passed by pump **90** into the bottom of the alkylation reaction vessel **91**. This vessel is provided with suitable means for maintaining an intimate mixture (preferably an emulsion) of the acid and hydrocarbon phases, such as the perforated plate **192**, which passes the mixture in the form of numerous jets under high velocity into the main portion of the reaction zone, which is maintained suitably under a pressure of about 180 pounds per square inch gauge in order to maintain the hydrocarbons therein in liquid phase at the reaction temperature of about 50° F.

The feed rate should be adjusted to provide a time of contact of the olefins in the reaction zone sufficiently long to secure reaction of at least the major portion of the olefins. This may range, for example, from about 0.5 hour to 1.5 hours or longer.

The mixture of acid leaving vessel **91** by line **92** is passed to a separator **93**, the lower acid layer separating therein being withdrawn by line **94** and recycled by line **95**. A portion of this acid is withdrawn from the system and replaced by fresh concentrated acid supplied by line **96** to maintain the desired acid strength in the alkylation vessel. A portion of the mixture in line **92** may also be recycled directly by line **97** if it is desired to prolong the time of reaction.

The upper, hydrocarbon layer from separator **93** is washed with alkali in vessel **98** to remove acid and is passed to column **99** from which a C_3 cut is separated from heavier hydrocarbons. These are passed to column **100**, which is operated to produce a distillate consisting substantially of isobutane, which is recycled by line **87** to the alkylation unit. The butanes in the original C_4 cut (after separation of olefins) are also conveniently introduced into the alkylation treatment through vessel **100** by line **101** in order to avoid passing the inert normal butane of this cut through the alkylation vessel. The normal butane and less volatile hydrocarbons are withdrawn from the bottom of tower **100** and passed to tower **102**, where excess C_4 and C_5 hydrocarbons above volatility requirements of the final alkylate may be removed as distillate through line **103**, the residue from this column passing to tower **104**, where an aviation alkylate fraction boiling up to about 300° F., for example, is separated as distillate from higher boiling residual products. The excess C_5 hydrocarbons removed through line **103** are essentially isopentane and this isopentane stream, preferably after separation of n-butane, may be recirculated in line **87** with the isobutane so that sufficient isopentane concentration can be built up in the alkylation reactor to alkylate this excess isopentane. While this step and the alkylation of the C_3, C_4 and C_5 olefins have been indicated to be carried out in a single alkylation reactor as indicated above, the amount of isopentanes passing to the alkylation treatment may be controlled by the operation of columns **20** and **32**; some isopentane may be withdrawn in the bottoms from these columns to meet volatility requirements in the gasoline blending operation. The individual olefin and isoparaffin alkylations may also be carried out in separate reactor systems.

As indicated above, the catalytically treated naphtha contains a substantial proportion of aromatic hydrocarbons and very little olefinic hydrocarbons. The U. S. Army specifications for nitration grade toluene require a purity of above 99% and also substantial freedom from paraffin and olefin hydrocarbons. This can be readily extracted in high yields from the above-described catalytically treated naphthas.

It is desirable to select for this extraction rather sharply cut naphtha fractions of narrow boiling range as this has been found to aid the separation of toluene from the other hydrocarbons present. The extraction may be conducted with any suitable selective solvent, for example, liquid sulfur dioxide may be used between about −20 and −60° F. A preferred method for separating toluene from such naphtha fractions involves subjecting the vaporized naphtha to treatment under distillation conditions with a solvent which is characterized by its ability to reduce the vapor pressure of aromatic hydrocarbons to a substantial extent, while at the same time reducing the vapor pressure of other types of hydrocarbons to a much smaller degree. Phenol is an illustrative solvent of this type. The separation of toluene with such a solvent is illustrated in the drawing.

The catalytically treated naphtha fraction in line **36**, boiling between about 175° F. and 300° F. is redistilled in tower **110**, a portion of the overhead being condensed and returned as reflux to provide a distillate fraction in line **111** cut sharply to an end point of about 250° F. The residue from this tower is a desirable aviation gasoline blending stock and may be withdrawn for this purpose by line **112**. The distillate in line **111** is passed as a vapor into the mid-portion of an absorption tower **113**, which is maintained at a temperature above the dew point (at the prevailing pressure) of the mixed hydrocarbon feed. Phenol is supplied to a higher level of the column at a temperature substantially equal to that prevailing in the column at the point of supply by line **114**. Heat is supplied to the bottom of the column by any suitable means, such as heat exchanger **115**, in order to increase the concentrating effect of aromatic hydrocarbons in the extract, and cooling means, such as heat exchanger **116**, are supplied at the top of the column in order to provide reflux and to prevent loss of phenol in the vapor raffinate removed by line **117**. This raffinate is also suitable blending stock for aviation gasoline.

A suitable column design permitting the required separation provides **30** theoretical plates between the phenol feed line **114** and the bottom of the tower **113**, **16** theoretical plates above the phenol feed to the raffinate withdrawal and a 1:1 by volume (cold liquid basis) reflux ratio based on the raffinate.

The absorption tower **113** is preferably operated at a low pressure in order to avoid excessive heat requirements and may be operated, for example, at a pressure of about 5 to 20 pounds' gauge with a bottom temperature of about 385° F. and a top temperature of about 230° F. Optimum temperatures will be found to vary to some extent in relation to the composition and boiling range of the feed stock and the operating pressures. The phenolic extract is passed by line **118** to a stripping or distillation tower **119** from which the extracted toluene is remove as distillate by line **120** and the phenol as residue by line **121**. This phenol may be recycled by line **114** to the absorption tower, preferably after cooling to about 250° F. to 300° F. About three volumes of phenol are passed through the absorber **113** for each volume of the total hydrocarbon feed (including any recycle extract fractions) supplied thereto. Other ratios of phenol to hydrocarbon, for example in the approximate range of 0.8 to 6 vols./vol. of hydrocarbon feed, may be used.

The extract distillate in line **120** contains a high proportion of toluene but requires further purification and refractionation to eliminate small amounts of solvent and of olefins, paraffins and other aromatic hydrocarbons that are generally present. It may, for example, be treated with sulfuric acid at about 80° F. (about 25 pounds of 98% sulfuric acid per barrel being usually sufficient) and then be washed in the acid treating and washing steps indicated diagrammatically as **122** and **123** respectively. The treated extract is then redistilled in tower **124** to produce a pure toluene fraction of nitration grade and boiling at 231° F. with a total deviation of plus or minus 1° F., which is withdrawn by line **125**. In the usual operation, where the distillation of the catalytically treated naphtha fraction prior to the absorption treatment is sufficiently sharp, toluene of this purity will be obtained as the overhead distillate from tower **124**, which will then be operated under the usual conditions with pump-back of a part of the distillate for reflux. If the initial fractionation of the treated naphtha is not sufficiently sharp, small amounts of low boiling products may be present in the extract feed to tower **124**; in this event, such low boiling fractions may be separated as overhead distillate and the pure toluene product is withdrawn as a sidestream by line **126** from the upper portion of the column several plates below the top. In order to secure this toluene distillate or sidestream fraction of the requisite purity, it is desirable to remove a substantial portion, for example, about 50% of the tower feed as bottoms therefrom. These contain a high concentration of toluene and are recycled through line **127** and vaporizer **128** to the absorption tower **113**. These bottoms in line **127** may also be redistilled to remove small amounts of higher boiling fractions or a portion of the bottoms may be removed by line **129** in order to prevent the accumulation of such high boiling fractions in the system.

A suitable method for conducting the processes of this invention will now be described, with reference to Figure III of the drawings. This process, as described, is intended to be conducted in the equipment illustrated in Figures II, II*a* and II*b* of the drawings, but it may be conducted in any other suitable type of equipment for carrying out the various treating steps and reactions which are involved.

Referring to Figure III, the quantities of the various streams are indicated on the flow plan as barrels per day. Hydrocarbons are indicated by the number of carbon atoms per molecule and olefins by the symbol =. Thus, isobutene is indicated by iso $C_4=$, propene by $C_3=$, pentenes by $C_5=$, and normal butenes by n—$C_4=$. The charge to the catalytic cracking unit is a distillate gas oil stock of 31.5 A. P. I. gravity, 179° F. aniline point and 650° F. midboiling point. The cracking operation is conducted with a powdered synthetic silica-alumina gel cracking catalyst with an average temperature in the cracking zone of 975° F. and a ratio of 5.8 pounds of catalyst per pound of oil in the feed to the cracking chamber, the oil being passed through this chamber at a rate of 3.0 pounds per hour per pound of catalyst present in the cracking chamber.

The naphtha cut (containing hydrocarbons from 6 carbon atoms per molecule up to those boiling at 400° F.), has a 49.7° A. P. I. gravity and a midboiling point of 250° F. It is passed to the catalytic naphtha treating unit in which it is subjected to an averaged reaction temperature of 900° F., using a powdered synthetic silica-alumina gel catalyst with a ratio of 8 pounds of catalyst per pound of oil in the feed to the treating chamber, the oil being passed through this chamber at a rate of 1.3 pounds per hour per pound of catalyst present therein. The light ends from both the catalytic cracking and treating units, including hydrocarbons of 4 carbon atoms per molecule, are passed through light end recovery equipment in which the C_4's and most of the C_3's are separated from the lighter gases. A portion of the C_3 cut, containing propene is passed to the alkylation unit. The C_4 cut is passed under sufficient pressure to maintain it in liquid condition, through an isobutene extraction unit, which is maintained at a temperature of 60° F. and is supplied with sulfuric acid of 65% strength in a proportion of about 1 to 2 mols of acid per mol of isobutylene in the hydrocarbons treated. The hydrocarbons remain in the extractor for about 50 minutes. The acid extract is diluted to an acid concentration of 45% and is stripped with steam, thus obtaining isobutene and some polymers, equivalent to 89 barrels/day of C_4's.

The raffinate is passed through a normal butene extractor maintained at a temperature of 95° F. and under sufficient pressure to maintain the hydrocarbons in liquid phase, at a rate permitting about three hours time of residence of the hydrocarbon in the extraction vessel. Sulfuric acid of 83% strength is supplied to this extractor in a proportion of about 1 mol per mol of butene in the feed hydrocarbons, the acid extract being diluted to an acid concentration of 62% in the regenerator or stripper in which normal butenes and some polymer are separated.

The normal butenes are dehydrogenated to butadiene by being passed with 9 volumes of steam per volume of hydrocarbon through a reaction vessel maintained at an average reaction temperature of 1150° F. and pressure of 7 pounds per square inch gauge, at such a rate as to permit a time of residence in the reaction zone of 0.3 second. The reaction zone is supplied with a suitable dehydrogenation catalyst, which maintains its activity in the presence of steam, for example, one containing about 70% magnesium oxide, 20% iron oxide, 5% potassium oxide and 5% copper oxide, unconverted normal butenes being separated from the product and recycled.

The raffinate from the butene extraction, polymer from the isobutene extraction, and the C_3 cut from the catalytic cracking and treating units are passed to an alkylation unit. Isobutene may also be passed to this unit or may be used separately for the preparation of synthetic rubber. Isobutene polymers and copolymers formed in the isobutene and butene extraction steps may also be passed to the alkylation unit or may be depolymerized to yield additional isobutene, if desired. C_5 cut from the catalytic cracking units is also supplied to the alkylation unit in an amount sufficient to make up the olefin requirements of this process. This is about 1 mol of total olefins (including those available by depolymerization of the isobutene polymers) per mol of isobutane supplied thereto. The alkylation reaction vessel is operated at a temperature of 50° F. and at a pressure sufficient to maintain the hydrocarbons therein in liquid condition. It is supplied with sulfuric acid in a ratio of about 1 volume per volume of hydrocarbon feed. The hydrocarbon feed is passed through the reaction vessel at a rate to provide a time of residence therein of about 30 minutes and in suitable proportions to maintain a ratio of 150 volumes of isobutane per volume of olefin therein. Unreacted hydrocarbons, particularly isobutane, are recycled to provide a ratio of about 5.5 volumes of isobutane per volume of olefin in the feed mixture supplied to the alkylation reactor.

The intermediate naphtha fraction of the product from the catalytic naphtha treating unit, boiling between about 175 and 255° F. is passed to the toluene extraction plant, preferably after treating with clay to remove any suitable olefinic or peroxide materials which may be present and would react with the phenol. The clay treatment may be conducted by passing the naphtha cut in vapor phase over Attapulgus clay of 30 to 60 mesh, for example, at a pressure of about 100 pounds per square inch and at a temperature of about 400° F., or to be more exact, at about the dew point of the material at the treating conditions. The naphtha feed rate is about 2.3 barrels (measured as cold liquid) per hour per ton of clay in the treating zone. Higher boiling polymers formed in this treatment are separated from the naphtha cut, which is then passed to the toluene extraction plant.

The toluene is suitably extracted by being scrubbed with phenol in an extraction vessel in which the naphtha is supplied at about 15 pounds per square inch gauge pressure and at a temperature just about its dew point under these conditions, the phenol being supplied at a temperature of about 250° F. in a proportion of about 3 volumes per volume of oil feed (both measured as cold liquid).

The following products may thus be obtained from a gas oil feed of 14,000 barrels per day:

Butadiene	standard tons per year	22,600
Isobutene	B./D [1]	414
Butane	B./D	292
C_4 polymers	B./D	87
Pentane (surplus above aviation gasoline requirements)	B./D	53
Tolene (nitration grade)	B./D	226
Aviation gasoline [2] (7 lb. Reid vapor pressure, 86.3 ASTM clear octane number)	B./D	5,178
For motor gasoline blending	B./D	415
Gas oil	B./D	5,200

[1] Equivalent to 18,800 long tons per year of butyl rubber.

[2] This, blended with 818 B./D. of 69 O. N. natural naphtha, gives 5496 B./D. of 100 octane aviation gasoline with 4 cc. TEL per gallon added.

While the invention has been described with particular reference to various types of apparatus and treating agents in each of the process steps described herein, the invention should not be so limited, for these have been presented as illustrative embodiments of the many variations that are readily apparent as being included within the scope of this invention.

We claim:

1. In a process for the catalytic conversion of relatively heavier hydrocarbon oils to relatively more volatile motor fuels and gaseous products, an improved method of utilizing said products comprising separating therefrom a fraction comprising mainly olefin and paraffin hydrocarbons of 3 to 5 carbon atoms per molecule, separating a mixture of hydrocarbons of 4 carbon atoms per molecule from said fraction, then removing isobutene from this mixture by selective extraction with sulfuric acid of a strength insufficient to react with the normal butene present, heating the acid extract and separating therefrom a mixture of isobutene polymers comprising mainly diisobutene, removing normal butenes from the remainder of said mixture, then subjecting a mixture of the remainder of said first mentioned fraction, the remainder of said fraction of 4 carbon atoms per molecule comprising n-butane and isobutane and the said isobutene polymers to alkylation conditions adapted to cause reaction of olefins with the isobutane present therein to form saturated isoparaffin alkylation products boiling in the motor fuel range and of high antiknocking characteristics.

2. Process for producing aviation gasoline, comprising cracking a higher boiling oil in the presence of a synthetic gel catalyst containing silica and alumina, to produce a highly olefinic product including a naphtha fraction boiling below about 400° F., and containing olefins in excess of the content permissible in aviation fuel, separating said naphtha fraction, subjecting said naphtha fraction to further treatment in the presence of a synthetic gel catalyst containing silica and alumina, to reduce the amount of unsaturates contained therein, separating an aviation gasoline fraction from the products of said second catalytic treatment, extracting toluene from said aviation gasoline fraction, also separating from the products of said cracking treatments a fraction comprising mainly olefin and paraffin hydrocarbons of 3 to 5 carbon atoms per molecule, separating at least a part of the olefins of 4 carbon atoms per molecule from said C_3—C_5 fractions, and subjecting the remainder of this fraction to alkylation conditions adapted to cause reaction of the olefins with the isoparaffins present therein, to produce an alkylate product comprising saturated isoparaffins, and mixing said alkylate product with the residue of said aviation gasoline product after said toluene extraction to yield an improved aviation grade gasoline of high octane number and low in unsaturates and in acid heat.

3. Process according to claim 2 in which the olefins of 4 carbon atoms are removed from the said hydrocarbon fraction of 3 to 5 carbon atoms per molecule before it is subjected to the said alkylation treatment.

4. Process according to claim 2 in which the normal butenes are removed from the said hydrocarbon fraction of 3 to 5 carbon atoms per molecule before it is subjected to the said alkylation treatment.

5. Process for producing aviation gasoline, comprising cracking a higher boiling oil in the presence of a cracking catalyst to produce relatively lower boiling motor fuel and normally gaseous products containing substantial proportions of olefins, separating from the cracked products a naphtha fraction boiling in the range comprising hydrocarbons from 6 carbon atoms per molecule at least up to those boiling at 200° F. and below 400° F. and containing olefins in excess of the amount permissible in aviation gasoline, then subjecting said naphtha fraction to a further treatment in the presence of a reforming catalyst under catalytic reforming conditions to reduce the amount of olefins therein, separating an aviation gasoline fraction from the products of said second catalytic treatment, also separating from the products of at least the first of said catalytic treatments a fraction consisting mainly of olefin and paraffin hydrocarbons of 3 to 5 carbon atoms per molecule, separating olefins of 4 carbon atoms per molecule from said fraction under conditions wherein the said separated olefins of 4 carbon atoms per molecule comprise substantially all of said olefins present in said $C_{3\text{-}5}$ fraction, subjecting the remainder of said fraction to alkylation conditions adapted to cause olefins and iso-paraffins present therein to form saturated iso-paraffins of 7 to 9 carbon atoms per molecule and of good antiknock characteristics and blending the product of alkylation with the aviation gasoline

fraction, polymerizing the separated isobutene to a low molecular weight polymer comprising mainly di-isobutene, said polymer being passed to said alkylation treatment.

6. Process for securing high yields of naphtha of aviation grade and alkylate adapted for blending with such naphtha, from catalytic cracking products of petroleum hydrocarbons, comprising carrying out the cracking under conditions to produce a large percentage of olefins, separating from the cracking product a naphtha fraction comprising normally liquid hydrocarbons boiling below about 400° F. containing hydrocarbons having from 6 carbon atoms per molecule at least up to those boiling at 200° F., said naphtha fraction having an olefin content in excess of that permissible in aviation fuel, also separating from the cracking product a fraction comprising mainly olefin and paraffin hydrocarbons of 3 to 5 carbon atoms per molecule, separating substantially all olefins of 4 carbon atoms per molecule from said fraction, then subjecting the remainder of said fraction to alkylation conditions adapted to cause reaction of the olefins of 3 and 5 carbon atoms with the iso-paraffins present therein, to form saturated iso-paraffins of 7 to 9 carbon atoms per molecule and having good antiknock characteristics, treating the said naphtha fraction to remove excess olefins and fit the naphtha fraction for use as an aviation fuel, as an incident of such treating, producing a fraction comprising mainly olefin and paraffin hydrocarbons of 3 to 5 carbon atoms per molecule, subjecting said less mentioned fraction to alkylation with admixture with the first mentioned fraction comprising mainly olefin and paraffin hydrocarbons of 3 to 5 carbon atoms per molecule, blending the resulting alkylate with said naphtha fraction which has been treated to remove excess olefins, extracting toluene from the naphtha fraction,

blending the remainder thereof with the alkylated product to yield an improved fuel of high antiknock value and relatively low acid heat.

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