

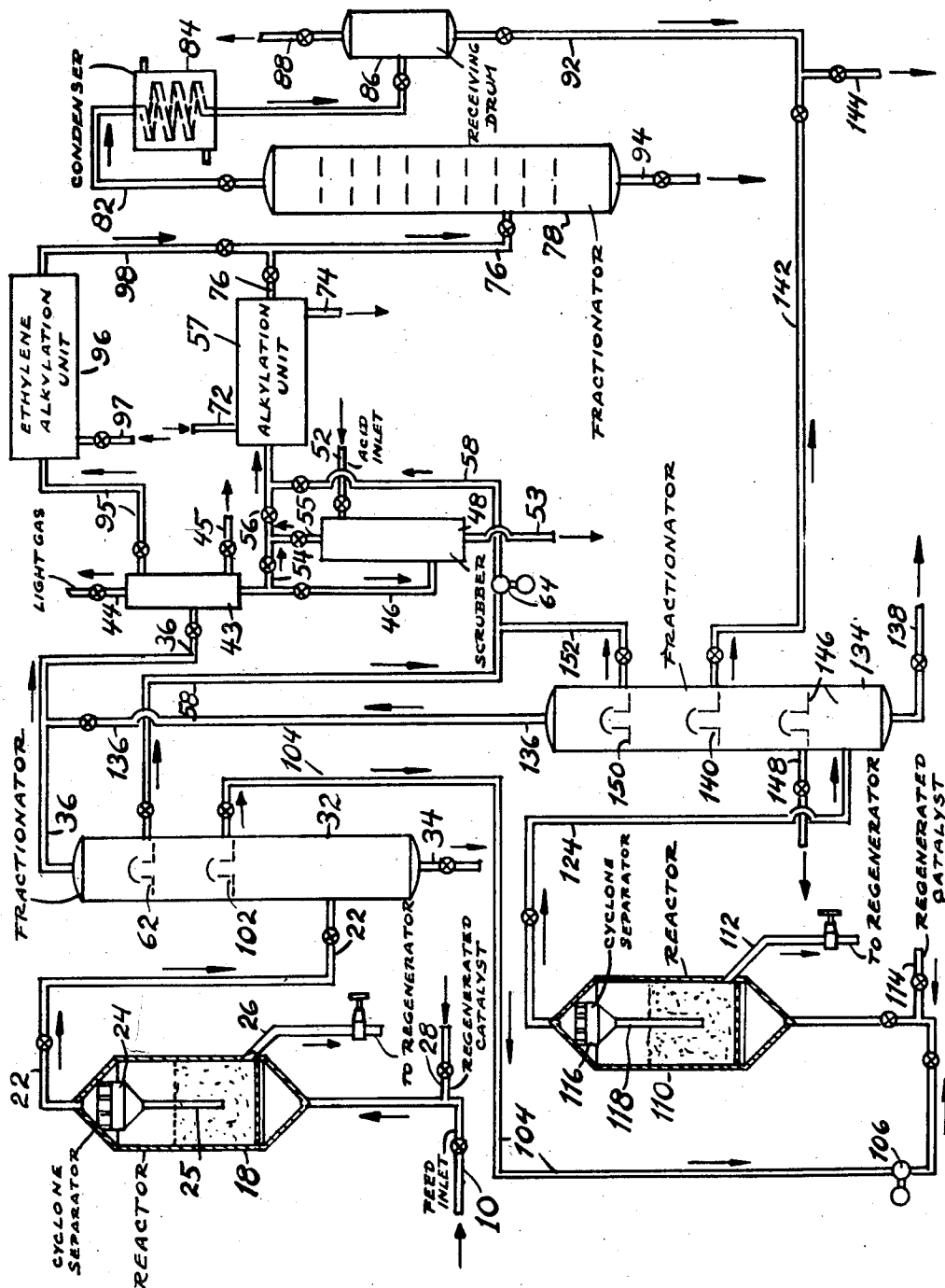
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TREATING HYDROCARBON FLUIDS

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## TREATING HYDROCARBON FLUIDS

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1 Claim. (Cl. 260-683.4)

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This invention relates to the production of aviation gasoline.

In the catalytic cracking of hydrocarbon oils, naphthas are produced which have a relatively high octane number, but as ordinarily produced, they are not of high enough quality for aviation gasoline. Various methods have been suggested for treating catalytically cracked gasoline or naphtha to produce aviation gasoline. My present invention is an improvement over such other processes.

According to my invention, a relatively heavy hydrocarbon, such as gas oil, is cracked in the presence of a catalyst at a relatively high temperature and from the cracked products are separated a light naphtha fraction, a heavy naphtha fraction, and a heavier oil fraction. The light naphtha fraction is alkylated with isobutane, and the heavy naphtha fraction is subjected to a catalytic re cracking operation. The products from these steps are then fractionated to separate light hydrocarbon fractions boiling in the aviation gasoline range, and the fractions are blended to produce a finished aviation gasoline of high stability, high octane number, high susceptibility to tetraethyl lead and high rich mixture performance. Furthermore, the ethylene and butylenes produced in the cracking and re cracking steps may also be subjected to alkylation with isobutane since the product alkylate is of high quality and augments the yield of aviation gasoline.

The light fraction of the catalytically cracked naphtha which is fed to the alkylation step should be substantially free of aromatics. The end point should be chosen to exclude benzene, if an appreciable amount is formed in the cracking step. For example, the end point may be 165 or 170° F. In some cases wherein the amount of benzene is very small the end point may be 200° or somewhat higher, but it should be borne in mind that the presence of even small amounts of aromatics in the alkylation feed stock results in rapid degradation of alkylation catalysts, as well as in lower yields and lower octane number products. This will be evident from the following Examples 1, 1A and 1B, Example 1 showing my preferred alkylation step and Examples 1A and 1B showing poorer results when selecting improper fractions.

### Example 1

A 60-150° F. fraction containing no aromatics from catalytically cracked gasoline was alkylated with isobutane at 45° F. employing a 10/1 isobutane/olefin ratio and sulfuric acid catalyst in a 1/1 acid/hydrocarbon ratio for 30 minutes contact time in a continuous run of 103 hours duration. An acid replacement rate of 0.5 to 0.7 pound per gallon of alkylate was required in or-

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der to maintain catalyst activity. The yield of aviation alkylate was 125% of the 60-150° F. fraction and the A. S. T. M. octane number was 87.5. The aviation octane number+4 cc. lead per gallon was equivalent to iso-octane+0.24 cc. lead per gallon.

### Example 1A

A 60-200° F. fraction from the same gasoline containing 8.8% aromatics when alkylated under the same conditions required an acid replacement rate of 1.5-1.8 pounds per gallon of alkylate in order to maintain activity. The yield of alkylate was 118% and the A. S. T. M. octane number was 85.

### Example 1B

If a 400° F. end point naphtha is subjected to alkylation, the yield is very low and the octane number of the product may actually be lower than that of the feed stock as a result of the absorption of aromatics by the catalyst and the alkylation of aromatics thus forming compounds boiling above the gasoline range.

In the alkylation step, the olefins react with isobutane to form saturated hydrocarbons of high clear octane number, high octane number appreciation on the addition of tetraethyl lead, high blending octane number, and high performance when employing rich fuel/air ratios as in take-off or under heavy loads as measured by the AFD-3C test method. Each of these factors is of prime importance in the production of large quantities of aviation gasoline having octane numbers of 100 or above. Removal or conversion of the olefins in the naphtha is necessary to achieve this end, and the alkylation of the light catalytic naphtha originally containing about 40% olefins lowers the bromine number from about 82 cgs./gm. to less than 1.

In the catalytic re cracking step, also, olefins are converted, so that the blend of alkylated light naphtha and catalytically re cracked heavy naphtha has a low bromine number and low acid heat and easily passes specifications. Since in the re cracking of the heavy naphtha lower boiling olefins are produced, in a preferred modification of my process the light naphtha produced in the re cracking step is passed to the alkylation unit along with the light naphtha produced in the catalytic cracking. In this manner there is produced an aviation gasoline of quite low olefin content and very high quality.

Apparently the olefin content is reduced in the catalytic re cracking step partly by polymerization and partly by hydrogenation through hydrogen exchange with naphthene hydrocarbons. The re cracking causes a sharp reduction in the amounts of naphthenes and paraffins present, particularly in the high boiling portions which are very high in aromatic content.

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The heavy fraction of the catalytically cracked naphtha which is subjected to catalytic re-cracking must likewise be a selected fraction if high yields of high octane number aviation gasoline are to be realized, as shown by the following examples. Example 2C shows improved yields obtained when catalytically re-cracking a selected heavy naphtha fraction, whereas Examples 2, 2A and 2B show that best results are not obtained with improperly selected fractions.

#### Example 2

A 70-410° F. naphtha produced by catalytic cracking at a temperature in the range 925-975° F. with powdered synthetic silica-alumina gel was re-cracked at 900° F. with the same catalyst and the product was fractionated. The yield of 335° F. end point aviation base stock exclusive of pentane was 46.8% and the yield of pentane was 25.9%. The aviation octane number+4 cc. tetraethyl lead per gallon of the feed stock to re-cracking was 88.7 while that of the depentanized aviation base product was 94.2.

#### Example 2A

A 110-220° F. fraction of the same gasoline as employed in Example 2 was re-cracked under the same conditions. The yield of aviation gasoline base exclusive of pentane was 58% and the yield of pentane was 14%, while aviation octane numbers+4 cc. lead of the feed and of the depentanized aviation base product were 86.4 and 92.6, respectively.

#### Example 2B

A 110-289° F. fraction of the same gasoline as employed in Example 2 was re-cracked under the same conditions, and yields of 61% of depentanized aviation base and 11.3% of pentane were obtained. The feed had an aviation octane number+4 cc. lead of 88, while that of the depentanized aviation base product was 92.5.

#### Example 2C

A 220-410° F. fraction of the gasoline employed in Example 2 was re-cracked under the same conditions. The feed stock contained 38.2% of material boiling in the aviation gasoline range below 335° F. The yield of depentanized aviation base was 58%, the pentane yield being 4.4%, and the yield of C<sub>4</sub> hydrocarbons being 5.5%. Whereas the aviation octane number+4 cc. lead of the feed stock was 87, that of the depentanized aviation base product was 98.2.

It has been found that the fraction of a catalytically cracked gasoline boiling between about 160° or 170° F. and about 220° F. has a low octane number, for example, about 84 aviation+4 cc. lead, and that re-cracking improves it only slightly, for example, to about 88. It is generally preferred to discard this fraction, which may amount to 10 or 12% of the catalytic gasoline, and to use it in automotive fuels. When discarding this fraction the charge to the alkylation unit is about 48% of the catalytic gasoline exclusive of C<sub>4</sub> hydrocarbons, and the 220-410° F. fraction charged to the re-cracking step amounts to about 40% of the catalytic gasoline.

As shown in Example 1, the yield from alkylation is 125% of the charge, or 60% based on the catalytic gasoline, and this alkylate has an aviation octane number+4 cc. lead greater than 100 (iso-octane+0.24 cc. lead). As shown in Example 2C, the yield of depentanized aviation base stock from the re-cracking step is 58% of the charge, or 23% based on the catalytic gasoline,

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and this base stock has an aviation octane number+4 cc. lead of 98.2. Blending of the alkylate and re-cracked aviation base stock gives a yield of 83% of aviation gasoline based on the 410° F. end point catalytic gasoline in addition to the pentane produced in re-cracking, and the aviation gasoline+4 cc. lead per gallon has an aviation octane number of 100 and a rich mixture performance equivalent to about iso-octane+1.8 cc. lead per gallon by the AFD-3C method.

As pointed out above, the yield and quality of the aviation gasoline may be augmented by alkylation of the ethylene and butylenes produced by cracking and re-cracking with the isobutane produced by cracking and re-cracking. In view of the requirements of normal butene and isobutylene as feedstocks in synthetic rubber production, it may be desirable to alkylate only the ethylene at the present time. The ethylene should be alkylated with isobutane in a separate unit not in the presence of sulfuric acid catalyst but in the presence of a halide catalyst, such as aluminum chloride or bromide, employing about 3/1 to 5/1 isobutane-ethylene ratio at 100-150° F. and 250-350 lbs./sq. in. pressure. The product contains 70-85% of C<sub>6</sub> hydrocarbons, predominantly 2,3-dimethyl butane which has a very high rich mixture rating on the AFD-3C scale.

The ethylene alkylate, or only the C<sub>6</sub> fraction therefrom, is blended with the aviation fractions produced by alkylation of the light catalytic naphtha and by re-cracking the heavy fraction of the catalytic naphtha. When operating so as to alkylate ethylene and C<sub>4</sub> olefins as well as the light catalytic naphtha, the yield of finished high quality aviation gasoline is more than 100% based on the original catalytic naphtha.

In contrast to ethylene alkylation, either the normal butenes or isobutylene or both can be alkylated with isobutane in the presence of sulfuric acid catalyst with good results, and it is preferred to do this simultaneously and in the same unit as employed in the alkylation of the light naphtha fractions.

In the drawing, the figure represents one form of apparatus which may be used to practice my process.

Referring now to the drawing, the reference character 10 designates a line through which the hydrocarbon oil feed stock is introduced to the system. For example, the feed may comprise gas oil vapors or other relatively heavy vaporized petroleum stock. When using powdered catalyst, it is also possible to start with a partly preheated liquid stock and to supply the heat of vaporization and conversion by contact with a sufficient quantity of hot catalyst. The hydrocarbons are cracked at atmospheric pressure or thereabouts at a temperature of about 900° F. to 1000° F., preferably about 975° F. when cracking a relatively heavy gas oil having an A. P. I. gravity of 25-30° and a mid-boiling point of about 600-750° F.

The catalyst may be any suitable cracking catalyst, such as synthetic silica alumina gel, synthetic silica magnesia gel, acid-treated bentonites, etc. For the preparation of aviation gasoline and relatively large amounts of olefins, it is preferred to use the synthetic silica alumina gel. The preparation of such a catalyst is well known and is not described here. Instead of using powdered catalyst, it is within the contemplation of my invention to use larger particles of

catalyst in a moving bed or to use larger particles in fixed bed operation. Preferably the powdered catalyst has a size of about 200 to 400 standard mesh or finer.

The hydrocarbon feed stock is passed through line 10 into the bottom portion of a reaction vessel 18 which contains dry powdered catalyst at reaction temperature. The velocity of the vapors passing through reaction vessel 18 is controlled so that the catalyst particles remain in the vessel for a much longer period of time than the vapors, and preferably such that a relatively dense layer of catalyst is present in the lower portion of the vessel. Suitable velocities lie in the range from 0.5 to 10, preferably 1 to 3, linear feet per second when employing 200-400 mesh catalyst having a density when freely settled of from 35 to 60 lbs./cu. ft. Under these conditions the relatively dense catalyst phase has a density of the order of 10 to 30 lbs./cu. ft. The relatively dense catalyst phase is aerated by the rising vapors and has the appearance of a violently boiling liquid, and possesses properties of liquids such as fluidity, the ability to exert hydrostatic pressure and a level or meniscus which is especially noticeable when low vapor velocities are employed. Also, when employing relatively low velocities, such as from 0.5 to 2 ft. per second, the carry-over of catalyst by the cracked products is very small, of the order of 0.003-0.01 lbs./cu. ft. of vapors.

The cracked products leave the top of the reaction vessel 18 through line 22, after passing through cyclone separator 24 where entrained powdered catalyst is separated therefrom. Cyclone separator 24 is preferably located inside the upper portion of vessel 18. Other forms of separating means may be used. Separated catalyst is returned to the reaction zone proper through line 25. During the conversion operation the powdered catalyst becomes contaminated with coke or carbonaceous material and it is necessary to regenerate the catalyst in any known manner, preferably by burning with air or oxygen-containing gas at about 1000-1100° F. to remove the carbonaceous deposit. Catalyst for regeneration is withdrawn from reaction vessel 18 through line 26 in a fluidized condition and is passed to a regenerator (not shown) which may be similar in construction to vessel 18. Hot regenerated catalyst is returned to line 10 and to the reactor through line 28 at a sufficient rate to maintain reactor temperature and catalyst activity at the desired levels, and if liquid feed stock is being supplied to the reaction, to absorb or vaporize the liquid completely. The weight ratio of catalyst to oil employed is generally above 3, for example, from 5 to 20.

While I have shown only one cyclone separator on the drawing, it is to be understood that more than one cyclone separator may be used in series to effect a better separation of powdered catalyst from the vaporous reaction products. The separated vaporous reaction products pass overhead from the separating means 24 through line 22 and are passed to a fractionating tower 32 for separating desired fractions from the cracked products. Condensate oil is removed from the bottom of the fractionating tower 32 through line 34 and may be recycled to the reaction zone 18 or withdrawn from the system.

The light uncondensed constituents comprising hydrogen, methane, ethane, ethylene, C<sub>3</sub> and C<sub>4</sub> hydrocarbons leave the top of the fractionating

tower 32 through line 36 and are subjected to fractionating and/or scrubbing operations to separate fractions rich in ethylene and in C<sub>4</sub> hydrocarbons. These operations, which are well known and need not be described in detail here, are indicated on the drawing by numeral 43. Light gases pass overhead through line 44. A C<sub>3</sub> fraction is withdrawn through line 45. The separated C<sub>4</sub> fraction withdrawn through line 46 contains isobutylene which is useful in the production of synthetic rubber and the isobutylene may be recovered by scrubbing with acid. The acid used is preferably sulfuric acid having a concentration of about 65% by weight. The C<sub>4</sub> fraction is introduced into the bottom portion of an acid scrubbing vessel 48, the acid is introduced at the top through line 52, and the acid extract is removed through line 53. In the scrubbing vessel 48 the temperature of the sulfuric acid is about 75° F. The isobutylene is recovered from the acid by treating with steam, thus raising the temperature to about 250° F. and lowering the acid concentration to 40-45%. Isobutylene and di-isobutylene are flashed overhead and the latter is cracked to form isobutylene. If isobutylene is not desired for synthetic rubber, the entire C<sub>4</sub> cut is by-passed around acid scrubber 48 through line 54 to line 56 leading to alkylation unit 57.

The rest of the C<sub>4</sub> fraction containing isobutane and butenes leaves scrubber 48 through the line 55 and is mixed with a light naphtha fraction introduced through line 58. This light naphtha fraction is withdrawn from the upper part of fractionating tower 32 wherein the catalytically cracked products are fractionated. The light naphtha fraction collects on trap-out tray 62 in the fractionating tower 32 and is passed through line 58 by pump 64. The light naphtha fraction contains olefins and paraffins, but as mentioned above, should be substantially free of aromatics. The light naphtha fraction has a boiling range of about 60° to about 170° F. or 200° F.

The mixture of the light cracked naphtha and the C<sub>4</sub> fraction is passed through line 56 to the alkylation unit or reactor 57 wherein the olefins are alkylated with isobutane to transform the olefins to branched paraffins. Any suitable alkylation catalyst is used, such as sulfuric acid, boron fluoride-water, hydrogen fluoride, etc. Where sulfuric acid is used, the titratable acidity of the acid is maintained above about 82%, preferably at about 85-90%, by continuous replacement with 94-98% acid. The temperature during alkylation is preferably in the range 45-80° F. The ratio of isobutane to olefins in the feed is generally maintained at 3/1 or higher by recycling isobutane separated from the products, and the instantaneous isoparaffin/olefin ratio in the reactor is maintained considerably higher, for example, 30/1 or 100/1 or greater, by recycling products which are low in olefins to the inlet of the reactor.

The acid for the alkylation unit is introduced through line 72 and spent acid sludge is withdrawn through line 74. The products of alkylation are passed through line 76 into a second fractionating tower 78 for separating the desired light hydrocarbons boiling in the aviation gasoline range from higher boiling constituents. The light hydrocarbon constituents pass overhead through line 82, are partially condensed in condenser 84, and passed to a separator 86 wherein gases are separated from liquid. The gases comprising C<sub>4</sub> and lighter pass overhead through line

88 and are fractionated in equipment (not shown) to separate isobutane which is recycled to the alkylation unit 57. The light aviation naphtha fraction is withdrawn from separator 86 as a liquid through line 92. This light fraction boils up to the end point of the desired aviation gasoline, generally 300-330° F. and is substantially free of olefins. Higher boiling constituents are withdrawn from the bottom of the fractionator 78 through line 94. These higher boiling constituents may be added to ordinary motor gasoline.

As mentioned earlier, it is frequently desirable to alkylate the ethylene produced in the cracking and re cracking operations with isobutane. To this end the ethylene separated in fractionating and scrubbing equipment 43 and which may have a purity from 25 to 80% is passed through line 95 to an alkylation unit 96 where it is alkylated with isobutane in the presence of aluminum chloride. Isobutane is introduced through line 97. The isobutane may come from cracked products in my process or from an extraneous source. The conditions of operation are similar to those employed in alkylation unit 57 except that the temperature is higher (100-150° F.) and the pressure may be 250-350 lbs./sq. in. The products are passed through line 98 into fractionator 78 along with the products from alkylation unit 57.

Returning now to the first-mentioned fractionating tower 32, the catalytically cracked products are further fractionated to separate a heavy naphtha fraction which is withdrawn from trap-out tray 102 through line 104 by pump 106. This heavy naphtha fraction has an initial boiling point from about 170° F. to about 220° F. and may have an end point of 350 or 400 or somewhat higher, and contains olefins, paraffins, aromatics and naphthenes. The paraffins and some of the olefins are of poor quality for aviation gasoline and it is desirable to convert them to higher quality constituents for aviation gasoline. Also some of the alkylated aromatics have a high boiling point and it is desirable to break off part of the chains of the alkylated aromatics to reduce their boiling point.

To improve the quality of the heavy naphtha fraction, it is passed through a second catalytic cracking operation in reactor 110. The re cracking unit is operated in the same manner as the cracking unit described earlier, employing powdered cracking catalyst of the same or different composition. Synthetic silica-alumina gel is a preferred catalyst. The temperature of operation is generally slightly lower than in cracking, for example, 700 to 950° F., particularly if the cracking unit is operated to give high conversions. With cracking conversions of the order of 60-80%, 900° F. is a suitable temperature for re cracking. A stream of catalyst is continuously withdrawn from the reactor through line 112, regenerated and returned through line 114. A cyclone separator 116 and return pipe 118 are used. A common regenerator is preferably employed for regenerating catalyst from the cracking and re cracking operations.

During the second cracking step paraffins, olefins and naphthenes are cracked, isomerized and dehydrogenated into isoparaffins and aromatics and at least some of the olefins are removed and others are reformed into higher quality constituents for aviation gasoline. The aromatic constituents originally in the heavy naphtha fraction passing to the reaction zone 110 remain as aromatics, but de-alkylation of alkylated aromatics

boiling above the aviation gasoline range reduces their boiling points and thereby increases the yield of aviation naphtha.

The vaporous reaction products pass overhead from reactor 110 through line 124 to a third fractionating tower 134. During the re cracking of the heavy naphtha fraction additional amounts of isobutane are formed together with other valuable light olefinic hydrocarbons. These light hydrocarbons are withdrawn from the top of the fractionating tower 134 through line 136 and are combined with the gaseous products leaving the first fractionator 32 through line 36. This mixture is then treated to separate isobutane and olefins from the other gases for use in the alkylation units 57 and 96.

The reaction products in the fractionator 134 are fractionated to separate an aviation naphtha fraction which collects on trap-out tray 140. This fraction is relatively heavy, boiling for the most part between about 190 and 335° F. and contains high quality constituents for aviation gasoline. The aromatic content of the naphtha is very high, particularly of the 220-335° F. fraction which may be 80-90% aromatics or higher. The naphtha fraction is withdrawn from trap-out tray 140 through line 142 and is mixed with the light alkylate fraction withdrawn through line 92 and the mixture is withdrawn through line 144 as an aviation gasoline. The addition of 4 or 4.5 cc. of tetraethyl lead per gallon and adjustment of the vapor pressure by adjustment of the isopentane content of the gasoline produces a finished aviation gasoline of high stability and high octane number by both the aviation octane number and the AFD-3C methods of testing.

A heavier fraction collects on lower trap-out tray 146 in the fractionating tower 134 and this fraction is withdrawn through line 148. This heavier fraction may be added to motor gasoline.

In a preferred modification, a light fraction of the re cracked products, and which contains olefins, is withdrawn from tower 134 by means of trap-out tray 150 and is passed through lines 152 and 58 to alkylation unit 57 with isobutane along with the light cracked naphtha of similar boiling range. In this case only the re cracked heavy naphtha fraction is passed directly through line 142 for blending with the alkylated naphtha.

While I have shown one form of apparatus and have given conditions for carrying out the different steps in my process, it is to be understood that these are by way of example and changes and modifications may be made without departing from the spirit of my invention.

I claim:

A method of producing aviation gasoline which comprises separating a catalytically cracked naphtha into a light naphtha fraction having a boiling range of about 60-165° F., an intermediate naphtha fraction having a boiling range of about 170-220° F., and a heavy naphtha fraction having a boiling range of about 220-410° F., alkylating the separated light naphtha fraction with isobutane to transform olefins to branched chain hydrocarbons, discarding the separated intermediate naphtha fraction, catalytically cracking the heavy naphtha fraction to higher aviation quality constituents and combining said alkylated products with said catalytically cracked heavy naphtha fraction to produce aviation gasoline.

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