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W. J. SWEENEY

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CONVERSION OF HYDROCARBON OILS

Filed Dec. 27, 1944

2 Sheets-Sheet 1

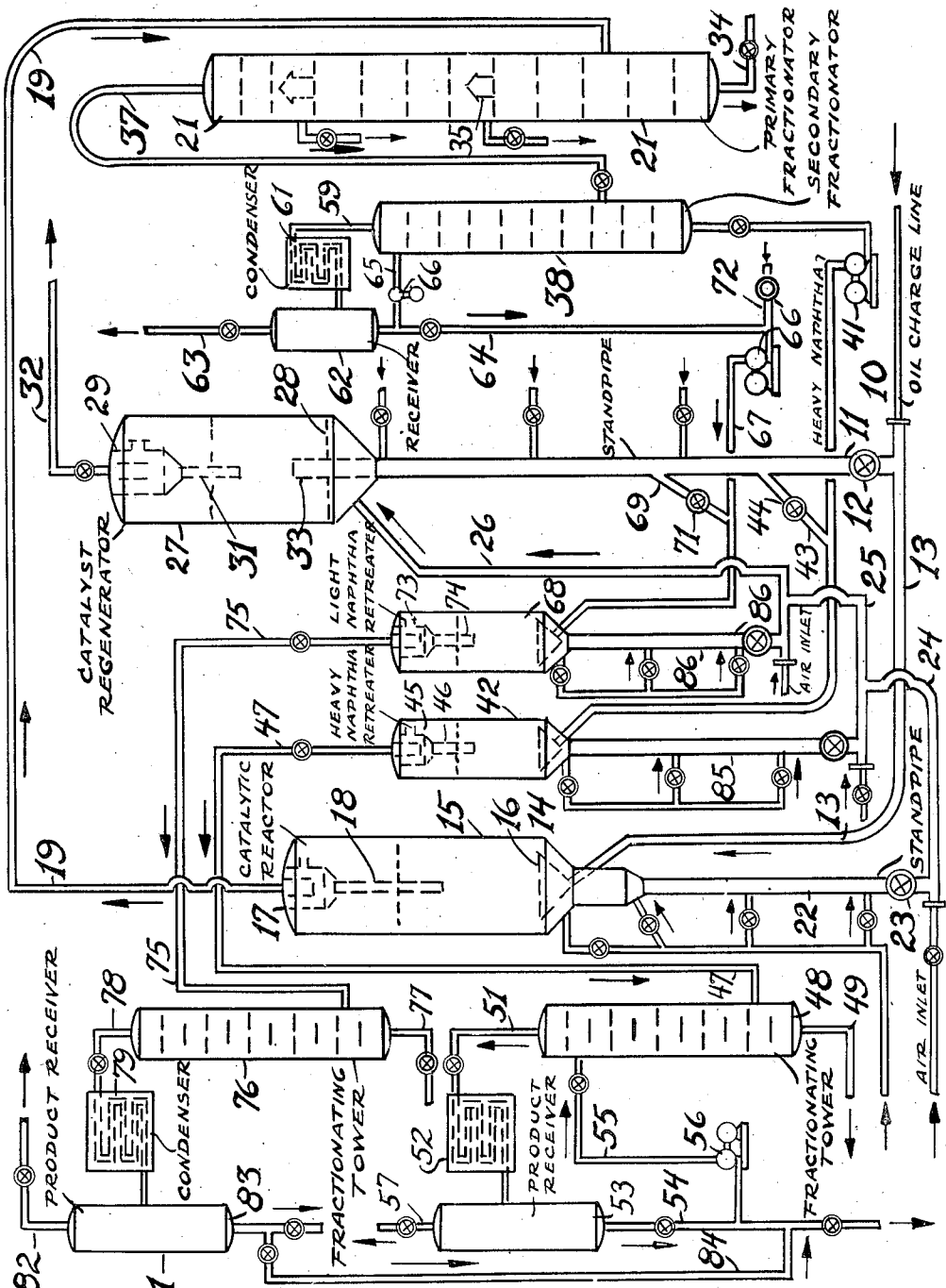


Fig. 1.

William J. Sweeney Inventor
By P. Young Attorney

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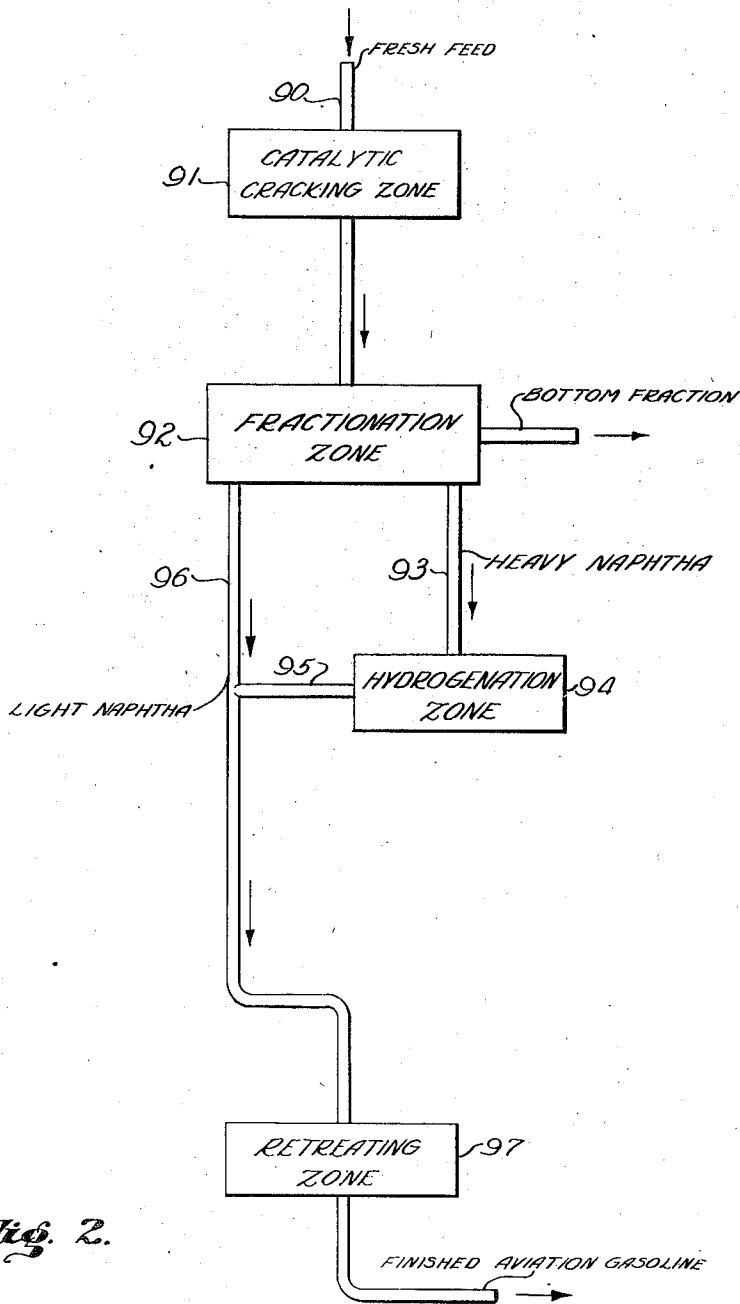


Fig. 2.

Inventor:
WILLIAM J. SWEENEY
By P. J. Whelan
Attorney

UNITED STATES PATENT OFFICE

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CONVERSION OF HYDROCARBON OILS

William J. Sweeney, Summit, N. J., assignor to
Standard Oil Development Company, a corporation of Delaware

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1 Claim. (Cl. 196—52)

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This invention relates to the conversion of hydrocarbon oils and pertains more particularly to the conversion of high-boiling hydrocarbons into high-quality aviation gasoline.

One of the objects of the present invention is to provide an improved method of producing aviation gasoline of superior quality.

Another object of the invention is to produce an aviation gasoline which will have exceptional rich-mixture performance.

Another object of the invention is to provide a process for converting high-boiling hydrocarbons into aviation gasoline and low-boiling olefinic hydrocarbons which may be utilized for the production of synthetic rubber or other valuable products.

It has heretofore been proposed to crack hydrocarbon oils in the presence of finely-divided catalysts under conditions controlled to produce a relatively high yield of butenes which may be further processed to produce butadiene for the production of synthetic rubber. Under conditions amenable to the production of high yields of butenes and other low-boiling olefins, the gasoline produced is not suitable for direct use for aviation fuel due to the presence of the relatively high percentage of olefinic material in the lower boiling fraction of the aviation gasoline.

It has been proposed to produce aviation gasoline by first cracking a gas oil or higher boiling fraction at high temperatures in the presence of a catalyst to form olefinic gasoline and thereafter subject the olefinic gasoline to further treatment in the presence of catalytic agents. I have now found that the quality of aviation fuel may be further improved by first separating the gasoline obtained from the initial catalytic cracking treatment of the higher boiling hydrocarbons into a light naphtha fraction having an end point between about 160° F. and 250° F., for example, and a higher boiling naphtha fraction.

The lower boiling fraction is then subjected to catalytic retreatment at relatively mild temperatures, such as a temperature of the order of from 500° F. to 850° F., preferably in the presence of added hydrogen or hydrogen donors, such as higher boiling naphthenic oils. The retreatment of the lower boiling fraction under relatively mild conditions materially reduces the amount of olefins contained in this fraction and thereby converts said fraction into constituents suitable for use in aviation and motor fuel.

The heavier naphtha fraction which is separated from the initial catalytic cracking treatment is predominantly aromatic and contains

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relatively little olefinic material. However, in addition to the aromatic constituents contained in the heavier fraction, which may amount to from 60% to 85% or 90%, there is a relatively small amount of non-aromatic constituents, ranging from 10% to 35%, which adversely affect the quality of the aviation fuel.

In accordance with the present invention, the heavier fraction is subjected to catalytic retreatment under relatively higher temperatures than are maintained during the cracking of the lower boiling fraction. This retreating temperature may, for example, be of the order of from 850° F. to 1000° F. Under these conditions, the non-aromatic constituents present in the heavier fraction are selectively cracked into lower boiling hydrocarbons without substantially affecting the aromatic constituents contained therein. These lower boiling hydrocarbons may then be separated from the aromatic constituents by simple fractionation, and the relatively pure aromatic so obtained may then be blended with the retreated light naphtha to form a balanced aviation fuel.

It has been found that the removal of the non-aromatic impurities from heavy naphtha materially improves the rich-mixture performance of the aviation fuel.

Having set forth the general nature and objects, the invention will be best understood from the more detailed description hereinafter in which reference will be made to the accompanying drawing wherein Fig. 1 is a diagrammatic illustration of equipment suitable for carrying the invention into effect and Fig. 2 is a flow plan illustrating a different embodiment of the invention.

Referring to the drawing, the reference character 10 designates a charge line through which the oil to be processed is introduced into the equipment. This oil may be a total crude, reduced crude, or a clean condensate stock, such as gas oil. In addition, the oil, instead of being derived from crude petroleum, may be obtained by synthetic processes such as by hydrogenation or by synthesis of carbon monoxide and hydrogen. The oil introduced through line 10 may be preheated to any desired temperature. The oil passing into the equipment through line 10 is intermixed with finely-divided cracking catalyst discharging into line 10 from standpipe 11 having a feed valve 12 for regulating the amount of catalytic material so introduced. The catalyst introduced into the oil stream may be any desired active cracking catalyst, such as naturally active

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or activated clays, synthetic compounds of silica-alumina, silica-zirconia, boric oxide-alumina, and the like. Best results have been obtained by utilizing synthetic silica-alumina catalysts formed by impregnating a purified silica hydrogel with an aluminum salt solution and thereafter decomposing the salt into alumina by ammonia. The catalyst introduced into the oil stream through standpipe 11 is preferably at a temperature of from 1000° F. to 1200° F. which is attained during the regeneration of the catalytic material, as later described.

The amount of catalyst introduced may be controlled to supply the bulk of the heat necessary for carrying out the cracking operation. In this case, the charging oil may be introduced through line 10 at substantially room temperature or at a mild preheat temperature. In general, the amount of catalyst admixed with the oil is between about 1 and 20 parts of catalyst per part of oil by weight.

In cases where it is desired to supply the bulk of the heat required for the cracking operation by hot catalyst introduced into the oil stream, the active catalytic material may be intermixed with a relatively inert diluent which may serve as a heat carrier. The mixture of catalyst and oil formed by the introduction of the catalyst into the oil stream is transferred through line 13 into a distributing cone 14 located in catalytic reactor 15. The distributing cone 14 is preferably provided with a perforated grid 16 positioned in the top thereof through which the suspension passes into the main body of the reactor. The distributing cone 14 is preferably of somewhat smaller diameter than the outer shell of the catalytic reactor 15 to form an annular space between the shell and the cone through which catalyst is removed from the reactor, as later described.

The velocity of the oil vapors passing upwardly through the reaction chamber is preferably controlled to permit the catalytic material contained therein to settle into a relatively dense mass which is maintained in a turbulent condition by the upward passage of the oil vapors there-through. To this end, the velocity of the oil vapors passing upwardly through the reactor 15 may be of the order of from 0.5 to 5 feet per second. Under well regulated conditions, a relatively dense layer of finely-divided catalytic material is formed within the reactor 15 superimposed by a dilute phase containing a relatively small amount of entrained solids.

The oil vapors passing through the reactor 15 are cracked under conditions controlled to produce a relatively high conversion, such as of the order of from 60% to 90%, as measured by the amount of feed disappearing during the cracking operation. Under high conversion conditions a substantial per cent of the oil is converted into butane-butene constituents. The amount of butane-butene constituents may, for example, range from 10% to 25% or more of the fresh feed, depending upon the conditions of operation. The temperature within the reaction chamber may be between 850° F. and 1050° F., and preferably between 900° F. and 1000° F. The time of passage of the oil vapors through the mass of finely-divided catalytic material through the reactor may range from 5 to 50 seconds and the weight of oil treated per hour per weight of catalyst within the reactor at a given instant may be of the order of from 0.5 to 10.

The oil vapors after passing through the bed

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of catalytic material within the reactor 15 are conducted to a cyclone separator 17 which may be positioned in the top of the reactor. Entrained catalytic material separated from the cracked vapors in the cyclone separator 17 may discharge through conduit 18 into the dense, turbulent mass of catalytic material therein. The cracked vapor products after passing through the cyclone separator 17 are removed overhead through line 19 to a fractionating tower 21 in which the products are subjected to initial fractionation to condense insufficiently cracked constituents. The initial condensate formed may contain a small amount of entrained catalytic material which is not removed by the cyclone separator 17.

During the course of the cracking operation, the catalytic material becomes contaminated with carbonaceous deposits which impair its activity. In order to maintain the desired activity, a portion of the catalytic material in the reactor 15 continuously discharges through the annular space formed between the distributing cone 14 and the outer shell into the bottom section of the reaction chamber. A stripping gas, such as steam, spent combustion gases or the like, may be introduced at one or more spaced points in the bottom section of the reaction chamber to remove gaseous reaction products from the catalyst. Following the stripping operation, the catalyst discharges from the bottom of the reaction chamber 15 into a standpipe 22 having a control valve 23 which feeds the catalytic material at a controlled rate into a stream of air passing through line 24. The stream of air carries the catalyst through lines 24, 25 and 26 into the bottom section of a regenerating chamber 27 below a perforated grid plate 28 located in the bottom portion thereof. A portion of the chamber below the grid plate 28 is preferably of reduced diameter to form a distributing zone for dispersing the catalyst into the regeneration zone. The velocity of the air stream passing through the regeneration zone is preferably controlled to permit the catalyst contained therein to settle into a relatively dense, fluidized mass of catalytic material which is maintained in a turbulent state by the upward passage of the regeneration gas therethrough. The density of the catalytic material in this dense layer within the regenerator may be of the order of from 10 to 25 pounds per cubic foot.

Within the regeneration chamber 27 the catalyst is subjected to oxidizing conditions to burn off carbonaceous deposits contained thereon, as previously described. During the burning operation, considerable heat is liberated and the catalyst temperature is raised. During regeneration it is desirable to control the temperature to avoid permanently impairing the activity of the material. The spent combustion gases after passing through the mass of catalytic material in the regenerator 27 are passed to a cyclone separator 29 located in the upper portion of the regenerator 27. Entrained catalytic material separated from the regeneration gases in the cyclone separator 29 may be returned to the main body of the catalytic material therein through line 31.

The spent regeneration gases after passing through the cyclone separator 29 are removed through line 32 and may, if desired, be passed to further purifying devices, such as Cottrell precipitators, scrubbing chambers, filter bags, and the like, for further removal of entrained catalytic material therefrom.

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The spent combustion gases may also be passed to a suitable heat absorber such as a waste heat boiler for recovery of heat therefrom prior to being vented to the atmosphere.

For the purpose of simplicity, these purifiers and heat exchangers have not been illustrated in the drawing.

The catalytic material after being subjected to the desired amount of regeneration within the regeneration chamber 27 is continuously withdrawn therefrom through standpipe 11 which has an internal extension 33 terminating within the dense layer of catalytic material at a point somewhat above the perforated grid 28. A portion of the regenerated catalytic material withdrawn from the regenerator through standpipe 11 is discharged into the oil stream, as previously described.

Returning again to the fractionating tower 21, the oil vapors introduced therein are subjected to fractionation to condense the insufficiently cracked constituents as reflux condensate. This fractionating tower may be provided with suitable trap-out trays for segregating the condensate into separate fractions of different boiling range. For example, the initial condensate formed in the bottom section of the tower and containing entrained catalytic material carried overhead from the reactor 15 may be withdrawn from the bottom of the fractionator through line 34. An intermediate condensate may be collected in trap-out tray 35 located at an intermediate point of the tower. This product may be withdrawn from the system and utilized as a diesel fuel, kerosene, heating oil or the like, or it may be returned to the reactor for further conversion by recycle line (not shown). The top of the fractionating tower 21 may also be provided with a trap-out tray 36 in which a heavy naphtha fraction may be collected, if so desired. This heavy naphtha may have an initial boiling point between 160°-250° F. and a final boiling point between 300°-450° F.

Vapors remaining uncondensed in the primary fractionating tower 21 are removed overhead through line 27 and may be passed to a secondary fractionating tower 38 in which further fractionation is carried out to segregate a heavy naphtha fraction, of the above-specified boiling range, and a lighter naphtha fraction. The heavy naphtha fraction formed as condensate in the fractionating tower 38 is removed therefrom through line 39 and is charged by means of pump 41 to a heavy naphtha retreating reactor 42. As illustrated, a portion of the regenerated catalyst from regenerator 27 may be introduced into the heavy naphtha stream through conduit 43 having a control valve 44.

The heavy naphtha retreating chamber 42 may be of the same general construction as the catalytic cracking reactor 15, except that the capacity may be substantially smaller since it is designed to process only the heavy naphtha fraction. The heavy naphtha vapors passing upwardly through the retreating chamber 42 are controlled to maintain a dense, turbulent mass of catalytic material therein. The products within the reaction chamber 42 are preferably maintained at a temperature of from 850° F. to 1050° F., and preferably between 900° F. and 1000° F. This temperature may be maintained by controlling the proportion of hot, regenerated catalyst introduced into the heavy naphtha stream through line 43, or the heavy naphtha may be subjected to preheating to any desired temperature prior to the admission of the catalyst thereto. The conditions within the retreating

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chamber 42 are controlled to preferentially crack the non-aromatic impurities contained in the heavy naphtha derived from the catalytic cracking process previously described. The amount of catalyst introduced into the heavy naphtha stream may, for example, range between 0.5 and 10 parts of catalyst per part of naphtha by weight. The time of residence of the heavy naphtha vapors within the reactor may range from 5 to 50 seconds. The heavy naphtha vapors after undergoing retreating in the reaction chamber 42 are passed to a cyclone separator 45 positioned in the top of the chamber for removal of entrained catalyst particles from the gases. The catalyst particles removed from the gases in the cyclone separator 45 are returned to the main body of catalytic material through conduit 46.

The retreated vapors after passing through cyclone separator 45 are removed overhead through line 47 and may be passed to a fractionating tower 48 wherein the vapors are subjected to fractionation. The condensate formed in the tower, which may comprise some high-boiling polymers formed during the operation, is removed from the bottom of the fractionating tower 48 through line 49. This polymer fraction may contain some entrained catalyst. The condensate fraction withdrawn through line 49 may, if desired, be recycled to the catalytic cracking unit 15 by suitable recycle line (not shown).

Vapors remaining uncondensed in fractionating tower 48 are removed overhead through line 51 to a condenser 52 in which the normally liquid constituents are condensed. Products from the condenser 52 then pass to a product receiver 53 in which the liquid separates from normally gaseous products formed during the retreating operation. Liquid distillate collected in product receiver 53 is removed therefrom through line 54. If desired, a portion of this distillate may be returned to the top of the tower 48 through line 55 and pump 56 to serve as a reflux medium therefor. Gases separated from the liquid distillate in product receiver 53 may be removed overhead through line 57 and may be subjected to further treatment for removal of the higher boiling hydrocarbon constituents, such as butanes, butenes, propylene and the like.

Returning again to the fractionating tower 38, the light naphtha vapors together with normally gaseous products formed during the catalytic cracking operation are removed overhead from the fractionating tower 38 through line 59 to condenser 61 in which the light naphtha constituents are condensed. Products from the condenser 61 are collected in product receiver 62 in which the light naphtha is segregated from normally gaseous products formed during the catalytic cracking operation. Uncondensed gases and vapors are removed from the product receiver 62 through line 63.

The gaseous products may include all of the butane-butene fractions as well as the lower boiling hydrocarbons, or, if desired, the temperature within the condenser may be controlled so as to retain the bulk of the butane-butene constituents in the light naphtha fraction. According to the preferred mode of operation, however, the butenes formed during the cracking operation are segregated from the cracked products and utilized as a source of raw material for the production of synthetic rubber.

The light naphtha fraction is removed from the product receiver 62 through line 64. If desired, a portion of the light naphtha removed from the product receiver 62 may be returned to the top of

the secondary fractionating tower 38 through line 65 and pump 66 as a reflux medium therefor. The light naphtha fraction removed from the receiver 62 is subjected to further retreating under temperature conditions substantially lower than those maintained during the retreating of the heavy naphtha fraction. To this end, the light naphtha from line 64 passes through pump 66' and line 67 to a light naphtha retreating chamber 68 which may be of the same construction as the heavy naphtha retreater 42. Finely-divided, hot, regenerated catalytic material from the standpipe 11 is discharged into the stream of light naphtha passing through line 67 through conduit 69 having a control valve 71 for regulating the quantity of catalytic material so introduced. The resulting suspension discharges into the light naphtha retreating chamber 68 and is subjected to treatment similar to that described with reference to the heavy naphtha, except that the temperature within the retreating zone may be of the order of from 500° F. to 850° F. The temperature within the retreating chamber may be controlled by regulating the proportion of the regenerated catalytic material introduced into the naphtha stream through line 69. In some cases, it may be desirable to cool the hot, regenerated catalytic material partially prior to introducing the same into the light naphtha stream.

It is also desirable to introduce into the naphtha stream undergoing treatment a naphthenic oil having a boiling range above the boiling range of the light naphtha. This naphthenic oil may serve to supply hydrogen for saturating the olefinic constituents contained in the light naphtha. The naphthenic oil may be obtained from an extraneous source or it may be produced by non-destructive hydrogenation of heavy aromatic naphtha produced in the process as hereinafter described. If desired, a naphthenic oil may be intermixed with the charging oil to the cracking reactor 15 to promote transfer of hydrogen during the main cracking step. The naphthenic oil may be introduced into the light naphtha stream through line 72. In place of naphthenic oils, hydrogen or other hydrogen donors may be intermixed with the light naphtha. The light naphtha vapors are retained within the retreating chamber 68 for a period sufficient to remove the olefin concentration therein to the desired minimum. Following this, the light naphtha vapors are passed through cyclone separator 73 positioned at the top of the retreating chamber 68. The catalyst separated from the light naphtha in the cyclone separator 73 may be returned to the main body of the reactor through line 74.

The light naphtha vapors after passing through the cyclone separator 73 are conducted through line 75 to a fractionating tower 76 in which constituents boiling above the end point of the desired light naphtha fraction are condensed. The condensate formed in the tower 76 is removed therefrom through line 77. The light naphtha which remains uncondensed in the fractionating tower 76 is removed overhead through line 78 to a condenser 79 in which the light naphtha fraction is condensed.

The products from the condenser then pass to a product receiver 81 in which the light naphtha distillate separates from normally gaseous constituents formed during the retreating operation. Normally gaseous constituents are removed from the product receiver through line 82. The light naphtha distillate is removed from the receiver 81

through line 83 and may be passed through line 84 to line 54 and blended with the heavy naphtha from product receiver 53 to form a balanced fuel.

The catalytic material is continuously withdrawn from the heavy naphtha retreater 42 through a standpipe 85 and discharged into a stream of air passing through line 25 which transports the catalyst to the regenerating chamber 27 for regenerative treatment. Likewise, catalytic material in the light naphtha retreater 68 is continuously withdrawn through a standpipe 86 and discharged into an air stream passing through line 26 which transports the material to the regenerator 27.

In order to effect circulation of the finely-divided material as previously described, it is necessary to build up or restore pressure on the catalytic material during circulation. As illustrated, this is accomplished by means of standpipes 11, 22, 85 and 86. In order to utilize the standpipes for developing pressure on the catalytic material undergoing circulation, it is essential to maintain the catalytic material in a fluidized, freely flowing state throughout its circulating path. To this end, a small amount of a fluidizing gas may be introduced at one or more spaced points along the various standpipes as indicated in order to maintain the catalytic material in the standpipes in a fluidized condition. The amount of aerating or fluidizing gas admitted into the standpipes is relatively small and is preferably only sufficient to effect the desired fluidity.

For simplicity, however, I have shown a single regenerator which is utilized for regenerating the catalytic material from both the catalytic cracking operation and the retreating operations. In some cases, it may be desirable to utilize separate regenerators for each of the treating operations and for the catalytic cracking operation. This is particularly suitable when different types of catalysts are employed for the three operations.

Fig. 2 is a flow plan illustrating a modification wherein the heavy naphtha resulting from the initial catalytic cracking operation is subjected to hydrogenation to convert the aromatic constituents thereof into naphthenes. The resulting naphthenes are then combined with the light naphtha passing to the treating zone.

Referring specifically to Fig. 2, the fresh feed is introduced through line 90 and is passed to conventional type of catalytic cracking apparatus 91, such as that illustrated in Fig. 1. The cracked products are then fractionated in a fractionating zone 92 wherein the cracked vapors are fractionated to segregate a light naphtha of the type previously described and a heavy naphtha. The heavy naphtha is passed through line 93 to a hydrogenating zone 94 wherein the products are hydrogenated under non-destructive conditions to saturate the aromatics and form naphthenes or hydroaromatics. The resulting naphthenes are then passed from the hydrogenating zone 94 through line 95 and combined with the light naphtha withdrawn from the fractionating zone 92 through line 96. The resulting mixture is then passed to a retreating zone 97 in which the light naphtha is subjected to retreating under conditions described with reference to Fig. 1. The products from the retreating zone 97 are subsequently fractionated to segregate the desired aviation gasoline therefrom.

What is desired to be protected by Letters Patent is:

A process for the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons

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suitable for motor fuel which comprises passing a stream of said higher boiling hydrocarbons through a cracking zone maintained at an active cracking temperature between 850° F. and 1000° F., contacting said hydrocarbons within said cracking zone with an active cracking catalyst, maintaining said oil within said cracking zone for a period sufficient to convert a major portion of said hydrocarbons into constituents outside the boiling range of said first-named hydrocarbons, fractionating the cracked products to segregate a light naphtha fraction containing a relatively high proportion of olefinic constituents and a heavy naphtha fraction containing a major portion of aromatic constituents, hydrogenating said heavy naphtha fraction under non-destructive conditions to convert at least a portion of said aromatic constituents into naphthenes, combining the hydrogenated heavy naphtha so formed with said light naphtha fraction, subjecting the combined mixture to further treatment with an active cracking catalyst at a temperature between about 500° F. and 850° F. to reduce the ole-

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fin content thereof, and fractionating the resulting treated product to segregate a motor fuel fraction therefrom.

WILLIAM J. SWEENEY.

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