Dec. 16, 1947. R. H. NEWTON 2,432,537

PRODUCTION OF MOTOR FUELS

Filed Jan. 12, 1945 2 Sheets-Sheet 1

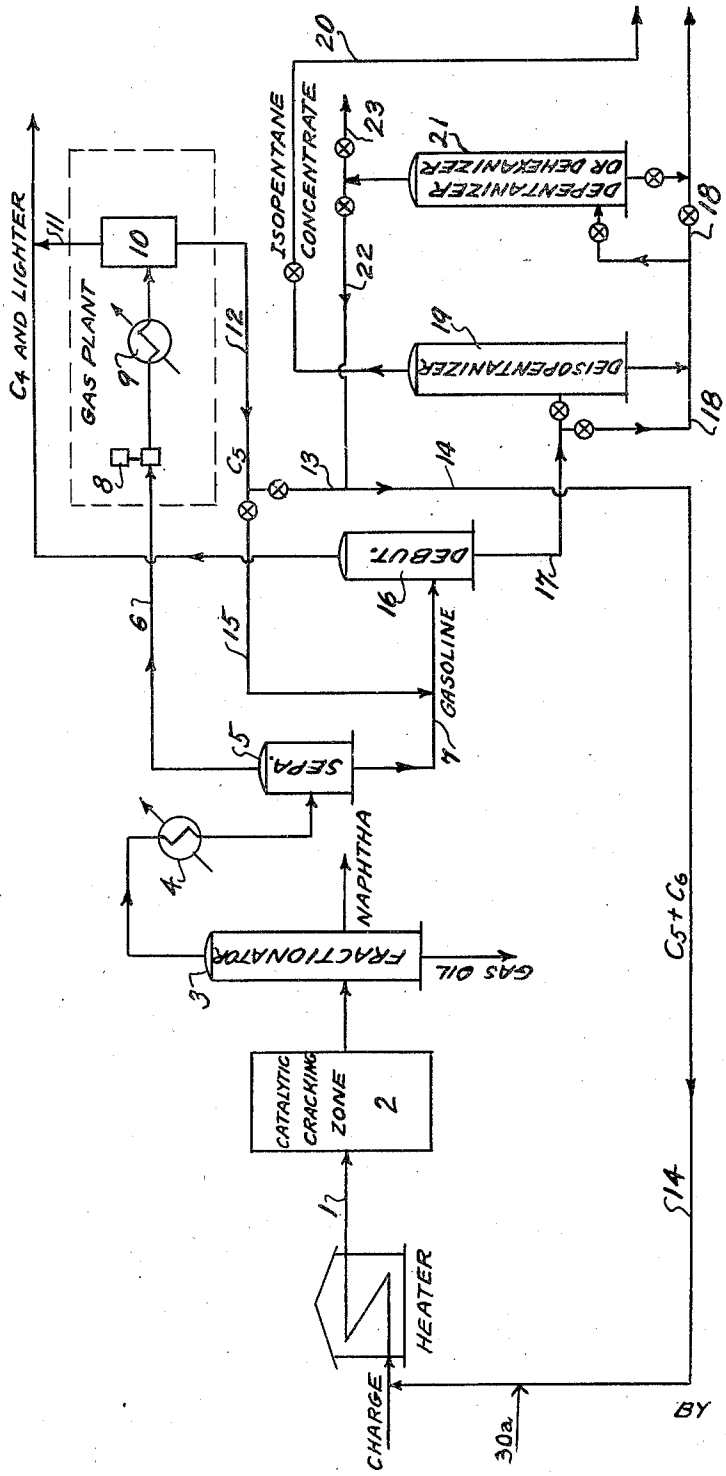


Fig. 1

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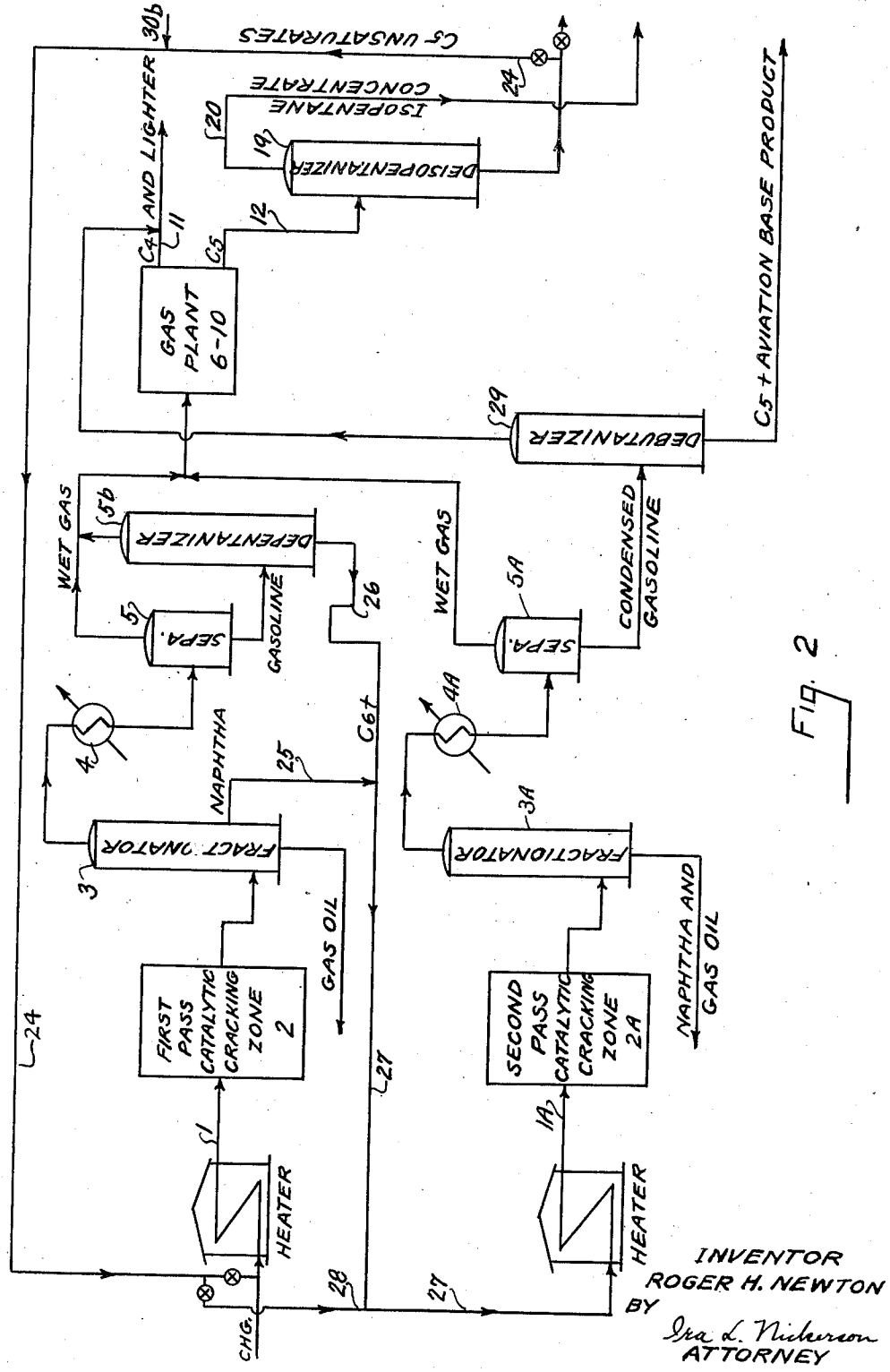


Fig. 2

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PRODUCTION OF MOTOR FUELS

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9 Claims. (Cl. 196—52)

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This invention relates to the catalytic conversion of hydrocarbons for the production of motor fuels including aviation base stock of superior quality.

One object of the invention is to improve acid heat of motor fuels, thereby to enhance lead susceptibility of the same and to obtain better leaded octane ratings which will be reflected in both the 1-C and 3-C tests for aviation fuels. Another object is to insure the production of non-corrosive motor fuels directly from cracking operations. Another object is to effect the above improvements in either one-pass or two-pass operations. Still another object is to utilize as part of the charge to a catalytic zone hydrocarbon material which during reaction will produce heat thereby supplying at least a portion of the heat necessary for the conversion or transformation of the remainder of the charge. Other objects will be apparent from the detailed description which follows.

The discovery has been made that the above objects can be attained by sending into a catalytic zone, along with the fresh charge to be converted, normally liquid low boiling unsaturated hydrocarbons, specifically C_5 unsaturates with or without C_6 unsaturates, and even at times some C_7 unsaturates. The unsaturates thus charged may be in whole or in part recycle material from a previous reaction in the same catalytic zone, or may come from an extraneous source. In general in a catalytic cracking operation the higher boiling the charge, the greater the quantity of olefins or unsaturates that are formed in the C_5 and C_6 cuts. For example with a light gas oil charge, of the order of 20 to 25% of the C_5 and C_6 cuts in the cracked product will be unsaturates; and when the charge is heavy gas oil the percentage of unsaturates in the said cuts may run up to 60%. The adverse effect of such a quantity of unsaturates on acid heat and lead susceptibility is only too apparent when it is realized that the C_5 and C_6 cuts normally amount to something like 50 to 55% of aviation base stock.

In accordance with the present invention it is advantageous to recirculate or recycle in the cracking zone C_5 and C_6 unsaturates when the production of the latter is 20% of such cuts or whenever sufficient of such unsaturates can be segregated so as to make up at least 5% of the gas oil or other charge to the cracking zone. C_5 and/or C_6 unsaturates should be recycled or recirculated through the cracking zone in such amount that the final product cuts of C_5's and

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C_6's contain not more than 10% of olefins or unsaturates; for best results, however, the operation should be conducted so as to reduce the olefin content of the C_5's and C_6's in the final product to about 3%.

In order to illustrate the invention and the manner of its use concrete embodiments of the invention are shown in the accompanying drawings which are entirely schematic in character and in which:

Fig. 1 is a diagrammatic view of a single pass operation; and

Fig. 2 is a similar view of a two pass operation.

In Fig. 1 preheated fresh charge, such as gas oil is admitted by line 1 to a catalytic cracking zone 2 containing one or more catalytic reactors of any desired type and the products of the cracking operation are fractionated in fractionator 3, the overhead from which, containing cracked gas and gasoline, is led through cooler 4 and separator 5 to effect division into wet gas and condensed gasoline fractions leaving separator 5 by lines 6 and 7, respectively. The wet gas fraction, which may contain paraffins and olefins up to and including a part of the C_6's, then passes through a gas plant of any desired type indicated schematically by compressor 8, cooler 9 and knock-out drums 10. For production of motor fuels of the aviation type, the C_4's and lighter are preferably withdrawn from the gas plant as by line 11, the higher boiling components of the wet gas, which may contain up to 50% olefins of 5 and 6 carbon atoms, being withdrawn by line 12 as a liquid stream, all or a portion of which may be led directly back to the catalytic cracking zone by lines 13, 14 and 1. Through control of the temperatures and pressures obtaining in cooler 4 and separator 5 any desired portion of the C_5 and C_6 olefins in the cracked products may be returned to the cracking zone. In the catalytic cracking zone 2 and C_5 and C_6 fractions so circulated have their olefinic content reduced to an extent controlled by regulation of the proportion of the total quantity of liquid in line 12 which is withdrawn as product, as for example, by line 15 and thence through the depentanizer 21 and line 23. As the ratio of recirculated to withdrawn material is increased the concentration in the latter of stable, high anti-knock components, such as isopentane, increases, especially when the catalytic material utilized in the cracking zone is capable of promoting polymerization and selective cracking reactions, among which are activated hydrosilicates of alumina and synthetic blends of silica

and alumina, silica and zirconia, alumina and zirconia, or any desired combination of them. Thus, the system disclosed may be operated to produce a stream of pure or substantially pure iso-pentane, or, alternatively, a motor or aviation fuel in which the C_5 components are composed practically entirely of this compound.

To effect withdrawal of iso-pentane concentrate or gasoline containing the same, the iso-pentane concentrate in line **15** may be combined with the condensed gasoline in line **7**, the combined streams debutanized in debutanizer **16** and the resulting debutanized gasoline withdrawn from the system by lines **17** and **18**. If desired, this gasoline may be fractionated in de-isopentanizer **19** to remove any desired part of the iso-pentane concentrate by line **20** for use as a blending agent for high quality fuels.

When gas plant condensate is sent by lines **12** and **15** to combine with condensed gasoline in line **7**, recirculation of the light olefin containing stream to the cracking zone **2** may be effected by subjecting the deisopentanized gasoline in line **18** to dependentanization or de-hexanization in a suitable fractionator **21**, the overhead from which comprising C_5 of C_5 and C_6 hydrocarbons may be led by line **22** to line **14** and thence to the catalytic cracking zone **2**, thus supplementing or replacing the stream of light material in line **13**. Whether recirculation is through line **13** or not, any small amounts of normal pentane that may remain in the C_5 fraction after recirculation may be withdrawn from the system as by use of a suitable withdrawal line, such as line **23**. In the event substantially all the C_5 fraction is passed to the gas plant through line **6** and condensate issuing from the gas plant by line **12** is processed in debutanizer **16**, deisopentanizer **19**, and dependentanizer **21**, the stream withdrawn in line **23** may be substantially pure normal pentane and the recycle stream in line **14** substantially isopentane free.

The produce from a normal single pass operation, which includes the bottoms from the gas separator line **7** and from the gas plant line **12** is usually corrosive to copper dish, and often requires further treatment to produce a satisfactory aviation fuel. By complete recirculation of the gas plant bottoms through lines **12**, **13** and **14**, the corrosion materials are removed and the products obtained from line **18** and the naphtha sidestream from fractionator **3** are non-corrosive and may be used directly in the final motor fuel products.

Fig. 2 illustrates a two-pass operation to produce very high quality fuels, for example base for combat grade aviation gasoline, which operation permits the use in the second catalytic pass of the comparatively severe operating conditions which affect beneficially the composition of the heavier portions of the first pass gasoline with a minimum of coke production. In this operation all or a part of the olefin rich light material, such as the C_5 fraction from the first pass cracking, is charged back to the first pass cracking zone. The olefin rich fraction is shown as being obtained by de-isopentanizing the heavy effluent of the gas plant and is the bottoms from the de-isopentanizing fractionator **19** which may be returned to the first pass cracking by line **24**. The wet gas from both first and second pass operations comprise the feed to the gas plant **6**—**10**, although separate gas plants may be used if desired. The second pass charge is composed essentially of C_6+ hydrocarbons obtained for example by de-pentanizing in dependentanizer **5b** liquid products from separator **5** resulting from the condensation of light overhead material from the primary fractionator **3** and combining the resulting de-pentanized material in line **26** with the motor naphtha fraction withdrawn from fractionator **3** through line **25**, the resulting motor gasoline being fed to the second pass catalytic cracking zone through line **27**. A part of the recirculated material in line **24** may be diverted through line **28** and into line **27** for charging to the second pass. By operating in this manner, full advantage may be taken of the very highly selective reactions which take place in second pass cracking under the comparatively severe conditions which are preferred with a charge containing only a small proportion of low boiling olefins. The reaction produces from olefinic C_5 charge a C_5 fraction highly concentrated in isopentane and practically free of pentenes and normal pentane. For this reason the C_5 content of the second pass product may be left in the final gasoline fraction, as for example by subjecting the condensed gasoline merely to debutanization in a suitable fractionator **29** and withdrawing the bottoms from the latter as final product.

Even in two pass operation the product from normal procedures, consisting of condensed gasoline from the gas separator and condensed C_5 fraction from the gas plant is frequently sufficiently corrosive to copper dish to require secondary treatment. However, when the wet gas from second pass is processed in the manner shown in Fig. 2 wherein the C_5 portion of this gas is recovered as isopentane concentrate in line **20** and as a concentrate of higher boiling material in line **24** with all of the latter being returned to the cracking zone or zones, the final product consisting of C_5+ aviation base from debutanizer tower **29** and isopentane concentrate from line **20** is non-corrosive and suitable for blending directly to the highest grades of aviation fuel.

The polymerization or other reaction which removes or converts in the cracking zone to more stable form the olefins contained in the recycled or recirculated streams produces heat in the catalytic zone, thus supplying at least a part of the heat needed to crack the fresh charge. This effect is of particular value when the catalytic cracking zones have moving catalyst reactors, for the exothermic heat of reaction of the olefins tends to reduce the quantity of heat input to the reactor from other sources as in the fresh charge and/or in regenerated or recirculated catalyst. Thus the point of admission of the olefinic stream may be selected to produce this heat at the most advantageous point or points in a moving catalyst reactor, as for example at or near the level of admission of the cracking stock or of regenerated or reheated catalyst. However, this production of heat is advantageous regardless of whether the catalytic reactors in the cracking zones are of the fixed bed, moving bed, or "fluid" types.

For purposes of supplying more exothermic heat of reaction in the cracking zone, the recycled olefinic feed may be augmented by olefins obtained from a source other than the effluent from the catalytic cracking zone itself, as for example propylenes, butylenes, pentenes and/or hexenes obtained from a cracking unit which produces highly olefinic material, such as a thermal cracker. In such event the additional feed may be ad-

mitted at a suitable point in the system, as at 30a to line 14 (Fig. 1) or at 30b to line 24 (Fig. 2).

Certain of the important advantages of the invention can be realized when the operation is conducted to produce motor fuel of the motor gasoline type rather than aviation gasoline, in which event the recirculated material rich in unsaturates may include butylenes. The gas plant would then be operated in normal manner for rejection of C_3's and lighter in the dry gas stream.

The following example illustrates use of the invention in a single pass operation as in Fig. 1:

A long gas oil boiling in the range of 440° to 900° F. was fed to a catalytic cracking zone containing active synthetic silica-alumina catalyst of about 35 activity index and maintained at average temperature of about 835° F., the pressure of the oil feed being 10 pounds per square inch gauge and the space rate (liquid volume of oil per volume of catalyst per hour) being 1.0. The finshed aviation gasoline base separated from the cracked products amounted to about 25% by volume of the gas oil charge. This aviation base had an acid heat of the order of 135° F., and 1-C and 3-C octane ratings (4.6 cc. of tetraethyl lead added) of about 88.5 and approximately

$$95\%\frac{S}{M}$$

respectively. (In the expression

$$95\%\frac{S}{M}$$

reference is made to a blend of 95% Standard Reference Fuel S having 100 octane by the 3-C method of test, and 5% Standard Reference Fuel M having O octane by that method.) When there was added to the gas oil charge light olefin containing condensate composed essentially of C_5 and C_6 hydrocarbons obtained by compression and cooling of the wet gas from the cracking operation, the resulting base stock exhibited reduced acid heat of about 100° F. and 1-C and 3-C octane ratings (4.6 cc. of tetraethyl lead added) of about 90 and

$$98\%\frac{S}{M}$$

(98% Fuel S and 2% Fuel M) respectively. These results were obtained after recirculation equilibrium had been reached, at which point the quantity of C_5 and C_6 hydrocarbons recharged to the catalyst was equivalent to about 8 to 10% of the gas oil charge.

In the two pass operation it is desirable to utilize, in second pass, synthetic cracking catalysts of high activity (at least 40 activity index) and in general more severe operating conditions, such as higher temperature or higher pressure or lower feed rate or a combination of these factors, in order to produce aromatics. This can be done without excessively heavy coke deposit on the catalyst since the unsaturates have already been substantially removed or converted in the first pass.

The cut of C_5 and C_6 unsaturates to be recycled in the cracking zone is usually within the boiling range of about 80° to 150° F. but the range may extend higher, as to 185° F., when some C_7 unsaturates are included, or extend lower if C_4 unsaturates are included.

I claim as my invention:

1. Process of making motor fuels of improved quality and lead susceptibility from higher boiling hydrocarbons which comprises subjecting the charge under cracking conditions to the action of cracking catalyst in a cracking zone, separating from the resulting cracked product a fraction rich in isopentane and a fraction rich in pentenes, and recirculating through said cracking zone along with the fresh charge the pentene rich fraction in order to reduce the quantity of C_5 unsaturates in the final motor fuel product.

2. Process of making motor fuels of improved quality and lead susceptibility from higher boiling hydrocarbons in a two pass operation which comprises sending the charge under cracking conditions into a first catalytic cracking zone, separating depentanized gasoline and naphtha from the effluent of said first cracking zone, and sending the same under cracking conditions at least as severe as in said first zone into a second catalytic cracking zone, separating an aviation base product from the effluent of said second cracking zone, combining the wet gas from both cracking zones, separating a normally liquid fraction containing C_5 unsaturates from said wet gas, and adding at least a part of said fraction to the charge to one of said cracking zones.

3. Process of making motor fuels of improved quality and lead susceptibility from higher boiling hydrocarbons in a two pass operation which comprises sending the charge under cracking conditions into a first catalytic cracking zone, separating depentanized gasoline and naphtha from the effluent of said first cracking zone and sending the same under cracking conditions at least as severe as in said first zone into a second catalytic cracking zone, separating an aviation base product from the effluent of said second cracking zone, combining wet gas containing C_5 hydrocarbons from both cracking zones, separating fixed gas and a fraction rich in isopentane from said wet gas, and adding at least a part of the remainder of the wet gas including C_5 unsaturates to the charge to said first cracking zone.

4. Process of making motor fuels of improved quality and lead susceptibility from higher boiling hydrocarbons in a two pass operation which comprises sending the charge under cracking condition into a first catalytic cracking zone, separating depentanized gasoline and naphtha from the effluent of said first cracking zone and sending the same under cracking conditions at least as severe as in said first zone into a second catalytic cracking zone, separating an aviation base product from the effluent of said second cracking zone, combining the wet gas from both cracking zones, separating said wet gas into a C_4 and lighter fraction, a fraction rich in isopentane, and a fraction containing C_5 unsaturates, and adding at least a part of said last named fraction to the charge to said first cracking zone.

5. Process of making motor fuels of improved quality and lead susceptibility from higher boiling hydrocarbons in a two pass operation which comprises sending the charge under cracking condition into a first catalytic cracking zone, separating depentanized gasoline and naphtha from the effluent of said first cracking zone and sending the same under cracking conditions at least as severe as in said first zone into a second catalytic cracking zone, separating an aviation base product from the effluent of said second cracking zone, combining the wet gas from both cracking zones, separating said wet gas into a C_4 and lighter fraction, a fraction rich in isopentane, and a fraction containing C_5 unsaturates, and adding at least a part of said last named fraction to the charge to both said first and said second cracking zones.

6. Process of making motor fuels of improved quality and lead susceptibility from higher boiling hydrocarbons in a two pass operation which comprises sending the charge under cracking condition into a first catalytic cracking zone, separating depentanized gasoline and naphtha from the effluent of said first cracking zone and sending the same under cracking conditions at least as severe as in said first zone into a second catalytic cracking zone, separating an aviation base product from the effluent of said second cracking zone, separating from the wet gas from said cracking zones a normally liquid light fraction containing C_5 unsaturates and recirculating said fraction through one of said cracking zones to be converted to more saturated and more stable hydrocarbons and to insure that the said aviation base product from said second cracking zone is free of components corrosive to copper dish.

7. The process of making motor fuels of improved quality and lead susceptibility from higher boiling hydrocarbons which comprises subjecting the charge under cracking conditions to the action of a cracking and polymerizing catalyst in a cracking zone, separating from resulting cracked products an essentially C_5 fraction rich in isopentane and an essentially C_5 plus C_6 fraction rich in olefines, and recirculating said C_5 plus C_6 fraction with the fresh charge through said cracking zone to increase the concentration of isopentane and to decrease the concentration of olefines in the products therefrom.

8. The process of making motor fuels of improved quality and lead susceptibility from higher boiling hydrocarbons which comprises subjecting the charge under cracking conditions in a cracking zone to the action of cracking catalyst, separating products of the cracking operation into a wet gas fraction containing pentanes and pentenes and a gasoline fraction, separating C_4's and lighter from said wet gas fraction to leave a normally liquid fraction containing C_5's, separating said normally liquid fraction into a fraction rich in isopentane and a fraction rich in pentenes, and recycling the latter through said cracking zone along with the charge thereto, whereby the distillate products of said cracking zone are relatively free of pentenes and relatively concentrated in isopentane.

9. In making motor fuels of improved quality and lead susceptibility, the process comprising subjecting cracking stock under cracking conditions in a cracking zone to the action of cracking catalyst, separating the products of cracking into a C_4 and lighter fraction, and a gasoline fraction containing C_5 and C_6 olefines and isopentanes, separating a fraction rich in isopentane from said gasoline fraction, separating from the remainder of the gasoline fraction a light normally liquid fraction rich in olefines, and recirculating said last named fraction to said cracking zone for conversion simultaneously with said cracking stock to produce isopentane and to reduce the quantity of light olefines in the final motor fuel product.

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