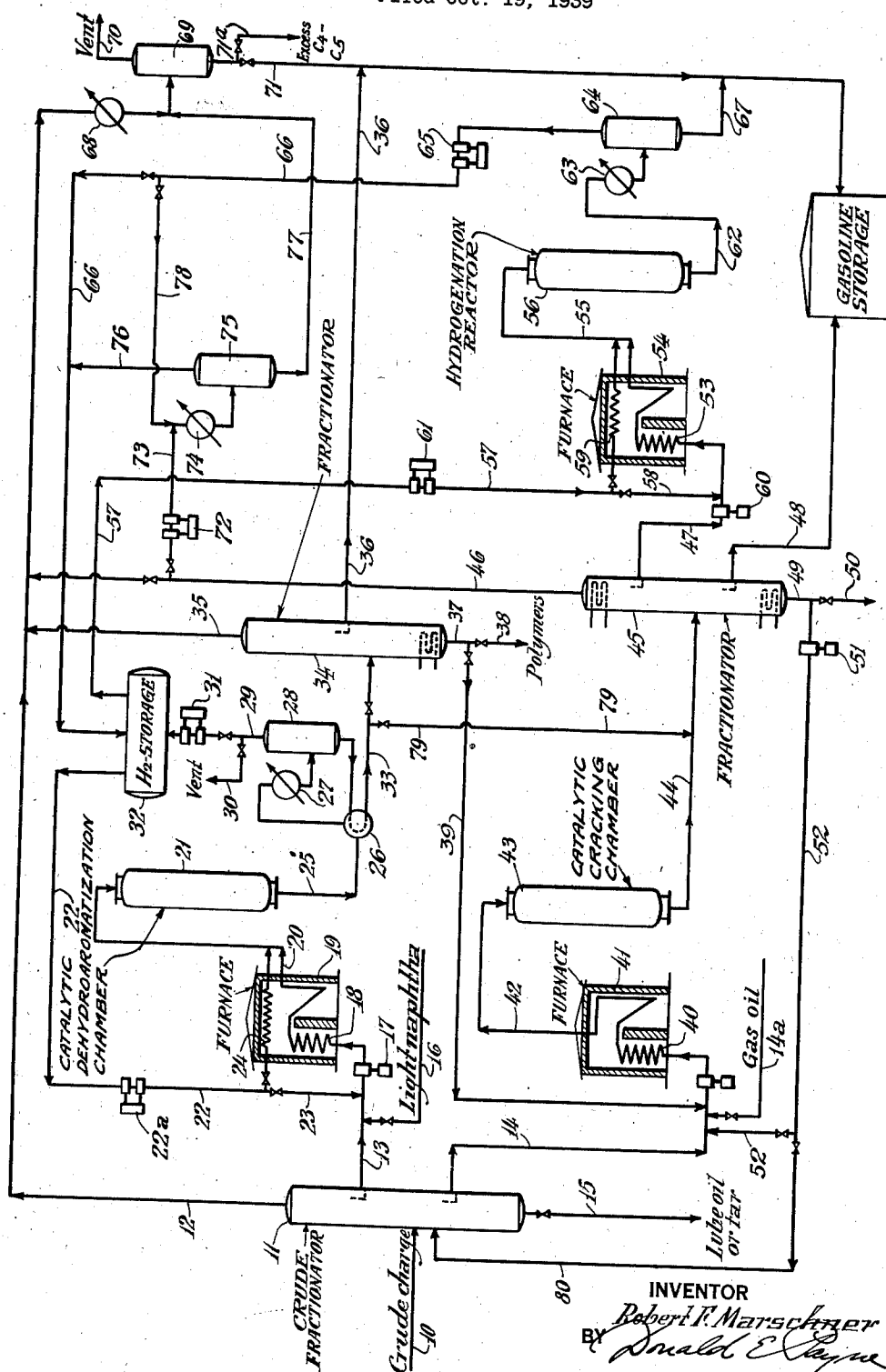


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CATALYTIC MOTOR FUEL PRODUCTION

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CATALYTIC MOTOR FUEL PRODUCTION

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This invention relates to the production of high quality motor fuel by catalytic processes and it pertains more particularly to the preparation of aviation gasoline in an improved system employing catalytic dehydro-aromatization, catalytic cracking and catalytic hydrogenation.

Motor fuel produced by catalytic cracking may be objectionable for aviation purposes because of its high olefinic content and its consequent high acid heat. The acid heat test is a common method for determining the unsaturated content of gasoline and is described, for example in volume IV of Science of Petroleum, page 2430. According to this test the acid heat number is expressed as the number of degrees F. rise in temperature, following the addition of 30 cc. of 66° Bé. sulfuric acid to 150 cc. of fuel to be tested in a Dewar flask. The mixture is thoroughly agitated and the temperature rise during a three minute period following the addition of the acid is expressed as the acid heat. An object of my invention is to catalytically produce a high knocking motor fuel which will be characterized by a low acid heat.

Benzol is objectionable as a motor fuel in many instances because of its low total heat content. However, benzol and alkyl substituted benzois have excellent antiknock properties. An object of the invention is to provide a motor fuel which contains substantial quantities of aromatics, which is characterized by a high octane number and which simultaneously meets rigid specifications with regard to total heat content.

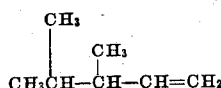
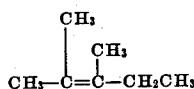
A further object of the invention is to provide an improved aviation gasoline which will meet rigid volatility specifications and in which the various components of different boiling range are chemically constituted to obtain maximum overall antiknock properties and to insure the most efficient engine performance. A further object is to provide a motor fuel with good lead response, i. e., one in which the addition of small amounts of lead tetraethyl will produce relatively large increases in octane number.

A further object is to provide a new combination of catalyst conversion systems with means for producing the hydrogen in one part of the system and utilizing said hydrogen in another part of the system. A further object is to provide an improved method for treating the components of a petroleum oil or oil fraction whereby maximum yields of high quality gasoline are obtained in each step with a minimum degradation to gas and coke.

A further object of the invention is more effec-

tively and efficiently to utilize catalytic cracking in a combination system involving dehydro-aromatization and hydrogenation. A further object is to provide an improved process wherein the hydrogenation step is applied only to a particular and relatively small fraction of the materials which have previously undergone catalytic conversion steps. Other objects will be apparent as the detailed description of the invention proceeds.

This invention is based on the discovery that certain naphtha, gas oil or heavy oil fractions require different conversion conditions than do other fractions and that heavy fractions produced by dehydro-aromatization are particularly amenable to catalytic cracking. I have found that it is unnecessary to hydrogenate the entire gasoline fraction from catalytic cracking in order to obtain a finished gasoline of desired low acid heat and high lead response and an important feature of my invention is the fractionation of catalytically produced gasoline prior to hydrogenation so that only the small fraction is subjected to hydrogenation. Furthermore, only partial hydrogenation of this fraction is necessary and even desirable. I have found that the desired chemical constitution of the individual hydrocarbons which make up finished gasoline is best obtained if: (a) the C₄ and C₅ fractions are kept out of the charging stock to the dehydro-aromatization unit; (b) the naphtha fractions are subjected to dehydro-aromatization; (c) the heavier fractions together with heavy products from dehydro-aromatization are subjected to catalytic cracking; and (d) the light catalytically cracked naphtha (which may include light aromatized naphtha) is partially hydrogenated without hydrogenating the heavy fractions. Referring more specifically to the partial hydrogenation, I have found that catalytically cracked gasoline contains two types of olefins: the unsubstituted olefins and the branched chain, substituted or iso-olefins. I have found that the unsubstituted olefins are hydrogenated much more easily than the substituted olefins. Thus the two hexenes



50 and

55 are equally branched; the first shows higher

blending octane number, but the second hydrogenates much more easily than the first.

Furthermore, the lighter paraffins such as iso- and n-pentanes show exceptionally high lead response, making hydrogenation of these cuts desirable. On the other hand hydrogenation of the heavy cuts is undesirable, even if carried out partially, since the less branched paraffins, although showing a high lead response, have extremely low octane numbers, causing an excessive fall in O. N. upon hydrogenation.

Partial hydrogenation of the lighter fraction of catalytically cracked gasoline, when effected to the extent of 20% to 90%, preferably about 60-75%, selectively leaves unhydrogenated the substituted olefins (to which much of the clear octane number of the gasoline may be attributed) and give a product of low acid heat which will have an increased lead tetraethyl response.

Complete hydrogenation of a cut boiling at 130-160° lowers the O. N. from 81 to 72, whereas hydrogenation of 225-250° cut lowers the O. N. from 80 to 62. This O. N. lowering is even greater in such fractions as the 350-400° cut.

The partial hydrogenation may be effected with the impure hydrogen produced in the system itself and the utilization of this hydrogen in the finished motor fuel results in increased gasoline yield. Not only may impure hydrogen be used for securing this partial hydrogenation, but the catalysts employed may likewise be of only moderate activity. They are therefore less expensive and are longer-lived than catalysts ordinarily employed for absolutely complete hydrogenation of olefins to paraffins.

In practicing my process I fractionate the charging stock into a C₅ and lighter fraction, a naphtha fraction and a heavy fraction. The C₄ and C₅ hydrocarbons may be blended directly with finished gasoline, any excess being withdrawn from the system. The naphtha is catalytically dehydro-aromatized to increase its knock rating and to supply hydrogen. The heavy fraction is catalytically cracked and fractionated. Light naphtha produced by catalytic cracking (which may have an end point of about 150 to 250° F. and which may include light naphtha produced by dehydro-aromatization) is then partially hydrogenated with the hydrogen produced in the dehydro-aromatization step. The heavy cracked naphtha, which may have an initial boiling point of about 150 to 250° F. and an end point of at least 350 to 400° F. is blended with the finished gasoline without hydrogenation. By means of this integrated catalytic system I obtain maximum yields of high octane number gasoline which when properly fractionated and blended not only meets motor fuel requirements but which meets the rigorous requirements of aviation gasoline.

The invention will be more clearly understood from the following detailed description read in conjunction with the accompanying drawing which forms a part of this specification and which is a simplified schematic flow diagram of my improved conversion system.

My invention is not limited to any particular feed; it may be either straight-run or cracked or it may be produced by the hydrogenation of carbonaceous materials, by the catalytic conversion of carbon monoxide and hydrogen or by any other known method. Preferably the original charge is straight-run or paraffinic hydrocarbon of wide boiling range and a relatively low octane number. In the preferred embodiment of the in-

vention I will describe the conversion of straight-run charge obtained from East Texas crude.

The catalyst employed for the naphtha reforming or dehydro-aromatization step is preferably an oxide of a VI group metal mounted on active alumina or "activated alumina" (a form of alumina obtained as a scale in aluminum ore purification) or alumina gel. About 2 to 10% of molybdenum oxide on alumina or about 8 to 40% of chromium oxide on alumina have been found to give excellent results. The minor ingredient of the catalyst is preferably an oxide or sulfide of molybdenum, chromium, tungsten or uranium or any mixture thereof mounted on bauxite, precipitated alumina, "activated alumina" or any other suitable catalyst support. Magnesium, aluminum or zinc chromites, molybdenites, etc. may be employed. Vanadium and cerium oxides have been found to be effective for this conversion. Oxides of copper, nickel, manganese, etc. may be included to facilitate regeneration or to supplement or promote catalyst activity. It should be understood, however, that the present invention is not limited to any particular catalyst but is applicable to the use of any dehydro-aromatization catalyst known to the art.

The catalyst may be made by impregnating "activated alumina" or other support with molybdic acid, ammonium molybdate or any other catalyst compound decomposable by heat. Also the aluminum and molybdenum oxides may be coprecipitated as a gel or the separate oxides may be mixed together as a paste, dried, extruded under pressure or pelleted and heated to a temperature of about 1000 to 1200° F. Since the preparation of the catalyst forms no part of the present invention it will not be described in further detail.

For the catalytic cracking step the catalyst is preferably an activated hydrosilicate of alumina or an active silica gel impregnated with a metal oxide, although it should be understood that cracking catalysts of any known type may be used. So-called "natural catalysts" may be made by treating fuller's earth or other natural clays with acid or with aqueous solutions of chlorides or sulfates of magnesium, aluminum, manganese, etc. the treated catalyst then being washed, dried and pelleted. An acid-treated clay of the type commonly marketed as Super-Filtrol has been found to be an excellent catalyst for cracking and is an example of the so-called "activated clay" commonly used in the decolorizing of lubricating oils, which activated clays are also good cracking catalysts.

Synthetic cracking catalysts may be prepared by depositing on silica gel oxides of such metals as aluminum, cerium, beryllium, thorium, zirconium, cadmium, copper, boron, titanium, manganese, magnesium, etc. Natural or artificial zeolites may be used as cracking catalysts when the alkali metals therein have been replaced by oxides of the metals hereinabove listed, particularly aluminum, copper, cadmium, manganese, magnesium, etc. The catalyst may be used in granular or pelleted form and it may for instance be made into a thick slurry or paste, molded, pelleted or extruded by conventional means, dried at about 300 to 400° F. and finally heated to about 800 to 1200° F. or higher. The preparation of the cracking catalyst forms no part of the present invention and it will not be described in further detail.

The catalyst in both cases may be employed in fixed beds, in movable beds or as a powder sus-

pendent in a gaseous stream, the conversion in all cases being in the vapor phase. The fixed bed catalyst may be positioned in tubes mounted for instance in the convection section of a furnace or they may be positioned in a single bed or plurality of beds in vertical towers or chambers. The moving catalyst may be charged to the top of a tower or tube either continuously or intermittently, the spent catalyst being withdrawn from the base of the tube at substantially the same rate; in this case the reaction takes place continuously and under substantially constant conditions of temperature and pressure, the regeneration being effected outside of the conversion zone. The powdered catalyst may be fed into a rapidly moving stream of vaporized naphtha and hydrogen, separated therefrom after reaction is completed and separately regenerated by oxygen while suspended in flue gas. Any of these specific catalyst reactors or their equivalents may be used in practicing the invention, but they will not be described in further detail.

Referring specifically to Figure 1, a crude East Texas petroleum is passed from a heater or pipe still (not shown) through line 10 to fractionator 11 from which a butane-pentane fraction is withdrawn overhead through line 12, a naphtha fraction is withdrawn through line 13 and a heavy fraction such as gas oil is withdrawn through line 14, lubricating oils or tarry fractions being withdrawn through line 15.

The naphtha fraction may be supplemented by other naphthas from outside sources introduced through line 16. Generally speaking, the boiling range of this fraction will be in the general range of from about 150 to 350° F. and it will contain predominantly hydrocarbons ranging from about 6 to 12 or 14 carbon atoms per molecule. This naphtha fraction is passed by pump 17 through coils 18 of furnace 19 and thence through transfer line 20 to catalyst chamber 21.

Hydrogen from line 22 may be passed by compressor 22a through line 23 for admixture with charging stock in line 13 or it may be passed through separate coil 24 in furnace 19 and then introduced into transfer line 20 or directly into catalyst chamber 21.

The reaction in the catalyst chamber is preferably effected at a space velocity of about 0.04 to 10, preferably about 0.2 to 2-volumes of liquid naphtha per volume of catalyst space per hour at a temperature of about 875 to 1075° F., preferably about 950° F., at a pressure of about 50 to 450 pounds per square inch, preferably about 200 pounds per square inch, and in the presence of about 4 to 8 mols of hydrogen to 1 mol of naphtha, preferably about 3 mols of hydrogen per mol of naphtha.

Reaction products and vapors leave reaction chamber 21 through line 25, are passed through heat exchanger 26 and cooler 27 and are then introduced into hydrogen separator 28 which is preferably maintained at substantially reaction pressure but at a temperature of about 35 to 105° F. Separated hydrogen is withdrawn through line 29 (any excess or unduly low grade hydrogen being vented through line 30) and passed by pump 31 to hydrogen storage 32. Liquid from separator 28 is withdrawn through line 33, heated in exchanger 26 and introduced into fractionator 34 from which gases are taken overhead through line 35 and aromatic gasoline is withdrawn as a side stream through line 36. Products boiling above the gasoline or motor fuel

boiling range (so-called "polymers") are withdrawn through line 37 and removed from the system through line 38 or preferably introduced through line 39, together with gas oil from line 14, into the coils 40 of pipe still 41. Outside gas oil may be introduced into line 14 thru line 14a when crudes containing high proportions of naphtha are charged to fractionator 11. The charging stock is heated in coils 40 to a temperature of about 875 to 925° F. under a pressure of about atmospheric to 50 pounds per square inch and is then introduced by transfer line 42 to catalytic cracking chamber 43. Space velocity in the cracking chamber is preferably about 0.5 to 2 volumes of liquid feed per volume of catalyst space per hour, and the average cracking temperature is preferably about 850 to 950° F.

Products from the catalytic cracking step are withdrawn through line 44 and introduced into fractionating column 45 which is provided with suitable reflux and reboiler means. Hydrogen and hydrocarbon gases are taken overhead through line 46. A light cracked naphtha fraction with an end point preferably within the range of 150 to 250° F. is withdrawn through line 47. Heavy cracked naphtha is withdrawn through 48 and gas-oil and heavier fractions are removed from the base of the column through line 49; these heavier fraction may either be removed from the system through line 50 or returned by pump 51 and line 52 to line 14 for further cracking. It should be understood, of course, that any number of side streams may be taken from this fractionator and that suitable side stream strippers or other expedients may be employed for obtaining the desired boiling range, flash point, end point, volatility, etc. of each fraction. Instead of employing only a single gasoline storage tank I may employ a number of tanks, particularly when motor fuel and aviation fuel of different grades are desired.

An important feature of the invention is the segregation of the light cracked naphtha for subsequent partial hydrogenation. As hereinabove pointed out, the partial hydrogenation of this particular fraction does not materially lower its octane number while it markedly lowers its acid heat and markedly improves its response to lead tetraethyl. This light cracked naphtha of about 150 to 250° F. end point, withdrawn through line 47 is passed through coils 53 of furnace 54 and then introduced through transfer line 55 to hydrogenation reactor 56. Hydrogen may be introduced from storage tank 32 and line 57 either through line 58 with incoming charging stock or through separating heating coil 59 which discharges into transfer line 55 or into the hydrogenation chamber 56. Pump 60 and compressor 61 are provided in lines 47 and 57, respectively, for maintaining the necessary hydrogenation pressure which may vary from 50 pounds or lower to upwards of 3,000 pounds, depending upon the catalyst temperatures, space velocities, etc. employed in the hydrogenation reactor.

The hydrogenation catalyst may be of any type known to the art. Oxides or sulfides of VI group metals such as molybdenum, tungsten, uranium, etc. may be used alone or in admixture with each other or with other metallic oxides and may be mounted on suitable supports such as "activated alumina", alumina gel, bauxite, etc. Alternatively, catalysts such as copper, cobalt or preferably nickel or the lower oxides of such metals supported on pumice, silica or preformed porcelain may be employed. In the case of the

VI group oxides or sulfides the hydrogenation conditions may be about the same as those used for dehydrogenation, except that space velocity and other operating conditions will be controlled to bring about only partial hydrogenation, i. e. a saturation of about 20% to 90% or preferably about 60 to 75% of the olefins in the cracked light naphtha. The pressure for such hydrogenation may be from about 200 to about 3000 pounds per square inch. The space velocity may be higher than that used in dehydrogenation, for instance about 1 to 5 volumes of charging stock per volume of catalyst space per hour. The temperature may be somewhat lower than that used for dehydrogenation, i. e. of the order of 550 to 850° F.

When catalysts such as nickel are employed dehydrogenation may be effected at lower pressures, ranging from atmospheric to 50 pounds. The temperatures may be from about 350 to 450° F. and space velocities may be of the order of 8 or 10 volumes of liquid charged per volume of catalyst space per hour. The hydrogenation step per se is, of course, well known in the art and I modify this well-known process by employing sufficiently higher space velocity or sufficiently lower temperature or pressure to obtain only partial instead of complete saturation of the olefins in the light cracked naphtha.

Products from the hydrogenation reactor 56 are passed by line 62 through cooler 63 to hydrogen separator 64. If the hydrogen is sufficiently pure for reuse it may be returned by pump 65 and line 66 to storage tank 32. The hydrogenated products are withdrawn from the base of the separator through line 67 and are further fractionated if such fractionation is necessary before being passed to the proper gasoline storage tank.

If the gases in line 46 do not contain appreciable amounts of hydrogen they may be passed directly to line 12. Butanes and pentanes from lines 12, 35 and 46 may then be passed through cooler 68 to separator, stabilizer or depropanizer tower 69, from which propane and lighter gases are taken overhead through line 70 and pentane, together with some butanes are withdrawn as a liquid through line 71. Excess butanes and pentanes may be vented through line 71a.

If the gases in line 46 contain sufficient hydrogen for recovery such gases may be compressed by compressor 72 and introduced through line 73 and cooler 74 to hydrogen separator 75, the hydrogen passing by line 76 to line 66. Liquid from separator 75 is preferably introduced by line 77 to tower 69. When the gases from separator 64 contain substantial quantities of hydrocarbons such gases may be passed by line 78 to line 73 for separately recovering hydrogen and hydrocarbons as hereinabove described.

The final gasoline is composed of two or more of the following products: (a) aliphatic C₈ hydrocarbons (containing also C₄ and C₆ hydrocarbons) from line 71; (b) aromatic hydrocarbons from line 36; (c) partially saturated branched chain aliphatic light naphtha from line 67; and (d) heavy cracked naphtha from line 48. Various blends of gasoline may be produced from these products, either for ordinary motor fuel or for aviation fuel. Such fuels will be characterized by a low acid heat, a very high octane number, a relatively high total heat content and a good lead tetraethyl response. The overall chemical compositions of such fuels will differ from any heretofore produced because the heavy fraction thereof will be more highly olefinic than

the light fractions and because of the aromatic and branched chain structures which result from the various conversion steps.

Instead of employing separate fractionating columns 34 and 45, as hereinabove described, I may eliminate fractionator 34 with its associated lines 35, 36, 37, etc. and pass the products from line 33 through line 79 to line 44 for fractionation in column 45. This effects considerable savings in investment costs. Furthermore, by fractionating materials from line 33 and line 44 in a common fractionating column I may hydrogenate the undesirable cracked olefins which are present in the light aromatic gasoline fractions along with the olefins present in the light cracked gasoline fraction, thereby increasing the overall heat content and markedly improving the lead response of the finished gasoline. In this modification the heavier-than-gasoline aromatic products are withdrawn through line 49 and they may either be returned by line 52, line 14 as hereinabove described, or they may be returned by lines 52 and 80 to crude fractionator 11.

While I have described in detail a preferred embodiment of my invention it should be understood that I do not limit myself to such details since many alternatives and modifications will be apparent to those skilled in the art.

I claim:

1. The method of producing high quality aviation fuel from petroleum hydrocarbons containing fractions of the naphtha boiling range and fractions boiling above the naphtha boiling range, which method comprises separating hydrocarbons of the naphtha boiling range from heavier hydrocarbons, dehydro-aromatizing the hydrocarbons of the naphtha boiling range to produce an aromatic gasoline fraction and a heavy fraction, catalytically cracking the combined heavier-than-naphtha fraction and the heavy fraction from the dehydro-aromatization step, separating the catalytically cracked products into a light cracked gasoline and a heavy cracked gasoline fraction, respectively, partially hydrogenating the light cracked gasoline fraction and blending the aromatic gasoline with the hydrogenated light cracked gasoline and the heavy cracked gasoline, respectively, to form a blended aviation fuel of low acid heat and high antiknock.

2. The method of claim 1 which includes the further step of separating butanes, pentanes and lighter hydrocarbons from the naphtha fraction prior to dehydro-aromatization, removing lighter hydrocarbons from said separated butanes and pentanes and blending said butanes and pentanes with the aromatic gasoline fraction, hydrogenated light cracked gasoline fraction and heavy cracked gasoline fraction, respectively, to form an aviation fuel of improved volatility, knock rating and lead response.

3. The method of claim 1 which includes the step by hydrogenating at least a part of the light aromatic gasoline simultaneously with the hydrogenation of the catalytically cracked gasoline.

4. The method of making high quality gasoline from a charging stock containing naphtha and gas oil which method comprises catalytically dehydro-aromatizing said naphtha to produce hydrogen, aromatic gasoline and an aromatic oil heavier than gasoline, catalytically cracking said gas oil in the presence of said aromatic oil heavier-than-gasoline, separating the catalytic cracking products into a light gasoline fraction and a heavy gasoline fraction, hydrogenating said light cracked gasoline fraction to effect saturation of

at least 20% but not more than 90% of the olefins contained therein with hydrogen produced in the dehydro-aromatization step and blending the hydrogenated product with the aromatic gasoline and the heavy cracked gasoline fractions, respectively.

5. The method of lowering the acid heat of catalytically cracked gasoline without unduly impairing its octane number and tetraethyl lead response, which method comprises fractionating said cracked gasoline into a light fraction having an end point of 150° to 250° F. and a heavy fraction, respectively, hydrogenating said light fraction to effect at least 20% saturation but not more than 90% saturation of the olefins contained therein and blending the partially hydrogenated light fraction with the unhydrogenated heavy fraction.

6. The method of lowering acid heat of catalytically cracked gasoline without unduly impairing its octane number and tetraethyl lead response, which method comprises partially hydrogenating a light fraction of said catalytically cracked gasoline having an end point of 150° to 250° F. to effect about 60% to 75% saturation of the olefins contained therein and blending the partially hydrogenated light fraction with an unhydrogenated heavy fraction of said catalytically cracked gasoline.

7. An integrated process for making low acid heat, high octane number gasoline from petroleum charging stocks containing hydrocarbons of the naphtha and gas oil boiling ranges, which method comprises dehydro-aromatizing a naphtha fraction of the charging stock for the production of an aromatic gasoline fraction, catalytically cracking a gas oil fraction of said charging stock, fractionating the products of the catalytic cracking step to obtain a light naphtha fraction having an end point of about 150 to 250° F., partially hydrogenating said light naphtha fraction to saturate at least 20% but not more

than 90% of the olefins contained therein and blending said partially hydrogenated light naphtha with said aromatic gasoline fraction to form a blended aviation fuel of low acid heat and high antiknock.

8. An integrated process for making low acid heat, high octane number gasoline from charging stocks containing naphtha and gas oil, which method comprises dehydro-aromatizing a naphtha fraction of said charging stock to produce hydrogen, a gasoline fraction and a fraction heavier than gasoline, catalytically cracking the fraction heavier than gasoline with a gas oil fraction from the charging stock, separating the catalytically cracked products into a light cracked gasoline fraction having an end point of 150° to 250° F. and a heavier fraction, hydrogenating the light cracked gasoline fraction to an extent sufficient to saturate at least 20% but not more than 80% of the olefins contained therein, effecting said hydrogenation with hydrogen produced in the dehydro-aromatization step and blending the hydrogenated cracked fraction with the gasoline produced by dehydro-aromatization to form a blended motor fuel of low acid heat and high antiknock properties.

9. The method of claim 8 wherein the hydrogenation is effected under conditions for obtaining saturation of at least 60% but not more than 75% of the olefins in the catalytically cracked gasoline fraction.

10. A hydrocarbon conversion process which comprises catalytically dehydro-aromatizing naphtha to produce hydrogen, a gasoline fraction and a fraction heavier than gasoline, catalytically cracking the heavier-than-gasoline fraction, separating a cracked gasoline having an end point of 150° to 250° F. from the products of the catalytic cracking step and partially hydrogenating the catalytically cracked gasoline with hydrogen produced in the dehydro-aromatization step.

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