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2,729,596

PRODUCTION OF DIESEL AND JET FUELS

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No Drawing. Application May 21, 1951,
Serial No. 227,527

7 Claims. (Cl. 196—53)

The present invention relates to the treatment of hydrocarbon oils and is particularly concerned with the production and treatment of liquid fuels of lower volatility than motor gasoline.

Ordinary automobile and aviation engines of the spark-ignited Otto cycle type operate more efficiently on light comparatively volatile liquid fuels in the gasoline boiling range. For this purpose hydrocarbon distillates in the gasoline range are preferred which are of high octane rating. Such high octane qualities obtain as a result of particular types of hydrocarbons present in the gasoline, which may be further supplemented by knock-reducing compounds, among which the more familiar are the tetra-alkyl lead compounds. The presence of increased proportions of aromatic hydrocarbons and highly branched chain aliphatic hydrocarbons in the gasoline generally favors good anti-knock qualities. Various methods have been extensively developed and employed in the art to obtain gasoline of improved octane quality and to treat gasoline and naphtha of poorer anti-knock quality to enhance the octane rating thereof.

In oil-burning engines other than the carburetor-supplied spark-ignition type, fuels less volatile than gasoline are ordinarily employed and methods of production and treatments favoring the obtention of higher octane motor fuels afford no advantage or perhaps are even disadvantageous as applied to these less volatile fuels.

The present invention is particularly concerned with the production of fuels of such less volatile type in increased yields and/or of improved qualities for their intended use. Such fuels lying in a boiling range generally above that of gasoline (although they may include lower ends within the gasoline range) are particularly suited for use in compression-ignition engines such as those of the diesel type, and in continuous combustion engines such as jet propulsion devices of the simple tube or turbo-jet type. These types of engines can be made to operate on a wide variety of fuels including for instance kerosene and sometimes low grade gasoline and on higher boiling liquid fuels up to heavy fuel oils, but not necessarily at equal or desired operating efficiency. Smooth burning is an important consideration in engines of this type which are often more sensitive to the ignition characteristics of the fuel than the ordinary spark-ignition engines. For maximum combustion efficiency coupled with high caloric content, freedom from carbon residue, economy of fuel consumption, as well as low volatility and safe flash point to better assure freedom from fire and vapor lock hazards (particularly in connection with jet fuels for aviation engines), exacting standards and requirements must be met. For use as diesel fuels, particularly in high speed engines, oils having an API gravity of about 30–45° and boiling in the range of about 350–750° F. are generally preferred. Cetane is the reference standard for diesel fuels and the ignition quality is generally given in terms of cetane number (or sometimes in terms of diesel index which is a function of the gravity and aniline point of the fuel).

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For use in "turbo-prop" and "turbo-jet" engines, good grades of kerosene have been generally considered acceptable except perhaps in cases where lower freezing point requirements prevail, but increasing demands for this type of fuel cannot be met by present methods employing catalytic cracking of hydrocarbons except at the expense of distillates required for other uses including motor and aviation gasoline.

From the standpoint of the hydrocarbon composition of the fuels, diesel and jet fuels can be distinguished from gasoline by high paraffinicity, low aromatic content and minimum possible unsaturation of the former. By usual commercial methods of catalytic cracking, the production of higher yields of aromatics is favored by increased cracking severity, resulting in degradation of components desired for diesel and jet fuels.

The present invention is based on the discovery that by controlled methods of cracking under high hydrogen pressures and in the presence of catalysts having both cracking and hydrogenating activity, a highly saturated synthetic crude is obtained, which although rich in naphthenes and having a fairly high content of aromatics, can be treated to separate out high yields of fractions having characteristics and qualities desired for diesel and jet fuels. It was also discovered that with increasing boiling range of progressive cuts of the synthetic crude from such hydrogenative cracking, there was an unexpected and striking increase in normal paraffin content and a corresponding decrease in iso-paraffins; a similar change in normal to iso content with increasing boiling range is not found in liquid products from the usual catalytic cracking process.

In accordance with the present invention a hydrocarbon charge stock boiling above the range of gasoline, and preferably a heavy gas oil cut from a petroleum crude, is subjected to hydrogenative cracking in the presence of a cracking catalyst having composited therewith a minor quantity of a hydrogenation-dehydrogenation promoter compound. The operating conditions employed in the conversion include temperatures in the range of 700–900° F., pressures of from about 1000–3500 pounds per square inch gauge, there being added to the reaction at least 3 mols hydrogen per mol of oil charged. Although space velocities above 3 to 4 volumes of oil (as liquid) per hour per volume of catalyst can be employed with tendency to increased yields of products in the gasoline boiling range, lower space velocities are preferred for reasons hereinafter appearing. The effluent is condensed and fractionated into cuts at points depending largely upon the boiling range desired for the jet and/or diesel fuels to be prepared therefrom, but in any event the cut points are selected to provide on the one hand a fraction consisting of, or rich in normal paraffins (which might also include the monomethyl substituted normal paraffins), particularly suitable for use as a jet or diesel fuel or as a high quality blending agent for such fuels, and on the other hand in a cut including hydrocarbons in the gasoline boiling range which is of superior octane value.

In a typical operation in accordance with the invention, for example, the product from hydrogenative cracking at the selected conditions stated, can be fractionated into cuts including a cut boiling up to about 200° F., a second cut boiling in the range of about 200–400° F., a 3rd cut boiling up to about 650° F., and a 4th cut (bottoms) comprising the products boiling above about 650° F. The first cut (which in some instances might be carried up to about 220° or 230° F.) which ordinarily will constitute about 25–35% of the total liquid product in the gasoline boiling range, is of fairly high octane quality and the ratio of iso-paraffins to normal paraffins in this cut is exceptionally high, being generally greater than

5/1 and often as high as 10/1 or above. The next higher boiling cut (up to about 400° F.), while it has an increased content of aromatics, the considerably lower ratio of iso-paraffins particularly in the higher boiling portion of this cut, largely accounts for the relatively poor octane value. Moreover, the iso-paraffins present are preponderantly of the monomethyl- and dimethyl-alkane type, which have relatively low octane numbers; hydrocarbons containing quaternary carbon, which would have high octane numbers, are not present in any significant amount. Because of the kind and quantity of naphthenes contained in this cut, however, it can be readily up-graded by known methods of reforming, such as by dehydrogenation. The up-graded fraction thus obtained can then be blended, if desired, with the lower boiling gasoline of the first cut. The third cut can be employed directly as a diesel fuel, since it will have a satisfactory cetane number (45-50 or above) and shows very good motor performance characteristics. This cut, or at least a lower boiling portion thereof is also suitable for use in jet fuels in the JP 1 or in the JP 3 boiling range. It is preferred, however, in the practical application of the invention, to subject this third cut to treatment improving its value as a diesel fuel. This cut is therefore best treated to separate out a fraction consisting of or rich in normal paraffins suitable as such or as a base stock for high quality diesel fuel, leaving behind a raffinate fraction comprising mainly naphthenes, aromatics and some iso-paraffins. This raffinate fraction provides an excellent charge stock for further hydrogenative cracking and can therefore be effectively recycled to that step in the operation, thus producing additional desirable products in the gasoline boiling range. The normal paraffins, pursuant to this embodiment of the invention, can be removed from the third cut by selective extractive fractionation, for instance by treatment with urea, as hereinafter described. The bottoms cut, boiling above about 650° F., can be recycled to hydrogenative cracking or otherwise cracked or treated as desired.

Instead of reforming the second cut, that is the higher boiling gasoline fraction up to about 400° F., this cut can be subjected to selective fractionation, for instance by treatment with urea, to separate out the normal paraffins (including some monomethyl paraffins), thus providing a raffinate of increased value on the one hand, and a straight chain paraffinic fraction which is suitable for jet fuels of JP 3 specifications, or as a light additive to improve the quality of diesel fuels. In some instances the second cut may be carried to a somewhat higher boiling point as up to about 450° F.

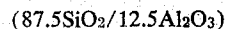
In operations wherein the production of increased yields of high quality diesel fuels are required rather than greater yields of gasoline, the higher boiling portion of the second cut may be combined with the third cut or with the lower boiling portion of the third cut and the whole subjected to a single extraction with urea; the raffinate being recycled to further hydrogenative cracking. Thus the initial effluent from hydrogenative cracking may be fractionated to provide a gasoline cut boiling up to about 350° F. and a diesel cut boiling thereabove up to about 650° F., which latter is subjected to urea extraction. The portion boiling above 350° F., even though it is highly aromatic, has been found of low octane value, believed largely due to the low ratio of iso-paraffins to normal paraffins therein (less than 1.5/1). Advantageously, for preparation of a superior jet fuel, a narrower cut is subjected to urea treatment, such as one boiling in the range of 350-450° F.

The low octane normal paraffin fraction or fractions obtained by urea extraction, as hereinbefore indicated, are particularly suited for use in jet and diesel fuels. Since this fraction contains substantially only straight chain paraffins, it can be readily fractionated by distillation to provide individual normal paraffins of high purity,

for use as such or as starting materials for the production of desired industrial chemicals.

The following experiment will serve to illustrate the adaptability and flexibility of the present invention.

5 A heavy gas oil (440°-950° F. boiling range) comprising the fraction obtained by removing from an East Texas crude oil the initial 56% of lower boiling materials and heavy ends up to 23% of the crude, was subjected to hydrogenative cracking for three hours over a catalyst comprising synthetic silica-alumina



10 impregnated with 2% nickel, at 825° F. under a pressure of 3500 pounds per square inch, and at a liquid space velocity of two volumes of oil (as liquid) per hour per volume of catalyst, six moles of hydrogen being added per mole of charge. The gasoline obtained (C₆+) was divided into a number of cuts which were examined for properties and analyzed for types of hydrocarbons present.

20 It was found that the fraction boiling below 220° F. and constituting about 30% of the total gasoline was of satisfactory motor fuel quality, having a high ratio of iso to normal paraffins (above 10/1) and an octane number above 72 (CFR-M clear). The middle portion of this cut particularly had a fairly high naphthene content, so that the cut can be brought to even higher octane number, if desired, by known methods of reforming including hydroforming. The next higher fraction boiling in the range of up to about 370° F. and comprising 50% of the total C₆+ gasoline, contained increasing amounts of normal paraffins and had a relatively poor octane value, averaging less than 55 for the blend. The content of normal paraffins was slightly less than that of the iso-paraffins. The poor octane values may be accounted for by a fairly high content of methyl-paraffins and to certain substituted naphthenes. This fraction can be up-graded by known methods of reforming.

30 A sample of the total hydrogenatively cracked gasoline was fractionated to provide a 180-420° F. cut, which cut was separated by silica gel chromatographic adsorption into 70 volume percent paraffin-naphthene fraction and a 30 volume percent aromatic-olefin fraction. The paraffin-naphthene fraction was then further divided into cuts including 220-300° F., 300-370° F., and 370-425° F. portions, respectively. Each of these portions was subjected to urea fractionation to separate out normal paraffins in the following manner:

35 Each portion was mixed with 2-5 times its weight of urea and a few milliliters of methanol. The mixture was cooled in an ice bath with occasional stirring and filtered through a Dry-Ice cooled Büchner funnel. The iso-paraffins and naphthenes were recovered in the filtrate, and the solid urea adduct constituted by n-paraffin-urea complexes was decomposed with water for recovery of the normal paraffins. The quantity of normal paraffins separated out from each cut is shown in the following table (on a loss free basis) and the calculated ratio of normal paraffins to iso-paraffins in each of the cuts is also reported.

Fraction, ° F.	Paraffin-Naphthene Cut		Calculated Percent of Cut	
	Vol. Percent n-paraffin	Vol. Percent i-paraffin+naphthene	n-paraffin	i-paraffin
220-300.....	5	95	4	46
300-370.....	25	75	18	24
370-425.....	41	59	25	9

40 The important discovery that the normal to iso-paraffin ratio increases with the boiling range of the hydrogenatively cracked fraction is contrary to expectation particularly in

view of the fact that additional isomers are possible for the larger molecules of higher boiling point.

A sample of a 410–635° F. cut from hydrogenative cracking (constituting about 42% of the cracked liquid effluent), was inspected for diesel fuel characteristics with the following results:

Aniline point.....	°F.....	148.5
° A. P. I.....		32.4
Diesel index.....		$\frac{148.5 \times 32.4}{100} = 48.1$
Cetane No.....		47.0
Motor performance characteristic.....		Good

Since the above sample contains a high ratio of normal to iso-paraffins in the lower boiling portion of the sample, which normal paraffins have cetane numbers in the order of about 80 and above, and fairly high amounts of C₁₆+ normal paraffins which have a cetane number of about 100, by urea extraction of the sample there is obtained a paraffinic fraction having properties closely approaching that of cetane, being of superior quality for use in diesel fuels or for upgrading diesel fractions of poorer quality by blending therewith. The cetane number of the urea extract will, of course, depend on the boiling range of the fraction so extracted. In any event, urea extraction of hydrogenatively cracked fractions boiling above normal heptane (which has a cetane number of about 57) will provide paraffinic extracts of high cetane number.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim as my invention:

1. The method of preparing liquid hydrocarbon fuels of high paraffinicity and having a cetane number of about 80 and which comprises the steps of subjecting a crude oil fraction boiling above the range of gasoline to hydrogenative cracking in contact with a catalyst composite comprising a predominating proportion of a cracking component and a minor proportion of a catalytic nickel material having hydrogenating activity, effecting conversion of said fraction in contact with said catalyst at a temperature above 700° F. and under a total pressure of at least 1000 pounds per square inch, at least three mols of hydrogen being added to the conversion reaction per mol of oil charged; separating the reaction products to provide a fuel cut boiling above 300° F. of high normal paraffin content, subjecting the fuel cut to selective treatment to separate out a portion thereof having an increased concentration of normal paraffins.

2. The method according to claim 1 wherein the conversion products are fractionated to provide a diesel cut and the latter is subjected to selective extraction to separate out a portion thereof having an increased concentration of normal paraffins.

3. The method according to claim 2 wherein such selective extraction includes the step of treating the said diesel cut with urea, thereby forming a solid urea addition complex of the normal paraffins present in the cut, separating the solid complex from unreacted liquid, and decomposing the solid urea complex to recover normal paraffins.

4. The process of preparing high quality jet fuel in accordance with the method defined in claim 1, which comprises separating from the reaction products in the catalytically converted effluent a fraction substantially free of products boiling below 200° F. and of products

boiling above 650° F., which fraction contains components boiling in the range of 350–450° F., and selectively treating said fraction to decrease the proportional concentration of iso-paraffins therein.

5. The method according to claim 1 wherein the effluent from the defined catalytic conversion is distilled to provide an intermediate cut containing components boiling in the range of 400–650° F. and substantially free from components boiling below 200° F., recovering by selective treatment of the said intermediate cut a fraction predominating in normal paraffins.

6. The method which comprises hydrogenatively cracking a mixture of a recycle stock and a heavy gas oil in the presence of a catalyst composite comprising synthetic silica-alumina gel containing a small amount of nickel having activity in promoting cracking and hydrogenation respectively, effecting such hydrogenative cracking at a pressure of 1000–3500 pounds per square inch while feeding said gas oil at a space rate of not more than three volumes of oil per volume of catalyst per hour, together with at least three mols of hydrogen per mol of oil, fractionating the hydrogenatively cracked effluent to provide at least three cuts including a gasoline cut, a diesel cut, and a bottoms cut; recycling the bottoms cut to further hydrogenative cracking, and treating at least a portion of the diesel cut with urea and an alcohol and cooling to separate out a fraction thereof having a cetane number of about 80 of increased normal paraffin concentration recovering a fraction of the diesel cut of very low paraffin concentration from said treatment with urea; and recycling said low paraffin fraction to further hydrogenative cracking.

7. The method of preparing a diesel fuel having a cetane number of about 80 which comprises: passing a mixture of a recycle stock and a hydrocarbon stock boiling above the gasoline range over a cracking catalyst comprising nickel within the temperature range of from 700 to 900° F. at a pressure of from 1000 to 3500 pounds per square inch and at a hydrogen to hydrocarbon mol ratio of about 3, and at a space velocity less than 3; fractionally distilling the effluent to recover a fraction boiling above the range of gasoline; subjecting said fraction to a selective extractive fractionation with several times its weight of a urea and a small quantity of an alcohol; cooling the thus treated fraction; filtering the cooled fraction to obtain a liquid filtrate providing said recycle stock; and decomposing the normal paraffin rich, high cetane number diesel fuel from the urea-complex.

References Cited in the file of this patent

UNITED STATES PATENTS

2,358,879	Redcay	Sept. 26, 1944
2,366,490	Cloud	Jan. 2, 1945
2,377,116	Voorhies et al.	May 29, 1945
2,415,700	Meier	Feb. 11, 1947
2,541,229	Fleming	Feb. 13, 1951
2,541,317	Wilson	Feb. 13, 1951

FOREIGN PATENTS

959,374	France	Mar. 28, 1950
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OTHER REFERENCES

"Production of Premium Diesel Fuels," Wood, part 2, The Petroleum Engineer, pages 58, 60, 62 and 64 (December 1936).