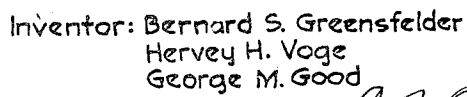


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CONVERSION OF HYDROCARBON OILS

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This invention relates to a new and improved process for the production of anti-knock gasoline and other valuable products from hydrocarbon oils boiling above the gasoline boiling range.

In the past, many methods for the production of gasoline have been suggested in which gasoline of improved anti-knock rating is produced through the agency of catalytic cracking. However, in general, if the production of anti-knock gasoline is improved through the use of catalytic cracking, the production of Diesel fuel suffers both in quality and quantity. Also, if the catalytic cracking is carried out under conditions optimum for the production of quality gasoline, reduced amounts of valuable olefins are produced. In practice it is usually necessary to strike a compromise between producing smaller amounts of gasoline of excellent anti-knock rating and producing a larger amount of gasoline of lesser anti-knock rating, and also upon striking a compromise between producing gasoline at the expense of other valuable products and producing other valuable products at the expense of gasoline.

The process of the present invention allows considerable amounts of valuable products such in particular as olefinic gases, lower olefins and Diesel fuel of high cetane number to be produced while at the same time producing excellent yields of gasoline of high anti-knock value. The excellent yields of these quality products are largely made possible through the action of, and at the expense of, relatively high boiling aromatic hydrocarbons. In the hitherto proposed processes, large amounts of highly aromatic gas oils of little value are produced. These are commonly blended with black oil or cracked residues and sold as fuel oil. In the process of the present invention, little of such products is formed. Also, many of the hitherto proposed processes involving catalytic cracking give substantially saturated gasoline. This results in an unfavorable hydrogen balance. In the process of the present invention, an olefinic gasoline is produced and this allows greater production of other products.

In the broader, more general aspects of the process of the invention, the oil feed boiling above the gasoline boiling range (400° F.) is subjected to a catalytic cracking treatment under relatively severe conditions. The product is separated into a fraction of normally gaseous products, a light gasoline fraction, a heavy gasoline fraction, a reflux condensate heavier than gasoline and a higher boiling residue. This separation is usually done in two steps. The reflux condensate is subjected to a catalytic hydrogenation treatment under conditions to produce a minor amount of destructive hydrogenation. The hydrogenated reflux condensate is then combined with the heavy gasoline fraction, and the mixture is subjected to a second

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catalytic cracking treatment under less severe cracking conditions. The product from the second catalytic cracking treatment is then separated into a fraction of normally gaseous products, a gasoline fraction, a reflux condensate heavier than gasoline, and a higher boiling residue. The gasoline separated from the reaction product of the second catalytic cracking treatment is blended with an amount of the first-mentioned light gasoline fraction to produce a gasoline of suitable volatility.

The process will be explained in more detail and with certain modifications in connection with the attached flow sheet.

The feed entering by line 1 is any hydrocarbon oil boiling above the gasoline boiling range. Petroleum gas oil is, for example, an excellent feed. However, other feeds such as vacuum flashed distillate or deasphaltized reduced crude may also be used. Although hydrocarbons in the gasoline boiling range are not desired in this feed, the presence of a small amount of hydrocarbons in this range can be tolerated. The process is particularly advantageous when the feed is from a naphthenic petroleum; also it is particularly advantageous when the petroleum contains large amounts of nitrogen bases and/or sulfur compounds. Thus the process is particularly advantageous for use with California and West Texas petroleum stocks.

The feed is passed to a catalytic cracking zone 2 where it is catalytically cracked under severe conditions. In general, catalytic cracking is carried out at temperatures between 750° F. and 950° F. at relatively low space velocities. In the process of the present invention, the catalytic cracking is preferably carried out at a temperature of at least 900° F. and preferably above 950° F., for example 1000° F. or even higher. When operating at temperatures above 1000° F., the method described in U. S. Patent No. 2,398,739 may be advantageously used. Otherwise any of the conventional cracking techniques or processes may be applied. The space velocity is also maintained lower than usual so as to produce a depth of cracking of at least 40% and preferably between 50% and 75% (depth of cracking is defined as 100 minus the percent of recovered oil boiling above 400° F.). In this primary catalytic cracking step, any of the conventional cracking catalysts may be used. While any of the clay type catalysts (see U. S. Patent No. 2,400,431) will give fair to excellent results, it is to be pointed out that hardly any two of these cracking catalysts are equivalent. In catalytic cracking many reactions take place. It has been found that the various catalysts differ widely in their ability or tendency to catalyze one or more of these reactions in preference to others. A preferred catalyst is a silica-magnesia cracking

catalyst (see, for example, U. S. Patent No. 2,343,295). Another preferred catalyst is boric oxide supported on alumina (see U. S. Patent No. 2,407,918).

The cracking is carried out in the absence of added hydrogen, and preferably in the presence of steam at slightly elevated pressure, for example 1.1-5 atmospheres. Under these conditions, and especially when using a feed stock having a nitrogen content of 0.2% or over, a large amount of valuable olefins, particularly butylenes and amylenes, is produced. The gasoline, although having a high anti-knock rating, is not of the best quality. However it is particularly amenable to the subsequent treatments of the process.

The total product from the catalytic cracking is passed by line 3 to a separation zone. This zone comprises a fractionation system. Here the product is separated into a fraction consisting of gasoline and gas, a reflux condensate boiling above the gasoline boiling range and a higher boiling residue. The higher boiling residue is withdrawn by line 4. The reflux condensate boiling from about 400° F. up to about 600° F. or 700° F. is withdrawn by line 5. The gasoline and gas are passed by line 6 to a second separation zone 7 wherein they are separated into a gas which is withdrawn by line 8, a light gasoline fraction having a final boiling point between 200° F. and 300° F. which is withdrawn by line 9, and a heavy gasoline fraction having an initial boiling point between 200° F. and 300° F. and a final boiling point of about 400° F. which is withdrawn by line 10.

The reflux condensate is passed to a hydrogenation zone 11 wherein it is treated with hydrogen in the presence of a sulf-active hydrogenation catalyst under conditions to produce a minor amount of destructive hydrogenation. The destructive hydrogenation should be carried out to such an extent that about 25% or somewhat less of the feed is converted into hydrocarbons of the gasoline boiling range. The hydrogenation is otherwise carried out with the conventional catalysts under the conventional conditions.

The product from the hydrogenation treatment is commingled with the described heavy gasoline fraction from line 10 and the mixture is passed to a second catalytic cracking zone 13. The cracking conditions in catalytic cracking zone 13 are conventional and preferably less severe than in catalytic cracking zone 2. Thus, the temperature is preferably in the common catalytic cracking range (750°-950° F.). Here again any of the clay type cracking catalysts may be used. However, due to the difference in the catalytic behaviors of the various catalysts, it is advantageous to utilize a different catalyst in the two zones. While the use of any two different catalysts will give some advantage, some combinations of catalysts are better than others. Particularly suitable combinations are, for example, silica-magnesia and acid-treated clay (Filtrol), boric oxide-alumina and acid-treated clay (Filtrol), boric oxide-alumina and silica-alumina, boric oxide-alumina and silica-magnesia, acid-treated clay (Filtrol) and activated carbon, activated carbon and silica-alumina, silica-magnesia and activated carbon, boric oxide-alumina and activated carbon. With these combinations there is little tendency for refractory hydrocarbon types to accumulate in the system.

The product from the second catalytic cracking

treatment is passed by line 14 to a separation zone 15 wherein it is separated by conventional methods into a gas fraction which is withdrawn by line 16, a gasoline fraction which is withdrawn by line 17, an intermediate oil fraction (reflux condensate) withdrawn by line 18, and a heavy higher boiling residue which is withdrawn by line 19. The gaseous fractions from lines 8 and 16 may be combined. This gas may be utilized to produce high octane fuel components by polymerization or alkylation or may be employed for chemical synthesis such as the production of butadiene, alcohol, etc. The gasoline from line 9 is blended with the gasoline in line 17 to produce an olefinic gasoline of suitable volatility. Any excess of the light gasoline fraction beyond that required to produce the required volatility may be withdrawn by line 20; this material constitutes an excellent source of valuable olefins for chemical synthesis, for example, the production of alcohols by the Oxo process. The heavy residues of lines 4 and 19 may be combined. This product is a superior quality fuel oil. It may be used as such or may be blended with inferior or under-grade material to make a salable fuel oil.

The character of the intermediate fraction (reflux condensate) withdrawn by line 18 may vary considerably. In some cases it may be very aromatic in nature. In such cases it is most advantageously combined with the first reflux condensate by lines 24 and 12. In other cases it may contain sizable amounts of paraffinic hydrocarbons. In such cases it may be advantageously passed to an extraction zone 22. Here the fraction, or a portion of it, is separated into two fractions, namely a hydrogen-rich fraction (raffinate) and a hydrogen-poor fraction (extract) by solvent extraction. The hydrogen-poor fraction is preferably withdrawn by line 12 and combined with the first reflux condensate. The raffinate fraction may be advantageously cycled to the first cracking step by lines 25 and 21. However, this raffinate fraction is an excellent Diesel fuel and may in most cases be more advantageously withdrawn by line 23. In still other cases the reflux condensate withdrawn by line 18 may contain sizable amounts of naphthenic hydrocarbons. In such cases it is usually more advantageous to combine it directly with the feed to the first cracking step by lines 26 and 21 or, if desired, to subject it to the described extraction step, in which case the raffinate only is cycled to the first cracking step and the extract again sent by line 12 to the hydrogenation zone. The character of this reflux condensate from the second cracking step depends primarily upon the conditions, and especially the catalysts, employed in the two cracking treatments. A typical application of the process is as follows:

The feed stock is a vacuum flashed distillate (from a California petroleum) having the following inspection:

Gravity, °A. P. I.	25.2
Viscosity, S. S. U. at 100° F.	90
Sulfur, % Wt.	1.0
Nitrogen, % wt.	0.25
A. S. T. M. distn., °F.:	
I. B. P.	421
10%	540
50%	697
90%	730
F. B. P.	---

The feed stock is catalytically cracked under the following conditions:

Reactor temperature, °F	993
Weight hourly space velocity	0.94
Catalyst/oil wt. ratio	22.3
Reactor pressure, top p. s. i. g.	12.3
Catalyst: 60% synthetic silica-alumina and 40% Super Filtrol.	

The product is separated into fractions as follows:

	Percent weight
Gas fraction	25.3
Light gasoline	14.5
Heavy gasoline	18.7
Reflux condensate	17.6
Bottoms	14.9
Coke	9.0

The inspections of these fractions are as follows:

Gas fraction	Percent weight
H ₂ S	1.7
H ₂	0.6
CH ₄	13.0
C ₂ H ₄	6.6
C ₂ H ₆	12.7
C ₃ H ₆	22.5
C ₃ H ₈	10.0
i-C ₄ H ₈	9.3
n-C ₄ H ₈	13.3
i-C ₄ H ₁₀	7.2
n-C ₄ H ₁₀	3.1

Heavy gasoline fraction

Gravity, °A. P. I.	35.5
Sulfur, % wt.	0.50
Bromine No., g./100 g.	63
Blending octane No., F-2	84
A. S. T. M. distn., °F.:	
I. B. P.	250
10%	272
50%	316
90%	381
F. B. P.	418

Light gasoline fraction

Gravit, °A. P. I.	74.4
Sulfur, % wt.	0.08
Bromine No. g./100 g. (% olefins about 85%)	181
Blending octane No., F-2	84
A. S. T. M. distn., °F.:	
I. B. P.	96
10%	111
50%	133
90%	182
F. B. P.	209

Reflux condensate

Gravity, °A. P. I.	22.1
Viscosity, S. S. U. at 100° F.	36
Sulfur, % wt.	0.80
A. S. T. M. distn., °F.:	
I. B. P.	413
10%	450
50%	515
90%	596
F. B. P.	662

The reflux condensate is subjected to hydrogenation under the following conditions:

Catalyst: Tungsten-nickel sulfide.
Temperature: 720° F.
Pressure: 1000 p. s. i. g.
Throughput: 2.0 L. H. S. V. hydrogen to oil mol ratio: 10.

About 10% of the charge is converted into hydrocarbons boiling in the gasoline boiling range.

The product from the hydrogenation treatment is blended with the above-mentioned heavy gasoline and the mixture is subjected to catalytic cracking under the following conditions:

15 Reactor temperature, °F	850
Weight hourly space velocity	1.0
Catalyst/oil weight ratio	15
Reactor pressure, top, p. s. i. g.	10
Catalyst	Synthetic silica-alumina

20 The product is separated into fractions as follows:

	Percent weight
Gas fraction	10
Gasoline	70
Reflux condensate	20
Bottoms	

This gasoline is blended with the above-mentioned light gasoline to produce a gasoline having suitable volatility characteristics. Excess light gasoline may be used as a source of lower olefins.

30 The yield of gasoline may be increased by combining the second reflux condensate with the flashed distillate feed to the first catalytic cracking step. This reflux condensate is of a different character than the first reflux condensate and is amenable to catalytic cracking.

Also the yield of gasoline may be increased and Diesel fuel of good quality may be produced by extracting this second reflux condensate and returning the extract to the hydrogenation zone. It may alternately be advantageous to extract only a portion of the reflux condensate (preferably a portion having the boiling range of the desired Diesel oil) and to cycle the remainder to the first catalytic cracking step, which simplifies the extraction treatment. If a catalyst which is more or less selective for the cracking of paraffin hydrocarbons (as for example boric oxide-alumina catalyst or activated carbon) were applied in the second catalytic cracking step, it would be more advantageous to either cycle the raffinate to the first cracking step or to cycle the reflux condensate without extraction to the first cracking step. On the other hand, if the conditions and catalyst in the second cracking step were such as to produce a reflux condensate of highly aromatic character, the reflux condensate would advantageously be combined with the first reflux condensate.

Most of the processes involving two or more catalytic treatments which have been heretofore proposed are designed to produce a gasoline containing little or no olefins which is suited for use in aviation gasoline. The gasoline produced in the present process is an olefinic gasoline usually having a bromine number of at least 80. It is eminently suited as so-called motor gasoline.

The invention claimed is:

70 1. Process for the conversion of hydrocarbon oils boiling above the gasoline boiling range into anti-knock gasoline and other valuable products which comprises subjecting said oil to catalytic cracking with a clay type cracking catalyst at a temperature above 950° F. for a time to effect

a depth of cracking between 50% and 75%, separating the resulting reaction mixture into a fraction of normally gaseous products, a light gasoline fraction having an end point between 200° F. and 300° F., a heavy gasoline fraction having an initial boiling point between 200° F. and 300° F., a reflux condensate heavier than gasoline, and a higher boiling residue, subjecting said reflux condensate to catalytic hydrogenation with a sulf-active hydrogenation catalyst under conditions to afford a minor amount less than 25% of destructive hydrogenation, combining the hydrogenated reflux condensate with said heavy gasoline fraction and subjecting the mixture to a second catalytic cracking treatment with a clay type cracking catalyst at a temperature between 750° F. and 950° F., separating the resulting product from said second catalytic cracking treatment into a fraction of normally gaseous products, a gasoline fraction and a reflux condensate heavier than gasoline, and combining said latter gasoline fraction with such an amount of the above-mentioned light gasoline fraction to produce an olefinic gasoline of suitable volatility.

2. Process according to claim 1 in which the hydrocarbon oil has a nitrogen content of at least 0.2%.

3. Process for the conversion of hydrocarbon oils boiling above the gasoline boiling range into anti-knock gasoline and other valuable products which comprises subjecting said oil to catalytic cracking with a clay type cracking catalyst at a temperature above 950° F. for a time to effect a depth of cracking between 50% and 75%, separating the resulting reaction mixture into a fraction of normally gaseous products, a light gasoline fraction having an end point between 200° F. and 300° F., a heavy gasoline fraction having an initial boiling point between 200° F. and 300° F., a first reflux condensate heavier than gasoline, and a higher boiling residue, combining said reflux condensate with an aromatic extract produced as hereinafter specified and subjecting the mixture to catalytic hydrogenation with a sulf-active hydrogenation catalyst under conditions to afford a minor amount less than 25% of destructive hydrogenation, combining the hydrogenated reflux condensate with said heavy gasoline fraction and subjecting the mixture to a second catalytic cracking treatment with a clay type cracking catalyst at a temperature between 750° F. and 950° F., separating the resulting product from said second catalytic cracking treatment into a fraction of normally gaseous products, a gasoline fraction and a second reflux condensate heavier than gasoline, separating from said second reflux condensate an aromatic extract, combining said aromatic extract with said first reflux condensate, and combining said latter gasoline fraction with such an amount of the above-mentioned light gasoline fraction to produce an olefinic gasoline of suitable volatility.

4. Process for the conversion of hydrocarbon oils boiling above the gasoline boiling range into anti-knock gasoline and other valuable products which comprises subjecting said oil in admixture with reflux condensate raffinate produced as hereinafter specified to catalytic cracking with a first clay type cracking catalyst at a temperature above 950° F. for a time to effect a depth of cracking between 50% and 75%, separating the resulting reaction mixture into a fraction of normally gaseous products, a light gasoline fraction having an end point between 200° F. and 300° F., a heavy gasoline fraction having an initial boiling

point between 200° F. and 300° F., a first reflux condensate heavier than gasoline, and a higher boiling residue, combining said reflux condensate with an aromatic extract produced as hereinafter specified and subjecting the mixture to catalytic hydrogenation with a sulf-active hydrogenation catalyst under conditions to afford a minor amount less than 25% of destructive hydrogenation, combining the hydrogenated reflux condensate with said heavy gasoline fraction and subjecting the mixture to a second catalytic cracking treatment with a second clay type cracking catalyst different than the first at a temperature between 750° F. and 950° F., separating the resulting product from said second catalytic cracking treatment into a fraction of normally gaseous products, a gasoline fraction and a second reflux condensate heavier than gasoline, separating from said second reflux condensate an aromatic extract, combining said aromatic extract with said first reflux condensate, subjecting the raffinate fraction of the second reflux condensate to catalytic cracking as above specified, and combining said latter gasoline fraction with such an amount of the above-mentioned light gasoline fraction to produce an olefinic gasoline of suitable volatility.

5. Process for the conversion of hydrocarbon oils boiling above the gasoline boiling range into anti-knock gasoline and other valuable products which comprises subjecting said oil to catalytic cracking with a clay type cracking catalyst at a temperature above 950° F. for a time to effect a depth of cracking between 50% and 75%, separating the resulting reaction mixture into a fraction of normally gaseous products, a light gasoline fraction having an end point between 200° F. and 300° F., a heavy gasoline fraction having an initial boiling point between 200° F. and 300° F., a reflux condensate heavier than gasoline, and a higher boiling residue, subjecting said reflux condensate to catalytic hydrogenation with a sulf-active hydrogenation catalyst under conditions to afford a minor amount less than 25% of destructive hydrogenation, combining the hydrogenated reflux condensate with said heavy gasoline fraction and subjecting the mixture to a second catalytic cracking treatment with an activated carbon cracking catalyst at a temperature between 750° F. and 950° F., separating the resulting product from said second catalytic cracking treatment into a fraction of normally gaseous products, a gasoline fraction and a reflux condensate heavier than gasoline, and combining said latter gasoline fraction with such an amount of the above-mentioned light gasoline fraction to produce an olefinic gasoline of suitable volatility.

6. Process for the conversion of hydrocarbon oils boiling above the gasoline boiling range into anti-knock gasoline and other valuable products which comprises subjecting said oil to catalytic cracking with a first clay type cracking catalyst at a temperature above 950° F. for a time to effect a depth of cracking between 50% and 75%, separating the resulting reaction mixture into a fraction of normally gaseous products, a light gasoline fraction having an end point between 200° F. and 300° F., a heavy gasoline fraction having an initial boiling point between 200° F. and 300° F., a reflux condensate heavier than gasoline, and a higher boiling residue, subjecting said reflux condensate to catalytic hydrogenation with a sulf-active hydrogenation catalyst under conditions to afford a minor amount less than 25% of destructive hydrogenation, combining the

hydrogenated reflux condensate with said heavy gasoline fraction and subjecting the mixture to a second catalytic cracking treatment with a second clay type cracking catalyst different than the first at a temperature between 750° F. and 950° F., separating the resulting product from said second catalytic cracking treatment into a fraction of normally gaseous products, a gasoline fraction and a reflux condensate heavier than gasoline and combining said latter gasoline fraction with such an amount of the above-mentioned light gasoline fraction to produce an olefinic gasoline of suitable volatility.

7. Process for the conversion of hydrocarbon oils boiling above the gasoline boiling range into anti-knock gasoline and other valuable products which comprises subjecting said oil in admixture with reflux condensate produced as hereinafter specified to catalytic cracking with a clay type cracking catalyst at a temperature above 950° F. for a time to effect a depth of cracking between 50% and 75%, separating the resulting reaction mixture into a fraction of normally gaseous products, a light gasoline fraction having an end point between 200° F. and 300° F., a heavy gasoline fraction having an initial boiling point between 200° F. and 300° F., a reflux condensate heavier than gasoline, and a higher boiling residue, subjecting said reflux condensate to catalytic hydrogenation with a sulf-active hydrogenation catalyst under conditions to afford a minor amount less than 25% of destructive hydrogenation, combining the hydrogenated reflux condensate with said heavy gasoline fraction and subjecting the mixture to a second catalytic cracking treatment with a clay type cracking catalyst at a temperature between 750° F. and 950° F., separating the resulting product from said second catalytic cracking treatment into a fraction of normally gaseous products, a gasoline fraction and a second reflux condensate heavier than gasoline, subjecting said second reflux condensate to catalytic cracking as above specified and combining said latter gasoline fraction with such an amount of the above-mentioned light gasoline fraction to produce an olefinic gasoline of suitable volatility.

8. Process for the conversion of hydrocarbon oils boiling above the gasoline boiling range into anti-knock gasoline and other valuable products which comprises subjecting said oil to catalytic cracking with a clay type cracking catalyst at a temperature above 950° F. for a time to effect a depth of cracking between 50% and 75%, separating the resulting product into a fraction of normally gaseous products, a light gasoline fraction having an end point between 200° F. and 300° F., a heavy gasoline fraction having an initial boiling point between 200° F. and 300° F., a reflux condensate heavier than gasoline, and a higher boiling residue, subjecting said reflux condensate in admixture with a second reflux condensate obtained as hereinafter specified to catalytic hydrogenation with a sulf-active hydrogenation catalyst under conditions to afford a minor amount less than 25% of destructive hydrogenation, combining the hydrogenated product with the above-said heavy gasoline fraction and subjecting the mixture to a second catalytic cracking treatment with a clay type cracking catalyst at a temperature between 750° F. and 950° F., separating the resulting product from said second catalytic cracking treatment into a fraction of normally gaseous products, a gasoline fraction and a second reflux condensate heavier than gasoline, combining said second reflux condensate with said first reflux condensate, and combining said latter gasoline fraction with such an amount of the above-mentioned light gasoline fraction to produce an olefinic gasoline of suitable volatility.

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