

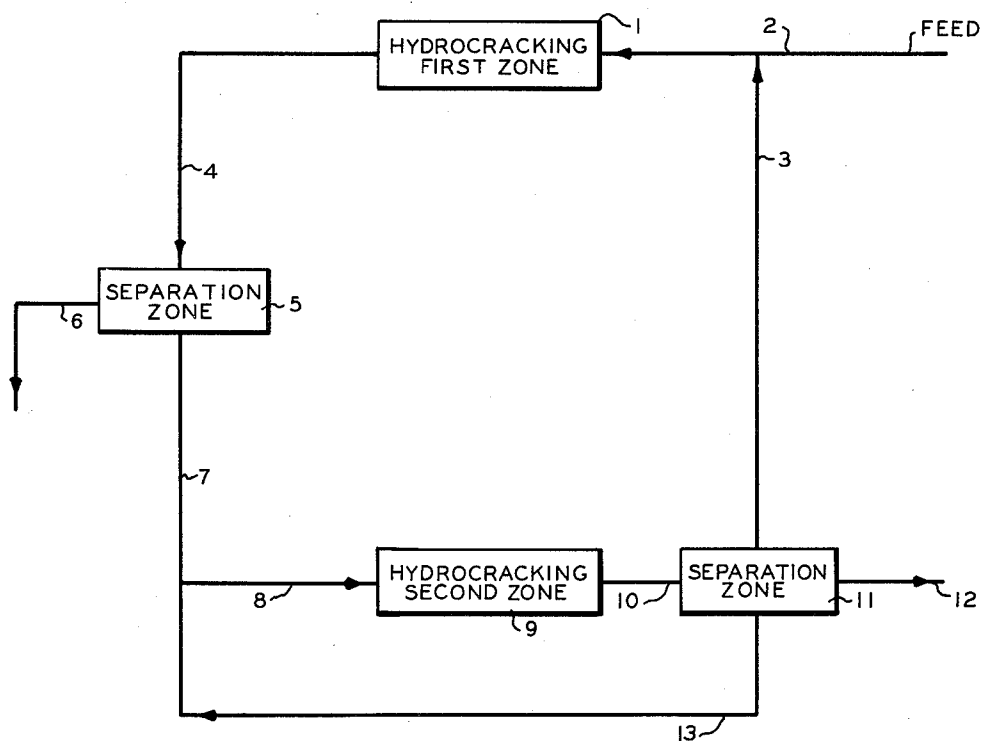
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HYDROCRACKING PROCESS

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1

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HYDROCRACKING PROCESS

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This invention relates to hydrocracking of hydrocarbon feedstocks. More particularly, the invention relates to a process comprising a combination of mutually interrelated and interdependent steps for the hydrocracking of hydrocarbons boiling above gasoline to produce gasoline boiling range hydrocarbons.

It has been found that when kerosene and gas oil feedstocks boiling in the range from about 400 to about 1000° F. are catalytically hydrocracked under conditions favoring the conversion of naphthenes to the desired aromatics, there results in addition to the desired gasoline boiling range aromatics some heavy aromatics which are quite refractory and are therefore not converted to the desired gasoline boiling range hydrocarbons under the conditions of the hydrocracking treatment.

It is an object of the invention, therefore, to provide a process for converting such kerosene or gas oil feedstocks substantially entirely to more valuable lower boiling hydrocarbons, principally in the gasoline boiling range, in an economical and efficacious manner.

The drawing is a schematic representation of my process.

Other objects, as well as aspects and advantages, of the invention will become apparent from a consideration of the accompanying disclosure.

The first step in my integrated process is the hydrocracking of my hydrocarbon feed having a boiling range in the range from 400 to 1000° F. in the presence of a hydrocracking catalyst under conditions favoring the dehydrogenation of naphthenes, employing a temperature in the range from 800 to 950° F., a pressure in the range from 300 to 1000 p.s.i.a., a liquid hourly space velocity (volumes/volumes/hour) of 0.2-10 and at least 1000 cubic feet of hydrogen at standard conditions per barrel of oil. An additional feedstock to this first hydrocracking step is a recycle gasoline fraction derived from a subsequent hydrocracking step, to be discussed later, and the space velocities and hydrogen ratios mentioned are on the basis of this total combined charge. This step is effected in hydrocracking zone 1 of the drawing, the hydrocarbon feed having a boiling range from 400 to 1000° F. entering in line 2 and the recycle gasoline fraction entering by way of line 3. The product from this first hydrocracking step is withdrawn through line 4 and includes light ends and gasoline of high octane number and the heavy fraction boiling above 400° F. This product is separated in separation zone 5 into a gasoline and lighter fraction boiling below 400° F. in line 6 and the heavy fraction boiling above 400° F. which is withdrawn through line 7 and introduced through line 8 to hydrocracking zone 9. This heavy fraction contains heavy, refractory aromatic hydrocarbons which are stable and cannot be converted to gasoline boiling range hydrocarbons under the conditions of the first hydrocracking step. This heavy cut is subjected in hydrocracking zone 9 to a second hydrocracking step in which all of its components can be converted to gasoline boiling range hydrocarbons (except for some unavoidable light ends formation), in the presence of a hydrocracking catalyst which can be the same or a different catalyst than employed in the first hydrocracking step, under conditions which favor the net hydrogenation of aromatics to naphthenes, employing a temperature in the range from 600 to 780° F., a pressure in the range from 500 to 2000 p.s.i.a., a liquid hourly spaced velocity in the range from 0.2-10, and hydrogen

2

in the amount of at least 1000 cubic feet per barrel of charge. In this hydrocracking step the refractory aromatics are converted to naphthenes and these are hydrocracked to lower molecular weight products. From the effluent which is passed through line 10 from this hydrocracking step there is separated in separation zone 11 a cut of the heavier portion of gasoline produced, and this gasoline is recycled through line 3 to the first hydrocracking step, as mentioned before. This cut usually has a boiling range from 400° F. down to 170° F., but is more often in the range from 400° F. down to about 200° F. The lighter portion of the gasoline from the second hydrocracking step and the light ends are taken as product through line 12, while the residue boiling above 400° F. is recycled to extinction through line 13 as part of the feed to the second hydrocracking step.

As before stated, the feeds to be treated in my process are hydrocarbon mixtures in the kerosene to gas oil boiling range, boiling in the range from 400° F. to 1000° F., although usually the end point of the feed employed is not over 800° F. These kerosenes and gas oils, as is well known, contain mixtures of hydrocarbon types, including naphthenes, aromatics, and paraffins.

The advantages of the process of the present invention are apparent. Thus, the heavy refractory materials which can not be converted in the first hydrocracking step are hydrogenated and hydrocracked in the second hydrocracking step to gasoline boiling range materials containing naphthenes which, when recycled to the first hydrocracking step, can be converted under the net dehydrogenation conditions of the first hydrocracking step to valuable aromatics in the gasoline boiling range. The simplicity of the combination of mutually interrelated steps of the process of the invention, together with the complete utilization of the feed to form valuable gasoline boiling range hydrocarbons (except for some unavoidable formation of light ends), results in a process of technical and economic importance.

While it has been stated that the minimum amount of hydrogen employed is at least 1000 standard cubic feet per barrel of oil in each of the hydrocracking steps, it is usually desirable that at least 3500 cubic feet per barrel of oil be employed. Although the upper limit of hydrogen can vary widely in either hydrocracking step, for economic reasons there is seldom employed over 40,000 cubic feet of hydrogen per barrel of charge.

For each of the hydrocracking steps described herein, specific ranges of conditions have been set forth as a guide. However, the hydrocracking conditions which will produce specific effects are well known in the art. It is noted that the conditions in the first hydrocracking step are such that there is a net dehydrogenation of naphthenes to aromatics. It is known, of course, that high temperature favors dehydrogenation, while high pressure suppresses dehydrogenation. Therefore, for any specific feed the temperatures and pressures in each of the hydrocracking steps must be properly correlated for the desired results. For instance, for any particular feedstock, operation of the first hydrocracking step at 800 p.s.i.a. will require a higher temperature within the disclosed range than operation at 500 p.s.i.a. In a like manner, in the second hydrogenation step, wherein the conditions are to favor hydrogenation of aromatics to naphthenes, for any specific feed, operation at 780° F. will require a higher pressure than will be required for operation at 600° F. Thus, optimum conditions for any specific feedstock can be established by mere routine tests over the ranges of conditions disclosed, with such conditions as a guide, with no need to resort to extensive experimentation in order to establish the conditions for dehydrogenation of naphthenes to aromatics in the first

hydrocracking step or the hydrogenation of aromatics to naphthenes in the second hydrocracking step.

Any known hydrocracking catalyst is applicable in either hydrocracking step of the present invention. Many such catalysts are available and are well known. A particular type of catalyst found to be applicable are catalysts containing from 0.05 to 10 weight percent of a group VIII metal selected from the group consisting of platinum, palladium, rhodium, iridium, nickel, and cobalt, deposited on a solid inorganic metal oxide cracking component, such as, for instance silica-alumina or alumina. Preferably, however, the cracking component is a material having more cracking activity than alumina; such materials are more acidic than alumina. Examples of such catalysts include the platinum-halogen-alumina catalysts of U.S. Patent 2,479,109, especially where such disclosed catalysts contain at least 1 percent by weight of the disclosed halogen, such as chlorine or fluorine, or both since the higher amount of halogen gives a more acidic catalyst having more cracking activity. Other examples of applicable highly acidic catalysts are the catalysts disclosed in U.S. Patent 2,478,916, such as the platinum or palladium deposited on a cracking component disclosed in that patent, e.g., silica-alumina, silica-zirconia, silica-magnesia, silica-thoria, silica-alumina-zirconia, alumina-boria, etc. Examples of specific catalysts of specific portions disclosed in the foregoing patents are also examples of catalysts applicable in either step of the process of my invention. A now particularly preferred catalyst for use in each step of the process of my invention is a catalyst consisting of 0.05 to 5 weight percent platinum, about 1-10 weight percent of a halogen, either chlorine or fluorine, or both, deposited on alumina. Specific examples of catalyst bases comprising a cracking component having more cracking activity and being more acidic than pure aluminum, on which there is deposited one of platinum, palladium, rhodium, iridium, nickel and cobalt to produce a preferred catalyst of my invention, are silica-alumina, silica-zirconia, silica-magnesia, silica-thoria, alumina-boria, silica-alumina-zirconia, silica-alumina-magnesia, silica-alumina-thoria, alumina containing from 1 to 10 weight percent chlorine or fluorine, or both, and silica-alumina containing 1 to 10 weight percent chlorine or fluorine, or both.

As is well known in the art, when hydrocracking over catalysts promoted with noble metals, nickel or cobalt, improved results are obtained if stocks containing appreciable sulfur compounds are first desulfurized. As is well known such a treatment is a mild hydrogenation effected under conditions which convert the sulfur compounds to H_2S and will reduce the olefin content of the feed, if present, but which hydrogenation conditions are too mild to hydrogenate aromatics present. Such a pretreatment step is well known in the art, and can be effected using a cobalt-molybdate type catalyst, for instance. Such a pretreatment step is an optional preliminary step to the practice of the present invention.

Example I

Hydrotreated kerosene (boiling range 457-535° F.) having a density at 20° C. of 0.82 was contacted with platinum-halogen-alumina catalyst containing about 0.4 weight percent platinum and 3 percent fluorine. One run was at about 842° F. and 500 p.s.i.g., and the other was at 779° F. and 800 p.s.i.g. Results of these tests were:

Run number	Run 1	Run 2
Process conditions:		
Avg. temp., ° F.	842	779
Pressure, p.s.i.g.	500	800
LHSV	2.0	2.1
H_2/HC , cubic ft./bbl.	3500	3600
Product octanrating, research +3 ml. TEL rating:		
C ₈ -200° F. product	92.7	83.6
200-400° F. product	98.2	
Density at 20° C. of residue above 400° F.	0.97	0.82

At 842° F. and 500 p.s.i.g. the gasoline had high octane rating; however, the high density (0.97) of the residue above 400° F. shows that it is highly aromatic and thus is comparatively stable at these conditions. On the other hand the gasoline product from the run at 779° F. and 800 p.s.i.g. had fairly low octane rating, but the residue above 400° F. had about the same density as the feed showing that it can be recycled and further converted to these conditions.

Example II

This example shows that gasoline produced at the low-temperature, high-pressure conditions of my second step is upgraded when processed at the high-temperature, lower-pressure conditions of the first step.

Hydrotreated kerosene similar to Example I was contacted with a platinum-boria-alumina catalyst containing about 0.4 weight percent platinum and 11.8 percent boria at 705-744° F., 800 p.s.i.g., 2 L.H.S.V., and with about 3400 cubic feet of H_2 per barrel of kerosene. The 200-400° F. gasoline product, having an octane rating (Research +3 mm. TEL) of 75.1, was then further processed by contacting with a similar platinum-boria-alumina catalyst at 500 p.s.i.g. and 839° F. The octane rating of the gasoline was considerably improved as is shown by the following data:

Process conditions:

Avg. temp., ° F.	839
Pressure, p.s.i.g.	500
LHSV	2
H_2/HC , cubic ft./bbl.	1700
Research +3 ml. TEL rating of gasoline product	97.6

Example III

Hydrotreated kerosene similar to that used in Examples I and II was processed over the same catalyst used in Example II at 768° F., 2 L.H.S.V., 800 p.s.i.g., and with about 3400 cubic feet of hydrogen per barrel of hydrocarbon. Approximately 630 volumes of feed containing about 51 liquid volume percent of aromatics were treated. The product boiling above 400° F., which was equal to 11.0 liquid volume percent of the feed, contained 7.5 volume percent aromatics. Thus, approximately 94.5 volumes (of the original 630) of aromatics boiling above 400° F. were fed to the hydrocracking step, and only about 5 volumes remained in the product boiling above 400° F. This is especially significant since the temperature was in the upper part of the range (600-780° F.). The density of the 400°+ F. product was 0.7926 using the 768° F. reaction temperature. When the run was repeated as before, but using a temperature of 744° F. the density was 0.7835, indicating still lower aromatic content.

Example IV

A hydrocarbon cut having a boiling range from 400-700° F. is charged continuously to a hydrocracking reactor containing these same catalysts described in Example I, employing a liquid hourly space velocity of 2, 500 p.s.i.g., 850° F. and a charge of 4000 cubic feet of hydrogen under standard conditions per barrel of feed charged. From the reaction product is separated the material boiling below 400° F., and the balance of the product boiling above 400° F. is charged to a second hydrocracking reactor over a hydrocracking catalyst as described in Example II. In this reactor the conditions are a space velocity of 1, a temperature of 730° F., a pressure of 800 p.s.i.g. and 7000 cubic feet of hydrogen per barrel of total charge. There is separated from the product of the second hydrocracking reaction the gasoline cut boiling in the range from 200 to 400° F., and this cut is continuously recycled to the first hydrocracking reactor as a part of the charge thereto, while the small portion of residue boiling above 400° F. is recycled to the second hydrocracking reactor as part of the charge to that reactor.

As will be evident to those skilled in the art, various modifications of this invention can be made or followed in the light of the foregoing disclosure and discussion without departing from the spirit and scope of the disclosure or from the scope of the claims.

I claim:

1. A process for conversion of hydrocarbons which comprises the steps of hydrocracking a hydrocarbon feed having a boiling range in the range from 400 to 1000° F., together with a heavy gasoline recycle feed described hereafter, in the presence of a hydrocracking catalyst containing 1-10 weight percent of a group VIII metal selected from the group consisting of platinum, palladium, rhodium, iridium, nickel and cobalt deposited on a solid inorganic metal oxide cracking component, under conditions favoring dehydrogenation of naphthenes to aromatics, employing a temperature from 800 to 950° F., a pressure from 300 to 1000 p.s.i.a., a liquid hourly space velocity of total hydrocarbon feed from 0.2 to 10, and a ratio of hydrogen to total hydrocarbon feed of at least 1000 s.c.f. per barrel; separating the residue fraction of the effluent boiling above 400° F. from the product gasoline fraction, hydrocracking said residue in another hydrocracking step in the presence of a catalyst of the foregoing description under conditions favoring hydrogenation of aromatics to naphthenes, employing a temperature from 600 to 780° F., a pressure from 500 to 2000 p.s.i.a., a liquid hourly space velocity of total hydrocarbon feed from 0.2 to 10, and a ratio of hydrogen to total hydrocarbon feed of at least 1000 s.c.f. per barrel; separating a heavy gasoline fraction from the effluent from said another hydrocracking step and recycling same as part of the said total feed to the first-mentioned hydrocracking step.

2. A process of claim 1 wherein the residue boiling above 400° F. in said another hydrocracking step is recycled thereto as a part of the total feed thereto.

3. A process for conversion of hydrocarbons which comprises the steps of hydrocracking a hydrocarbon feed having a boiling range in the range from 400 to 1000° F., together with a heavy gasoline recycle feed described hereafter, in the presence of a hydrocracking catalyst containing 1-10 weight percent of a group VIII metal selected from the group consisting of platinum, palladium, rhodium, iridium, nickel and cobalt deposited on a solid inorganic metal oxide cracking component having more cracking activity than pure alumina, under conditions favoring dehydrogenation of naphthenes to aromatics, employing a temperature from 800 to 950° F., a pressure from 300 to 1000 p.s.i.a., a liquid hourly space velocity of total hydrocarbon feed from 0.2 to 10, and a ratio of hydrogen to total hydrocarbon feed of at least 1000 s.c.f. per barrel; separating the residue fraction of the effluent boiling above 400° F. from the product gasoline fraction; hydrocracking said residue in another hydrocracking step in the presence of a catalyst of the foregoing description under conditions favoring hydrogenation of aromatics to naphthenes employing a temperature from 600 to 780° F., a pressure from 500 to 2000 p.s.i.a., a liquid hourly space velocity of total hydrocarbon feed from 0.2 to 10, and a ratio of hydrogen to total hydrocarbon feed of at least 1000 s.c.f. per barrel; separating a heavy gasoline fraction from the effluent from said another hydrocracking step and recycling same as part of the said total feed to the first mentioned hydrocracking step.

4. A process for conversion of hydrocarbons which comprises the steps of hydrocracking a hydrocarbon feed having a boiling range in the range from 500 to 800° F., together with a heavy gasoline recycle feed described hereafter, in the presence of a hydrocracking catalyst con-

taining 1-10 weight percent of a group VIII metal selected from the group consisting of platinum, palladium, rhodium, iridium, nickel and cobalt deposited on a solid inorganic metal oxide cracking component having more cracking activity than pure alumina, under conditions favoring dehydrogenation of naphthenes to aromatics, employing a temperature from 800 to 950° F., a pressure from 300 to 1000 p.s.i.a., a liquid hourly space velocity of total hydrocarbon feed from 0.2 to 10, and a ratio of hydrogen to total hydrocarbon feed of at least 1000 s.c.f. per barrel; separating the residue fraction to the effluent boiling above 400° F. from the product gasoline fraction; hydrocracking said residue in another hydrocracking step in the presence of a catalyst of the foregoing description under conditions favoring hydrogenation of aromatics to naphthenes employing a temperature from 600 to 780° F., a pressure from 500 to 2000 p.s.i.a., a liquid hourly space velocity of total hydrocarbon feed from 0.2 to 10, and a ratio of hydrogen to total hydrocarbon feed of at least 1000 s.c.f. per barrel; separating a heavy gasoline fraction boiling in the range of from 200 to 400° F. from the effluent from said another hydrocracking step and recycling same as part of the said total feed to the first mentioned hydrocracking step.

5. A process for conversion of hydrocarbons which comprises the steps of catalytically hydrocracking a hydrocarbon feed having a boiling range in the range from 400 to 1000° F., together with a heavy gasoline recycle feed described hereafter, under conditions favoring dehydrogenation of naphthenes to aromatics, employing a temperature from 800 to 950° F., a pressure from 300 to 1000 p.s.i.a., a liquid hourly space velocity of total hydrocarbon feed from 0.2 to 10, and a ratio of hydrogen to total hydrocarbon feed of at least 1000 s.c.f. per barrel; separating the residue fraction of the effluent boiling above 400° F. from the product gasoline fraction; catalytically hydrocracking said residue in another hydrocracking step under conditions favoring hydrogenation of aromatics to naphthenes, employing a temperature from 600 to 780° F., a pressure from 500 to 2000 p.s.i.a., a liquid hourly space velocity of total hydrocarbon feed from 0.2 to 10, and a ratio of hydrogen to total hydrocarbon feed of at least 1000 s.c.f. per barrel; separating a heavy gasoline fraction from the effluent from said another hydrocracking step and recycling same as part of the said total feed to the first-mentioned hydrocracking step.

6. A process for conversion of a hydrocarbon feed stock boiling in the range from 400 to 1000° F. which comprises subjecting same to a first hydrocracking step under conditions effecting dehydrogenation of naphthenes therein to aromatics, from the product of said first step separating a residue boiling above 400° F. and subjecting same to a second hydrocracking step under conditions effecting hydrogenation of aromatics to naphthenes, from the product of said second step separating a heavy gasoline fraction and recycling same as additional feed to said first hydrocracking step.

References Cited in the file of this patent

UNITED STATES PATENTS

1,995,604	Davis	Mar. 26, 1935
2,009,717	Peck	July 30, 1935
2,279,550	Benedict et al.	Apr. 14, 1942
2,334,159	Friedman	Nov. 9, 1943
2,360,622	Roetheli	Oct. 17, 1944
2,428,692	Voorhies	Oct. 7, 1947
2,464,539	Voorhies	Mar. 15, 1949
2,479,109	Haensel	Aug. 16, 1949
2,703,308	Oblad et al.	Mar. 1, 1955