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COMBINATION PROCESS FOR UPGRADING
LIGHT OLEFINS

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This invention relates to the upgrading of light boiling olefinic fractions. More particularly this invention relates to the upgrading of light cracked gasoline fractions by a combination of hydro-processes.

Light cracked gasoline fractions comprising normal olefins having from four through six carbon atoms per molecule have a high octane rating, particularly blending octane rating. However, their presence in motor gasoline in recent years has been increasingly undesirable because of their high sensitivity. By sensitivity it is meant the difference in octane rating determined by the Research Method (F-1) and the octane rating determined according to the Motor Method (F-2).

It is known that olefins can be converted to the corresponding saturated hydrocarbons by hydrogenation, usually by a catalytic process employing a catalyst comprising a hydrogenation component on an inert support, such as the conventional cobalt molybdenum on alumina catalyst. However, while the Research octane rating of normal olefins is relatively high, the Research octane rating of the normal paraffin product obtained by simple hydrogenation is often very much lower. Therefore, simple hydrogenation processes have not been looked upon with favor since the refiner can rarely tolerate the loss in Research octane rating.

It has been proposed to hydroisomerize olefins by means of a dual function catalyst comprising a hydrogenation component associated with an acid-acting support. In such a process, normal olefins are converted at an elevated temperature and pressure into isoparaffins. Isoparaffins have a considerably higher octane rating than the corresponding normal paraffins, thus, the hydroisomerization product is not only of the desired degree of saturation, but, owing to the increase in isoparaffin content, is of a higher Research octane rating than the product obtained by a conventional simple hydrogenation process. Further details of the hydroisomerization of olefins are disclosed and described in copending application Serial No. 39,818, filed June 30, 1960, by Joost C. Platteuw and Johannes H. Choufoer.

The mechanism by which normal olefins are converted into isoparaffins in the presence of a dual function catalyst is not fully understood, although the simplest explanation is that the olefins are first isomerized to an isoolefin which is then hydrogenated to the corresponding isoparaffin. That the isomerization reaction proceeds before the hydrogenation reaction is supported by the observation that normal paraffins are substantially unaffected by the catalyst at the conversion conditions. However, although normal olefins such as normal butene, normal pentene and normal hexene are converted primarily to isoparaffins, side reactions leading to the formation of higher boiling compounds also occur to an appreciable extent. The presence of the low octane heavy boiling side reaction products has a detrimental effect on octane quality of the isomerizate. Alternately, removal of the higher boiling material from the isomerizate results in a lower yield of high octane product.

It is an object of this invention to provide an improved process for upgrading light olefins. A further object of this invention is to convert light boiling olefin hydrocarbons to high octane gasoline components of low sensitivity. A particular object of the invention is to provide

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a combination process for converting a light cracked gasoline fraction to a high octane, low sensitivity, gasoline component. These and further objects will become more apparent to those skilled in the art from the following detailed description of the invention.

It has now been found that light olefin hydrocarbons can be converted into high octane low sensitivity gasoline components by contacting the light olefin hydrocarbons in the presence of hydrogen with a hydroisomerization catalyst under hydroisomerization conditions, separating the isomerizate into a light boiling fraction and a heavy boiling fraction, and catalytically reforming the heavy boiling fraction.

The olefins which are to be upgraded by the process of the invention are the light olefins having from four to about six carbon atoms per molecule. The olefin feed can be a single olefin, a mixture of olefins, or a mixture of olefins and other hydrocarbons. A particularly preferred feed to the process of the invention is a light cracked gasoline fraction, comprising primarily C₅ and C₆ hydrocarbons, boiling up to about 200° F. and preferably up to about 185° F. The light cracked gasoline fractions are recovered from the catalytic or thermal cracking of hydrocarbon oils boiling above the gasoline boiling range and are often available in the refinery as a separate hydrocarbon stream.

In the process of the invention the olefin feed is hydroisomerized over a suitable hydroisomerization catalyst comprising a hydrogenation component deposited on an acid-acting support. The hydrogenation component should have a relatively weak hydrogenation activity. One of the main functions of the hydrogenation component is to promote the hydrogenation of highly unsaturated compounds, such as diolefins which are present in the feed or are formed as an intermediate reaction product, which would tend to deposit on the catalyst as a polymerization product. Rapid deactivation of the isomerization function of the catalyst is prevented in this manner and at the same time, through hydrogenation of diolefins to monoolefins which can then take part in the isomerization reaction, a higher yield of branched hydrocarbons is obtained. The use of a component with too strong a hydrogenation action, such as nickel, will result in hydrogenation of the monoolefins before the isomerization component has been able to perform its action.

Highly suitable hydroisomerization catalysts comprise a solid acid-acting support catalyst containing a sulfide of one or more of the metals of the left-hand column of Group VI (chromium, molybdenum, tungsten) and/or a sulfide of one or more of the metals of Group VIII (iron, cobalt, nickel) of the Periodic Table. By solid acid-acting support it is meant those which when absorbing butter yellow and other weaker basic indicators, show a color change of these indicators, indicating the transition to the acid form. Suitable acid-acting supports for the dual function catalyst of the invention are acidic refractory oxides, particularly compounds of silica and alumina, such as silica-alumina cracking catalyst, compounds of silica and zirconium dioxide, compounds of boron trioxide and alumina, compounds of boron trioxide and silica, compounds of alumina and halogen, such as alumina and chlorine and the like. A catalyst consisting of silica-alumina compounds, in particular those having a silica content of at least 60% by weight and an alumina content of about 1-40% by weight are preferred. Nickel sulfide and/or cobalt sulfide deposited or distended on silica-alumina are particularly preferred olefin hydroisomerization catalysts.

The amount of metal sulfide applied to the acid isomerization catalyst can vary within wide limits and is generally in the range from about 0.5-15% by weight based on the total catalyst. Thus, for example, a catalyst containing silica and alumina, and having a silica content

of at least 60% by weight (based on the total catalyst) and to which is applied 5 to 10% by weight of nickel sulfide (based on the total catalyst) is an excellent catalyst for use in the process of the invention. The metal sulfide can be applied to the acid isomerization catalyst, for instance silica-alumina cracking catalyst, by any suitable method known per se. For example, the metal sulfide can be applied by impregnating the acid catalyst with a solution of a salt of the corresponding metal, for instance nickel nitrate, followed by drying, calcining and finally sulfiding with hydrogen sulfide or a gas containing hydrogen sulfide.

The hydroisomerization conversion is carried out in the presence of hydrogen at elevated pressure, preferably at a total pressure not exceeding 1500 p.s.i., for instance, in the range of from 150 to 1200 p.s.i.g., and particularly from about 300 to 900 p.s.i.g. The hydrogen partial pressure can vary within wide limits and is preferably from 50 to 90% of the total pressure. It is not necessary to employ pure hydrogen since hydrogen-containing gases such as hydrogen enriched gases formed in a subsequent reforming step or in the reforming of other hydrocarbon oils are also suitable.

Hydroisomerization of the light olefin hydrocarbon is conducted at a temperature in the range of from about 400° F. to about 900° F. and preferably from about 500° F. to about 750° F. The liquid hourly space velocity used is in the range of from 0.5 to 20 barrels of liquid fresh feed hydrocarbons per hour per barrel of catalyst, although lower or higher space velocities may be used if desired.

Hydroisomerization of olefins is an exothermic reaction and consequently, a large increase in temperature results from the heat of reaction which is liberated. The increase in temperature can be sufficient to promote hydrocracking, which is also an exothermic reaction, and thus lead to so-called runaway hydrocracking. Thus, excessive temperature increases in the reaction zone can result in loss in yield, increased carbonaceous deposits on the catalyst, and possible harm to the catalyst itself. If desired, any suitable conventional method of preventing excessive temperature increases in the reaction zone can be employed, such as subdivision of the catalyst into a number of separate beds connected in series with cooling of the reaction mixture between the beds, or by recycling liquid product. A preferred means is to admix with the olefinic hydroisomerization feed a straight-run naphtha fraction which then undergoes desulfurization and denitrification in the hydroisomerization reaction zone.

In the hydroisomerization reaction zone, the light olefin starting material is converted primarily into isoparaffin hydrocarbons. However, the hydroisomerization reaction is accompanied by the formation of an appreciable quantity of hydrocarbons boiling higher than the starting material. For example, in the hydroisomerization of hexene-1 at 650° F., 600 p.s.i.g., 2.25 LHSV and 10/1 hydrogen/oil molar ratio over a catalyst comprising nickel sulfide on silica-alumina cracking catalyst, the yield of C₇ and higher hydrocarbons is about 20% by weight. For pentene-2, the yield is approximately 21% by weight. At a slightly lower temperature and pressure, the yield of C₇+hydrocarbons from hexene-1 is about 27% by weight. Surprisingly, it is found that the higher-boiling hydrocarbons obtained in the hydroisomerization of light olefins contain appreciable quantities of cyclic hydrocarbons. For example, in the hydroisomerization of hexene-1, it was found that the 165° F.+ product fraction contained about 23% naphthenes and 3% aromatics. Thus, the higher-boiling isomerizate fraction is suitable as a catalytic reformer feed.

Therefore, in the process of the invention, liquid isomerizate recovered from the hydroisomerization process is separated, e.g., by fractional distillation, into a light fraction boiling substantially below a cut point in the

range of about 170° F. to 230° F. and a heavy fraction boiling substantially above such cut point. Preferably the isomerizate is separated into a light fraction boiling below about 185° F. and a heavy fraction boiling above about 185° F. If desired, any normally gaseous hydrocarbons present in the isomerizate can be removed before or after the above separation. The light fraction containing a high proportion of isoparaffins, is an excellent motor gasoline component. The heavy fraction, comprising C₇ or C₈ and higher hydrocarbons is passed at an elevated temperature and pressure together with hydrogen over a reforming catalyst at catalytic reforming conditions.

In commercial distillation there is normally an overlap of boiling range of products and in the above discussion the term "cut point" is a temperature within the overlap between light and heavy fractions, or if there is no overlap, a temperature between the boiling ranges of the fractions. It is preferred that the distillation be sufficiently precise and that the cut point is above the ASTM Method D-86, 90% point of the light fraction and below the 10% point of the heavy fraction.

Suitable catalytic reforming conditions are known to the art. Catalytic reforming operations are ordinarily carried out at temperatures of 850°-1000° F. and a pressure in the range of about 50 to 1000 pounds per square inch. A hydrogen/oil molar ratio from about 2/1 to about 15/1 is generally used and the liquid hourly space velocity is about 0.5 to about 5.

Catalysts for the reforming process comprise a hydrogenation-dehydrogenation component on a suitable carrier such as alumina. Particularly suitable reforming catalysts comprises a small amount, e.g., 0.1/2% of a noble metal, e.g., Pt, Pd, and Rh, supported on a carrier such as alumina, alumina-silica composites, and the like, and are frequently promoted with small amounts, e.g., 0.1-3% of chlorine and/or fluorine. Platinum on halogenated alumina is a highly effective and widely used catalyst. However, the older so-called hydroforming catalysts such as compounds of such elements as molybdenum, chromium, cobalt and the like supported on a base, e.g., 10% by weight molybdenum on alumina, are also suitable reforming catalysts.

In the reforming process there is generally a net production of hydrogen. Hydrogen from the reforming process can suitably be used in the hydroisomerization process wherein hydrogen is consumed.

The heavy isomerizate fraction can be reformed alone or admixed with other suitable reforming feed. It is preferred to reform the heavy isomerizate together with naphtha fractions such as straight-run naphtha. Reforming feed naphthas boil in the range from about 200° F. to about 390° F.

The reformate obtained in the reforming process can be used as a gasoline blending component or blended with the light isomerizate.

The process of the invention will be illustrated by means of the following example.

EXAMPLE I

A light catalytically cracked fraction having a boiling range of 95° F. to 212° F., an F-1-1.5 octane of 98 and a sensitivity of 13 was hydroisomerized over a catalyst comprising nickel sulfide on silica-alumina cracking catalyst. The hydroisomerization reaction was carried out at an inlet temperature of 608° F., a pressure of 88 p.s.i.g. (60 atm.), an LHSV of 0.5 volumes of hydrocarbon per hour per volume of catalyst, a ratio of product recycle/fresh feed of 3, and a hydrogen/oil ratio, basis total feed, of 10/1.

The hydroisomerization liquid product was separated by distillation into two fractions, the distillation cut-point being 185° F. The fraction boiling below about 185° F. had an F-1-1.5 octane of 96 and a negligible sensitivity. The heavy fraction boiling above 185° F., comprising ap-

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proximately 25% by weight of the total product, had an octane of only 78 F-1-1.5. Of this heavy fraction, approximately 35% by weight boiled above 212° F. Naphthene content of the material boiling above 212° F. was about 60% by weight.

The heavy fraction boiling above 185° F. was catalytically reformed with a commercial platinum catalyst comprising about 0.75% Pt, 0.30% Cl, and 0.40% F on alumina. Reforming conditions and feed and product properties are summarized in Table I.

Table I

REFORMING HEAVY ISOMERIZATE

Conditions:			
Pressure, lbs./sq. in.	285		
Temperature, ° F.	914		
H ₂ , s.c.f./bbl. feed	6,700		
LHSV	2.0		
C ₈ + yield (percent by weight)	80		
	Feed	Product	Product
Properties:			
ASTM-distillation (° F.)—			
IBP	196	109	
10%	201	165	
30%	208	205	
50%	217	226	
70%	235	243	
95%	385	336	
99%	430	385	
FBP	0.7256	0.7710	0.7897
d ₄ ²⁰			
Hydrocarbon Type, percent by weight—			
Paraffins	60.0	35.0	26.3
Olefins	1.5	0.7	0.5
Naphthenes	35.5		
Aromatics	3.0	64.3	73.2
Octane Number—			
F-1-1.5	abt. 78	68.5	103.3
F-2-1.5	abt. 78	87.3	89.1

We claim as our invention:

1. A process for converting an olefin feed consisting essentially of an olefin having from four through six carbon atoms per molecule into a high octane low sensitivity gasoline blending component which comprises contacting said olefin feed with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising a hydrogenation component deposited on an acid-acting support, separating the hydroisomerization liquid effluent into a light fraction boiling substantially below a cut point in the range of about 170° F. to 230° F. and a heavy fraction boiling substantially above said cut point, and contacting the heavy fraction with hydrogen at reforming conditions in the presence of a reforming catalyst.

2. A process for converting an olefin feed consisting essentially of an olefin having from four through six carbon atoms per molecule into a high octane low sensitivity gasoline blending component which comprises contacting said olefin feed with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising nickel sulfide on silica-alumina cracking catalyst, separating the hydroisomerization liquid effluent into

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a light fraction boiling substantially below a cut point in range of about 170° F. to 230° F. and a heavy fraction boiling substantially above said cut point, and contacting the heavy fraction with hydrogen at reforming conditions in the presence of a platinum-containing reforming catalyst.

3. A process for converting a light catalytically cracked hydrocarbon fraction consisting essentially of normal olefins having from five through six carbon atoms per molecule boiling up to about 200° F. into a high octane low sensitivity gasoline blending component which comprises contacting said hydrocarbon fraction with hydrogen at a temperature of from about 400° F. to about 900° F. and a pressure of about 150 to about 1500 pounds per square inch in the presence of a hydroisomerization catalyst comprising nickel sulfide on silica-alumina cracking catalyst, separating the hydroisomerization liquid effluent into a light fraction boiling below a cut point in the range of about 170° F. to 230° F. and a heavy fraction boiling above said cut point, and contacting the heavy fraction with hydrogen at reforming conditions in the presence of a reforming catalyst.

4. A process for converting a normal olefin feed consisting essentially of an olefin having from four through six carbon atoms per molecule into a high octane low sensitivity gasoline blending component which comprises contacting said olefin feed with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising a hydrogenation component deposited on an acid-acting support, separating the hydroisomerization liquid effluent into a light fraction boiling below a cut point in the range of about 170° to 230° F. and a heavy fraction boiling above said cut point, and contacting the heavy fraction with hydrogen at reforming conditions in the presence of a reforming catalyst.

5. A process for converting a normal olefin feed consisting essentially of an olefin having from four through six carbon atoms per molecule into a high octane low sensitivity gasoline blending component which comprises contacting said olefin feed with hydrogen at a temperature of from about 400° F. to about 900° F. and a pressure of about 150 to about 1500 pounds per square inch in the presence of a hydroisomerization catalyst comprising nickel sulfide on silica-alumina cracking catalyst, separating the hydroisomerization liquid effluent into a light fraction boiling below a cut point in the range from about 170° F. to 230° F. and a heavy fraction boiling above said cut point, and contacting the heavy fraction with hydrogen at reforming conditions in the presence of a reforming catalyst.

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