

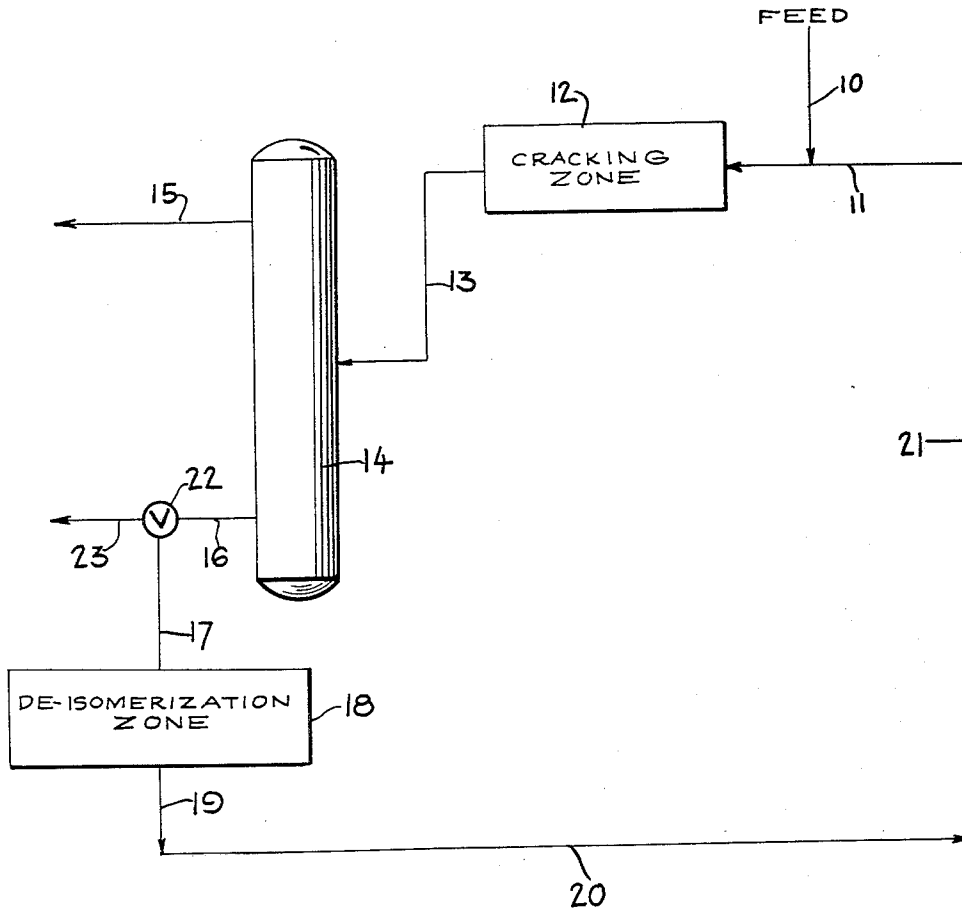
Aug. 23, 1960

P. B. WEISZ

2,950,240

SELECTIVE CRACKING ALIPHATIC HYDROCARBONS

Filed Oct. 10, 1958



INVENTOR
Paul B. Weisz
BY
Raymond W. Barclay
ATTORNEY

1

2,950,240

SELECTIVE CRACKING OF ALIPHATIC
HYDROCARBONSPaul B. Weisz, Media, Pa., assignor to Socony Mobil
Oil Company, Inc., a corporation of New York

Filed Oct. 10, 1958, Ser. No. 766,619

6 Claims. (Cl. 208—70)

This invention relates to a process for effecting selective cracking of aliphatic hydrocarbons including normal and isoaliphatics from a mixture of the same with cyclic hydrocarbons. Such hydrocarbon mixtures are normally present in petroleum and selected fractions of petroleum distillates or processing streams including for example, mixtures of normal paraffins, normal olefins, iso-paraffins, iso-olefins, naphthenes, aromatics, alkyl-aromatics, etc.

It is well known that the above mixtures of hydrocarbons may undergo catalytic cracking in the presence of cracking catalysts such as synthetic composites of silica and alumina or acid activated naturally occurring clays. It is also well known that cracking in the presence of these catalysts proceeds with different relative ease by different classes of hydrocarbons, namely in the order of decreasing ease of cracking:

- (1) Alkyl-aromatics, particularly with alkyl groups of two or more carbon atoms to dealkylated cracking products;
- (2) Naphthenes;
- (3) Iso-aliphatics;
- (4) Normal aliphatics.

The process of the present invention involves a cracking process which is unique in the order of reactivity toward the different classes of hydrocarbons as compared to the above-noted familiar processes.

In one embodiment, the present invention provides a continuous process which preferentially cracks normal aliphatic hydrocarbons, i.e. normal olefins or normal paraffins, from a hydrocarbon mixture or petroleum charge stock containing iso-aliphatic hydrocarbon and cyclic hydrocarbon components to the substantial exclusion of cracking of said components whether they be naphthenic or aromatic and regardless of the type and size of alkyl groups contained therein.

In accordance with the process of the invention, the charge stock initially containing normal aliphatic, iso-aliphatic and cyclic hydrocarbons is introduced into a continuous system comprising a catalytic de-isomerization zone and a catalytic cracking zone, the latter containing as catalyst a crystalline zeolite having rigid three-dimensional networks bearing catalytic surfaces active in hydrocarbon cracking and having uniform interstitial dimensions sufficiently large to sorb normal aliphatic components contained in the charge but sufficiently small to exclude the hydrocarbon components of larger molecular size, i.e. iso-aliphatic and cyclic hydrocarbons. Under such conditions, the normal aliphatic hydrocarbon components of the charge mixture capable of entering the interior pore structure of the above catalyst undergo cracking to lighter highly olefinic materials while the iso-aliphatic and cyclic hydrocarbon components, because of their larger molecular size are unable to penetrate the porous catalyst structure and accordingly undergo little or no catalytic cracking. The product emerging from the cracking zone containing uncracked charge components and products resulting from cracking of the normal aliphatic components is conducted to the de-isomerization zone where iso-aliphatic components are converted to normal aliphatic hydrocarbons. The prod-

2

uct from the de-isomerization operation is then recycled to the cracking zone where the normal aliphatic hydrocarbons produced during the de-isomerization step undergo cracking. The above cyclic cracking and de-isomerization operations are repeated any desired number of cycles. Generally, it is preferred to continue the recycle operation until the charge is substantially free of aliphatic hydrocarbons leaving a useful concentrate of cyclic hydrocarbons. The products resulting from the selective cracking step prior to de-isomerization, may be subjected to a suitable intermediate separation operation, such as by fractionation or other feasible means, wherein light materials produced, i.e. those boiling below the initial charge stock are removed and the remaining materials, of equal or higher boiling range than the charge stock, are then subjected to de-isomerization and thereafter recycled in the above continuous cracking and de-isomerization system until the desired extent of concentration of cyclic hydrocarbons is achieved.

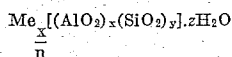
The process of the invention is useful for a number of applications. For example, jet fuels or other high energy fuels require a low aliphatic hydrocarbon content. Thus, the process applied to kerosine range petroleum fractions achieves selective cracking of aliphatic hydrocarbons leaving an energy-rich fuel of cyclic compounds which may be used as obtained or after being subjected to hydrogenation. Also, the process described herein is useful in production of aromatic oils and solvents. For such purpose suitable boiling range petroleum fractions are subjected to catalytic cracking of aliphatic hydrocarbon components to obtain a cyclic concentrate. The light materials resulting from cracking with the crystalline zeolite catalyst employed in such step are highly olefinic in character. Separation of these light olefinic materials from the heavier components before recycling the latter accordingly affords products susceptible to a wide variety of useful applications. Such products may be employed, for example, in the formation of high octane alkylate; they also may be used for the alkylation of benzene to form cumene or other alkyl benzenes; or they may be polymerized to liquid fuels or to form plastics such as polyethylene and polypropylene.

The charge material conducted to the present process is a mixture of normal aliphatic hydrocarbons, iso-aliphatic hydrocarbons and cyclic hydrocarbons. The normal aliphatic hydrocarbons may be normal paraffins or normal olefins or a mixture of the two. Likewise, iso-aliphatic hydrocarbons contained in the charge mixture may be iso-paraffins or iso-olefins or a mixture of the two. Cyclic hydrocarbons include naphthenes or aromatics or a mixture of the two. It will thus be apparent that the charge material may be a relatively simple hydrocarbon mixture or a complex mixture of hydrocarbons which may contain minor proportions of other materials such as sulfur, nitrogen and oxygen-containing components. Representative of the latter type mixtures is petroleum and various fractions thereof. A preferred charge for use in the present process is a petroleum fraction characterized by an aliphatic, iso-aliphatic and cyclic hydrocarbon content and having an approximate boiling range of 200 to 600° F. and in particular, a fraction of 180 to 320° F. boiling range obtained from a 98 octane number reformat characterized by an approximate boiling range of 180 to 400° F.

It is contemplated that the reaction conditions heretofore used in effecting catalytic cracking will be employed in the cracking step of the present process. Thus, catalytic cracking with the crystalline size-selective zeolite catalyst described herein may be carried out by contacting a hydrocarbon charge at catalytic cracking conditions employing a temperature within the approximate

range of 700° F. to 1200° F. and preferably between about 800° F. and about 1050° F. and under a pressure ranging from sub-atmospheric pressure up to several hundred atmospheres. The liquid hourly space velocity of the charge may range from 0.2 to 4.0 and preferably from 0.5 to 2.0. The catalyst may be used as pellets in a fixed bed operation or they may be used in a compact moving bed operation or in a fluidized operation. The contact time of the hydrocarbon charge with the catalyst is adjusted in any case according to the conditions, the particular charge stock and the particular results desired to give a substantial amount of cracking of the normal aliphatic hydrocarbon components to lower boiling products.

The cracking operation is particularly characterized by the presence of a catalyst comprising a crystalline synthetic or natural zeolite having a uniform pore size which permits passage of normal aliphatic hydrocarbons but excludes larger molecular size components. It is preferred to use as cracking catalyst a synthetic zeolite having uniform pore dimensions of about 5 Angstrom units made by dehydrating a synthetic metal aluminosilicate salt. The resulting dehydrated crystalline zeolites have the atoms thereof arranged in a definite crystalline pattern. Such structure contains a large number of small cavities interconnected by a number of still smaller channels. These cavities and channels are precisely uniform in size. It is essential for the present process that the zeolite catalyst have a uniform pore structure permitting entry into the interior thereof of normal aliphatic hydrocarbons but excluding entry of iso-aliphatic hydrocarbons, cyclic hydrocarbons and other components characterized by a molecular size greater than that of normal aliphatics. Generally, a catalyst fulfilling the above requirements has a uniform pore size of about 5 Angstrom units. Thus, if the pore size is materially smaller than 5 Angstrom units, the pores are too small to permit entry into the crystalline catalyst structure of normal aliphatics. If the pores are materially larger, the large hydrocarbon molecules, i.e. iso-aliphatics and cyclic hydrocarbons are able to enter the pores of the catalyst structure so that selective catalytic cracking of the normal aliphatic components cannot thereby be achieved. Chemically, the zeolites employed herein as catalysts in the cracking zone may be represented by the general formula:



where Me is a metal cation,

$$\frac{x}{n}$$

is the number of exchangeable metal cations of valence n , x is also the number of aluminum ions combined in the form of aluminate, y is the number of silicon atoms, and z is the number of water molecules, removal of which produces the characteristic channel system. In the above formula,

$$\frac{y}{x}$$

is a number from 1 to 5 and usually from 1 to 2. Zeolites having the above characteristics have sometimes been referred to as molecular sieves. At the present time, there are commercially available molecular sieves having channels of about 5 Angstroms in diameter. Such material known as "Molecular Sieve 5A" is essentially the crystalline calcium aluminosilicate prepared by base-exchange of a crystalline sodium aluminosilicate having channels of about 4 Angstroms in diameter, known as "Molecular Sieve 4A" and characterized by the formula: $\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$, it being understood that calcium replaces sodium in the ratio of one calcium ion for two sodium ions.

Such molecular sieves consist fundamentally of a three-dimensional tetrahedral structure of silicon and aluminum. These tetrahedra are joined by sharing oxygen atoms in such a manner that the ratio of atoms of oxygen to the total number of atoms of aluminum and silicon is equal to two. The electrovalence of the tetrahedra containing aluminum is balanced by the inclusion in the crystal of a cation, for example, an alkali metal or an alkaline earth metal cation. This equilibrium can be expressed by the formula wherein the ratio of Al_2 to the number of the various cations such as Ca, Sr, Na_2 , K_2 or Li_2 , is equal to unity. One cation may be exchanged either in entirety or partially by another cation utilizing ion exchange techniques. The spaces between the tetrahedra are occupied by molecules of water prior to dehydration.

The above molecular sieves are ordinarily prepared initially in the sodium form of the crystal. The sodium ion in such form may, as desired, be exchanged for other alkali metal or other alkaline earth metal cations. In general, the process of preparation involves heating, in aqueous solution, an appropriate mixture of oxides, or of material whose chemical composition can be completely represented as a mixture of oxides Na_2O , Al_2O_3 , SiO_2 and H_2O at a temperature of approximately 100° C. for periods of 15 minutes to 90 hours or more. The product which crystallizes within this hot mixture is separated therefrom and water washed until the water in equilibrium with the zeolite has a pH within the range of 9 to 12. The material is thereafter activated by heating until dehydration is attained.

It is to be noted that the sodium form of the above zeolite, i.e. "Molecular Sieve 4A" is catalytically inactive for use as a cracking catalyst in the process of the present invention. However, such inactive form may be rendered highly active in catalytically selectively cracking normal aliphatic hydrocarbons in the present process by the simple procedure of cation exchange of calcium for sodium after crystallization. By base-exchanging the sodium aluminosilicate salt with a calcium ion-containing solution, the salt becomes catalytically active in selectively cracking normal aliphatic hydrocarbons and has a resulting uniform pore diameter of about 5 Angstrom units.

While calcium aluminosilicate characterized by uniform pores of approximately 5 Angstroms in diameter, i.e. "Molecular Sieve 5A" is preferred for use as the catalyst in the cracking step of the present process, it is contemplated that other metal aluminosilicates having a uniform pore size of about 5 Angstrom units may also suitably be employed as the cracking catalyst. Thus, aluminosilicate salts, containing a divalent metal ion and in particular an alkaline earth metal such as strontium or magnesium, capable of sorbing at least 10 percent of their weight of n -hexane but negligible amounts of iso-hexanes when brought into contact with liquid hexane at substantially atmospheric pressure and a temperature of about 25° C. are suitable for use in the cracking step of the present process. The sodium form of the above zeolite exchanged with calcium or other of the above-indicated divalent metals possesses larger pores than the unexchanged material. An unusual characteristic of the calcium or other divalent metal exchanged zeolite is that the opening of the pores is not accomplished progressively as the sodium ions are replaced by calcium or other divalent ions but is produced within a fairly narrow range of composition. When the exchange is 25 percent or less, the substance possesses substantially the same pore characteristics as the sodium form of the zeolite, namely a pore diameter of about 4 Angstrom units. However, when the exchange is in substantial excess of about 25 percent, the pore characteristics become those of the calcium form of the zeolite, i.e. a pore diameter of about 5 Angstrom units. Accordingly, it will be appreciated that the crystalline aluminosilicate zeolite employed as

cracking catalyst in the process of the present invention may be a mixed salt of sodium and calcium or of sodium and one or more of the other above-indicated suitable divalent metal ions, it being essential that the pore diameter of the resulting composition be sufficiently large to admit normal aliphatic hydrocarbons and sufficiently small to exclude hydrocarbons having a molecular size exceeding that of the aliphatics.

It is also contemplated that the size-selective catalyst may be a composite comprising a major proportion of the above-described crystalline zeolite and a minor proportion of one or more materials which may act as promoters or activators or otherwise enhance the desired catalytic conversion while the crystalline zeolite is responsible for the major size-selective characteristics. In this regard, the crystalline zeolite may suitably be composited with activated clays, vanadia, thoria, zirconia, molybdena, silica, alumina or combinations thereof. Such composites may be prepared by impregnation of the crystalline zeolite with the added substance or by mechanical admixture of the two materials usually followed by shaping of the resulting composite into particles by casting, pelleting, extrusion or other suitable means.

The product from the cracking zone is conducted to a de-isomerization zone. As an aid in the understanding of the action taking place in the de-isomerization zone, it is to be recognized that thermodynamic equilibria between normal and isomeric aliphatics requires substantial quantities of both of these components to be present in the equilibrium product. Thus, an isomerization reaction will effect a net shift to isomeric products when the feed stock is rich in normal aliphatic hydrocarbons, or a net conversion to normal aliphatics when the feed stock is rich in isomer components. The latter will be the case in the process of the present invention since the selective cracking action taking place in the cracking zone, and removal of light cracked products, results in an iso-enriched product which is conducted to the de-isomerization zone. It will accordingly be understood that this zone has been termed "de-isomerization zone" to characterize the unconventional method of use as well as resultant chemical conversion, although the de-isomerization step is carried out under conditions and in the presence of catalysts conventionally employed in isomerization reactions. Thus, the catalyst employed may be a Friedel-Crafts type catalyst such as aluminum chloride, aluminum bromide, aluminum iodide, aluminum fluoride, boron trifluoride, iron chloride, complexes thereof with organic and inorganic compounds and other halogen-containing catalysts such as hydrogen fluoride. Generally, however, it is preferred to employ, as a catalyst, a metal-acidic oxide type isomerization catalyst which affords substantial de-isomerization without appreciable material losses by cracking reactions. Suitable catalysts of such type include generally, metals of group VIII of the periodic system such as cobalt, nickel, platinum, and palladium supported upon carriers such as silica, alumina or composites thereof. Also, an isomerization catalyst made up of a mechanical mixture of a platinum metal deposited on alumina and a silica-alumina cracking component may be utilized as the catalyst. Isomerization using the latter mechanically mixed catalyst is described in my co-pending application Serial Number 633,189 filed January 9, 1957, now U.S. Patent No. 2,892,003.

Generally, the de-isomerization step will be carried out at a temperature between about 650° F. and about 900° F., at a liquid hourly space velocity between about 0.5 and about 20, employing a hydrogen to hydrocarbon molar ratio of between about 0.5 and about 20, and a pressure of between about 50 p.s.i.g. and about 1000 p.s.i.g. All of the aforementioned variables are interrelated. As a practical matter, the temperature of operation is generally fixed as a result of primary choice with respect to other variables and the desired conversion level.

In the de-isomerization zone, the iso-aliphatic components contained in the charge are converted to normal aliphatic hydrocarbons. The products resulting from the cracking zone prior to introduction to the de-isomerization zone are suitably separated into light materials boiling below the range of the initial charge stock and materials of equal or higher boiling range than the initial charge stock. The latter are subjected to de-isomerization and thereafter recycled to the cracking zone. The lighter materials removed are highly olefinic and are suitable for use in a variety of applications described hereinabove.

A schematic flow diagram of the process of the present invention is shown in the attached figure. Referring more particularly to such figure, the hydrocarbon feed initially containing normal aliphatic hydrocarbons, iso-aliphatic hydrocarbons, and cyclic hydrocarbons is conducted through lines 10 and 11 to cracking zone 12. Selective catalytic cracking of the normal aliphatic hydrocarbon components takes place in the cracking zone in the presence of the above-described crystalline size-selective zeolite catalyst maintained under catalytic cracking conditions. The product emerges from the cracking zone through line 13 and is conducted to a fractionating column 14. Light materials, highly olefinic in content, boiling below the initial charge stock are removed as overhead through line 15. Materials having a boiling point at least equal to that of the initial charge are removed as bottoms from fractionating column 14 through line 16 and conducted through line 17 to de-isomerization zone 18 wherein the iso-aliphatic hydrocarbon components are converted in the presence of a suitable isomerization catalyst to normal aliphatic hydrocarbons. The product from the de-isomerization zone is recycled through lines 19, 20, 21 and 11 to the cracking zone 12. When a product of desired cyclic hydrocarbon content is obtained, the same is removed from the system by adjusting valve 22 permitting all or a portion of the product stream flowing through line 16 to be withdrawn through conduit 23.

The following example will serve to illustrate the process of the invention without limiting the same:

A petroleum distillate containing approximately 35 percent by weight aliphatic and approximately 65 percent by weight cyclic constituents and boiling in the range of 400 to 500° F. is used as the charge stock. The aliphatic component of such charge contains about 20 percent by weight of normal paraffins and about 15 percent by weight of iso-paraffins. The charge in the ratio of 1 part of fresh stock to 3 parts of recycle stock is subjected to cracking in the presence of a catalyst of Molecular Sieve 5A at a temperature of 900° F. and a liquid hourly space velocity of ½ based on fresh feed. The product resulting from cracking is then distilled. The fraction boiling substantially below 400° F., constituting about 32 weight percent of the distillation charge, is continuously withdrawn. This product consists essentially of gasoline and gas range hydrocarbons, primarily light normal paraffins and olefins. The fraction boiling above 400° F. is divided into two streams. One stream constituting 67 weight percent of such fraction serves as the recycle charge. Before returning such recycle charge to the cracking zone, the same is passed through a de-isomerization zone containing a platinum-silica-alumina isomerization catalyst at a temperature of 770° F., a total pressure of 300 p.s.i.g. with admixture of hydrogen in a molar ratio of 6 to 1 in relation to the hydrocarbon flow rate. The remaining 23 weight percent of the fraction boiling above 400° F. is withdrawn as cyclic concentrate product, containing less than 10 percent by weight of total paraffins.

It will be understood that the above description is merely illustrative of preferred embodiments of the invention, of which many variations may be made within

the scope of the following claims by those skilled in the art without departing from the spirit thereof.

I claim:

1. A continuous method for selectively cracking aliphatic hydrocarbons from a mixture of the same with cyclic hydrocarbons and obtaining a resultant cyclic hydrocarbon concentrate which comprises conducting a charge initially containing normal aliphatic, iso-aliphatic and cyclic hydrocarbon components in a continuous system to a cracking zone maintained under catalytic cracking conditions and containing a cracking catalyst comprising a crystalline zeolite having a uniform pore structure of sufficient size to afford entry into the catalyst structure of normal aliphatic hydrocarbon components while excluding hydrocarbon components of larger molecular size whereby said normal aliphatic hydrocarbon components are selectively cracked, subjecting the resulting mixture of cracked and uncracked components to de-isomerization in the presence of an isomerization catalyst and under catalytic isomerization conditions whereby iso-aliphatic components are converted to normal aliphatic hydrocarbons, recycling the resulting product to said cracking zone, repeating the aforesaid treatment on a continuous cyclic basis to yield a concentrate of cyclic hydrocarbons and removing said concentrate from said continuous system.

2. A continuous method for selectively cracking aliphatic hydrocarbons from a mixture of the same with cyclic hydrocarbons and obtaining a resultant cyclic hydrocarbon concentrate which comprises contacting a charge initially containing normal aliphatic, iso-aliphatic and cyclic hydrocarbon components under catalytic cracking conditions with a cracking catalyst comprising a crystalline zeolite having a uniform pore structure of sufficient size to afford entry into the catalyst structure of normal aliphatic hydrocarbon components while excluding hydrocarbon components of larger molecular size whereby said normal aliphatic hydrocarbon components are selectively cracked, subjecting the resulting product mixture to fractionation, removing as overhead the lighter materials having a boiling point below that of the initial charge mixture, removing as bottoms a fraction having a boiling point at least equal to that of the initial charge mixture, subjecting said bottoms to de-isomerization in the presence of an isomerization catalyst and under catalytic isomerization conditions whereby iso-aliphatic components are converted to normal aliphatic hydrocarbons, recycling the product from de-isomerization to said cracking zone and repeating the aforesaid treatment on a continuous cyclic basis to yield a concentrate of cyclic hydrocarbons and removing said concentrate from said continuous system.

3. A continuous method for treating a petroleum fraction characterized by a normal aliphatic, an iso-aliphatic, and cyclic hydrocarbon content and having an approximate boiling range of 200 to 600° F. which comprises contacting said mixture in a cracking zone maintained under catalytic cracking conditions with a cracking catalyst comprising a crystalline zeolite having a pore size of about 5 Angstrom units in diameter whereby said normal aliphatic hydrocarbon components are selectively cracked, contacting the resulting mixture of cracked and uncracked components to de-isomerization in the presence of an isomerization catalyst and under catalytic isomerization conditions whereby iso-aliphatic components are converted to normal aliphatic hydrocarbons, recycling the resulting product to said cracking zone, repeating the aforesaid treatment on a continuous cyclic basis to yield a concentrate of cyclic hydrocarbons and removing said concentrate from said continuous system.

4. A continuous method for treating a petroleum fraction characterized by a normal aliphatic, an iso-aliphatic, and cyclic hydrocarbon content and having an approximate boiling range of 200 to 600° F. which comprises contacting said mixture in a cracking zone maintained

under catalytic cracking conditions with a cracking catalyst comprising a crystalline zeolite having a pore size of about 5 Angstrom units in diameter whereby said normal aliphatic hydrocarbon components are selectively cracked, subjecting the resulting product mixture to fractionation, removing as overhead the lighter materials having a boiling point below that of the initial charge mixture, removing as bottoms a fraction having a boiling point at least equal to that of the initial charge mixture, subjecting said bottoms to de-isomerization in the presence of an isomerization catalyst and under catalytic isomerization conditions whereby iso-aliphatic components are converted to normal aliphatic hydrocarbons, recycling the product from de-isomerization to said cracking zone and repeating the aforesaid treatment on a continuous cyclic basis to yield a concentrate of cyclic hydrocarbons and removing said concentrate from said continuous system.

5. A continuous method for selectively cracking aliphatic hydrocarbons from a mixture of the same with cyclic hydrocarbons and obtaining a resultant cyclic hydrocarbon concentrate which comprises contacting a charge initially containing normal aliphatic, iso-aliphatic and cyclic hydrocarbon components under catalytic cracking conditions with a cracking catalyst comprising a crystalline calcium aluminosilicate having a pore size of about 5 Angstroms in diameter whereby said normal aliphatic hydrocarbon components are selectively cracked, subjecting the resultant mixture of cracked and uncracked components to de-isomerization in the presence of an isomerization catalyst and under catalytic isomerization conditions whereby iso-aliphatic components are converted to normal aliphatic hydrocarbons, recycling the resulting product to said cracking zone, repeating the aforesaid treatment on a continuous cyclic basis to yield a concentrate of cyclic hydrocarbons and removing said concentrate from said continuous system.

6. A continuous method for selectively cracking aliphatic hydrocarbons from a mixture of the same with cyclic hydrocarbons and obtaining a resultant cyclic hydrocarbon concentrate which comprises contacting a charge initially containing normal aliphatic, iso-aliphatic and cyclic hydrocarbon components under catalytic cracking conditions with a cracking catalyst comprising a crystalline calcium aluminosilicate having a pore size of about 5 Angstroms in diameter whereby said normal aliphatic hydrocarbon components are selectively cracked, subjecting the resulting product mixture to fractionation, removing as overhead the lighter materials having a boiling point below that of the initial charge mixture, removing as bottoms a fraction having a boiling point at least equal to that of the initial charge mixture, subjecting said bottoms to de-isomerization in the presence of an isomerization catalyst and under catalytic isomerization conditions whereby iso-aliphatic components are converted to normal aliphatic hydrocarbons, recycling the product from de-isomerization to said cracking zone and repeating the aforesaid treatment on a continuous cyclic basis to yield a concentrate of cyclic hydrocarbons and removing said concentrate from said continuous system.

References Cited in the file of this patent

UNITED STATES PATENTS

1,840,450	Jaeger et al. -----	Jan. 12, 1932
2,326,779	Houdry -----	Aug. 17, 1943
2,469,733	Kearby -----	May 10, 1949
2,666,022	Johnson -----	Jan. 12, 1954

FOREIGN PATENTS

487,392	Canada -----	Oct. 21, 1952
715,474	Great Britain -----	Sept. 15, 1954

OTHER REFERENCES

"Isomerization of Pure Hydrocarbons," Egloff et al., publisher, Reinhold Publishing Corp., 1942, New York, N.Y., pages 232 to 235.