

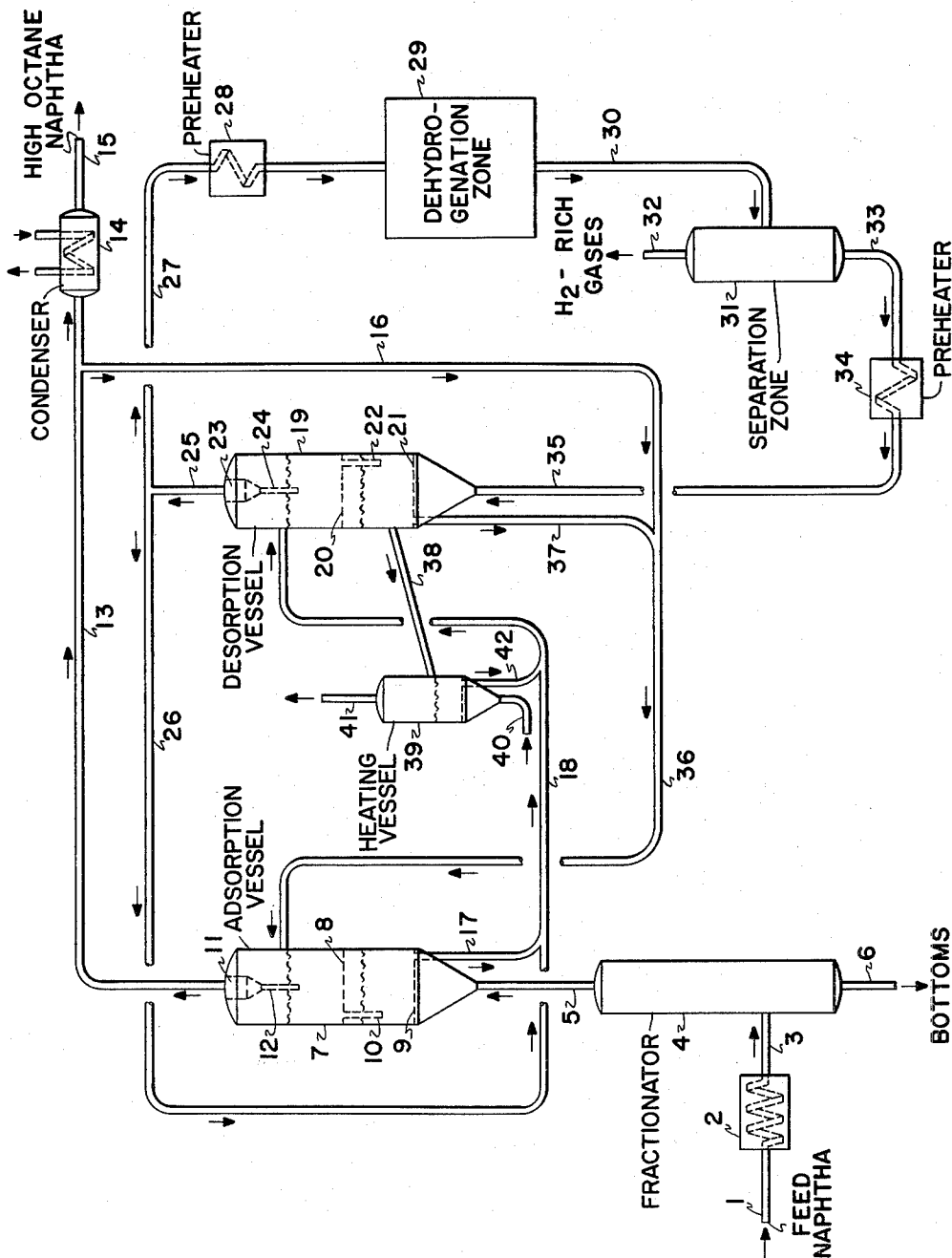
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MOLECULAR SIEVE PROCESS FOR UPGRADING NAPHTHA WHEREIN THE
DESORBED STRAIGHT CHAIN HYDROCARBONS ARE DEHYDROGENATED
AND USED AS DESORBING AGENTS

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MOLECULAR SIEVE PROCESS FOR UPGRADING NAPHTHA WHEREIN THE DESORBED STRAIGHT CHAIN HYDROCARBONS ARE DEHYDROGENATED AND USED AS DESORBING AGENTS

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The present invention relates to the preparation of high octane motor fuels and more particularly relates to an improved process for upgrading naphtha for use as a blending stock in the preparation of high octane gasolines.

The increasing demand for gasolines having higher octane numbers has in recent years necessitated a considerable change in the blending stocks utilized by petroleum refiners for the preparation of gasolines. Present octane levels require the use of large quantities of relatively high octane blending stocks such as catalytic naphtha, polymer gasoline, hydroformate and the like and permit the inclusion of much lesser amounts of light virgin naphtha than were formerly used in gasoline blending. This trend away from the use of light virgin naphtha as a blending stock has created surpluses of such naphtha at many refineries. At the same time the production of the higher octane blending stocks in quantities sufficient to supply the demand for premium quality gasolines in an expanding market has become a serious problem for many refineries.

The octane deficiency of light virgin naphtha is due primarily to the presence therein of low molecular weight normal paraffins, particularly normal pentane and normal hexane. Since these compounds which are extremely low in octane number often constitute 35 percent or more of the total light naphtha fraction, they severely depreciate the overall value of the naphtha as a blending stock. The present invention provides an improved process for upgrading light naphtha wherein such normal paraffins are converted into olefins having much higher octane blending values.

In accordance with the process of the invention, the light virgin naphtha to be upgraded is first fractionated to obtain a C₅ to about 175° F. fraction and this fraction is then contacted with a molecular sieve adsorbent in order to segregate the normal paraffins present in the fraction from the higher octane isoparaffins and cyclic compounds. The normal paraffins recovered from the molecular sieve are dehydrogenated to form olefins. The olefins thus prepared are used as the sieve desorbent for removing adsorbed normal paraffins and are in turn replaced by more normal paraffins during the succeeding adsorption step. The olefins leave the process with the unadsorbed isoparaffins and cyclic compounds, forming a naphtha stream which has a significantly higher octane value. This particular combination of process steps has been found to be especially advantageous in that the preparation of olefins from the normal paraffins permits effective utilization of these low octane constituents of the naphtha and results in high overall yields for the process. The olefins are used for desorption of the molecular sieve and are then passed directly into the product naphtha stream, eliminating the necessity for intermediate separation steps. The process is a continuous one and results in a significant improvement in the light virgin naphtha fraction.

The molecular sieve adsorbents employed for the sep-

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aration of normal paraffins from isoparaffins and cyclic compounds in the process of the invention are crystalline zeolite compounds. It has long been recognized that certain such zeolites possess selective adsorptive properties. These properties are due to the presence in the zeolite crystals of minute pores which are extremely uniform in size. These pores may have diameters of from about 3 Angstrom units to about 13 or more Angstrom units, depending upon the composition of the zeolite and the conditions under which the crystals were formed. Adsorption upon the zeolites takes place within these minute pores and therefore only those compounds whose molecules are small enough to enter the pores can be adsorbed. Because of this particular adsorption action, such zeolites are commonly referred to as molecular sieves.

Molecular sieves are normally alkali metal or alkaline earth metal aluminosilicates, and may be either natural or synthetic in origin. Analcite and chabazite are typical naturally-occurring molecular sieves and have the formulae NaAlSi₃O₈·H₂O and NaAl₂Si₄O₁₂·6H₂O, respectively. Other natural zeolites having molecular sieve properties are described in an article entitled "Molecular Sieve Action of Solids," which appeared in Quarterly Review, volume 3, pages 293-320 (1949), published by the Chemical Society (London). U.S. Patent 2,306,610 describes a synthetic molecular sieve having the formula (CaNa₂)Al₂Si₄O₁₂·2H₂O. U.S. Patent 2,522,426 teaches the preparation of a synthetic molecular sieve represented by the formula 4CaO·Al₂O₃·4SiO₂. Numerous other references to similar synthetic molecular sieve adsorbents may be found in the chemical and patent literature.

A particularly effective synthetic molecular sieve of high adsorptive capacity and suitable for use in the process of the present invention may be prepared by heating sodium aluminate and sodium metasilicate together at a temperature between about 180 and 200° F. to form crystals having pore diameters of about 4 Angstrom units. The crystals thus formed are treated with a calcium salt such as calcium chloride in a base exchange reaction to produce a molecular sieve of 5 Angstrom unit pore diameters. This sieve may then be mixed with a suitable binder such as bentonite or sodium silicate and extruded into pellets which, after drying and calcining, are suitable for use under fluidized solids conditions.

The dehydrogenation step of the process of the invention is preferably a catalytic one, although thermal reforming and other similar dehydrogenation processes well known in the art may be employed. Metal oxides such as chromium oxide are preferred dehydrogenation catalysts for the process.

The exact nature of the invention can be more fully understood from the following detailed description and the accompanying drawing which illustrates a preferred embodiment of the invention.

Referring now to the drawing, a light virgin naphtha introduced through line 1 and vaporized in preheater 2 is passed through line 3 into fractionator 4. An overhead fraction boiling up to about 175° F. is taken off through line 5 and a bottoms fraction boiling above about 175° F. is removed through line 6 for further processing or storage. The overhead fraction contains substantial quantities of n-pentane and n-hexane, as well as isomeric compounds. This fraction is introduced through line 5 into adsorption vessel 7 where it is contacted with a 5 A. molecular sieve adsorbent under fluidized solids conditions. As will be apparent later, the molecular sieve particles present in adsorption zone 7 have olefins adsorbed therein. These particles containing olefins are present in vessel 7 in a finely divided form and may range in size from about 100 to 400 mesh. The particles are maintained in a dense turbulent mass or bed within the vessel by the upflowing naphtha vapors. The bed is pref-

erably maintained in two or more separate stages interconnected by downcomers in order to achieve maximum contacting efficiency between the naphtha and adsorbent. The vapor velocity through the bed is preferably controlled within the range of about 0.5 to 5.0 feet per second. Vessel 7 may be provided with perforated plates 8 and 9 or with other suitable members for supporting the stages of the bed and obtaining even distribution of vapor over the bed cross-section. Downcomer 10 provides for transfer of solids from the upper to the lower stage of the bed. A cyclone separator 11 in the upper portion of the vessel serves to remove sieve particles entrained in the vapor as it leaves the upper stage of the fluidized bed. Particles of sieve removed by the separator are returned to the bed through dip pipe 12. It will be understood that although a fluidized bed having two stages is depicted in the drawing, it may be desired to employ additional stages in order to achieve maximum adsorption.

The temperature within adsorption vessel 7 is preferably maintained in the range from about 100 to 500° F. and the pressure may range from atmospheric to about 500 p.s.i.g. Temperatures of about 250 to 400° F. and pressures of about 50 to about 150 p.s.i.g. are particularly preferred. Heating coils or a suitable jacket may be provided for purposes of temperature control. As the naphtha vapor passes upward through the molecular sieve bed under these conditions, normal paraffins are adsorbed by the sieve, replacing the olefins contained therein, while branched chain and cyclic constituents pass through unadsorbed and leave the vessel with the desorbed olefins through line 13. The major portion of these unadsorbed constituents of the naphtha and desorbed olefins is then condensed in condenser 14 and withdrawn as product through line 15. This stream may be employed directly as a blending stock for the preparation of high octance gasoline. A minor portion of the uncondensed olefins, isoparaffins and cyclic compounds is withdrawn from line 13 through line 16 and recycled to the adsorption zone as a conveying gas, as will be explained below.

As the normal paraffins are adsorbed upon the molecular sieve particles in vessel 7, the particles move downwardly from the upper stage of the bed to the lower stage through downcomer 10. Sieve particles containing adsorbed normal paraffins are continuously withdrawn from the lower stage in vessel 7 through standpipe 17 and are suspended in a gas stream flowing through line 18 into desorption vessel 19. The conveying gas in line 18 may be a stream of normal paraffins recycled from the desorption vessel as will be explained below. The sieve particles carried through line 18 are introduced into the upper section of desorption vessel 19 into the upper stage of a staged, fluidized bed similar to that maintained in vessel 7. Perforated plates 20 and 21 or similar members are provided to support the stages of the bed and a downcomer 22 interconnects the stages. Again more than the two stages shown may be employed if desired. Temperatures in the desorption vessel are maintained somewhat higher than those in vessel 7 and are preferably from about 100 to 200° F. above the adsorption temperatures. Suitable jacketing, heat coils or the like may again be provided for purposes of temperature control. The pressure in the desorption vessel is maintained from about 10 to about 50 p.s.i.g. below that in vessel 7 and may range between about atmospheric and about 450 p.s.i.g. The normal paraffins contained in the sieve interstices are replaced by olefins in vessel 19 under these conditions. The liberated normal paraffins pass upwardly through a cyclone separator 23, where entrained sieve particles are removed and returned through dip pipe 24 to the upper stage of the fluidized bed, and are withdrawn from the desorption vessel through line 25. The normal paraffins used as a conveying gas for carrying the sieve particles from vessel 7 into vessel 19 pass through the cyclone separator and are withdrawn with the desorbed normal paraffins. A portion of this stream

is then recycled from line 23 through line 26 and into line 18 to again serve as the conveying gas.

The remainder of the normal paraffin stream removed overhead from desorption vessel 19 through line 25 is passed through line 27 and preheater 28 into dehydrogenation zone 29 where the normal paraffins are partially dehydrogenated into olefins. Thermal reforming and other processes well known in the art for producing olefins from saturated aliphatic compounds may be utilized for the purposes of the invention but it is preferred that the dehydrogenation reaction be carried out catalytically in the presence of a chromium oxide catalyst supported upon a suitable carrier. Alumina carriers are preferred. Other catalysts which may be employed for the dehydrogenation reaction include oxides of the transition metals of groups IV, V and VI of the periodic table and mixtures of such oxides. The dehydrogenation temperature may range between about 750° F. and about 1300° F., temperatures between about 900° F. and about 1200° F. being preferred. The dehydrogenation reaction is preferably conducted at about atmospheric pressure and the space velocity may range between about 500 and 5000 volumes of normal paraffins per volume of catalyst per hour. Space velocities on the order of from 1000 to 3000 volumes per volume per hour are preferred. Two or more dehydrogenation reactors may be employed in parallel in order to permit regeneration of the catalyst by burning off carbonaceous deposits with air or other oxygen-containing gases, or instead a fluidized system wherein the catalyst is continuously circulated between a reactor and a regenerator may be employed. The use of such a fluidized system is normally preferred.

Sieve particles containing adsorbed olefins are continuously withdrawn from the bottom of vessel 19 through standpipe 37 at an equilibrium rate and returned as a suspension in a gaseous stream of isoparaffins, olefins and cyclic compounds through line 36 to the upper stage of the fluidized bed in adsorption vessel 7. The stream of isoparaffins, olefins and cyclic compounds recycled from line 13 through line 16 is utilized for this purpose. Upon reaching vessel 7 the conveying gas passes through cyclone separator 11 and is again discharged through line 13 with the unadsorbed materials.

The products from dehydrogenation zone 29 include sizable amounts of hydrogen and other normally gaseous products as well as olefins and unconverted normal paraffins. Normally gaseous products are separated from the olefins and normal paraffins by passing the product stream withdrawn from dehydrogenation zone 29 through line 30 and separation zone 31. Hydrogen-rich gases are taken overhead from the separation zone through line 32, and olefins and unconverted normal paraffins are withdrawn as a bottoms product through line 33. These olefins and normal paraffins are vaporized in preheater 34 and passed through line 35 into desorption zone 19. The upflowing vapors maintain the bed in zone 19 in a fluidized state. The normal paraffins contained in the sieve interstices are replaced by olefins under these conditions. The normal paraffins introduced with the olefins pass through the desorption zone unaffected and are removed, together with the liberated normal paraffins, through line 25.

During the adsorption and desorption of normal paraffins by the molecular sieves, small amounts of water and other polar compounds, such as sulfur-containing materials, picked up from the feed stream by the sieves result in a reduction in the sieve adsorption capacity. These components have a higher affinity for the sieve pores than do hydrocarbons and hence are not desorbed by replacement. The buildup of these materials is generally relatively slow, but as they accumulate they must be removed in order to maintain the sieve capacity at a high level. A small side stream, comprising from about 1 to about 10 percent of the material in desorber 19, is continuously or intermittently withdrawn through aerated

line 38 to a heating vessel 39 wherein the withdrawn solids are preferably maintained in a fluidized state, as described in connection with adsorber 7 and desorber 19. Hot flue gas, air or inert gas is admitted into vessel 39 through line 40 in order to supply heat and act as a flushing medium for the sieve. The gases are preferably at a temperature of from about 700 to 850° F., and a residence time on the order of about 10 to 120 seconds is maintained in order to desorb the polar contaminants. Hydrocarbons such as methane or ethane may also be used for this reactivation purpose. A suitable source of such hydrocarbons is the low molecular weight gases remaining after hydrogen has been removed from the normally gaseous products from dehydrogenation zone 29. The use of such hydrocarbons is preferred because it results in a minimum transfer of non-hydrocarbon gases into the desorption vessel. Hot gases are removed from regeneration zone 39 through overhead line 41 and the regenerated sieve is withdrawn through standpipe 42, entrained in the normal paraffin stream passing through line 18, and returned to desorption vessel 19.

The process of the invention may be further illustrated by considering a typical application of the process in a commercial refinery processing approximately 100,000 barrels per day of West Texas crude. This crude contains about 15 percent by volume of light naphtha boiling below about 200° F. and upon fractionation a C₅ to 175° F. cut of approximately 9000 barrels per day is obtained. The composition and octane values of this C₅-175° F. cut are as follows.

Table I

Component	B./D.	Vol. Percent	RON Clear	RON+3 cc. TEL
n-paraffins	3,032	32.8	44.8	78.3
Isoparaffins and Cyclics	6,200	67.2	87.1	100
Total Cut	9,232	100	73.4	94.6

The normal paraffin contained in this fraction are segregated and dehydrogenated to form C₅ and C₆ olefins in the manner described above.

The product naphtha fraction obtained from the process has the following composition and octane values:

Table II

Component	B./D.	Vol. Percent	RON Clear	RON+3 cc. TEL
Isoparaffins and Cyclics	6,200	72	87.1	100
Olefins	2,424	28	96.7	100.3
Total Cut	8,624	100	90.5	100.1

From the foregoing tables it can be seen that the process permits an increase in leaded octane number of from 94.6 to 100.1 with a 94.3 percent yield based upon the total C₅-175° F. fraction. In addition, 1.58 million standard cubic feet of hydrogen per day and 1.65 million standard cubic feet of light hydrocarbon gases per day are produced. These gases may be employed in hydrodesulfurization, various polymerization processes and the like and therefore constitute a net credit to the process.

The process of the invention may be readily combined with other processes known in the art to achieve even greater improvements in total octane value. In some instances it may, for example, be highly advantageous to hydroform the fraction of the light naphtha boiling above 175° F. to produce a further 100+ octane stream. It has been found that, although light virgin naphtha itself in some cases does not constitute a good feed stream for the hydroforming process, the fraction of the naphtha boiling above 175° F. may be advantageously treated in this manner.

It will be understood that the foregoing description of

the invention and the attached drawing are intended to exemplify the invention but are not intended as limitations as to the scope thereof. Many modifications which may be made in the process of the invention will be apparent to those skilled in the art.

What is claimed is:

1. A process for upgrading a light virgin naphtha containing normal paraffins in the C₅ to 175° F. boiling range which comprises: contacting said naphtha with a molecular sieve adsorbent having pore diameters of about 5 A., selectively adsorbing said normal paraffins upon said molecular sieve and desorbing olefins adsorbed thereon, said olefins having the same number of carbon atoms per molecule as said normal paraffins; withdrawing and recovering a product stream containing said desorbed olefins and unadsorbed constituents of said naphtha; desorbing said normal paraffins from said adsorbent and concomitantly adsorbing olefins having the same number of carbon atoms per molecule as said normal paraffins thereon; dehydrogenating at least part of the said desorbed normal paraffins to the corresponding olefins in a dehydrogenation zone; and thereafter passing thus formed olefins and unconverted normal paraffins from said dehydrogenation zone to said normal paraffin desorption step.

2. A process as defined by claim 1 wherein said normal paraffins are catalytically dehydrogenated to olefins.

3. A process as defined by claim 1 wherein said normal paraffins are adsorbed upon said molecular sieve adsorbent in a staged fluidized bed.

4. A process as defined by claim 1 wherein said normal paraffins are adsorbed upon said molecular sieve adsorbent at a temperature in the range of from about 250° to about 400° F. and at a pressure of from about 50 to about 150 p.s.i.g.

5. A process as defined by claim 1 wherein said normal paraffins are desorbed from said molecular sieve adsorbent at a temperature of from about 100° to 200° F. above the adsorption temperature and at a pressure of from about 10 to about 50 p.s.i. below the adsorption pressure.

6. A process for preparing high octane gasoline blending stocks which comprises contacting a vaporized C₅ to 175° F. light virgin naphtha fraction in an adsorption zone with a molecular sieve adsorbent having pore diameters of about 5 A. and containing adsorbed C₅ and C₆ olefins, selectively adsorbing normal paraffins from said fraction and desorbing said olefins upon said adsorbent at a temperature of from about 100° to about 500° F. and a pressure of from about atmospheric to about 500 p.s.i.g., withdrawing a product stream from said adsorption zone comprising said desorbed olefins and unadsorbed constituents of said naphtha fraction, passing adsorbent containing adsorbed normal paraffins to a desorption zone, desorbing said normal paraffins and adsorbing C₅ and C₆ olefins from a dehydrogenation zone upon said adsorbent at a temperature of from 100° to 200° F. above the temperature in said adsorption zone and a pressure about 10 to 50 p.s.i. below the pressure in said adsorption zone, converting at least part said desorbed normal paraffins to C₅ and C₆ olefins in a dehydrogenation zone at a temperature of from about 750° to 1300° F. in the presence of a dehydrogenation catalyst, passing C₅ and C₆ olefins and unconverted normal paraffins from said dehydrogenation zone to said desorption zone, and passing adsorbent containing adsorbed C₅ and C₆ olefins from said desorption zone to said adsorption zone.

7. A process as defined by claim 6 wherein said adsorbent is maintained in staged fluidized beds in said adsorption and said desorption zones.

8. A process as defined by claim 6 wherein said adsorbent has a particle size of from about 100 to about 400 mesh.

9. A process as defined by claim 6 wherein said dehydrogenation catalyst is chromium oxide.

10. A process as defined by claim 6 wherein said adsorbent is regenerated by withdrawing adsorbent from

said desorption zone, contacting said withdrawn adsorbent with air at a temperature of from about 700° to about 850° F., and reintroducing said adsorbent into said desorption zone.

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