

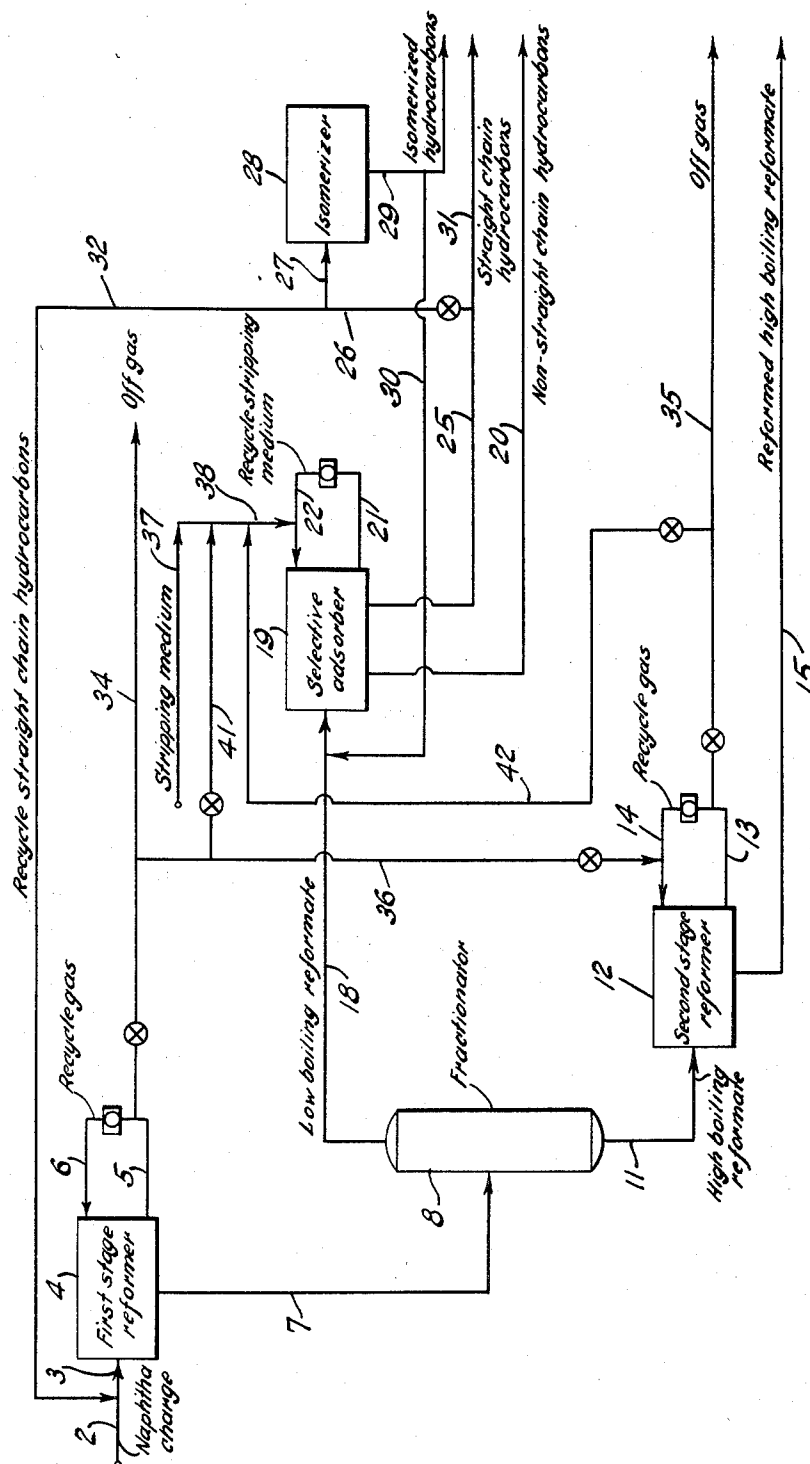
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HYDROCARBON CONVERSION PROCESS

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HYDROCARBON CONVERSION PROCESS

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9 Claims. (Cl. 208—65)

This invention relates to a hydrocarbon conversion process. More particularly, it is directed to the treatment of naphtha stocks containing naphthenes and paraffins for the manufacture of high octane number motor fuels or motor fuel components.

In accordance with the process of this invention, naphtha stocks containing paraffins and naphthenes are contacted with a platinum-alumina catalyst in the presence of hydrogen in a first reaction zone under reforming conditions selected to effect selective dehydrogenation of naphthenes and formation of aromatics and hydrogen with substantial freedom from the formation of carbonaceous deposits. The effluent from the said first reaction zone is subjected to fractional distillation to produce a light fraction boiling below about 250° F. and a heavy fraction. The aforesaid heavy fraction is contacted with a catalyst comprising a compound of chromium in the presence of hydrogen in a second reaction zone under reforming conditions selected to effect dehydrogenation and cyclization of paraffins to form aromatics and hydrogen. In a preferred embodiment of the process of this invention the aforesaid light fraction is contacted with a solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to effect adsorption of straight chain hydrocarbons from said light fraction. The straight chain hydrocarbons from said light fraction may be improved in octane number by subjecting to isomerization in a separate isomerization zone or by recycling at least a part thereof to said first reaction zone. The present invention is an improvement in the two stage reforming process of Carter, Riordan and Hess described in their copending application Serial Number 393,699, filed November 23, 1953, now abandoned, of which one of us is coinventor.

Petroleum fractions such as, for example, straight run and cracked naphthas, are complex mixtures of hydrocarbons of varying octane number and varying susceptibility to improvement by treating processes employed to upgrade such fractions. A variety of treating processes have been employed to improve the octane numbers of such fractions, for example, isomerization, thermal and catalytic cracking and thermal and catalytic reforming processes. These treating processes have been employed singly and in combination to effect the dehydrogenation of naphthenes to aromatics, isomerization of normal paraffins to isoparaffins, isomerization of five carbon atom naphthenes to six carbon atom naphthenes, and the dehydrocyclization of paraffins to form naphthene and aromatic hydrocarbons. Because these various upgrading reactions do not proceed equally well under the same conditions, single step treating processes employing several of these upgrading reactions have the disadvantage that the optimum conditions for all of the upgrading reactions desired cannot be obtained simultaneously. On the other hand, multistep treating processes have a disadvantage in that large volumes of feed material are

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handled in each step with the result that handling and investment costs reduce the economic and commercial attractiveness of such schemes. A further disadvantage of such multistep processes is that in some steps components may be included in the feed stock which are not improved under the treating conditions employed. In fact, under some conditions, a component of the feed stock may be destroyed or the quality impaired. In accordance with our invention a combination treating process is employed wherein a petroleum fraction is converted into high octane motor fuel components and wherein only a portion of the fraction is subjected to multiple treating steps.

The herein described process provides a method of reforming naphtha to obtain products of extremely high octane value. Hitherto, it has been impossible to obtain extremely high octane values of the order of about 100 without such high losses in liquid product as to make the processes unattractive. The present process is conducted under such highly selective conditions that the reforming of the naphtha even to high octanes is effected with unusually low yields of hydrocarbon gases.

An advantage of the process of this invention is that hydrocarbon components of a naphtha are treated under conditions selected to promote the reactions by which the fractions are most susceptible to improvement.

Another advantage of the process of this invention is that hydrocarbon components of naphthas are diverted from processing steps in which the particular component would serve only as a diluent or be converted to less valuable products.

The process of this invention is particularly applicable to the treating of naphtha fractions boiling within the range of about 175 to 450° F. Although naphtha fractions produced by thermal or catalytic cracking may be processed, we prefer to employ a heavy straight run naphtha containing straight chain and non-straight chain hydrocarbons and which might have the following composition.

Hydrocarbon type:	Percent by volume
Naphthenes	0 to 75
Aromatics	0 to 50
Paraffins (including normal paraffins and isoparaffins)	3 to 90
Unsaturates (including normal olefins and iso-olefins)	0 to 50

A typical straight run stock with a boiling range of about 175 to 400° F. may comprise about 40% naphthenes, 50% paraffins and 10% aromatics. The normal paraffinic components may consist of about 6 to 100% of normal paraffins. The naphthene component of such a stock will ordinarily comprise about equal proportions of five carbon ring compounds and six carbon ring compounds.

In the first stage of the process, the platinum-alumina catalyst is highly selective in catalyzing isomerization of substituted five carbon rings to form six carbon rings and dehydrogenating six carbon rings to the corresponding aromatic hydrocarbons. The extent of the reaction in the first stage is limited so that the paraffins are largely unreacted. The catalyst and conditions employed in the first stage are such that the reaction is highly selective in promoting dehydrogenation and the reaction is accompanied by a minimum of cracking, splitting off of hydrocarbon radicals and the formation of hydrocarbon gases. The result is that the gaseous products of the first stage reaction consist of at least 75 volume percent hydrogen and may typically comprise 95 percent hydrogen. To achieve maximum selectivity, the first stage reaction is advantageously conducted in a manner short of complete re-

action of the naphthenes and with substantial freedom from the formation of carbonaceous deposits on the catalyst.

The reformed naphtha, liquid product from the first stage, comprises aromatics, unreacted paraffins and a relatively small proportion of unreacted naphthenes. The reformed naphtha is then subjected to fractional distillation to produce a relatively low boiling fraction having a boiling range below about 250° F., for example, below about 210° F., and a remaining relatively heavy fraction. The relatively heavy fraction boiling within the range of about 210 to about 475° F. is subjected to further reforming in a second stage over a catalyst comprising a compound of chromium in an atmosphere of hydrogen under conditions selected to effect dehydrogenation and cyclization of paraffins and dehydrogenation of residual naphthenes from the first stage. Extensive cracking is avoided although some hydrocracking occurs and there is a moderate formation of olefins and deposition of coke on the catalyst. The catalyst is subjected to regeneration by burning the coke deposits with an oxygen-containing gas, for example, air or air diluted with flue gas. In the second reforming stage, the naphthene and paraffin content of the naphtha is reduced and the aromatic content further increased.

The relatively light fraction of reformat may be blended directly in motor fuel with the reformed high boiling reformat from the second stage reforming step. In this case, a greater number of barrels of naphtha are produced having a given octane number than are produced if all of the first stage reformat is charged to the second stage reformer. This is accounted for by the fact that the low boiling reformat consists of hydrocarbons which are not susceptible to improvement by reforming over a chromium type catalyst but are converted to hydrocarbons boiling below the motor fuel distillation range.

However, motor fuel fractions of increased octane number can be separated from the low boiling reformat by subsequent treating. For example, we may employ the selective adsorption process described in our copending application Serial Number 534,299 filed September 14, 1955, now U.S. Patent No. 2,888,394. In one embodiment of the process of this invention, said light or low boiling fraction is contacted with a solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said light fraction. The resulting treated light fraction, substantially free of straight chain hydrocarbons, exhibits a substantially higher octane number than the untreated fraction.

The adsorbed straight chain hydrocarbons are desorbed from the adsorbent. The desorbed straight chain hydrocarbons have a relatively low octane number. This fraction may be diverted from motor fuel uses requiring high octane number fractions and in fact the straight chain fraction may be valuable as a solvent or in the manufacture of specialty products. However, the straight chain fraction may be further processed to improve the octane number by other processing methods, for example, isomerization, thermal reforming or catalytic reforming. In isomerization, the straight chain hydrocarbons are converted to non-straight chain hydrocarbons of higher octane number. In thermal reforming, the straight chain hydrocarbons, in this case paraffins are cracked to produce olefins which have an increased octane number. In catalytic reforming of low boiling hydrocarbons, such as those produced in our process, octane number improvement is effected largely as a result of isomerization of the straight chain hydrocarbons to non-straight chain hydrocarbons.

The catalyst employed in the first stage of the process of this invention is platinum on alumina. It is desirable that the catalyst be substantially free from acidic constituents which tend to promote cracking or hydrocrack-

ing. The platinum-alumina catalyst contains small proportions of platinum in the range of about 0.1 to 2 percent. Catalysts comprising about 0.5 percent platinum on gamma alumina and 0.6 percent platinum on eta alumina are effective in the process of this invention. The first stage is conducted under a pressure in the range of about 200 to 700 pounds per square inch gage at temperatures in the range of about 850 to 975° F. and with space velocities in the range of about 3 to 20 volumes of oil per hour per volume of catalyst. The operation is conducted in the presence of hydrogen recycle gas containing about 80 to 95 percent hydrogen which is recycled at a rate in the range of about 4,000 to 8,000 cubic feet per barrel of liquid charge. In a typical operation, the naphtha is contacted with a platinum alumina catalyst at a temperature of 875 to 925° F. a pressure of 250 pounds per square inch gage, a space velocity of 3 volumes of oil per hour per volume of catalyst and with a recycle gas rate of 8,000 cubic feet per barrel of naphtha.

The catalyst in the second stage comprises a compound of chromium. A catalyst consisting of chromia on alumina is well-known and readily available and usually contains about 10 to 20 percent of chromia on an alumina base. Here again, it is desirable to exclude components which may promote cracking. Advantageously, the catalyst may also include small amounts of potassia and ceria which may function to reduce cracking activity and stabilize the catalyst. The high boiling reformed naphtha from the first stage is contacted with the chromium-type catalyst in the second stage at temperatures of about 875 to 1000° F. and at space velocities in the range of about 0.1 to 2 volumes of oil per hour per volume of catalyst. Pressures below 700 pounds per square inch gage are preferred and the second stage may be advantageously operated at atmospheric pressure. It is desirable to conduct the operation in an atmosphere of hydrogen and accordingly hydrogen-rich gas may be recycled at rates up to about 2,000 cubic feet per barrel of feed. Since the first stage produces an excess of hydrogen, the excess may be directed to the second stage to supply at least a part of the hydrogen required therein and thereby supplement or supplant recycle of gas in the second stage. Coke or carbonaceous deposits are laid down on the catalyst in the second stage and it is desirable to regenerate the catalyst. This stage may be conducted as a fixed-bed operation employing intermittent catalyst regeneration, or it may be conducted as a moving bed or fluidized catalyst operation employing continuous catalyst regeneration. In a typical embodiment of the process of this invention, a high boiling reformed naphtha is contacted in the second stage with a chromia alumina catalyst at a temperature of 925° F., a pressure in the range of about 0 to 25 pounds per square inch gage, a space velocity in the range of about 0.4 to 8 volumes of oil per volume of catalyst with a gas recycle rate of about 1,250 cubic feet per barrel of feed.

Any solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons can be employed in the process of this invention for the treatment of the low boiling reformed naphtha. It is preferred, however, to employ as the adsorbent certain natural or synthetic zeolites or aluminosilicates, such as a calcium aluminosilicate, which exhibit the properties of a molecular sieve, that is, adsorbents made up of porous matter or crystals wherein the pores are of molecular dimension and are of uniform size. A particularly suitable solid adsorbent for the adsorption of straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons is a calcium aluminosilicate manufactured by Linde Air Products Company and designated Linde type 5A molecular sieve. The crystals of this particular calcium aluminosilicate, apparently actually a sodium calcium aluminosilicate, have a pore size or pore diameter of about 5 Angstrom units, a pore size sufficient to admit

straight chain hydrocarbons such as the n-paraffins, to the substantial exclusion of the non-straight chain hydrocarbons, such as the naphthenic, aromatic, iso-paraffinic, and iso-olefinic hydrocarbons.

Other solid selective adsorbents may be employed in the practice of this invention. For example, it is contemplated that adsorbents having the property of selectively adsorbing straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons in the manner of a molecular sieve may be obtained by suitable treatment of various oxide gels, especially metal oxide gels of the polyvalent amphoteric metal oxides.

Other suitable selective adsorbents are known and include the synthetic and natural zeolites which, when dehydrated, may be described as crystalline zeolites having a rigid three dimensional anionic network having interstitial dimensions sufficiently large to adsorb straight chain hydrocarbons but sufficiently small to exclude the non-straight chain hydrocarbons. The naturally occurring zeolite, chabazite, exhibits such desirable properties. Another suitable naturally occurring zeolite is analcite, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, which, when dehydrated, and when all or part of the sodium is replaced by an alkaline earth metal such as calcium, yields a material which may be represented by the formula $(\text{Ca}, \text{Na})\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ and which, after suitable conditioning, will adsorb straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Naturally occurring or synthetically prepared phacolite, gmelinite, harmotome and the like or suitable modifications of these products by base exchange are also applicable in the practice of this invention.

Other solid adsorbents which selectively adsorb straight chain hydrocarbons, such as n-paraffins and n-olefins, to the substantial exclusion of non-straight chain hydrocarbons are known.

In the selective adsorption step, the low boiling reformate is contacted with a solid adsorbent such as an alkaline earth metal aluminosilicate, preferably a calcium aluminosilicate, to effect the adsorption separation of straight chain hydrocarbons therefrom. Adsorption conditions in the adsorber may include a temperature within the range of about 300 to 750° F., and a pressure in the range of about 0 to 2,000 pounds per square inch gage. It is preferred to maintain the adsorption conditions such that the fraction undergoing treatment is in the vapor phase. After contact within the adsorber to effect the adsorption of straight chain hydrocarbons, the treated fraction is separated substantially free of or at least having a reduced content of straight chain hydrocarbon.

On completion of the adsorption operation, the adsorber is subjected to desorption conditions to effect the removal of the adsorbed straight chain hydrocarbons. Suitable desorption conditions include a temperature in the range of about 500 to 1100° F. and a pressure in the range of about 0 to 1000 pounds per square inch gage. It is preferred to carry out the desorption operation under such conditions that the straight chain hydrocarbons are desorbed or recovered in the vapor phase. Desorption of the straight chain hydrocarbons is facilitated by the introduction of a stripping medium to displace the desorbed straight chain hydrocarbons from the adsorption zone. Gases suitable as stripping media include hydrogen, nitrogen, carbon monoxide, carbon dioxide, steam, and normally gaseous hydrocarbons. Reformer off-gases, from either stage of the herein described process, comprising hydrogen and small quantities of normally gaseous hydrocarbons are suitable.

The accompanying drawing diagrammatically illustrates the process of this invention. Although the drawing illustrates one arrangement of apparatus in which the process of this invention may be practiced, it is not intended to limit the invention to the particular apparatus or material described.

Referring to the drawing, a naphtha fraction, such as, a heavy straight run naphtha having an initial boiling point in the range of 150 to 250° F. and an end-point in the range of 350 to 475° F., is introduced through lines 2 and 3 into first stage reformer 4. In the first stage reformer 4, the naphtha charge is contacted with a platinum-alumina catalyst in the presence of hydrogen to effect selective conversion of naphthenes to aromatics and hydrogen. Gaseous products rich in hydrogen are recycled through lines 5 and 6. Naphtha reformate, the liquid product from the first stage reformer, is withdrawn through line 7 and transferred to fractionator 8. In fractionator 8, the reformate is separated into an overhead light fraction and a relatively heavy bottoms fraction. The light fraction boils below about 250° F., for example, 210° F. and may comprise as much as 60% by volume of the reformate. The heavy fraction is withdrawn through line 11 and is transferred to second stage reformer 12. In second stage reformer 12, the high boiling reformate is contacted with a catalyst comprising a compound of chromium in the presence of hydrogen to effect substantial dehydrogenation and cyclization of paraffins and further dehydrogenation of naphthenes. Gaseous products rich in hydrogen are recycled through lines 13 and 14. Reformated high boiling reformate of high octane number is withdrawn through line 15 and is discharged to external storage not shown for motor fuel blending.

The light or low boiling reformate fraction produced in fractionator 8 is withdrawn through line 18 and transferred to selective adsorber 19. In adsorber 19, the low boiling reformate is contacted with a solid adsorbent, for example, a sodium calcium aluminosilicate, to effect the adsorptive separation of straight chain hydrocarbons therefrom. The treated light fraction substantially free of or having a reduced straight chain hydrocarbon content is discharged through line 20 to external storage, not shown, for motor fuel blending. Straight chain hydrocarbons are desorbed from the solid adsorbent by stripping medium recycled to adsorber 19 through lines 21 and 22. Desorbed straight chain hydrocarbons are discharged from adsorber 19 through line 25. The light straight chain hydrocarbon fraction may be further processed by transfer through lines 26 and 27 to isomerizer 28 from which isomerized hydrocarbons of increased octane number are discharged through line 29 to external storage not shown. Advantageously, the products of the isomerization step may be returned to the selective adsorption step through line 30 so that only non-straight chain hydrocarbons are withdrawn from the system and unconverted components of the isomerization effluent are retained in the system for further treatment. In the alternative, the light straight chain hydrocarbons may be withdrawn from adsorber 19 and discharged from the system without further processing through line 31 for utilization where high octane number is not required. The light straight chain hydrocarbons may be processed for octane number improvement, if desired, by recycling to first stage reformer 4 through lines 25, 26, 32 and 3.

Both the first stage reformer and second stage reformers produce hydrogen-rich off-gas. Off-gas from the first stage reformer may be discharged from the system for external utilization not shown through lines 5 and 34. Off-gas from the second stage reformer may be discharged through lines 13 and 35. The hydrogen concentration of the recycle stream employed in the second stage reformer may be increased by adding at least a part of the off-gas from the first stage reformer, which generally has a higher hydrogen concentration, through line 36 and discharging reformer off-gas from both reforming stages from the recycle stream of the second stage reformer through lines 13 and 35.

Make-up stripping medium from an external source, not shown, is added to the selective adsorber through lines 37 and 38. Reformer off-gas may be employed as

stripping medium for the selective adsorber by adding reformer off-gas from the first stage reformer through lines 34, 36, 41 and 38. Off-gas from the second stage reformer may be employed as stripping medium by passing the gas from line 35 through line 42 to stripping medium supply line 38. The hydrogen gas produced in the process may be employed advantageously by discharging off-gas from the first stage reformer to the recycle gas system of the second stage reformer, and discharging off-gas from the second stage reformer to the selective adsorber to supply make-up requirements of stripping medium.

Illustrative of the practice of this invention, a heavy straight run naphtha having a boiling range of 222 to 380° F.; containing 11.6 volume percent aromatics, 44.2 percent naphthenes, and 44.2 percent paraffins; and having ASTM Research octane numbers of 49.8 clear and 73.5 with 3 ccs. of tetraethyl lead per gallon, is reformed with a platinum-alumina catalyst under the conditions and with the results shown in Table I.

Table I

Average reactor temperature, ° F.	911
Reactor inlet pressure, p.s.i.g.	600
Recycle gas (83.4% hydrogen) cu. ft./bbl.	8250
Space velocity, vol. oil/hr./vol. catalyst.	3.1
Yield of catalytic reformat, vol. percent.	83.4
ASTM Research octane number of catalytic reformat, clear.	87.1

The catalytic reformat shown in Table I is fractionated to separate a low boiling and a high boiling fraction. The low boiling fraction boils within the range of 75 to 209° F., comprises 41.5 volume percent of the total reformat and has an ASTM Research octane number of 72.7 clear. The high boiling reformat boils in the range of 209 to 440° F., comprises 58.5 volume percent of the total reformat and has an ASTM Research octane number of 94.5 clear.

The low boiling reformat fraction is contacted with a calcium aluminosilicate solid adsorbent to effect adsorption of straight chain hydrocarbons. A treated fraction of reduced straight chain hydrocarbon content is separated comprising 54.7 volume percent of the low boiling reformat and having an ASTM Research octane number of 84.7 clear. A fraction comprising straight chain hydrocarbons is desorbed from the adsorbent comprising 45.3 volume percent of the low boiling reformat and having an ASTM Research octane number of 52.6 clear.

The high boiling reformat fraction is reformed in a second stage in contact with a chromia catalyst at a temperature of 1000° F., a space velocity of 0.2 volume of oil per hour per volume of catalyst and at atmospheric pressure to produce a re-reformed naphtha having an ASTM Research octane number equivalent to iso-octane +0.14 cc. of tetraethyl lead per gallon at a yield of 89.0 volume percent of the heavy reformat.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for upgrading a naphtha stock containing paraffins and naphthenes which comprises contacting said naphtha in a first reaction zone with a platinum-alumina catalyst in the presence of hydrogen under reforming conditions selected to effect selective dehydrogenation of naphthenes with the production of aromatics and hydrogen with substantial freedom from the formation of carbonaceous deposits, separating from the effluent from said first reaction zone a first gas rich in hydrogen and a liquid fraction, recycling a portion of said first gas rich in hydrogen to said first reaction zone, fractionating said liquid fraction to produce a light fraction boiling

below about 250° F. and a heavy fraction, contacting said heavy fraction in a second reaction zone with a catalyst comprising a compound of chromium under reforming conditions selected to effect dehydrogenation and cyclization of paraffins to produce aromatics and hydrogen, separating from the effluent from said second reaction zone a second gas rich in hydrogen and a liquid fraction of improved octane number, contacting said light fraction in an adsorption zone with a solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to remove straight chain paraffins from said light fraction, recovering from said adsorption zone a light fraction of improved octane number and having a reduced straight chain paraffin content and stripping adsorbed straight chain paraffins from said solid adsorbent by passing a gas rich in hydrogen produced in the process through said adsorption zone under desorbing conditions.

2. The process of claim 1 in which the gas used to strip adsorbed straight chain paraffins from the solid adsorbent comprises the second gas rich in hydrogen.

3. The process of claim 1 in which the gas used to strip adsorbed straight chain paraffins from the solid adsorbent comprises the first gas rich in hydrogen.

4. The process of claim 1 in which the desorbed straight chain paraffins are returned to the first reaction zone.

5. The process of claim 1 in which the catalyst comprising a compound of chromium comprises chromium oxide on alumina.

6. The process of claim 1 in which the solid adsorbent comprises an alkaline earth metal aluminosilicate.

7. The process of claim 6 in which the solid adsorbent comprises sodium calcium aluminosilicate.

8. A process of upgrading a naphtha stock containing paraffins and naphthenes which comprises contacting said naphtha in a first reaction zone with a platinum-alumina catalyst in the presence of hydrogen and under reforming conditions selected to effect selective dehydrogenation of naphthenes and formation of aromatics and hydrogen with substantial freedom from the formation of carbonaceous deposits, separating a gaseous fraction rich in hydrogen and a liquid effluent fraction from said first reaction zone, recycling a portion of said gaseous fraction to said first reaction zone, fractionating said liquid effluent from said first reaction zone to produce a light fraction boiling below about 250° F. and a heavy fraction, contacting said light fraction with a solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said light fraction and to produce a fraction comprising a light fraction of reduced straight chain hydrocarbon content, stripping said solid adsorbent with a portion of said gas rich in hydrogen from said first reaction zone to effect desorption of said straight chain hydrocarbons, separating from the desorption effluent a fraction comprising light straight chain hydrocarbons, and contacting said heavy fraction in a second stage reaction zone with a catalyst comprising a compound of chromium under reforming conditions selected to effect dehydrogenation and cyclization of paraffins to form aromatic hydrocarbons and hydrogen.

9. A process of upgrading a naphtha stock containing paraffins and naphthenes which comprises contacting said naphtha in a first reaction zone with a platinum-alumina catalyst in the presence of hydrogen and under reforming conditions selected to effect selective dehydrogenation of naphthenes and formation of aromatics and hydrogen with substantial freedom from the formation of carbonaceous deposits, separating a first gaseous fraction rich in hydrogen and a liquid effluent fraction from said first reaction zone, recycling a portion of said gaseous fraction to said first reaction zone, fractionating said liquid effluent from said first reaction zone to produce a light fraction

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boiling below from about 250° F. and a heavy fraction, contacting said light fraction with a solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said light fraction and to produce a fraction comprising a light fraction of reduced straight chain hydrocarbon content, stripping said solid adsorbent with a gaseous stripping medium to effect desorption of said light straight chain hydrocarbons from said adsorbent, separating from the desorption effluent a fraction comprising light straight chain hydrocarbons, contacting said heavy fraction in a second stage reaction zone with a catalyst comprising a compound of chromium in the presence of hydrogen and under reforming conditions selected to effect dehydrogenation and cyclization of paraffins to form aromatic hydrocarbons and hydrogen, separating a second gaseous fraction rich

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in hydrogen and a liquid effluent fraction from said second reaction zone, recycling a portion of said second gaseous fraction to said second stage reaction zone, and passing a portion of said first gaseous fraction to said second stage reaction zone, said gaseous stripping medium comprising a gas rich in hydrogen produced in the process.

References Cited in the file of this patent

UNITED STATES PATENTS

2,409,695	Laughlin	Oct. 22, 1946
2,522,426	Black	Sept. 12, 1950
2,740,751	Haensel et al.	Apr. 3, 1956
2,758,062	Arundale et al.	Aug. 7, 1956
2,767,124	Myers	Oct. 16, 1956
2,818,455	Ballard et al.	Dec. 31, 1957