

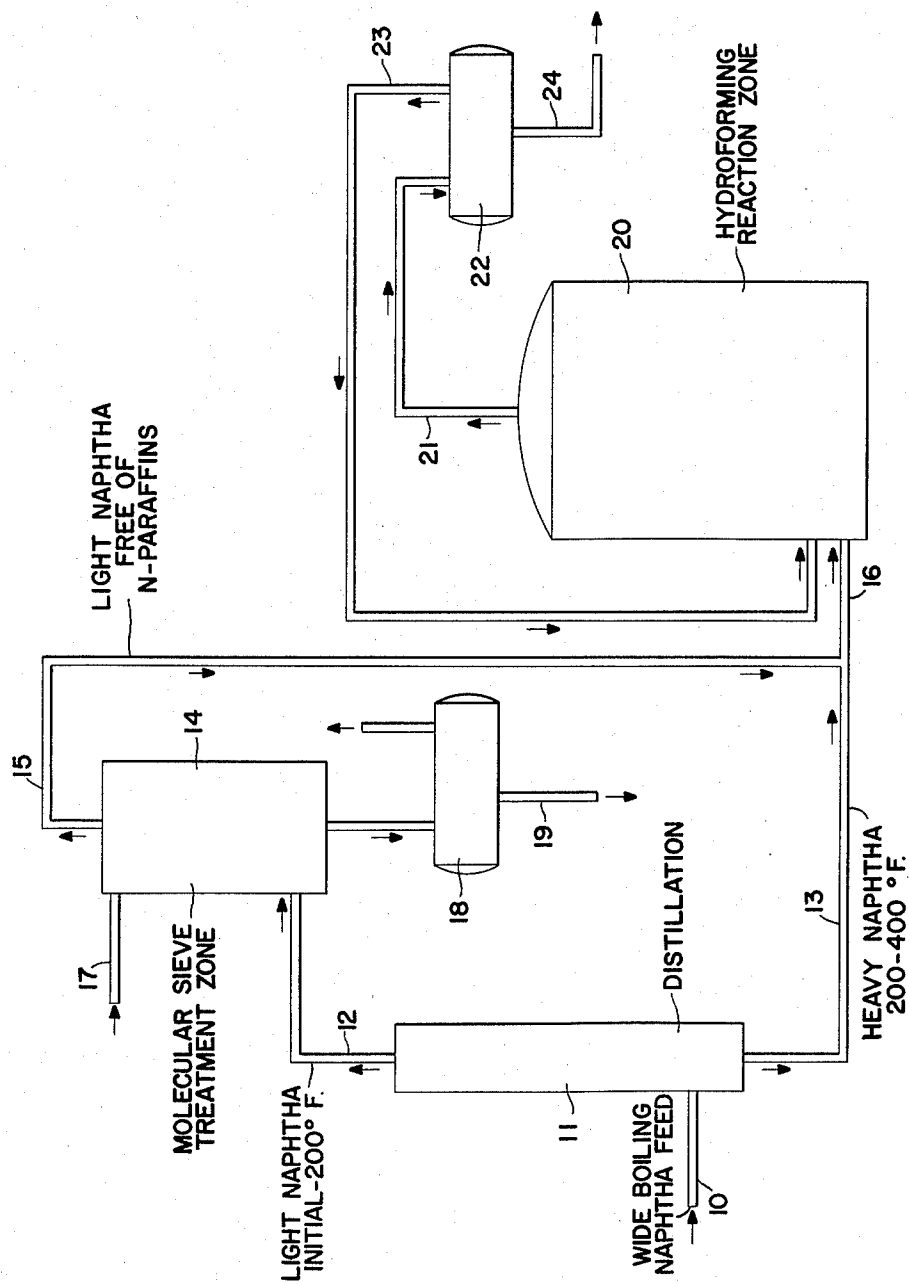
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NAPHTHA REFORMING PROCESS

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NAPHTHA REFORMING PROCESS

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The present invention relates to the conversion of hydrocarbons and particularly to an improved method for upgrading wide boiling range, low octane number naphthas into high octane number motor fuels in high yields.

Hydroforming is a well known and widely used process for upgrading hydrocarbon fractions boiling in the motor gasoline or naphtha boiling range to increase their octane numbers and to improve their burning or engine cleanliness characteristics. In hydroforming, the hydrocarbon fraction or naphtha is contacted at elevated temperatures and pressures and in the presence of hydrogen or hydrogen-rich process gas with solid catalytic materials under conditions such that there is not net consumption of hydrogen and ordinarily there is a net production of hydrogen in the process. A variety of reactions occur during hydroforming including dehydrogenation of naphthenes to the corresponding aromatics, hydrocracking of paraffins, isomerization of straight chain paraffins to form branch chain paraffins, dehydrocyclization of paraffins, and isomerization of compounds such as ethylcyclopentane to form methylcyclohexane which is readily converted to toluene. In addition to these reactions some hydrogenation of olefins and polyolefins occurs, if such hydrocarbons are present, and sulfur or sulfur compounds are eliminated by conversion to hydrogen sulfide or to metal sulfides on the catalyst, making the hydroformate burn cleaner or form less deposits when used as the fuel in internal combustion engines.

Hydroforming is usually applied to a rather wide boiling range naphtha, i.e., to one having a boiling range of about 125 to about 400–430° F. It has been known that the lower boiling naphthas are not substantially improved by hydroforming processes as ordinarily conducted. The extensive report entitled "An Appraisal of Catalytic Reforming" in Petroleum Processing for August 1955, for example states at page 1174 "Optimum reformer utilization is obtained by not using feed stock constituents boiling much below 200° F. which do not contribute greatly to increased octane during reforming as these merely take up reformer capacity better used for high boiling materials more susceptible to octane upgrading." In view of the continuing demand for more and higher octane number gasolines, however, it is becoming increasingly important to upgrade these lower boiling fractions which constitute from about 5 to 12% based on the entire crude.

It has been proposed to bypass these light naphthas around the reforming reaction zones. While this serves to save reformer reactor capacity it leaves the problem of blending off substantial quantities of low octane naphtha. It has also been proposed to distill off a light naphtha fraction and to hydroform it separately under conditions which are more or less optimum for the conversion of light naphthas. This is not too satisfactory, however, because it requires a separate reactor or essentially a second hydroforming reaction system.

It is the object of this invention to provide the art with an improved method for reforming or upgrading a wide boiling range naphtha.

It is also the object of this invention to provide a simple

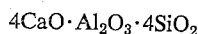
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and effective method for hydroforming a wide boiling range naphtha in a single reaction zone and which will effect a substantial improvement in octane number of the light naphtha constituents.

These and other objects will appear more clearly from the detailed specification and claims which follow.

It has now been found that wide boiling range naphthas can be hydroformed in a single reaction zone and still effect a substantial improvement in the octane number of the light naphtha components, if the naphtha is distilled to separate a light naphtha (initial to about 200° F. boiling range) fraction and a heavy or 200 to 400° F. boiling range fraction, removing the normal paraffin constituents from the light naphtha fraction by treatment with a selective solid adsorbent, combining the light naphtha fractions substantially free of normal paraffins with the heavy naphtha fraction and subjecting this mixture to hydroforming under conditions normally applied to a wide boiling range naphtha. Under these conditions a substantial increase in octane number of the light naphtha components is achieved. In addition, the low octane number, low boiling normal paraffins are eliminated from the end product where they would depress the octane number. Also, the presence of the normal paraffins in the hydroforming reaction zone, where they can adversely affect the hydroforming results, is completely avoided.

The scientific and patent literature contains numerous reference to the sorbing action of natural and synthetic zeolites. Among the neutral zeolites having this sieving property may be mentioned chabazites. A synthetic zeolite with molecular sieve properties is described in U.S. Patent No. 2,442,191. Zeolites vary somewhat in composition but generally contain the elements silicon, alumina and oxygen as well as an alkali metal and/or an alkaline earth metal element e.g. sodium and/or calcium. The naturally occurring zeolite, analcite, for instance has the empirical formula $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$. Barrer U.S. Patent No. 2,306,610 teaches that all or part of the sodium is replaceable by calcium to yield on dehydration a molecular sieve having the formula $(\text{CaNa}_2) \text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$. Black, U.S. Pat. No. 2,522,426 describes a synthetic molecular sieve zeolite having the formula



A large number of other naturally occurring zeolites having molecular sieve activity, i.e. the ability to adsorb a straight chain hydrocarbon and exclude or reject the branch chain isomers and aromatics because of differences in molecular size are described in an article entitled "Molecular Sieve Action of Solids" appearing in Quarterly Reviews, vol. III, pages 293–320 (1949), published by the Chemical Society (London). For the purposes of this invention molecular sieve separation vessel is charged with a natural or synthetic zeolite of the class described above having a pore size of approximately 5 Angstrom units which will readily adsorb the normal paraffins contained in the feed but will not adsorb the isoparaffins, naphthenes or aromatics contained therein.

Reference is made to the accompanying drawing which illustrates diagrammatically a flow plan of the process in accordance with the present invention.

Referring to the drawing, a wide boiling naphtha feed, for example one having an end point of about 400° F. is supplied to inlet line 10 of distillation column 11. The naphtha feed is separated by distillation into a light naphtha fraction boiling in the range from about 110° F. to 200° F. which is taken off the distillation column via line 12 and a heavy naphtha fraction boiling in the range of 200–400° F. which is taken off the bottom of the distillation column through line 13.

The light naphtha fraction is passed, preferably in

vapor phase, at temperatures of about 200 to about 350° F. into the adsorption zone or tower 14 where it is subjected to treatment in contact with molecular sieves. The adsorbent or molecular sieve is a natural or synthetic zeolite of the molecular sieve type heretofore described and having a pore diameter of about 5 Å. The molecular sieve is arranged in any desired manner in the adsorption zone or tower 14. It may, for example, be arranged on trays or packed therein with or without supports. Conditions maintained for the molecular sieve treatment in the adsorption zone or tower 14 are flow rates of 0.1 to 5 v./v./hr., temperatures of about 175°–350° F., and pressures of from atmospheric pressure to several hundred pounds per square inch. Molecular sieves of the 5 Å. type having a pore diameter of approximately five Angstrom units are capable of readily adsorbing the normal paraffins contained in the naphtha feed but are incapable of adsorbing the isoparaffins and naphthenes contained in the light naphtha. Accordingly, there is removed overhead from the molecular sieve treatment zone 14 a stream of light naphtha which is essentially free of normal paraffins and which is passed through transfer line 15 to line 13 where the normal paraffin-free, light naphtha is combined with the heavy naphtha fraction from the distillation column 11.

The mixture of normal paraffin-free, light naphtha and heavy or 200°–400° F. boiling range naphtha is passed via line 16 to hydroforming reaction zone 20 where the mixture is subjected to hydroforming reaction conditions essentially the same as have been applied to wide boiling range naphtha. The hydroforming reaction zone diagrammatically shown at 20 may assume various forms. For example, the hydroforming may be effected in a fluidized solids reactor system in which case separate reactor and regenerator vessels are provided with continuous circulation of catalyst between these vessels. Alternatively, the hydroforming may be carried out in fixed bed or moving bed type operations. In general, fluid or moving bed operations are preferred where the reaction conditions are such that frequent regenerations of the catalyst are necessary and particularly in any operation where the catalysts are capable of withstanding the grinding or disintegrating forces to which they are subjected.

Hydroforming may be effected in contact with group VI metal oxides, preferably molybdenum oxide dispersed on alumina-containing supports such as activated alumina or the like. A suitable catalyst is one containing about 10 wt. percent molybdenum oxide dispersed upon an activated alumina support which contains about 2 to 5 wt. percent of silica as a stabilizer. Reaction conditions for hydroforming with this type of catalyst are temperatures of about 850–975° F., preferably about 925° F. and pressures of from about 50 to 500 p.s.i.g., preferably about 200 p.s.i.g. Hydrogen or hydrogen-rich recycle gas is supplied to the hydroforming reaction zone at rates of from about 2000–8000 cubic feet per barrel of liquid feed in order to minimize carbon formation and extend the life of the catalyst. Feed rates vary depending upon the age of the catalyst and the desired octane number of the product and may be about 0.1 to about 1.5 w./hr./w.

The hydroforming may also be carried out in contact with platinum group metal catalysts, for example with catalysts containing 0.01 to 1.0 wt. percent platinum, or 0.1 to 2.0 wt. percent palladium dispersed upon a highly pure alumina support such as is obtained from aluminum alcoholate as per U.S. Pat. No. 2,636,865 or from an alumina hydrosol prepared by hydrolyzing aluminum metal with dilute acetic acid in the presence of very small catalytic amounts of mercury. A suitable catalyst comprises about 0.1 to 0.6 wt. percent of platinum widely dispersed upon alumina in the eta phase derived from aluminum amylate and having a surface

area of about 150–220 sq. meters per gram. A preferred catalyst for fluidized solids operations is one comprising a mixture of a platinum catalyst concentrate consisting essentially of 0.3 to 2.0 wt. percent platinum on alumina microspheres formed by spray drying an alcoholate-alumina hydrosol prepared in accordance with U.S. Pat. No. 2,656,321 and mixed with sufficient unplatinated alumina to form a catalyst composition containing about 0.01 to 0.2 wt. percent platinum. Reaction conditions for hydroforming with platinum type catalysts are temperatures of from about 850–975° F. preferably about 925° F. and pressures of from about 200–700 p.s.i.g., preferably about 350 p.s.i.g. Hydrogen or hydrogen-rich recycle gas is supplied to the hydroforming reaction zone at rates of from about 1000 to 6000 cubic feet per barrel of liquid feed. Feed rates vary depending upon the age of the catalyst and the desired octane number of the product and may be about 0.5 to about 4 w./hr./w. When operating at pressures below about 400 p.s.i.g., carbonaceous deposits are formed upon the platinum catalyst and must be removed to maintain catalyst activity. Regeneration of the platinum catalyst may be effected as required by burning the carbonaceous deposits therefrom with oxygen-containing gas at temperatures of from 900 to 1200° F., preferably about 1000°–1100° F. Excess air is used for the regeneration to insure the complete removal of carbon or coke from the catalyst prior to the reactivation treatment to be described. The regenerated or carbon-free catalyst can advantageously be treated with air or oxygen-enriched gas at temperatures of from about 900°–1100° F. for about from 1 to 4 hours. The regenerated catalyst is then contacted with chlorine gas, or a mixture of chlorine gas and air, in order to reactivate the catalyst, restore its chlorine content, and disperse or break up the large platinum crystallites that form during use of the catalyst.

The chlorine partial pressure during reactivation may be in the range of from 0.001 to 2 atmospheres, preferably 0.01 to 1 atmosphere. The quantity of chlorine supplied is in the range of 0.1 to 2.0 wt. percent preferably about 0.15 wt. percent based on the catalyst. The chlorine treatment may be carried out for periods of from about 15 seconds to 1 hour, preferably from about 1 to 15 minutes. While the chlorine treated catalyst may be subjected to air stripping to remove excess chlorine, it is usually preferred to avoid stripping chlorine from the reactivated catalyst since the chlorine content governs the hydrocracking activity of the catalyst which in turn controls the volatility of the hydroformate. In general, the total amount of chlorine, i.e. both chemically combined and adsorbed, remaining on the catalyst when employing a catalyst at 0.6 wt. percent platinum may be in the range of 0.2 to 1.25 wt. percent and is preferably about 0.5 to 1.0 wt. percent.

The naphtha is maintained in the hydroforming reaction zone 20 for a period sufficient to raise the octane number of the naphtha to the desired level. In general, the octane number of the hydroformate withdrawn from the reaction zone 20 should be above about 90 research O.N. clear, and preferably is about 95 to 100 research O.N. The reaction products are withdrawn from the hydroforming reaction zone via line 21 and passed through cooling or condensing means and thence passed into gas-liquid separator 22. Hydrogen-rich gas is withdrawn from separator 22 via line 23 and is compressed and recycled to the hydroforming reaction zone after scrubbing, if desired, to remove contaminants such as hydrogen sulfide or to increase the hydrogen content by removing gaseous hydrocarbons. High octane number hydroformate is withdrawn from separator 22 through line 24 and is passed to product storage or blending.

When the molecular sieves in the adsorption zone or tower 14 become saturated with normal paraffins as may

be readily determined by conventional means, such as refractive index, gravity, or spectrographic analysis of the effluent, the flow of light naphtha is stopped and the desorption cycle or regeneration of the sieves begins. Desorption is effected by passing an olefin-containing gas, preferably one containing a substantial proportion of propylene, from line 17 through the exhausted bed of molecular sieves. For example, cracked refinery gases containing propylene is a convenient and highly satisfactory desorbing gas. The stripping or desorbing gas is preferably heated to about 200° to 300° F. prior to introduction into the molecular sieve treating zone. Thus, without changing the temperature of the adsorption zone or tower, the stripping or desorbing gas replaces the adsorbed paraffins with an olefin such as propylene. The desorbed normal paraffins are withdrawn from the adsorption zone and cooled and separated from the desorbing gas in the gas-liquid separator 18. The desorbed normal paraffins are withdrawn through line 19 and may either be passed to storage for use for example, as jet fuel or, if desired, they may be subjected to further processing as for example by aromatization or hydroisomerization under well known or conventional conditions for upgrading the same for admixture with high octane number motor fuel components.

The following example is illustrative of the present invention.

Example

A virgin naphtha having a research O.N. of 53.1 obtained from West Texas crude is distilled to separate 28% of a light naphtha boiling (5% to 95%) in the range of 162° to 191° F. and 72% of a heavy naphtha boiling (5% to 95%) in the range of 237 to 312° F. The light naphtha is then separated by vapor phase (240° F.) contacting with molecular sieves having about 5 Angstrom pores into a normal paraffin fraction (6.7% on total naphtha) and a non-normal hydrocarbon fraction (21.3% on total naphtha) which contains 54% naphthenes, 43% iso-paraffins, and 3% aromatics and has a research clear O.N. of 82. A blend of the normal paraffin-free fraction with the heavy naphtha is hydroformed by contacting with a catalyst comprising 10% molybdenum oxide deposited on alumina at a temperature of 900° F., a pressure of 200 pounds per square inch, and in the presence of 2000 cubic feet of added hydrogen per barrel of feed at various feed rates between 0.2 and 0.5 weights of naphtha per hour per weight of catalyst. A sample of the original total naphtha is hydroformed under the same operating conditions to provide comparative data. Correlated yield data for various octane levels are summarized in the following table.

Feed to Hydroformer	Total Naphtha	Heavy Naphtha Plus N-Paraffin-Free Light Naphtha
Vol. Percent of Total Naphtha.....	100	93.3
Octane No., Research Clear.....	53.1	56.5
Product Yields, Vol. Percent on Total Naphtha:		
90 Octane No. Hydroformate.....	80.2	81.0
95 Octane No. Hydroformate.....	74.0	76.4
98 Octane No. Hydroformate.....		72.4
N-C ₈ -C ₇ Hydrocarbons.....	0	6.7

The above data show that the removal of the normal paraffins boiling below about 200° F. (on an ASTM distillation) from a light virgin naphtha greatly improves its quality as a hydroformer feed. The hydroformate yields are improved even when based on the origin total naphtha and disregarding the separated n-paraffins, which represent valuable by-product fractions useful as jet fuels, solvents, specialty uses, etc. In addition, removal of the light normal paraffins allows achievement of a higher octane number product; the total naphtha cannot be hydro-

droformed to as high as 98 octane number with a feasible feed rate.

The foregoing description contains a limited number of embodiments of the present invention. It will be understood however, that this invention is not limited thereto, since numerous variations are possible without departing from the scope of the following claims.

What is claimed is:

1. A method of upgrading a wide boiling range low octane number naphtha into high octane number motor fuels in high yields which comprises distilling the naphtha boiling in the range of about 125° to 400° F. to separate a light naphtha fraction containing hydrocarbon components boiling up to about 200° F. from a heavy naphtha fraction boiling above 200° F., treating the light naphtha fraction with a molecular sieve of the 5 A. type in order to remove relatively low octane number, normal paraffins from the light naphtha fraction, recombining the light naphtha essentially free of normal paraffins with said heavy naphtha fraction and hydroforming the resultant mixture to an octane number above 90 research clear by passing the mixture through a single hydroforming reaction zone maintained at active hydroforming reaction conditions.

2. The method as defined in claim 1 in which the hydroforming reaction zone is charged with a molybdenum oxide on alumina catalyst.

3. The method as defined in claim 1 in which the hydroforming reaction zone is charged with a platinum on alumina catalyst.

4. The method as defined in claim 1 in which the hydroforming reaction zone is charged with a molybdenum oxide on alumina catalyst and is maintained at temperatures of about 850° to 975° F. and pressures of about 50 to 500 p.s.i.g. and the naphtha is charged thereto at the rate of about 0.1 to about 1.5 w./hr./w. in admixture with about 2000 to 8000 cubic feet of a hydrogen-rich gas per barrel of liquid naphtha feed.

5. The method as defined in claim 1 in which the hydroforming reaction zone is charged with a platinum on alumina catalyst and is maintained at a temperature of from about 850° to 975° F. and pressures of from about 200 to 700 p.s.i.g. and the naphtha is charged thereto at the rate of about 0.5 to 4.0 w./hr./w. in admixture with about 1000 to 6000 cubic feet of hydrogen-rich gas per barrel of liquid naphtha feed.

6. A method of upgrading a wide boiling range low octane number naphtha into a high octane number motor fuel in high yield, said naphtha containing a substantial amount of normal paraffins boiling in the range of about 125° to about 400° F., which comprises distilling the naphtha to separate therefrom a light naphtha fraction containing the normal paraffins boiling up to about 200° F. from a heavy naphtha fraction, treating the light naphtha fraction to remove therefrom normal paraffins boiling up to about 200° F., and thereafter hydroforming the light naphtha fraction essentially free of normal paraffins and said heavy naphtha fraction containing normal paraffins boiling above 200° F. to obtain a hydroformate product having an octane number above about 90 from both the light fraction freed of normal paraffins and the heavy naphtha fraction containing normal paraffins under hydroforming reaction conditions.

References Cited in the file of this patent

UNITED STATES PATENTS

2,375,573	Meier	May 8, 1945
2,442,191	Black	May 25, 1948
2,689,208	Murray et al.	Sept. 14, 1954
2,818,455	Ballard et al.	Dec. 31, 1957
2,886,508	Hess et al.	May 12, 1959

OTHER REFERENCES

Sachanen: Chemical Constituents of Petroleum" (1945), Reinhold Publishing Corp., pages 200-201.