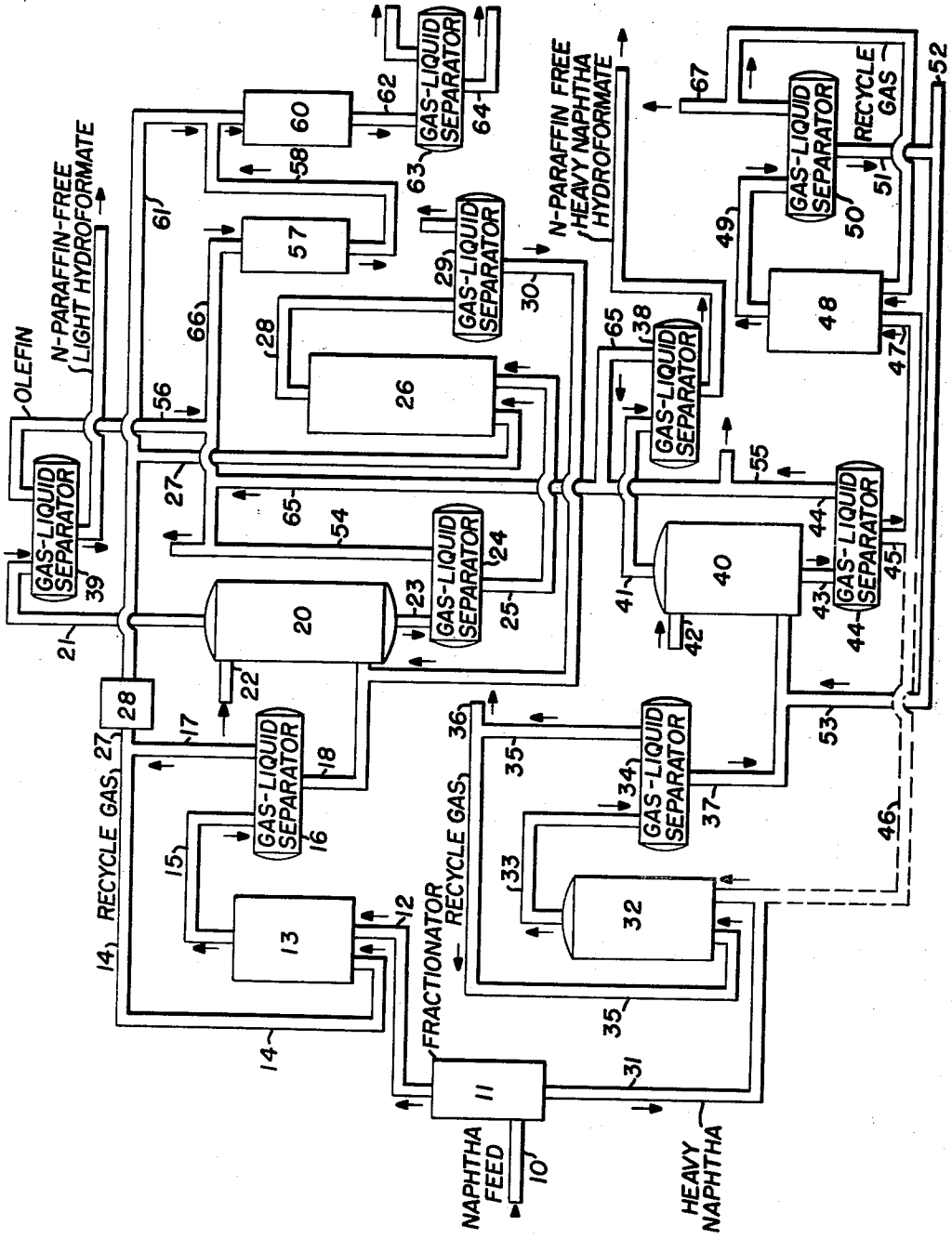
July 5, 1960 C. N. KIMBERLIN, JR., ET AL 2,944,001

NAPHTHA REFORMING PROCESS

Filed May 29, 1956



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United States Patent Office 2,944,001 Patented July 5, 1960

2,944,001

NAPHTHA REFORMING PROCESS

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Filed May 29, 1956, Ser. No. 587,999

2 Claims. (Cl. 208—80)

The present invention relates to the hydroforming of hydrocarbons and particularly to an improved combination of process steps for converting low grade, light or full boiling range 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 no 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 when such compounds 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 engine deposits when used as the fuel in an internal combustion engine.

Hydroforming is usually applied to a rather wide boiling range naphtha, i.e., one having a boiling range of from about 125° F. to about 400 to 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 on page 1174 "Optimum reformer utilization is obtained by not using feed stock constituents boiling much below 200° F. which do not contribute greatly to the 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.

It is the object of this invention to provide the art with an improved method for reforming or upgrading naphthas.

It is also an object of this invention to provide the art with an improved process for reforming or upgrading a low octane, wide boiling range naphtha into high octane number motor fuels.

It is a further object of this invention to provide the art with an integrated process for upgrading low octane, wide boiling range naphthas which will effectively upgrade the lower boiling as well as the higher boiling constituents of the naphtha.

It is also a further object of this invention to provide an integrated process for producing high yields of high octane number motor fuels.

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

It has now been found that high yields of high octane number motor fuels may be prepared in an integrated process if the virgin naphtha feed having, for example, a boiling range of about 110° to about 400° F. is first fractionated to separate a light naphtha fraction comprising the initial to 200° F. end point fraction and a heavy naphtha comprising the 200–400° F. end point fraction. These two fractions are then separately hydroformed under the optimum conditions for upgrading each. Both hydroformates are then subjected to treatment with molecular sieves having pore diameters of about 5 A. units which adsorb the normal paraffins while passing the higher octane number isoparaffins and aromatics. The latter materials are used as high octane number motor fuels or they may be blended with other gasoline components to form high octane number motor fuels. The light normal paraffins recovered from the molecular sieve treatment are thereupon subjected to hydroisomerization using make-gas from the hydroforming operation to provide the desired hydrogen partial pressure. The resultant hydroisomerizate is then recycled to the molecular sieve treatment in order that the branch chain compounds formed by this treatment may be recovered and added to the other non-normal paraffin constituents. The heavy normal paraffins recovered from the molecular sieve treatment of the heavy hydroformate are not particularly suited as a feed to an isomerization treatment. These heavy normal paraffins, however, do form a satisfactory feed for an aromatization treatment or, if desired, they may be recycled to the heavy naphtha hydroformer vessel. In accordance with a further embodiment of the present invention, propylene and/or n-butylene, or a cracked refinery gas stream which contains these olefins is utilized to desorb the normal paraffins from the molecular sieves. In accordance with this invention the olefins utilized for desorption are separated from the normal paraffins and passed to a polymerization unit and the resultant polymer may thereafter be subjected to a hydrogenation treatment utilizing make-gas from the hydroformer operation in order to hydrogenate the polymer and render it suitable for blending with the other motor fuel constituents produced in accordance with this invention.

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

Referring to the drawing, a wide boiling range naphtha feed is supplied to the system through inlet line 10 into fractionator 11 where the feed is separated into an overhead light naphtha fraction boiling up to about 200° F. and a heavy naphtha fraction boiling in the range of about 200° to 400° F. The light naphtha fraction is withdrawn through line 12 and supplied to low pressure platinum hydroformer 13. Catalysts that may be used for hydroforming the light naphtha fraction in reactor 13 are those 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. Patent 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 platinum widely dispersed upon alumina in the eta phase derived from alumi-

num amylate and having a surface area of about 150 to 220 square meters per gram.

The pressure in the hydroforming reaction zone **13** should be in the range of 0 to 125 p.s.i.g. and is preferably about 50 p.s.i.g. It has been found that in the pressure range of about atmospheric pressure to 125 p.s.i.g. it is possible with the platinum-containing catalysts described above to upgrade light virgin naphthas having a mean average boiling point of 169° F. and a Research Clear octane number of 66 into a hydroformate having a Research O.N (Clear) of around 92 and higher in yields of about 75 vol. percent and into a hydroformate having a Research O.N. (clear) of around 97 or higher in yields of about 68 vol. percent at 200 p.s.i.g. With a molybdenum oxide-alumina catalyst the hydroformate produced is of only about 81 Research O.N. at yields of about 75 vol. percent or about 85 Research O.N. in yield of about 68 vol. percent. In further contrast thereto, hydroforming of this light naphtha at 200 p.s.i.g. with platinum-containing catalysts produces a hydroformate of only 85 Research O.N. at 75 vol. percent yield. Moreover, it was found impossible to increase the octane number much above 85 by hydroforming this light naphtha with platinum-containing catalysts at 200 p.s.i.g.

The temperature of the catalyst bed in reactor **13** should be in the range of from 800°–975° F., preferably from 875° to 950° F. The naphtha feed is preheated to temperatures in the range of from 900°–1050° F., preferably about 975° to 1000° F., preparatory to charging to the hydroforming reaction zone **13**. Hydrogen or hydrogen-rich process or recycle gas is supplied to the hydroformer **13** by line **14** and is preheated to 900°–1300° F., preferably about 1200° F., preparatory to charging to the hydroforming reaction zone. If desired, the naphtha and hydrogen-rich gas may be heated together in which event the preferred preheat temperature is in the range of from 900°–1000° F.

The hydrogen-rich or recycle gas normally contains about 65–90 mol. percent hydrogen with the remainder being light hydrocarbon gases. The exact composition of the recycle gas depends upon the hydroforming reaction conditions and upon the pressure and temperature at which the recycle gas is separated from the hydroformate. The amount of recycle gas employed may vary from 500–5000 and is preferably about 1000–3000 standard cubic feet per barrel of naphtha feed.

In addition to preheating the naphtha feed and recycle gas, the additional heat load may be supplied to the hydroforming reaction zone **13** by the sensible heat of the regenerated catalyst in the event that a fluidized solids operation is employed or by circulating reactor catalyst through a heating zone or by arranging heating coils in the catalyst bed or jacketing the reactor and circulating hot flue gases, mercury, Dowtherm, or the like therethrough.

Under the reactor conditions maintained in hydroformer **13**, there is a tendency for carbon to form on the catalyst and it therefore becomes necessary to regenerate the catalyst by burning the carbonaceous deposits from the catalyst. Regeneration is preferably effected with diluted air to facilitate control of the temperature of regeneration and it is preferred to contact the regenerated or carbon-free catalyst with undiluted air or oxygen-enriched gas at temperatures of about 850°–1100° F. for from about 1–4 hours. It is also desirable to provide means for subjecting the regenerated catalyst or a portion of it in continuous operation to reactivation with a halogen or halogen compound such as chlorine or hydrogen chloride. A free halogen such as chlorine is the preferred treating agent for reactivation. Aside from the accumulation of poisons the deactivation of hydroforming catalysts proceds by two mechanisms: (1) the loss of chlorine or other halogen which is normally present as part of the catalyst composition and that contributes substantially to the catalyst activity and (2) the agglomeration of the platinum metal into relatively large or massive crystals having diameters in excess of about 50 A. units. Treatment of the catalyst with a halogen compound such as hydrogen chloride or the like is effective in restoring the halogen content of the catalyst to the desired level and to this extent it is effective in restoring the activity of deactivated or partially deactivated catalyst. On the other hand, treatment of the catalyst with an elementary halogen, such as chlorine or the like, not only restores the catalyst halogen content to the desired level but also acomplishes the redispersion of the platinum metal by breaking up the large platinum crystalites.

Regeneration of the catalyst is effected as required by burning carbonaceous materials therefrom with oxygen-containing gas at temperatures of 900°–1200° F., preferably at 1000°–1100° F. The pressure in the regeneration operation may be the same as during hydroforming or it may, if desired, be lowered to near atmospheric pressure. In burning off the carbonaceous deposits, a certain amount of water is formed by combustion of hydrogen in said deposits. This water is stripped from the catalyst and passes overhead with the flue gases and is removed from the system. Excess air is used for the regeneration to insure the complete removal of carbon or coke from the catalyst and to effect reactivation in admixture with chlorine. The regenerated or carbon-free catalyst can advantageously be treated with air at temperatures of 850°–1100° F. for from about 1–4 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 redisperse or break up the large platinum crystalites that formed during the 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 may be in the range of 0.1 to 2.0 wt. percent, preferably, about 0.5 wt. percent based on the catalyst. The chlorine treatment may be carried out for periods of from about 15 seconds to 1 hour, preferably, about 1–15 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. The amount of chlorine which is desirable to have remaining on the stripped catalyst is related to the platinum content of the catalyst. With high platinum content catalysts a relatively high chlorine content is desirable and a correspondingly lower chlorine content is desirable for lower platinum contents. In general, the total amount of chlorine (i.e., both chemically combined and adsorbed) remaining on the catalyst when employing a catalyst of 0.6 wt. percent platinum content may be in the range of about 0.2 to 1.25 wt. percent and is preferably about 0.5 to 1.0 wt. percent.

Reaction products are taken overhead from hydroformer **13** by line **15** and are cooled to condensation temperatures and passed into gas-liquid separator **16**. Hydrogen-rich recycle gas is withdrawn from the separator by line **17** and is returned to the hydroformer by line **14**. Liquid hydroformate is withdrawn from the bottom of the separator by line **18** and it is supplied to molecular sieve separation vessel **20**, preferably, after preheating to 200°–300° F. or sufficiently high to completely vaporize the hydroformate.

The scientific and patent literature contain numerous references to the sorbing action of natural and synthetic zeolites. Among the natural 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, aluminum 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 $NaAlSi_2O_6.H_2O$. Barrer in 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 $(CaNa_2)\ Al_2Si_4O_{12}$. Black, U.S. Patent No. 2,522,426 describes a synthetic molecular sieve zeolite having the formula

$$4CaO.Al_2O_3.4SiO_2$$

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).

The molecular sieve separation vessel **20** is charged with a natural or synthetic zeolite of the class described above having a pore size of approximately 5 A. which will readily adsorb the normal paraffins contained in the hydroformate but will not adsorb the isoparaffins or aromatics contained therein. If desired, the hydroformate can be passed through a guard zone containing a molecular sieve material having pore diameters of 4 A. or smaller which will serve to remove any water or hydrogen sulfide or the like contained in the hydroformate. This is highly desirable since both water and certain sulfur compounds are more strongly adsorbed than most hydrocarbons and it is difficult to desorb them. Since these contaminants frequently occur in hydroformates in small amounts, continued use of the 5 A. sieves would require periodic interruptions to desorb the contaminants and restore adsorbent capacity. By using a guard bed of molecular sieves having pore openings of 4 A. or less, the contaminants are removed, but the hydrocarbons are not adsorbed. Since the capacity of the 4 A. and smaller sieves for water is high, the total volume or amount of this sieve as compared to the total volume or amount of the 5 A. molecular sieve is small. Ordinarily, it is preferred to arrange the adsorbent units in pairs so that one unit may undergo desorption or regeneration while the other unit is on stream. Water may be desorbed from the guard bed by passing hot gases such as dry air therethrough. It should be understood, however, that if the hydroformate is dry and /or substantially free of sulfur compounds, it is not necessary to provide a guard bed.

The hydroformate feed is passed in vapor phase, preferably, at temperatures of about 200°–300° F., into the molecular sieve separation zone or tower **20**. The adsorbent or molecular sieve material is arranged in any desired manner in the adsorption zone or tower. 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 are flow rates of 0.1 to 5 v./v./hr., temperatures of about 175°–350° F., and pressures from atmospheric pressure to several hundred pounds per square inch.

The light naphtha hydroformate substantially free from straight chain paraffins is withdrawn from the adsorption zone or tower by line **21** and is sent to storage or used for blending or for direct employment as a high octane number motor fuel.

When the molecular sieves in the adsorption zone or tower **20** become saturated with normal paraffins as may be determined by conventional means, such as refractive index, gravity, or spectrographic analysis of the effluent, the flow of hydroformate is stopped and the desorption or regeneration of the sieves begins. Desorption is effected by passing an olefin-containing gas, preferably, one containing a substantial proportion of propylene, preheated to 200°–250° F. through the bed of molecular sieves via line **22**. The stripping gas may be passed through a guard bed similarly to the hydroformate if necessary to remove the contaminants that might become absorbed on the molecular sieve. Cracked refinery gases containing propylene and/or n-butylene are preferred as the stripping gas, not only because of their availability and efficacy in stripping off the adsorbed normal paraffins but also because of the value of these olefins after separation from the absorbate as a feed to a polymerization unit. Without changing the temperature of the adsorption zone or tower the stripping or desorbing gas replaces the adsorbed paraffins with the propylene and/or other olefins. The desorbed normal paraffins and the non-olefinic constituents of the stripping gas and any iso-butylene are withdrawn from the tower **20** via line **23**, cooled or condensed and passed into gas-liquid separator **24**. The unadsorbed stripping gases are removed through line **54**. If sufficient iso-butylene is present, this gas stream may be passed to polymerization zone **57** for co-polymerization with propylene and/or n-butylene recovered from gas-liquid separators **38** and/or **39**. However, for desorbing C_6 and C_7 normal paraffins, propylene will usually be preferred. For higher boiling normal paraffins, such as C_8–C_{12} paraffins, either propylene or n-butylene may be used, preferably, n-butylene. In some instances, the molecular sieve may have sufficient catalytic activity to polymerize iso-butylene. In such instances, it may be preferred to use iso-butylene-free gas or to remove this isomer by selective conversion in the polymerization zone before use as a desorbing gas in the molecular sieve towers. The light, normal paraffins are withdrawn from gas-liquid separator **24** via line **25** and supplied to hydroisomerization reactor **26**. Isomerization of the light normal paraffins is preferably carried out as hydroisomerization or by means of Friedel-Crafts catalyst, such as $AlCl_3$, in which case a substantial partial pressure of hydrogen will advantageously be employed to promote selectivity and prolong catalyst life. Although a number of catalytic materials may be employed to promote hydroisomerization, nickel deposited on silica-alumina or platinum deposited on silica-alumina are particularly useful for this purpose. For example, 5 wt. percent nickel on silica-alumina may be employed at a pressure of about 350 p.s.i.g. and at a temperature of about 700° F. to isomerize a wide range of normal paraffins falling within the gasoline range. Hydrogen partial pressure in the hydroisomerization reaction zone may be provided by withdrawing excess or tail gas from line **17** by line **27**. It is usually desirable to employ a sulfur removal or guard zone **28** in the hydrogen feed line so as to avoid deactivation of the catalyst in the reactor vessel **26**. The hydroisomerizate is withdrawn from reactor vessel **26** by line **28** and is cooled and condensed and discharged into gas-liquid separator **29**. The liquid hydroisomerizate is withdrawn from separator **29** by line **30** and recycled to molecular sieve separation zone **20** for recovery of isoparaffins along with non-normal hydrocarbons and the aromatics formed in the hydroforming zone.

The heavy naphtha or the 200°–400° F. fraction is withdrawn from fractionator **11** by line **31** and passed to high pressure hydroformer **32**.

The heavy naphtha fraction is hydroformed in reactor **32** under essentially conventional or well known conditions. For example, the heavy naphtha may be hydroformed in contact with 10 wt. percent molybdic oxide on activated alumina catalyst at temperatures of about 850°–1000° F., preferably, about 925° F. at pressures up to about 750 p.s.i.g., preferably, about 200 p.s.i.g., and in the presence of from about 2000–8000 cu. ft. of hydrogen-rich gas per barrel of feed. Alternatively, the heavy naphtha may be hydroformed in contact with a catalyst consisting essentially of about .5 wt. percent platinum upon eta alumina, derived from alcoholate alumina, at temperatures of from 800°–975° F., preferably, about 925° F., and at pressures of from 200–500 p.s.i.g. in a regenerative or cyclic type operation, or at 500–750 p.s.i.g. in a continuous or non-regenerative operation. The

heavy naphtha hydroformate is taken overhead from the hydroformer 32 by line 33 and passed through coolers or condensers and thence into gas-liquid separator 34. Hydrogen rich or recycle gas is removed from separator 34 by line 35 for recycling to the hydroformer 32. Excess hydrogen-rich gas is removed from the system by discharge line 36. The heavy naphtha hydroformate is withdrawn from separator 34 by line 37 and passed to molecular sieve separation zone or tower 40. Tower 40 is similar to tower 20 and is charged with the same type of zeolite or molecular sieve and is operated in essentially the same way as tower 20, i.e., at a temperature sufficiently high to maintain the hydroformate in vaporous form.

Heavy naphtha hydroformate essentially free of normal paraffins is withdrawn from the molecular sieve separation tower 40 by line 41, through gas-liquid separator 38, and is then passed to storage or blending or is used directly as a high octane number motor fuel. When the molecular sieves in the adsorption zone 40 become saturated with normal paraffins, they are regenerated by supplying an olefin-containing gas via line 42 as described above for the regeneration of the molecular sieve material in tower 20. The desorbed heavy normal paraffins and the unadsorbed components of the desorbing gas are withdrawn from tower 40 via line 43 and cooled prior to discharge to gas-liquid separator 44. The unadsorbed gases are removed through lines 55 and may be vented or passed to polymerization zone 57 for conversion of iso-butylene, if desired. The heavy, normal paraffins are withdrawn from separator 44 via line 45 and are passed or recycled via line 46 to the high pressure hydroformer 32 or are passed via line 47 to aromatizer 48 where they may be subjected to known aromatization catalysts and reaction conditions to convert the heavy paraffins to aromatics. For example, the heavy normal paraffins may be aromatized in contact with such catalysts as chromia-alumina, chromia-magnesia-alumina, platinum-alumina, molybdena-alumina, etc. at temperatures of about 850°–1050° F., at pressures below about 500 p.s.i.g., preferably, below about 200 p.s.i.g., and in the presence of about 2000–8000 cu. ft of hydrogen-rich gas per barrel of feed The aromatizate is withdrawn from reactor 48 via line 49, condensed and passed to gas-liquid separator 50. The liquid aromatizate is withdrawn from separator 50 via line 51 and either passed to blending or storage via outlet line 52 or is recycled via line 53 to molecular sieve separation zone 40.

Olefinic displacement gas is withdrawn from separator 39 via line 56 and from separator 38 via line 65 and these streams are combined and passed through line 66 into polymerization zone 57 where the gaseous olefins, preferably, the C_3's and C_4's, used to displace the normal paraffins from the sieve adsorbent, are polymerized to yield additional quantities of high octane fuel components. Isobutylene may be obtained through lines 54 and 55 as already indicated. Usually it will be desirable to hydrogenate the polymer if the gaseous olefin feed is predominantly normal and isobutene. In this case the polymer is withdrawn from zone 57 via line 58 and passed to hydrogenation tower 60. Hydrogen from the hydroformer zone 13 may be supplied to the hydrogenation zone 60 by connecting lines 61, 27 and 17. Additional hydrogen may be supplied via lines 36 and 67. The hydrogenated polymer is discharged from hydrogenation zone 60 through line 62 into gas-liquid separator 63 and is withdrawn as liquid product through line 64 for transfer to storage or for use as a blending agent in the preparation of high octane number motor fuel.

It may readily be seen that the foregoing operation is a highly integrated process which permits the conversion of the various components of the naphtha feed under optimum conditions to the highest octane components and permits the most effective separation of the normal paraffins, the poorest octane components, so that they may be further processed to improve their octane numbers and increase their value for blending into the motor gasoline pool and which utilizes to the full excess hydrogen produced in the hydroforming processes as well as the olefinic gases used for regenerating the molecular sieves.

Example I

A light virgin naphtha from West Texas crude, boiling (5% to 95%) in the range of 162° to 191° F. and having an API gravity of 67.9° and a Research clear octane number of 66.1, is hydroformed by contacting with a catalyst comprising 0.6 wt. percent platinum deposited on alcoholate alumina at a temperature of 900° F., a pressure of 50 pounds per square inch, a feed rate of 1.2 weights of naphtha feed per hour per weight of catalyst, and in the presence of 2000 cu. ft. of recycle hydrogen per barrel of feed for a processing period of 8 hours. There is obtained a yield of 73.0 vol. percent of C_5+ product having a Research O.N. clear of 93.0.

The C_5+ hydroformed naphtha is combined with stabilized isomerizate, vaporized, and passed at 240° F. through a bed of molecular sieves having pore openings of about 5 A. until the sieves are about 90% saturated with normal paraffins. The adsorbed normal paraffins are then desorbed with propylene at the same bed temperature and are passed to a hydroisomerization zone consisting of a fixed-bed of 4.5% nickel on silica-alumina catalyst at 675° F., 400 pounds per square inch pressure, 0.8 weight of n-paraffins per hour per weight of catalyst, and with 8000 cu. ft. of hydrogen per barrel of hydrocarbon. The isomerizate is stabilized to remove small amounts of C_5 and lighter hydrocarbons and is combined with the hydroformate for molecular sieve treating as indicated. The combined n-paraffin-free hydroformate and the isoparaffins amount to 72.5 vol. percent based on fresh naphtha feed. The Research octane number of the blend is 99.1. If the naphtha is hydroformed directly to this octane level, the yield of C_5+ hydroformate is 62.6 vol. percent.

Example II

A 53.1 Research O.N., virgin naphtha is fractionated to obtain 28 vol. percent of a light naphtha (157°–254° F.) and 72% of heavy naphtha (228°–330° F.). The 66.1 octane number light naphtha is hydroformed, the C_5+ hydroformate treated with molecular sieves to remove normal paraffins, and the normal paraffins desorbed from the sieves by propylene displacement and hydroisomerized as in Example I.

The 48.0 octane number heavy naphtha is hydroformed by contacting with a 10% molybdena-on-alumina catalyst at 900° F., 200 pounds per square inch pressure, 0.4 weight of naphtha feed per hour per weight of catalyst, and in the presence of 2000 cu. ft. of recycle hydrogen per barrel of feed for a processing period of 4 hours. The C_5+ hydroformate obtained has an octane number of 96.0 and is combined with aromatized, heavy n-paraffins, vaporized, and passed at 350° F. through a bed of molecular sieves having pore openings of about 5 A. until the sieves are about 90% saturated with normal paraffins. The adsorbed normal paraffins are then desorbed at the same bed temperature with n-butylene contained in a refinery gas stream at 22% concentration. The normal paraffins (11 vol. percent on C_5+ hydroformate) are aromatized at 1000° F. and 10 pounds per square inch pressure over 10% MoO_3-on-$ZnAl_2O_4$ and combined with the heavy hydroformate for molecular sieve treating as indicated.

Propylene concentrate obtained from the molecular sieve column used for removal of normal paraffins from the light hydroformate and hydroisomerizate and n-butylene concentrate obtained from the sieve column used for removal of normal paraffins from the heavy

hydroformate and heavy, n-paraffin aromatized product are combined and polymerized with a P_2O_5-kieselguhr catalyst at 450° F. and 1000 pounds per square inch pressure.

Blending the light hydroformate-isoparaffin fraction and the heavy hdroformate-C_8+ aromatics fraction with the propylene-butylene polymer gives, on the basis of naphtha feed, an 80.1 vol. percent yield of 100.4 Research octane number product. The highest octane number attained in direct, once-through hydroforming at practical plant throughput is 96–98. Under these conditions, the yield is 69 vol. percent.

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 for producing high octane number motor fuels which comprises fractionating the naphtha to form a 200° F. end point light naphtha fraction and a 200° to 350° or 400° F. end point heavy naphtha fraction, hydroforming the light naphtha fraction in contact with a platinum-alumina catalyst at temperatures of from 800°–975° F. and pressures below 125 p.s.i.g. and in the presence of from 500 to 5000 cu. ft. of hydrogen-rich gas per barrel of liquid feed, treating the light naphtha hydroformate with molecular sieves having pores of about 5 A. diameter to separate the normal paraffins contained therein, separating the normal paraffins from the sieves by passing olefin-containing gases therethrough, treating the separated normal paraffins under isomerizing conditions to convert normal paraffins to branch chain isomers, passing the isomerizate to the molecular sieves for the recovery of the branch chain isomers along with the non-normal paraffin constituents of the light naphtha hydroformate, subjecting the heavy naphtha fraction to catalytic hydroforming at temperatures of from 850°–1000° F. and at pressures above about 200 p.s.i.g. in the presence of from 2000 to 8000 cu. ft. of hydrogen-rich gas per barrel of liquid feed, treating the heavy naphtha hydroformate with molecular sieves having pores of about 5 A. diameter to separate the normal paraffins contained therein, separating the normal paraffins from the molecular sieves by passing olefin-containing gases therethrough, aromatizing the normal paraffins separated from the heavy naphtha hydroformate and recycling the resultant aromatizate to the molecular sieve treatment for the recovery of branch chain paraffins and aromatics therein with the non-normal paraffins in the heavy naphtha hydroformate, separating the olefin-containing desorption gases from the molecular sieves, polymerizing the separated olefins to form additional gasoline boiling range products and passing the resultant polymerizate, the light naphtha products and heavy naphtha products to blending and storage.

2. The method for converting low octane number naphtha feeds into high octane number motor fuels which comprises fractionating the naphtha to form a 200° F. end point light naphtha fraction and a 200° to 350 or 400° F. end point heavy naphtha fraction, hydroforming said light naphtha fraction in contact with a solid catalytic material at elevated temperatures and pressures for a period sufficient to substantially improve the octane number of the light naphtha fraction, separating the hydroformate from the normally gaseous materials, vaporizing the hydroformate, passing the hydrofromate vapors through a bed of molecular sieves having pore diameters of about 5 A. units which selectively adsorbs the normal paraffins from the hydroformate vapors, recovering from said molecular sieve separation hydroformate substantially free from normal paraffins, desorbing the normal paraffins from the molecular sieves by passing olefin-containing gases therethrough, hydroisomerizing the separated normal paraffins, recycling the hydroisomerizate to the molecular sieve separation step, separately subjecting said heavy naphtha fraction to catalytic hydroforming by contacting said heavy fraction in admixture with hydrogen with a solid catalytic material at elevated temperatures and pressures for a period sufficient to substantially improve the octane number of the heavy naphtha fraction, separating the heavy hydroformate from the normally gaseous materials, vaporizing the heavy hydroformate, passing the heavy hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. units which selectively adsorbs the normal paraffins from the heavy hydroformate vapors, recovering from said molecular sieves heavy hydroformate substantially free from normal paraffins, desorbing the heavy normal paraffins removed from the heavy hydroformate vapors from the molecular sieves by passing olefin-containing gases therethrough, aromatizing said heavy normal paraffins separated from the heavy naphtha hydroformate, recycling the resultant aromatizate to the heavy naphtha molecular sieve treatment for the recovery of branch chain paraffins and aromatics therein with the non-normal paraffin constituents in the heavy naphtha hydroformate, separating olefin-containing desorption gases from the molecular sieves and polymerizing the separated olefins to form additional gasoline boiling range products.

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