Nov. 1, 1960 C. N. KIMBERLIN, JR., ET AL 2,958,644

PRODUCTION OF HIGH OCTANE MOTOR FUELS

Filed May 1, 1957 4 Sheets-Sheet 1

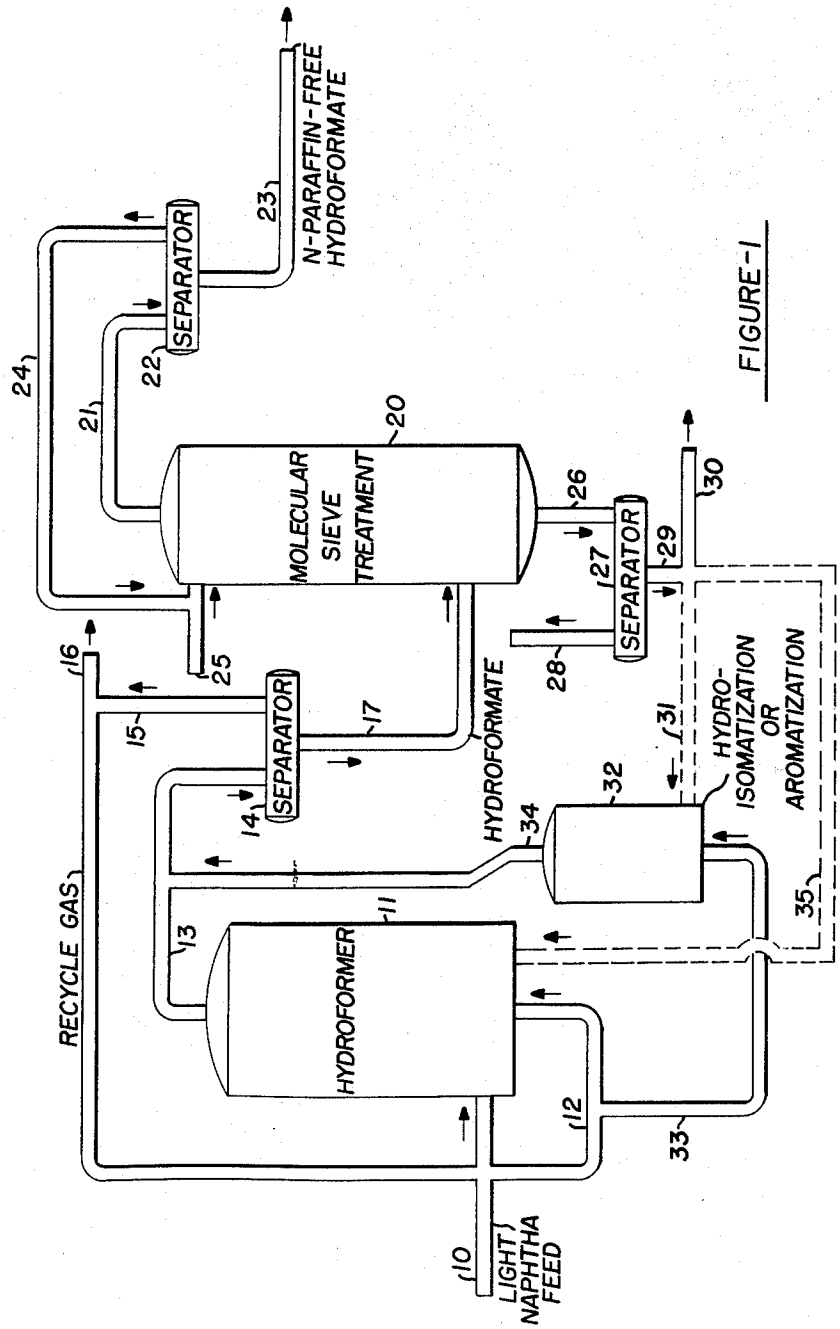


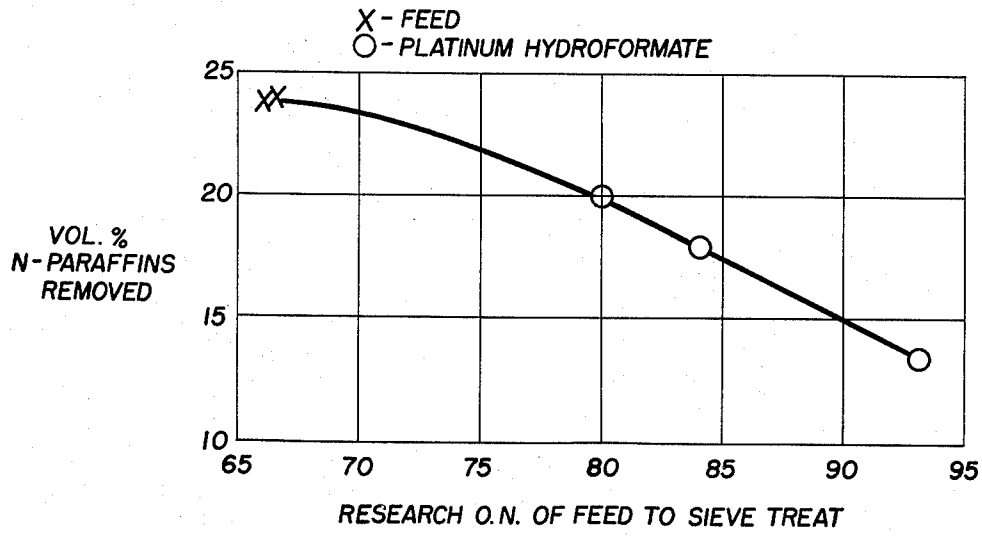
FIGURE-1

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FIGURE-2

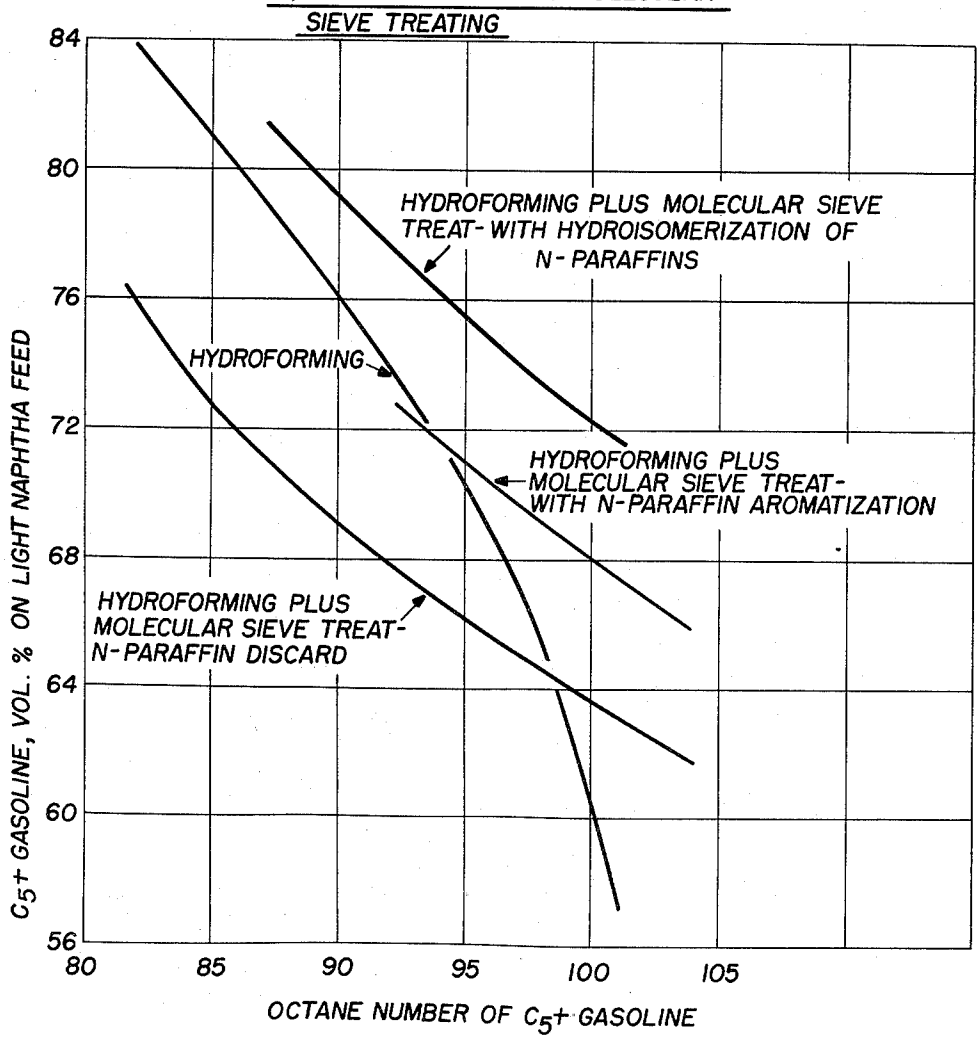
PLATINUM REFORMING OF LIGHT NAPHTHA PLUS MOLECULAR SIEVE TREAT-N-PARAFFINS REMOVED VS. OCTANE NUMBER OF REFORMATE



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FIGURE-3

REFORMING LIGHT VIRGIN NAPHTHA
YIELD-OCTANE NUMBER RELATIONSHIPS
FOR
1) 50 PSIG PLATINUM HYDROFORMING
2) HYDROFORMING PLUS MOLECULAR
SIEVE TREATING

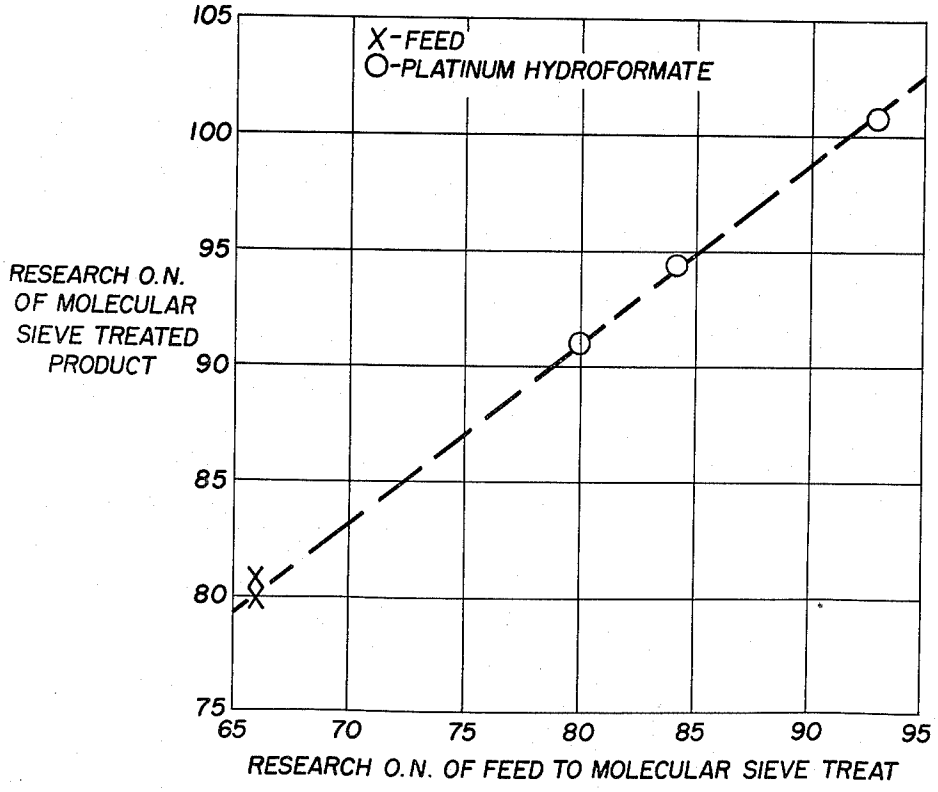


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FIGURE - 4

PLATINUM REFORMING OF LIGHT NAPHTHA PLUS MOLECULAR SIEVE TREAT
OCTANE NUMBER OF TREATED MATERIAL
VS.
OCTANE NUMBER OF REFORMATE



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2,958,644

PRODUCTION OF HIGH OCTANE MOTOR FUELS

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14 Claims. (Cl. 208—64)

The present invention relates to the reforming of hydrocarbons and particularly to an improved method for hydroforming of naphtha fractions to produce 100+ octane number motor fuels.

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 if such compounds are present and sulfur or sulfur compounds are eliminated by conversion to metal sulfides and/or hydrogen sulfide making the hydroformate burn cleaner or form less deposits when used as the fuel in an internal combustion engine.

Hydroforming is usually applied to a rather wide boiling range naphtha, i.e. to one having a boiling range of from about 125° F. 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 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 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 naphthas to even higher octane levels and in this connection it is becoming essential to improve the octane number of 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 the object of this invention to provide a simple and effective method for hydroforming petroleum naphthas boiling in the range of from about 110°–400° F., preferably from about 150°–350° F.

It is a further object of this invention to provide the art with a relatively simple, effective method for converting light petroleum naphthas having end points of 225° to 250° F. into 100+ octane number products in high yields.

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

It has now been found that naphtha fractions can be advantageously upgraded to 100+ octane number products by hydroforming the same in contact with hydroforming catalysts of the molybdenum oxide type as well as of the platinum metal type at temperatures of about 850°–975° F., preferably 875°–950° F., and at pressures up to about 400 p.s.i.g. and at feed rates sufficiently high that the hydroformate has an octane number of about 90 to about 95 and thereafter contacting the hydroformate with molecular sieves or synthetic alumino-silicate zeolites which selectively remove the normal paraffins from the hydroformate.

In a preferred embodiment, light petroleum naphtha fractions are converted into very high (100+) octane number light naphtha products with an unexpectedly high yield advantage by hydroforming them in contact with platinum-containing catalysts at pressures below 125 p.s.i.g. and preferably at pressures of from 50 to 100 p.s.i.g. to an intermediate octane number level of about 90 and thereafter treating the hydroformate with molecular sieves of the proper type to remove n-paraffins. By this particular combination of process steps it is possible to obtain a light naphtha hydroformate having an octane number of 100 or more with at least about a 5 vol. percent yield advantage, even without utilization of the separated n-paraffins, over hydroforming the same feed stock to the same octane number directly. In addition, by the combination process of this invention it is possible to increase the feed rates to a hydroforming unit, in some cases as much as three or fourfold increase over that necessary to produce hydroformates having an octane number of 100 or higher.

It has, of course, been known for some time that certain zeolites, both naturally occurring and synthetic, sometimes termed molecular sieves, have the property of separating straight chain from branched chain hydrocarbon isomers, as well as from cyclic and aromatic compounds. These zeolites have innumerable pores of uniform size and only molecules small enough to enter the pores can be adsorbed. The pores may vary in diameter from 3 or 4 Angstroms to 15 or more, but it is a property of these zeolites or molecular sieves that any particular product has pores of substantially uniform size.

The scientific and patent literature contains 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. Pat. 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 $NaAlSi_2O_6 \cdot H_2O$. Barrer (U.S. 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 (Ca, Na_2) $Al_2Si_4O_{12}$. Black (U.S. Pat. 2,522,426) describes a synthetic molecular sieve zeolite having the formula $4CaO \cdot Al_2O_3 \cdot 4SiO_2$. 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).

Although it has, in the past, been proposed to effect the separation of straight chain hydrocarbons from isoparaffins and aromatics it has been found that a very

special combination of process steps is required to obtain the yield advantage achieved in accordance with the present invention. For example, if light virgin naphtha feed is freed of normal paraffins by molecular sieves prior to hydroforming, a yield of about 50 vol. percent on the total light naphtha feed is obtained at 100.8 research octane number. If, on the other hand, the total light naphtha feed is hydroformed to 100.8 research octane number, a yield of about 58 vol. percent on total naphtha feed is obtained. Furthermore, if the total light naphtha feed is hydroformed to about 80 research octane number and the hydroformate treated with 5 A. molecular sieves, a treated product of 91 research octane number is obtained in yields of about 68 vol. percent whereas the total light virgin naphtha feed can be hydroformed to 91 research octane number with yields of about 75 vol percent based on the total naphtha feed. However, by hydroforming the total light naphtha feed to about 93 research octane number and treating the hydroformate with 5 A. molecular sieves, a treated product of 100.8 research octane number is obtained in yields of about 63–64 vol. percent whereas, as noted above, hydroforming of the total light virgin naphtha feed to 100.8 research octane number would give a yield of only about 58 vol. percent based on the total light naphtha feed.

Similar results are obtainable with heavy naphtha hydroformates. While it is necessary to go to somewhat higher levels in the case of heavy naphthas, there is a very definite yield advantage when forming 103–105 and higher octane products. The octane level race has already reached the point where there is a definite need for improved hydroforming processes for producing 105 O.N heavy naphtha hydroformates.

The combination process of the present invention offers further, important process advantages in that it permits substantially longer process cycles in fixed bed operations and permits longer catalyst residence times in the reactor in fluid hydroforming operations. For example, if a 225° F. end point naphtha is hydroformed to 100.8 research octane number in a 50 p.s.i.g. fixed bed platinum hydroforming operation, the run would have to be terminated after about 1 hour and the catalyst regenerated and reactivated. If, on the other hand, that naphtha is hydroformed to only 93 research octane number the run may be continued for about 8 hours before regeneration and reactivation of the catalyst becomes necessary. Since the number of regenerations that a charge of catalyst can undergo before it becomes deactivated to a point where it is necessary to replace it with a fresh charge of catalyst is limited, it is obvious that the process of the present invention offers the further advantage of giving long catalyst life.

Reference is made to the accompanying drawings in which Fig. 1 is a diagrammatic flow plan of the process in accordance with the present invention and Figures 2, 3 and 4 show graphically several correlations that are illustrative of the results obtained by the process of this invention.

Referring to Fig. 1, naphtha feed is supplied through inlet line **10** to hydroformer **11** where it is contacted, in admixture with hydrogen-rich recycle gas supplied through line **12**, with a hydroforming catalyst under conditions of temperature, pressure and the like as described below. While hydroformer **11** is shown as a single vessel it will be understood that this may comprise several reactor vessels in series with reheating means between each. The hydroformer may be a fixed or moving bed reactor or the reactor system may utilize the fluidized solids technique.

Hydroformate is taken overhead from hydroformer **11** through line **13**, cooled or condensed and passed to gas-liquid separator **14**. Hydrogen-rich recycle gas is removed from separator **14** via line **15** and returned to the hydroformer via inlet line **12**. Excess gas is discharged from the reactor system through vent line **16**.

Hydroformate is withdrawn from separator **14** through line **17**, heated to vaporization temperatures and charged to vessel **20** where the vapors are contacted with suitable molecular sieve materials having an average pore diameter of 5 Angstrom units. A suitable 5 A. molecular sieve may be prepared as follows: A solution of 600 g. of granular sodium metasilicate (composition 29.1 wt. percent Na_2O, 28.7 wt. percent SiO_2, 42.2 wt. percent H_2O) in one liter of water is placed in a burette. A second solution of 370 g. of sodium aluminate in 538 ml. of water is placed in a second burette. The two solutions are added dropwise with vigorous stirring over a period of two hours to 510 ml. water containing a little NaOH to give an alkaline solution at a temperature of 190° F. A slight excess of the metasilicate solution over the aluminate solution is maintained during the addition. At the end of the addition, heat is removed and stirring is continued for 10 minutes. The mixture is filtered and washed. The precipitate, sodium alumino silicate is 4 A. sieve.

To prepare the 5 A. sieve, 35 g. of the wet filter cake is stirred at room temperature for 1 hour in 600 g. of a 20% calcium chloride solution. The mixture is filtered, washed and then dried at 135° C. The dried product is calcined at 850° F. for 4 hours. The adsorbent or molecular sieve material is arranged in any desired manner in the adsorption tower or vessel **20**. 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 vessel **20** are flow rates of 0.1 to 5 v./v./hr., pressures from atmospheric to several hundred p.s.i.g., and temperatures sufficiently high to maintain the hydroformate in vaporous form i.e. —175–325° F. for light naphtha and up to 400 or 425° F. for heavy naphtha.

Hydroformate substantially free from straight chain paraffins is withdrawn from the adsorption zone or tower **20** via line **21**, cooled or condensed and passed to gas-liquid separator **22** to separate a stabilized liquid product which is withdrawn via line **23** and passed to product storage or blending. Gaseous materials, including normally gaseous olefins used for regenerating the molecular sieves are withdrawn from separator **22** through line **24** for recycling to the molecular sieve treatment vessel.

When the molecular sieve material in vessel **20** becomes saturated with normal paraffins, the flow of hydroformate is stopped and desorption or regenertaion of the sieves is begun. Desorption is preferably effected by passing an olefin-containing gas such as propylene or a cracked refinery gas rich in propylene or butylene preheated to about 200°–250° F. through inlet line **25** into vessel **20**. Thus without substantially changing the temperature of the adsorption zone or vessel **20**, the stripping or desorbing gas replaces the adsorbed paraffins with propylene and/or other olefins. The desorbed normal paraffins and the non-olefinic constituents of the stripping gas are withdrawn from vessel **20** via line **26**, cooled or condensed and passed into gas-liquid separator **27**. Gases are withdrawn from separator **27** through line **28**. Desorption can also be effected by passing hydrogen or natural gas through the bed or by raising the temperature or lowering the pressure in the bed, or by a combination of two or more of the foregoing expedients.

The desorbed normal paraffins are withdrawn from separator **27** via line **29** and may be discharged through line **30** to n-paraffin product storage for use as solvents or jet fuel or the like. If desired, however, the n-paraffins may be passed from line **29** through line **31** to an isomerization or aromatization reactor **32** or through line **35** into hydroformer reaction zone **11** for retreatment under hydroforming conditions. Isomerization of the light normal paraffins is preferably carried out as a hydroisomerization treatment or by means of a Friedel-Crafts catalyst such as aluminum chloride in which case a substantial partial pressure of hydrogen will advantageous-

ly be employed to promote selectivity and prolong catalyst life. Although a number of catalytic materials may be employed to promote hydroisomerization, nickel deposited upon silica-alumina or platinum on alumina or silica-alumina are particularly useful for this purpose. For example, 5 wt. percent nickel on silica-alumina may be employed at pressures of about 350 p.s.i.g. and at temperatures 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 hydrogen-rich recycle gas from line 12 through line 33. Ordinarily it is preferred to pass the hydrogen through a suitable guard bed or purifying zone to remove sulfur or hydrogen sulfide therefrom which would have an adverse effect upon the isomerization catalyst. The isomerization products are removed from reactor 32 through line 34 and passed into line 13 for cooling and recovery of the non-normal paraffin constituents along with the hydroformate. Alternatively the normal paraffins may be treated in contact with an aromatization catalyst such as chromia-alumina, chromia-titania or MoO_3 on zinc aluminate spinel at temperatures of from 850–1050° F. and at pressures from atmospheric to about 150 p.s.i.g.

The virgin naphthas that may be treated in accordance with the present invention may be a wide cut boiling in the range of from about 110–375° F., or it may be a narrow cut such as 110°–250° F. or preferably 150°–200° F. light naphtha or a heavy naphtha cut boiling in the range of from about 200 to about 350° F. The C_5 fraction, boiling below about 150° F., is not upgraded by the process to as great an extent as the C_6 and C_7 hydrocarbons and therefore the C_5 fraction is not a particularly desirable component of the feed. On the other hand, the presence of C_5 in the feed is not particularly harmful so that it may be preferred to include this fraction in the feed if doing so will avoid an additional distillation step in the feed preparation. The fraction boiling above 200° F. up to 225° F. or 250° F. responds fairly well to the conventional hydroforming processes employing either molybdenum oxide or platinum catalyst at about 200 p.s.i.g. or higher and may be included in the feed to such processes. On the other hand, this fraction also responds well to the present low pressure platinum process so that the method of handling this particular fraction of the virgin naphtha feed will depend upon circumstances such as availability of equipment and the volumes of the different boiling range fractions which it is desired to process.

In general it is preferred to process a wide boiling range naphtha or say a 200 to 350° F. cut under essentially conventional conditions, i.e. with a conventional hydroforming catalyst such as 10% MoO_3 upon activated alumina or silica stabilized activated alumina at 100–400, preferably about 200 p.s.i.g. and at temperatures of 850–975° F. or with a catalyst consisting essentially of about 0.6 wt. percent platinum upon highly pure alumina, for example, eta alumina prepared by hydrolysis of aluminum amylate, aging to convert the hydrolyzate to beta alumina trihydrate, drying and calcining. Pressures and temperatures for hydroforming with this platinum catalyst are essentially the same as for hydroforming with the molybdenum oxide catalyst.

It has been found that in the pressure range of from about atmospheric pressure to 125 p.s.i.g. it is possible with platinum-containing catalysts to upgrade a light virgin naphtha having a mid-boiling point of 169° F. and a research octane number of 66 into a hydroformate having a research clear octane number of around 90 and higher in yields of about 75 vol. percent and into a hydroformate having a research clear octane number of around 95 or higher in yields of about 68 vol. percent. In contrast thereto, hydroforming of this naphtha at 200 p.s.i.g. with a molybdenum oxide catalyst produces a hydroformate of only about 81 research octane number in yields of about 75 vol. percent or about 85 research octane number in yields 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 octane number at 75 vol. percent yield. Moreover, it was found impossible to increase the research octane number much above about 85 by hydroforming this light naphtha with platinum-containing catalysts at 200 p.s.i.g.

Under these reaction conditions 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 of platinum-containing catalysts 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 850°–1100° F. for from about 1 hour to 4 hours. The hydroforming reaction may be carried out in fixed bed, moving bed, or fluidized solids type operations, the latter being preferred when reaction conditions are such that frequent regenerations are necessary and particularly when MoO_3 catalysts are used.

It is also desirable to provide means for subjecting the regenerated platinum-containing 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 platinum hydroforming catalysts proceeds by two mechanisms, viz., (1) the loss of chlorine or other halogen that 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 Angstrom 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 is effective in restoring the activity of deactivated or partially deactivated catalysts. 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 accomplishes the redispersion of the platinum metal by breaking up the large platinum crystallites. This treatment, therefore, is entirely effective in restoring the activity to deactivated catalysts whose activity loss was not due to the accumulation of poisons such as arsenic or the like.

Platinum-containing catalysts that may be used for hydroforming the naphthas in accordance with the present invention 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 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 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. Patent 2,656,321 and mixed with sufficient unplatinized alumina to form a catalyst composition containing about 0.01 to 0.2 wt. percent platinum. A suitable molybdenum oxide-containing catalyst is one containing 5 to 15 wt. percent preferably about 10 wt. percent MoO_3 dispersed

or supported upon activated alumina, alumina gel and the like.

The pressure in the reaction zone should be in the range of 0 to 400 p.s.i.g. and is preferably about 50 p.s.i.g., in the case of light naphtha hydroforming with platinum catalysts, 200 p.s.i.g. for MoO_3 catalysts and about 300 p.s.i.g. for platinum catalysts when hydroforming a higher boiling feed such as the 200°–350° F. virgin naphtha cut. The temperature of the catalyst bed should be in the range of from 800 to 975° F. In view of the fact that under the conditions of low pressure and low recycle gas rates applied in accordance with this invention the dehydrogenation activity of the platinum metal catalysts is extremely high, the reaction temperatures may be somewhat lower than used previously. The preferred temperature range is from 875°–950° F.

The naphtha feed is preheated to temperatures in the range of from 900°–1050° F., preferably about 975° F. to 1000° F. preparatory to charging to the hydroforming reaction zone. Hydrogen or hydrogen-rich process or recycle gas is preheated to 900 to 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 preheated 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 to 5000 and is preferably about 1000 to 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 by the sensible heat of the regenerated catalyst in fluidized solids operations 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 vapor, Dowtherm or the like therethrough.

The hydroformate and process gases are removed from the reaction zone, passed through suitable catalyst recovery equipment, if desired or necessary, and then passed through suitable heat exchanger and condenser equipment and thence into a gas-liquid separator. The gaseous products are removed from the separator and any excess gas is rejected from the system. The recycle gas may, if desired, be scrubbed to remove hydrogen sulfide and passed through a drier if excessive amount of water appear therein.

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 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 prior to reactivation with chlorine. The regenerated or carbon-free platinum catalyst can advantageously be treated with air at temperatures of 850–1100° F. for 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 redisperse or break up the large platinum crystallites that form during use of the catalyst.

The chlorine partial pressure 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 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. The amount of chlorine which it 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% 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.

The hydroformate is withdrawn from the gas-liquid separator and is further treated with molecular sieves in accordance with the present invention. Essentially, the molecular sieve treatment is effected by vaporizing the hydroformate and passing the vapors through one or more zones or chambers charged with suitable molecular sieve materials. In order to separate the normal paraffins from the isoparaffins and aromatics in the hydroformate, the vapors should be treated with molecular sieves having a pore size of approximately 5 Angstrom units, which will readily adsorb the normal paraffins contained in the hydroformate but will not adsorb the isoparaffins or aromatics. If desired, the hydroformate can be passed through a guard-bed consisting of molecular sieve material having a pore diameter of 4 Angstrom units or smaller which will serve to remove any water or hydrogen sulfide or the like. 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 sieve of 4 A. or smaller pore diameter 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 the 4 A. and smaller molecular sieves as compared to the total volume or amount of the 5 A. molecular sieves, 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 is passed, preferably in vapor phase at temperatures of about 200 to 400° F., into the adsorption zone or towers. The adsorbent, any natural or synthetic zeolite of the molecular sieve type heretofore described having a pore diameter of about 5 A., 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 in the molecular sieve treatment in the adsorption zone or tower are flow rates of 0.1 to 5 v./v. hr. temperatures of about 175–425° F. and pressures of from atmospheric pressure to several hundred pounds per square inch.

Hydroformate substantially free from straight chain paraffins is withdrawn from the adsorption zone or tower and is cooled or condensed and 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 becomes 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 cycle or regeneration of the sieves is begun. Desorption, as described above, may be effected by passing an olefin-containing gas, preferably one containing a substantial proportion of propylene and preheated to 200°–250° F., through the exhausted bed of molecular sieves. The stripping gas may be passed through a guard-bed similarly to the hydroformate if necessary to remove contaminants that might become adsorbed upon the molecular sieve. Cracked refinery gases containing a major proportion of ethane and propane may also be used for stripping the adsorbed normal paraffins from the sieves. Without changing the temperature of the adsorption zone or tower, the stripping or desorbing gas replaces the adsorbed paraffins with the olefins or propylene. The desorbed normal paraffins are withdrawn from the adsorption zone or tower and either passed to storage for use, for example, as jet fuel or, if desired, subjected to further processing such as aromatization or hydroisomerization under well known or conventional conditions for admixture with fresh hydroformate for passage through the molecular sieve treatment in order to recover further quantities of aromatics or non-straight-chain paraffins.

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 66.3, was 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, and in the presence of 2000 cubic feet of added hydrogen per barrel of feed for processing periods of 16 hours. The feed rate was varied to change hydroforming severity. The hydroformate was then stabilized by distillation to yield a C_5+ product which was vaporized and passed at 240° F. over a 5 A. molecular sieve to adsorb normal paraffins. The 5 A. sieve is particularly well suited to the selective removal of n-paraffins, the lowest octane components of the hydroformate. Figure 2 shows a correlation of the vol. percent of n-paraffins removed as a function of the hydroformate octane number.

Table I shows gasoline yield data obtained at different levels of hydroforming severity.

Table I.—Platinum hydroforming plus molecular sieve treating

Test Number	1*	2	3
First Stage Hydroformate:			
Hydroforming Conditions—			
Temperature, ° F		900	900
Pressure, p.s.i.g.		50	50
Hydrogen, 2,000 C.f./b.		2,000	2,000
Process Period, Hrs.		16	16
W./H./W.		2.7	0.75
Research Octane No.	66.3	80.0	93.0
Octane Increase by Hydroforming	0	13.7	26.7
Yield of Hydroformate, Vol. Percent	100	85.4	73.0
Sieve Treated Hydroformate:			
Research Octane No.	82.0	91.2	100.8
Yield, Vol. Percent on Naphtha Feed	76.0	68.3	63.1
Once-through Hydroforming Yield to same Octane No.	84.0	75.0	58.0
Yield Improvement by Combination Process	−8	−7	+5

*Without hydroforming; molecular sieve treat on naphtha feed.

As shown by the data obtained in Test #3, reforming the light naphtha to 93 research octane number followed by 5 A. molecular sieve treating gives 100.8 octane product in 5% better yield than direct reforming to the same octane number. This yield advantage is obtained without recycle or any reforming treatment of the separated n-paraffins. However, correlations of gasoline yield as a function of octane level or reforming severity, Figure 3, show yield advantages for the combined hydroforming-sieve treatment when producing gasolines above about 98 octane number. To attain this octane level in the combination treat requires an initial hydroformate of about 89–90, as shown in Figure 4.

At the 100 octane number level, further processing of the n-paraffin fraction by aromatization gives an additional 5 vol. percent yield advantage over direct platinum hydroforming alone.

In addition to the yield advantage, the combination operation allows the production of 100+ octane numbers with a reasonable cycle length in a fixed-bed, 50 p.s.i.g. platinum operation and at a considerable increase in feed rate or plant capacity.

EXAMPLE II

A straight run virgin naphtha from South Lousiana crude boiling (5 to 95%) in the range of 225° F. to 306° F. and having an API gravity of 57.3 and a research clear octane number of 48.8 was hydroformed by contacting with a catalyst comprising 10 wt. percent MoO_3 deposited upon activated alumina containing about 2 wt. percent silica as a stabilizer at a temperature of 900° F., a pressure of 200 pounds per square inch and in the presence of 5000 cubic feet of hydrogen-rich recycle gas per barrel of feed in a fluidized solids reactor system. The naphtha feed rate was varied from about 0.2 to 1.0 w./w./hr. at a catalyst to oil weight ratio of 0.9 to 1.0 to produce hydroformates of various octane number. The hydroformates were stabilized by distillation to yield a C_5+ product which was vaporized and passed at 370°–400° F. over a 5 A. molecular sieve to adsorb normal paraffins. The following tabulation shows a comparison of hydroformate yields at various octane levels both with and without molecular sieve treating.

Table II. — Molybdena- alumina hydroforming plus molecular sieve treating

Test Number	4	5	6	7
Research Octane Number	65.1	98.3	101.0	105.0
C_5+ Yields, Vol. Percent of St. Run Feed:				
Hydroforming Only	88.6	70.5	65.5	58.1
Hydroforming Plus 5 A. Sieve Treating	[1] 76.0	67.0	65.0	62.1
Yield Advantage for Combination Process	−12.6	−3.5	−0.5	+4.0
W./hr./w. Advantage for Combination Process		3.2/1	3.6/1	4.3/1
N-Paraffin Yield, Vol. Percent of St. Run Feed	24.0	11.4	8.9	5.5

[1] Without hydroforming; molecular sieve treat on naphtha feed.

The results obtained with the heavy naphtha feed show a very definite yield advantage for the combination process employing molecular sieves to remove unconverted normal paraffins when producing fuels above about 102 research octane number. In addition to the yield advantages, the combination process operates at greatly increased feed rates of 3 to 4 times that required for the production of 100 to 105 octane number fuels by hydroforming alone. The combination process also produces 5 to 10 vol. percent of high purity normal paraffins when operated at this octane level. In hydroforming without sieve separation, these paraffins are converted to gas and coke.

The invention as described herein is a continuation-in-part of our co-pending application Serial No. 588,105, filed on May 29, 1956, now abandoned.

The foregoing description contains a limited number of embodiments. It will be understood 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 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 110–375° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a hydroforming catalyst at temperatures of 800–975° F. and at pressures up to about 400 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a Research Clear octane number of at least 90, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, and recovering hydroformate substantially free from normal paraffins.

2. A method for producing 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 150°–225° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a catalyst consisting essentially of a platinum group metal dispersed upon alumina at temperatures of 800–975° F. and at pressures between about 50 and 100 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 90, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, and recovering hydroformate substantially free from normal paraffins.

3. A method for producing 102+ research octane number motor fuels from hydrocarbon fractions boiling in the range of from about 200–350° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a hydrofoming catalyst at temperatures of 800–975° F. and at pressures of up to about 400 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 95, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, and recovering hydroformate substantially free from normal paraffins.

4. The process as defined in claim 3 in which the hydroforming catalyst consists essentially of platium upon alumina and the pressure is about 300 p.s.i.g.

5. The process as defined in claim 3 in which the hydroforming catalyst consists essentially of molybdenum oxide upon alumina and the pressure is about 200 p.s.i.g.

6. A method for producing 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 110° to 250° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a catalyst consisting of 0.01 to 1.0 wt. percent platinum upon an alcoholate alumina support at temperatures of 800° to 975° F. and at pressures below about 125 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 90, separating the hydroformate from the the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, and recovering hydroformate substantially free from normal paraffns.

7. A method for producing 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 150° to 225° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a catalyst consisting of 0.01 to 1.0 wt. percent platinum upon an alcoholate alumina support at temperatures of 800–975° F. and at pressures between about 50 and 100 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 90, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, and recovering hydroformate substantially free from normal paraffins.

8. A method for producing 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 110 to 375° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a hydroforming catalyst at temperatures of 800–975° F. and at pressures up to about 400 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 90, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, recovering hydroformate substantially free from normal paraffins from the molecular sieve treatment, desorbing normal paraffins from the molecular sieves, subjecting the desorbed normal paraffins to isomerization and combining the isomerizate with the hydroformate.

9. A method for producing 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 110 to 375° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a hydroforming catalyst at temperatures 800–975° F. and at pressures up to about 400 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 90, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, recovering hydroformate substantially free from normal paraffins from the molecular sieve treatment, desorbing normal paraffins from the molecular sieves, subjecting the desorbed normal paraffins to aromatization and combining the aromatizate with the hydroformate.

10. A method for producing 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 150°–225° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a catalyst consisting essentially of a platinum group metal dispersed upon alumina at temperatures of 800–975° F. and at pressures between about 50 and 100 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 90, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, recovering hydroformate substantially free from normal paraffins from the molecular sieve treatment, desorbing normal paraffins from the molecular sieves, subjecting the desorbed normal paraffins to isomerization and combining the isomerizate with the normal paraffin-free hydroformate.

11. A method for producing 102+ research octane

number motor fuels from hydrocarbon fractions boiling in the range of from about 200–350° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a hydroforming catalyst at temperatures of 800–975° F. and at pressures of up to about 400 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 95, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, recovering hydroformate substantially free from normal paraffins from the molecular sieve treatment, desorbing normal paraffins from the molecular sieves, subjecting the desorbed normal paraffins to isomerization and combining the isomerizate with the normal paraffin-free hydroformate.

12. A method for producing 102+ research octane number motor fuels from hydrocarbon fractions boiling in the range of from about 200–350° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a hydroforming catalyst at temperatures of 800–975° F. and at pressures of up to about 400 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 95, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, recovering hydroformate substantially free from normal paraffins from the molecular sieve treatment, desorbing normal paraffins from the molecular sieves, subjecting the desorbed normal paraffins to aromization and combining the aromatizate with the normal paraffin-free hydroformate.

13. A method for producing 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 110° to 250° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a catalyst consisting of 0.01 to 1.0 wt. percent platinum upon an alcoholate alumina support at temperatures of 800° to 975° F. and at pressures below about 125 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 90, separating the hydroformate from the accompanying normally gaseous materials vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, recovering hydroformate substantially free from normal paraffins from the molecular sieve treatment, desorbing normal paraffins from the molecular sieves, subjecting the desorbed normal paraffins to isomerization and combining the isomerizate with the hydroformate.

14. A method for producing 100+ research octane number products from hydrocarbon fractions boiling in the range of from about 150° to 225° F. which comprises contacting said fractions in admixture with a hydrogen-rich gas with a catalyst consisting of 0.01 to 1.0 wt. percent platinum upon an alcoholate alumina support at temperatures of 800–975° F. and at pressures between about 50 and 100 p.s.i.g., maintaining said hydrocarbons in contact with the catalyst for a period sufficient to produce a C_5+ hydroformate having a research clear octane number of at least 90, separating the hydroformate from the accompanying normally gaseous materials, vaporizing the hydroformate, passing the hydroformate vapors through a bed of molecular sieves having pore diameters of about 5 A. which selectively adsorbs normal paraffins from the hydroformate vapors, recovering hydroformate substantially free from normal paraffins from the molecular sieve treatment, desorbing normal paraffins from the molecular sieves, subjecting the desorbed normal paraffins to isomerization and combining the isomerizate with the hydroformate.

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