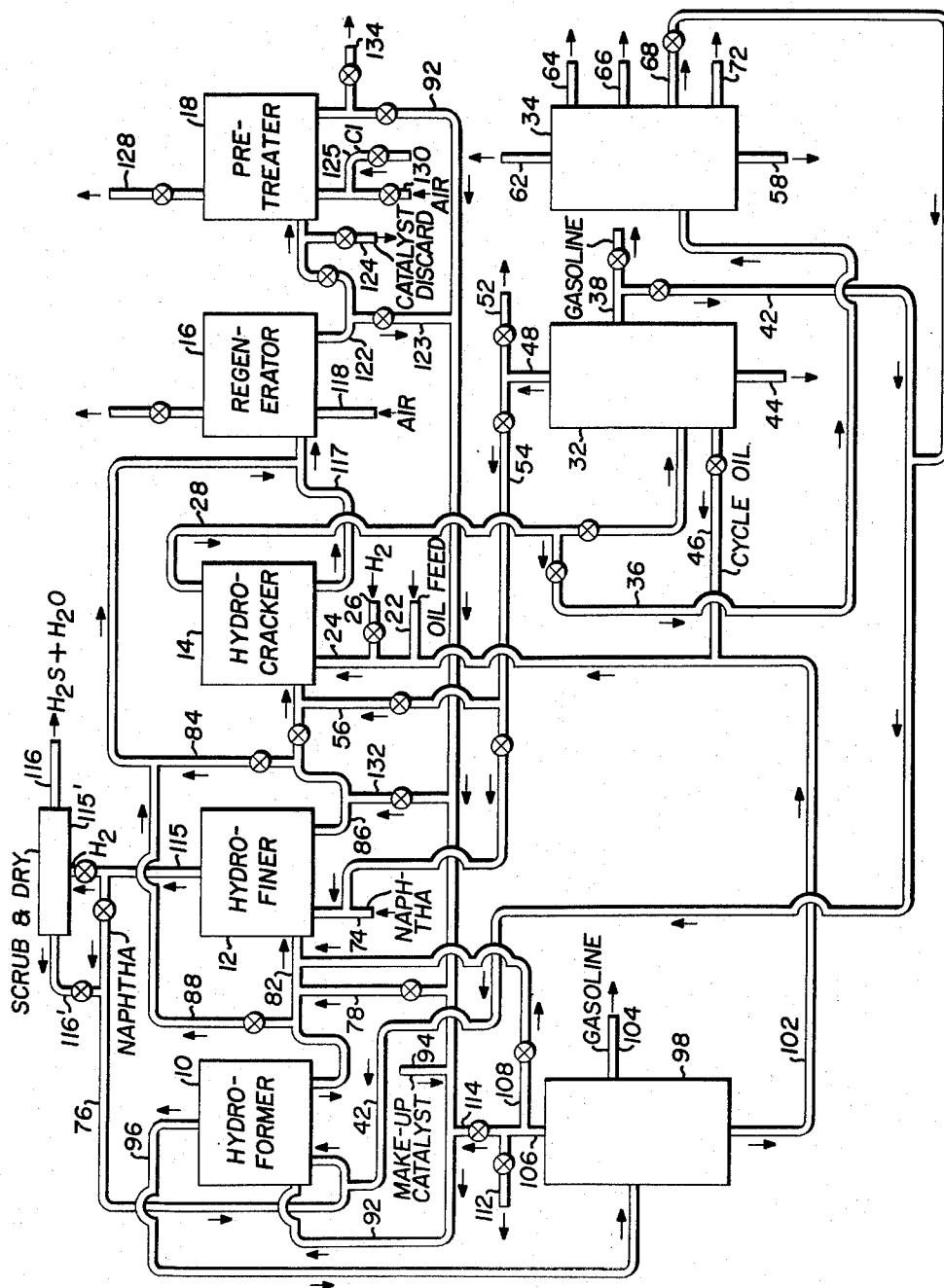


Nov. 1, 1960

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HYDROCRACKING OF A SULFUR CONTAINING
GAS OIL WITH A PLATINUM
ON ETA ALUMINA CATALYST
Filed Oct. 5, 1955

2,958,651



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HYDROCRACKING OF A SULFUR CONTAINING GAS OIL WITH A PLATINUM ON ETA ALUMINA CATALYST

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Filed Oct. 5, 1955, Ser. No. 538,722

9 Claims. (Cl. 208—112)

This invention relates to the conversion of hydrocarbons and more particularly relates to catalytic hydrocracking of relatively heavy hydrocarbon oil fractions to produce motor fuels such as gasoline. More particularly the oil feed to be converted is cracked in the presence of added hydrogen and a platinum-containing catalyst while maintaining the conversion or cracking zone under a relatively low pressure and at an elevated temperature.

In one form of the invention relatively high boiling oil feed stocks are hydrocracked to produce high yields of gasoline of high leaded motor octane number and low sulfur in the liquid products. The gasoline formed is highly saturated and accordingly is more stable than catalytically cracked gasolines.

In another form of the invention the gasoline fraction is separated into fractions and a heart cut fraction is passed to a hydroforming reaction zone to produce a higher octane product. In this case the other gasoline fractions are sent to the gasoline pool. Or the entire gasoline fraction may be passed to a hydroforming zone to increase the octane number of the gasoline product, but the selection of a heart cut fraction for further hydroforming is preferred.

In another form of the invention a naphtha fraction is hydrofined and then hydroformed, gas oil or other heavy oil feed is hydrocracked in the presence of a catalyst and hydrogen and the gasoline from the hydrocracked products is passed to the hydroforming zone. The catalyst for this form of the invention first is used in the hydroforming zone and then passed to the hydrofining zone from which it is passed to the hydrocracking zone. Then the catalyst is passed to the regeneration zone. Following regeneration the catalyst is passed to a pretreating zone where it is treated with acid such as a dilute mixture of hydrochloric acid plus nitric acid or perchloric acid or hypochlorous acid or an acid gas such as nitrosyl chloride or a mixed aqueous solution of aluminum chloride and nitrate or a halogen such as chlorine in an oxidizing atmosphere such as air or oxygen. The catalyst is then returned to the hydroforming zone. The catalyst comprises a small amount of platinum on eta alumina and may be used as finely divided fluidized catalyst, as moving bed pill catalyst or as a fixed bed catalyst.

The present invention is especially adapted for cracking poor cracking stock such as shale oil or very high sulfur containing crude oils or heavy gas oils high in sulfur to produce a gasoline of acceptable octane number without having to use a hydrogenating step prior or subsequent to cracking. The sulfur content of gas oil feed stocks may vary from 0.2 weight percent for low sulfur gas oil to 4 weight percent for high sulfur gas oil. The gasoline product recovered on hydrocracking according to the present invention has a low sulfur content and further the sulfur is easily removed from the gasoline product which is not true of catalytically cracked gasoline. The gasoline product obtained on hydrocracking according to the present invention contains more aromatic hydrocarbons and more saturated hydrocarbons and less olefins and un-

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saturated hydrocarbons than the gasoline product obtained on catalytic cracking of gas oils using conventional silica-alumina catalyst.

The pressure in the present hydrocracking process is preferably between about 200 and 700 lbs. per square inch gage (p.s.i.g.) and the temperature is preferably between about 975° and 1035° F. Generally, decreasing the pressure to about 200 p.s.i.g. increases octane number of the gasoline. Cracking at a temperature of about 1000° to 1015° F. at about 200–400 p.s.i.g. gives the highest octane number gasoline without excessive degradation to gas. When the product or fractions thereof are recycled to the hydroformer, pressures between about 400 and 700 p.s.i.g. and temperatures between 975° and 1000° F. are desirable because of the greater yield of product boiling in the gasoline range even though this product has a lower octane number.

At the lower pressures more coke is formed than at the higher pressures and with the present invention it is necessary to regenerate the catalyst by removing the coke or carbonaceous deposits from the catalyst. This may be done in various ways but preferably it is done by burning off the carbon or coke with air. Using the platinum catalyst of the present invention, it was noted that during hydrocracking the catalyst lost activity gradually with time on stream but after reactivation by (a) regenerating the catalyst with air or (b) regenerating with air followed by rejuvenation with a high pressure (200 to 1000 p.s.i.g.) air soak at 950°–1150° F. for 1–12 hours or (c) regenerating with air followed by a chlorine treat in the presence of air, the activity of the catalyst was substantially restored.

In the drawing, the figure represents diagrammatically one form of apparatus adapted to carry out processes according to the present invention.

Referring now to the drawing, the reference character 10 designates a hydroforming vessel, the reference character 12 designates a hydrofining vessel, the reference character 14 designates a hydrocracking vessel, the reference character 16 designates a catalyst regeneration zone and the reference character 18 designates a catalyst pretreating zone. In a fluid catalytic process according to this invention the catalyst will flow generally from the vessel 10 to the vessels 12, 14, 16 and 18 in that order and then back to vessel 10. In a fixed bed operation the process is carried out to follow these steps in the same manner. A heavy oil feed such as heavy or light gas oil, shale oil or blended residuum, or blends of these fractions is passed through line 22 and into the hydrocracking vessel 14 through line 24. The oil feed is heated in any suitable manner to a temperature of about 700° to 900° F. and is contacted with hydrocracking catalyst in the hydrocracking vessel 14 which is preferably maintained at a pressure of about 200 to 700 lbs. per square inch and a temperature between about 975° and 1035° F. The catalyst used in the different vessels is the same and preferably comprises platinum on eta alumina. The eta alumina is the form of alumina produced by heating the beta trihydrate of alumina to about 500°–1400° F. The amount of platinum may vary in the range between about 0.001–5% platinum, preferably 0.05–1% platinum.

One method of preparing eta alumina is to hydrolyze aluminum alcoholate with an aqueous solution containing ammonium hydroxide. The aluminum alcoholate may be prepared in any suitable manner. One method of preparation of aluminum alcoholate is given in Kimberlin U.S. Patent No. 2,636,865. Aluminum alcoholate is hydrolyzed with good agitation with from about 1 to 10 volumes of ammonium hydroxide per volume of aluminum alcoholate, preferably two to three volumes of ammonium hydroxide per volume of aluminum alcoholate, the concentration of NH_3 being in the range of about

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1.8 to 3.4 weight percent. The temperature of hydrolysis is preferably kept within a range of about 35° to 100° F. Upon hydrolysis an alumina slurry is obtained and this slurry is aged for a period of ½ to 15 hours, preferably 1 to 8 hours at room temperature. The aging is preferably carried out in the range of about 35°–80° F.

The alumina slurry contains alumina in the beta trihydrate form and the slurry is first dried at a temperature of about 200° to 400° F. to remove the ammonia and water to recover dry alumina. Crystalline eta alumina is formed by further dehydrating the beta alumina trihydrate and it has been found that the conversion to the eta form is essentially quantitative when the activating temperature is in the range of about 450°–1100° F. The activation is generally in the presence of air but can be done in the presence of inert gases.

The eta alumina is used as a support for platinum and is impregnated with an aqueous solution of water soluble inorganic platinum containing compounds such as chloro-platinic acid, platinum sulfide, etc. The term "water soluble" also includes platinum-containing compounds which form colloidal solutions.

A preferred solution is one containing 15 grams of $H_2PtCl_6 \cdot xH_2O$ (40% Pt) per liter. This strength of solution can be employed to yield catalysts containing about 0.6% platinum but the strength of the solution may be varied to obtain a catalyst containing about 0.001 to 5% platinum by weight. The alumina support is impregnated with the platinum solution, is then heated to dryness conveniently at temperatures of about 100°–600° F., preferably about 250° F. at atmospheric pressure and this results in removal of a substantial portion of the water. Thereafter the catalyst is calcined at a temperature between about 800° and 1250° F., preferably about 1100° F. The calcining step is preferably carried out for about 1 to 24 hours.

Before impregnating the eta alumina base with the platinum compound, it is also within the contemplation of this invention to calcine the eta alumina and this can be done at a temperature between about 800° and 1600° F. for 1 to 24 hours.

In some cases it is also desirable to treat the platinum catalyst or the eta alumina base either before or after calcination with an aqueous dilute mixed acid solution such as one containing nitric acid, perchloric acid, or hypochlorous acid, together with a hydrogen halide such as HCl, HF, HI and HBr. The mixture containing nitric acid and hydrochloric acid is preferred. An amount of nitric acid based on the total catalyst of about 0.1 to 8 weight percent is preferred. The HCl is employed in an amount of about 1 to 30 weight percent based on the total catalyst. The nitric and hydrochloric acids are contained in about 50–500 weight percent of water on the total catalyst.

In acid treating the catalyst, the catalyst is mixed with the acid solution, heated on a steam bath at about 150° to 180° F. for at least one hour, the acid solution is then drained off and the catalyst is washed thoroughly with distilled water. The washed catalyst is then dried at about 250° F. and recalcined for about 1 to 4 hours at between about 800° and 1250° F., preferably about 1100° F.

In a specific example the alumina support for a catalyst was obtained by hydrolysis of aluminum alcoholate solution by the method discussed above. The alumina after drying at about 250° F. was pulverized to pass through a 20 mesh screen and was then heated and activated at about 1100° F. for about 4 hours. To each 100 grams of activated alumina was added a solution made by dissolving 1.5 grams of H_2PtCl_6 (40% platinum) in about 65 cc. of distilled water. The composition was well mixed and dried overnight at room temperature. The catalyst was then dried at 250° F., screened and piled. The piled catalyst was calcined for 1 hour at about 1100° F.

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The piled and calcined catalyst was then treated with a solution containing 7 weight percent on catalyst of a concentrated HCl and 4 weight percent on catalyst of concentrated HNO_3 and 200 weight percent on catalyst of distilled water. The catalyst pills were slurried in the acid solution on a steam bath for about one hour. The temperature of the solution was about 150°–190° F. The acid solution was then drained off and the catalyst washed with distilled water. The washed catalyst was dried at 250° F. and calcined at 900°–1100° F. for at least 1 hour.

In a specific example for acid treating the alumina base, the calcined alumina base was treated with a solution containing 7 weight percent on the alumina base of concentrated HCl and 4 weight percent on the alumina base of concentrated HNO_3 and 200 weight percent on the alumina base of distilled water. The temperature of the acid treatment was about 150°–190° F. After draining the acid solution and washing the alumina base, the alumina base was dried at 250° F. and calcined for 4 hours at 1100° F. The calcined base was then impregnated with H_2PtCl_6 solution, dried at 250° F. overnight, piled and then calcined one hour at 1100° F.

Hydrogen is introduced into the hydrocracking zone 14 through line 26 and line 24 and the amount of hydrogen used in the hydrocracking vessel including recycle hydrogen is about 3,000 to 15,000 cubic feet per barrel of oil, preferably 5,000 to 10,000 cubic feet of hydrogen per barrel of total oil feed. It is preferred to have the hydrogen contact the feed before the feed contacts the catalyst. The hydrocracked vaporous products pass overhead from the hydrocracking vessel 14 through line 28 to either a first fractionating vessel 32 or second fractionating vessel 34 through line 36. Where a good cracking stock is used and motor gasoline is desired, the hydrocracked products may be passed to the fractionating vessel 32 and motor gasoline recovered through line 38. If higher octane number motor gasoline is desired, at least a portion of the motor gasoline from line 38 is recycled through line 42 to the hydroforming vessel 10 as will be hereinafter described in greater detail.

Bottoms from the fractionating vessel 32 are withdrawn through line 44 and can be sent on to other units for further processing or the cycle oil boiling above about 430° F. is withdrawn as a sidestream through line 46 and recycled through line 24 to the hydrocracking vessel 14. Hydrogen-containing gas is withdrawn overhead through line 48 and at least a portion of this hydrogen-containing gas may be withdrawn through line 52 and used as hydrogen in other hydrogenation processes. If desired, the hydrogen-containing gas may be passed to an absorption zone to increase the concentration of the hydrogen in the gas being withdrawn from the fractionating vessel 32 and/or may be scrubbed to remove hydrogen sulfide. All or a part of the hydrogen-containing gas withdrawn through line 48 is passed through line 54 and recycled to the hydrofining vessel 12. If desired, a portion of this hydrogen-containing gas is returned to the hydrocracking vessel 14 through line 56 and line 86 for supplying additional hydrogen to the vessel 14. It is preferred to contact hot catalyst with hydrogen before the hot catalyst contacts feed.

Where the gas oil feed or other heavy oil feed going to the hydrocracking vessel 14 is a poor cracking stock and contains a relatively high percentage of sulfur, the hydrocracked products from line 28 are preferably introduced into the second fractionating tower 34 for separating the hydrocracked products into a plurality of fractions. The hydrocracked products are separated into a bottoms fraction boiling above 430° F. and withdrawn through line 58 and which may be recycled to the hydrocracking vessel 14 or which may be diverted to other processing or used as a fuel.

A hydrogen-containing gas is withdrawn overhead

through line 62 and may be withdrawn from the process for use in other processes utilizing hydrogen or may be recycled to any or all of vessels 10, 12 and 14. The hydrogen-containing gas may be treated to concentrate the hydrogen and/or scrub out hydrogen sulfide. A light C_4 fraction is withdrawn as a side stream through line 64 from the fractionating tower 34. A higher boiling fraction comprising a C_5 to 200° F. cut is withdrawn through line 66. A paraffinic heart cut higher boiling fraction is withdrawn through line 68 and comprises a 200–360° F. fraction which is preferably recycled to hydroforming vessel 10 through lines 68 and 42 to improve the octane number of this fraction. A higher boiling side stream is withdrawn through line 72 and comprises a 360–430° F. fraction. The C_5 to 200° F. fraction and the 360–430° F. fraction are combined and passed to the gasoline pool because the 360–430° F. fraction has an acceptable octane number and the C_5 -200° F. fraction is excessively degraded to gas if recycled. The heart cut fraction may be a wider cut than above described and may comprise a 200–380° F. fraction. In general, the C_5 -200° F. fraction and the 380–430° F. fraction comprises about 15–20% of the product. The 200–380° F. fraction comprises about 60–70% of the product.

Naphtha feed which may be, for example, a 200–330° F. West Texas virgin naphtha is passed through line 74 at a temperature of about 600° to 750° F. into the hydrofining vessel 12 maintained under a pressure of about 200 to 700 p.s.i.g. and at a temperature between about 600° and 800° F. The hydrofining vessel 12 contains the same kind of catalyst above described in connection with the hydrocracking vessel 14 but the catalyst is somewhat more active than the catalyst in the hydrocracking vessel 14. The hydrofining vessel 12 is in effect a desulfurization zone for removing sulfur from the naphtha feed which is then passed through line 76 into the hydroforming vessel 10. The hydrofining vessel 12 receives some regenerated catalyst through line 78 which is mixed with the catalyst leaving the hydroforming vessel 10 through line 82. The hydrofining or desulfurizing vessel 12 is operated at preferably the same pressure as the hydroforming vessel 10 but at a lower temperature and at higher feed rates. The amount of hydrogen introduced into hydrofining zone 12 may be between about 500 and 15,000 standard cubic feet per barrel of oil.

From the hydrofining vessel 12 some of the withdrawn catalyst is passed to the regeneration vessel 16 through line 84, but most of the catalyst is passed through line 86 to the hydrocracking vessel 14. The amount of catalyst passing through line 84 compared to that passing through line 86 to the hydrocracking vessel 14 is in the ratio of about 0.1 to 1 to 1 to 1.

The hydrofined or desulfurized naphtha together with gasoline from line 42 is passed to the hydroforming vessel 10 through line 76 as hereinbefore described and the naphtha is subjected to a hydroforming treatment in the presence of freshly regenerated and/or treated platinum on eta alumina catalyst as was described above. The amount of hydrogen introduced into hydroformer 10 may be between about 3000 and 15,000 standard cubic feet per barrel of oil feed. The pressure in the hydroforming vessel 10 is maintained between about 200 and 700 p.s.i.g. and at a temperature between about 850° and 1050° F., preferably 850°–1000° F. The catalyst during the hydroforming reaction loses some activity and the less active catalyst is then passed into the hydrofining vessel 12 through line 82 as above described. A portion of the less active catalyst from the hydroforming vessel 10 is passed from line 82 through line 88 to the regeneration vessel 16. The proportion of catalyst passing through line 88 compared to that passing through line 82 to vessel 12 is in the ratio of about 1 to 1 to 0.1 to 1. Hot regenerated and/or pretreated catalyst is passed

through line 92 to the hydroforming vessel 10. Make-up catalyst is introduced into line 92 through line 94.

The hydroformed products in vapor form pass overhead from the hydroforming vessel 10 through line 96 and are introduced into a fractionating tower 98. The bottoms fraction comprising the polymer fraction is withdrawn through line 102 and preferably recycled via line 24 to the hydrocracking vessel 14. However, the polymer fraction may be withdrawn and used as kerosene, jet fuel etc. A high octane number gasoline is withdrawn as a side stream through line 104. Hydrogen-containing gas passes overhead through line 106 and a portion of this gas is passed through line 108 to hydrofining vessel 12 preferably being introduced into the line 82 passing catalyst from the hydroforming vessel 10 to the hydrofining vessel 12. Another portion of the hydrogen-containing gas may be withdrawn from the process through line 112 and used in other hydrogen consuming processes or in other processes utilizing hydrogen. Another portion of the hydrogen-containing gas is preferably passed through line 114 into the line 92 carrying catalyst from the pretreating vessel 18 to the hydroforming vessel 10. Hydrogen is also supplied to the hydroforming zone via products line 76. In some cases it is preferred to purify the products in line 76 by removing sulfur before returning the hydrogen-containing stream to hydroformer 10. In such cases the hydrofined products are passed through line 115 to scrubbing and drying zone 115' and water and H_2S are removed through line 116 and discarded, and the purified hydrofined products are passed through line 116' to hydroformer 10 via line 76. If desired, the hydrogen-containing gas passing overhead through line 106 may be treated as in an absorption zone to concentrate the hydrogen and the more concentrated hydrogen gas may be used in any of the recycle streams just described.

From the hydrocracking vessel 14, the catalyst is withdrawn through line 117 and introduced into the regeneration vessel 16 where carbonaceous material deposited on the catalyst during hydrocracking is removed. The regeneration may be carried out in a number of ways but preferably the catalyst is regenerated with air or flue gas introduced into the regeneration vessel 16 through line 118. During regeneration the pressure is maintained between about 0 to 700 p.s.i.g. and the temperature is maintained between about 800° and 1150° F.

The hot regenerated catalyst is withdrawn from the regeneration vessel 16 through line 122 and introduced into the pretreating vessel 18, and/or the pretreating vessel can be bypassed by sending the catalyst through line 123 to line 92. Bypassing is desirable in some cases because of improvement in gasoline and carbon selectivity with reduced halide on the catalyst. If desired, at least a portion of the used catalyst passing through line 122 may be withdrawn from the system through line 124 and discarded. In the pretreating zone 18 the platinum on eta alumina is treated to enhance activity of the regenerated catalyst. A non-metallic halide or chlorine is introduced through line 125 into the pretreating vessel 18 for treating the regenerated catalyst. Using air as a diluent during chlorine treating accelerates platinum crystal size reduction and hence enhances activity. It is preferable to do the treating in an oxidizing atmosphere. For this purpose air is introduced through line 130. This air or flue gas is also used to dry the catalyst after any treatment. The excess air is taken off through line 128 and/or may be recycled to line 130 or to line 118. Pretreatment can also be carried out by a mixed aqueous solution of aluminum chloride plus aluminum nitrate or a dilute solution of HCl plus HNO_3 . When the solutions are used it is necessary to cool the catalyst, preferably by heat exchangers with the feed stream or with water to form steam, to a temperature of 150°–250° F. The catalyst is washed after the treatment, dried, heated, by

heat exchange with the catalyst entering the pretreater, for example, and returned via line 92 to the system.

The regenerated and pretreated catalyst is withdrawn from the pretreating vessel 18 through line 92 and the major part of this catalyst is returned to the hydroforming vessel 10. The catalyst as was previously indicated, is preferably treated with H_2 before contacting feed. This can be done in line 92 with H_2 introduced via line 114 or it may be carried out in a separate vessel. The H_2 pretreat is also preferred when the catalyst is sent to vessels 12 and 14. As above pointed out, a portion of this regenerated catalyst may be passed through line 78 to the hydrofining vessel 12. In addition another portion of the pretreated regenerated catalyst from line 92 may be passed through line 132 to the hydrocracking vessel 14. If desired or if necessary, some of the pretreated catalyst may be withdrawn from the system through line 134. This is especially useful when it is desired to remove catalyst to change the platinum content thereof as will be hereinafter pointed out in greater detail.

Where finely divided catalyst is used in the fluidized process, the catalyst has a particle size of about 100–400 standard mesh or finer and preferably comprises particles having an average size between about 20 and 80 microns. To maintain the finely divided catalyst in a fluidized condition the velocity of the gasiform material passing upwardly through the vessels 10, 12, 14, 16 and 18 is maintained preferably between about 1 and 4 feet per second to obtain a dense turbulent fluidized mixture of solids having a dilute phase thereabove. Auxiliary equipment such as pumps, cyclone separators etc. has not been included in the drawing or in the description but it is clear that one skilled in the art knowing the fluidized process can supply such details.

In the hydroforming vessel 10, the feed may be a relatively narrow boiling virgin naphtha or it may be a full boiling range straight run naphtha or it may be a blend of virgin and coker naphtha or it may be a naphtha produced by hydrogen donor diluent cracking, by Fischer-Tropsch synthesis thermal reforming, etc. Or it may be the hydrocracked product gasoline or fractions thereof especially the heart cut 200–380° F. fraction. The yield-octane obtained on any feed in hydroforming is a function of the paraffin content and the type of naphthenes present. Because of the high selectivity and stability of the platinum on eta alumina catalyst, the conditions in the hydroformer can be adjusted for any feed to obtain any desired octane, even octanes in the range of about 100 research octane clear. C_8+ yield volume percent at 95 research octane number will vary from 79–82 for a feed with a characterization factor of 11.94 to 86–88 for a feed with a characterization factor of 11.72.

The temperature in the hydroforming zone is maintained between about 850° and 1000° F. and the pressure is maintained between about 50 and 700 p.s.i.g. The W./Hr./W. (weight of oil per hour per weight of catalyst) may be varied between about 0.1 and 20 in the hydroforming vessel 10.

The hydrofining or desulfurization vessel 12 is maintained at a temperature between about 600° and 800° F. and under a pressure between about 200 and 700 p.s.i.g. The W./Hr./W. is between about 0.5 and 20.

In order to obtain a high octane number gasoline during hydrocracking, the temperature is limited to a range of about 975° to 1035° F. and the pressure is maintained between about 200 and 700 p.s.i.g. At low pressures there is a loss of selectivity to gasoline, whereas at pressures above about 700 p.s.i.g. there is a marked loss in octane number. At the higher pressures less carbon is laid down on the catalyst. The W./Hr./W. in the hydrocracking vessel 14 is between about 0.1 and 20, preferably 0.5–8 W./Hr./W. Especially good results are obtained in the 2–4 W./Hr./W. region.

The regeneration vessel 16 is maintained between a temperature of about 800° and 1150° F. and a pressure between about 0 and 700 p.s.i.g. The regeneration is carried out by first contacting the catalyst with dilute air until a flame front passes through the catalyst bed, and then increasing the concentration of air until the desired level of combustion is obtained. This may be followed by an air soak at 950–1150° F. for 1–12 hours at high pressure (200–1000 p.s.i.g.) in either vessel 16 or vessel 18. This treatment with high pressure at 950° F.–1150° F. for 1–12 hours in the presence of air or oxygen reduces platinum crystal size and hence restores activity.

In the pretreating vessel 18 the pressure is maintained between about 0 and 700 p.s.i.g. and the temperature is maintained between about 800° and 1150° F. When using chlorine, the amount of chlorine used is between about 0.005 and 0.05 lbs. per lb. of catalyst. When using a liquid treating agent the temperature in the pretreating vessel is between about 150–250° F.

In the hydrocracking stage, relatively low pressure hydrocracking over platinum on eta alumina catalyst of the present invention results in a combination cracking and reforming process. With the present process, high yields of gasoline of high leaded motor octane number are obtained. In addition less carbon or coke is laid down on the catalyst than with catalytic cracking processes. Also there is less sulfur in the liquid hydrocracked products. The gasoline which is formed is highly saturated and accordingly is more stable than catalytically cracked naphthas obtained on cracking gas oil in the presence of silica-alumina catalyst.

EXAMPLE 1

An East Texas gas oil with about 0.3% sulfur was hydrocracked over an acid-treated platinum on eta alumina catalyst to a 65% conversion level. Another aliquot of the gas oil was cracked over conventional silica-alumina catalyst to the same conversion level. The data given in Table 1 demonstrate the advantages for the hydrocracking process. The platinum catalyst was prepared as follows.

Aluminum amylate was prepared by reacting pure aluminum metal with mixed amyl alcohols (1 part normal, 2 parts secondary and 1 part tertiary) in a hydrocarbon distillate (50% of the volume of the mixed alcohols) having a boiling range between about 200° and 500° F. in the presence of HgO catalyst. 589 grams of aluminum metal were reacted in 16 liters of the mixed alcohol hydrocarbon distillate solution in the presence of 0.3 gram HgO . The aluminum amylate solution was hydrolyzed in distilled water containing 10 volume percent concentrated ammonium hydroxide solution. 8 liters of aluminum amylate solution were hydrolyzed in 16 liters of distilled water containing 1.6 liters of concentrated (15 N) ammonium hydroxide. The hydrolysis was carried out at about 80° F. by introducing the aluminum amylate below the surface of the ammoniacal solution for a one hour period. The solution was stirred vigorously while the aluminum amylate was being introduced and the stirring was continued for a period of ½ hour after the addition of the aluminum amylate was complete. The resultant alumina slurry was aged for 5 days at ambient temperature (around 80° F.).

The alumina slurry was then dried at 250° F. and an X-ray analysis showed the material to be essentially pure beta alumina trihydrate. The dried alumina was then calcined 4 hours at 1100° F. X-ray analysis of the calcined alumina showed it to be essentially pure eta alumina and spectrographic analysis showed no metals present in more than trace quantities. After calcination 2431 grams of eta alumina (from several batches of alumina prepared using the proportions indicated above) were impregnated in 3 batches of 810.3 grams each with 567 cc. of aqueous chloroplatinic acid solution containing 12.2 grams of chloroplatinic acid (40% platinum).

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The impregnated alumina was allowed to stand at room temperature for about 18 hours and was then dried for about 24 hours at about 250° F. in a drying oven. The dried material was then passed through a 20 mesh screen, piled, and calcined for about 1 hour at 1100° F.

2245 grams of pills were acid treated in 4 batches at 561 grams each with 1500 cc. of solution containing about 86.4 cc. of concentrated hydrochloric acid and about 23 cc. of concentrated nitric acid. The mixture was put on a steam bath and held for 1 hour at about 180° F. The pills were then washed with distilled water, dried for about 24 hours at 250° F. and calcined for 1 hour at 1100° F. The finished catalyst contained 0.6 weight percent platinum.

Table 1

Catalyst.....	Pt on Al ₂ O ₃	SiO ₂ -Al ₂ O ₃	
Pressure, p.s.i.g.	400	0	0
Temperature, °F.	1,015	948	1,015
Space Velocity, W./Hr./W.	3.7	0.9	3.9
Conversion (430° F.) wt. percent	65.5	65.5	56
Gasoline Yields, Vol. percent	42.3	43.6	32.9
Hydrogen, s.c.f. per Bbl. of oil	5,000	None	None
Selectivity, Wt. percent:			
C ₅ -430° F. Gasoline.....	59	60	53
Carbon.....	5	9.0	5
Octane Numbers:			
Motor +3 cc.....	88.5	87.5	86.5
Research clear.....	90	94.5	96
Composition of Gasoline:			
Aromatics.....	48	36	41
Naphthenes and Saturates.....	47	42	17
Olefins.....	5	22	42
Sulfur in Gasoline, Wt. percent.....	0.01	0.06	0.04

Thus, the advantages are (1) less carbon for a given yield of gasoline, (2) less sulfur, (3) high leaded motor octane, (4) highly saturated gasoline, and (5) more aromatics in the gasoline in place of olefins. Moreover it will be noted that a higher leaded motor O.N. is obtained for this invention without increasing the Research Octane number. For the same Research O.N. the hydrocracking process of this invention gives a 3-5 octane advantage on the motor +3 cc. scale.

EXAMPLE 2

The advantage in octane number for operating at a temperature of about 1015° F. is shown by the following data.

Table 2

EFFECT OF TEMPERATURE ON OCTANE NO. ETGLO-5000
S.C.F. H₂/BBL. OF OIL
[4 W./Hr./W. for one-hour period]

Process.....	400 p.s.i.g. Pt Hydro- cracking		
Temperature, °F.	950	1,015	1,050
430° F. Conversion, wt. percent	53	66	70
Octane Numbers:			
Research, Clear.....	73	90	90
Motor +3 cc.....	82	88	86
Gasoline Composition:			
Percent Aromatics.....	33	48	49
Percent Olefins.....	6	5	8
Percent Saturates.....	61	47	43
Selectivity to C ₅ -430° F.	72	59	52

The above data show that a temperature of about 1015° F. gives the highest Motor +3 cc. lead octane number and going to 1050° F. reduces this octane number.

EXAMPLE 3

An East Texas gas oil with about 0.3% sulfur was cracked over 0.6% platinum on eta alumina catalyst in the presence of carbon tetrachloride. These results are compared to hydrocracking over the same catalyst without treating with carbon tetrachloride and from the data

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it will be seen that there is a slightly higher octane number product produced when using the carbon tetrachloride. The hydrocracking was carried out in the presence of about 5000 Standard cubic feet of hydrogen per barrel of oil feed.

Table 3

Catalyst.....	Acid Treated 0.6% Pt on Al ₂ O ₃	Acid Treated 0.6% Pt on on Al ₂ O ₃	
CCl ₄ (wt. percent on oil feed calculated as Cl).....	0.3	None	None
Pressure.....	200	200	400
W./hr./w.....	6.7	4	8
Conversion, Wt. Percent.....	63	55	57
Leaded Octane Nos.:			
Research.....	96.5	94	94
Motor.....	85.4	85.1	84.5

EXAMPLE 4

A West Texas gas oil of about 1.33% sulfur (25.4° API; 177° F. Aniline Pt; I.B.P. 450° F.; F.B.P. 910° F.) was hydrocracked over the same type of platinum on eta alumina catalyst used in Example 1 and the data are given in the following Table 4.

Table 4

30	Hydrocracking Over High Sulfur Feed, 5000 s.c.f. H ₂ /bbl. of Oil	
	Pressure p.s.i.g.	400
	Temperature, ° F.	1015
	W./Hr./W.	4
35	430° F. conversion, wt. percent	60
	C ₅ + gasoline yield, wt. percent	36
	Carbon, wt. percent	1.7
	Sulfur, wt. percent in gasoline	0.04
	Octane numbers:	
40	Motor +3 cc.	83
	Research clear	85

The stability of the platinum on eta alumina catalyst of the present invention in the hydrocracking of sulfur containing gas oils is shown by the following data in Table 5 in which the catalyst was regenerated in air followed by an air soak at a temperature of about 950° F. and a pressure of about 400 p.s.i.g. for 4 hours and maintained good activity for at least 19 cycles. The feed-stock used in this study had been stored for a long period of time before use and analysis showed it contained 9 p.p.m. peroxides and 130 p.p.m. H₂O. Despite the presence of these reputed platinum catalyst poisons, the catalyst maintained excellent activity and selectivity.

Table 5

Cycle No.	1	2	5	9	17	19
No. of Regenerations.....	0	1	4	8	16	18
Feed.....	490-700° F. ETGLO (0.23% S)					
430° F. Conversion.....	59.5	53.5	53	55.5	50	52
Hours on stream.....	1	2	6	12	22	24
Gasoline to carbon yield ratio.....		19.2	20	23.4	33.9	34.5

In practice, especially in fixed bed operation, it is preferable to operate at the lowest temperature feasible for the desired quality product and increase the temperature gradually as the catalyst deactivates. When the desired quality and conversion is no longer obtained, the catalyst is regenerated and reused without pretreatment with acid or chlorine. When the activity declines so that the desired quality product cannot be produced in the optimum temperature range of 975°-1035° F. the cat-

alyst is regenerated and pretreated. In general, increasing the temperature increases conversion and reduces carbon make.

The stability of the platinum on eta alumina catalyst in the hydroforming of virgin naphtha is shown by the data in Table 6. In a regenerative process study with a 200–330° F. Coastal virgin naphtha containing 0.07% sulfur, the catalyst showed no change in activity for at least six cycles.

Table 6

ACTIVITY MAINTENANCE STUDIES

[920° F. Temp., 200 p.s.i.g., 4 W./Hr./W.]

Cycle No.....	1	2	3	4	5	6
Research Octane Number.....	94.9	95.6	95.6	95.0	94.8	94.6

The form of alumina and its method of preparation are important variables in the preparation of high activity catalysts. The platinum catalysts with highest initial activity have been made from pure eta alumina. The presence of even 10% of another alumina phase can decrease catalyst activity by about 20% at the 95 Research octane number level. The usual methods of making alcoholate alumina result in a mixture of gamma and eta alumina. These catalysts have relative activities of 100–125%. Increasing the eta content of the alumina to essentially 100% (by varying the preparation procedure), increases the initial relative activity to 170%. The experimental data are summarized in Table 7. Commercial aluminas such as Alcoa, H41 or F10 have relative activities less than 100% of reference. All these catalysts were compared at the same chloride level, about 0.6 weight percent on catalyst. Platinum carbon catalysts are less active than the poorest aluminas. The platinum on carbon catalyst was prepared by impregnating activated carbon with chloroplatinic acid and then the catalyst was dried and calcined in nitrogen. The catalyst contained substantially the same amount of platinum as is present on the catalyst of the present invention.

Table 7

EFFECT OF ETA ALUMINA ON CATALYST PERFORMANCE
[900° F. Temperature, 200–330° F. virgin naphtha, 200 p.s.i.g., 4 W./Hr./W.]

Percent Eta in Alumina.....	5	60	90	100	Carbon
Research Octane Number.....	90.5	92	94	95	<80
Relative Activity, Percent of reference.....	95	115	150	170	<50

Relative activity of a catalyst (percent of reference) is defined as the ratio of the space velocity used with the unknown catalyst to the space velocity required by a standard catalyst to obtain the same octane number at constant temperature.

The form of alumina also appears to be an important variable in producing catalyst stability. The stability against deactivation by aging (i.e., crystal growth of platinum through prolonged use and repeated regenerations) is indicated in Table 8. These catalysts were given an accelerated aging test by heating at 1250° F. for 64 hours in air. This treatment is much more severe than that encountered in a year of regenerative operation. It can be seen that the catalyst with the eta alumina base is decidedly superior to that with the gamma alumina base. The eta alumina catalyst is more active after deactivation than the fresh gamma alumina catalyst. Furthermore, it can be noted that upon heat aging, the catalyst made with eta alumina decreases only 2 octane numbers, whereas the catalyst made with gamma alumina decreases about 6 octane numbers.

Table 8

EFFECT OF ETA ALUMINA CONTENT ON ACTIVITY AND STABILITY OF PLATINUM CATALYSTS

[200 p.s.i.g.; 900° F.; 4 W./Hr./W.; 6/1 H₂/Hydrocarbon 200–330° F. Virgin naphthas (0.004% sulfur); catalyst composition 0.6 Pt–99.4 Alcoholate alumina]

Alumina Phase, Percent		C ₅ + Research Clear Octane No.		
Eta	Gamma	Fresh	Heat Aged	Delta ¹
100	0	100.3	98.0	–2.3
83	17	99.6	96.8	–2.8
57	43	97.5	94.0	–3.5
4	96	95.1	89.5	–5.6

¹ The lower the absolute value of Delta, the more stable the catalyst.

A reactivation treatment carried out in a separate pretreating vessel with mixed salt or acid solutions does not materially alter the alumina so that the support may be used for an extended period of time. One such treatment consists of contacting a "spent" catalyst, which has received an oxidizing treatment, with sufficient dilute aqueous HCl to wet the catalyst. Upon drying to remove water, the platinum on the catalyst is characterized by small crystal size and an activity comparable to or better than that of a "fresh" catalyst. It is necessary to oxidize the used platinum catalyst before pretreating with acid.

The data in the following Table 9 give a comparison between catalytic cracking using conventional silica-alumina catalyst and hydrocracking East Texas light gas oil using a platinum on eta alumina catalyst prepared as above described in Example 1 with 5000 standard cubic feet of hydrogen per barrel of oil feed. These data show that with the platinum catalyst at the 200 p.s.i.g. level, the gasoline product has a much lower sulfur content than with the silica-alumina catalyst.

Table 9

	Pt on Al ₂ O ₃		SiO ₂ –Al ₂ O ₃	
	400	200	0	0
Pressure, p.s.i.g.....	47.3	52.0	56.5	56
430° F. Conversion, Wt. Percent.....	1,000	1,000	950	1,000
Temperature, ° F.....	0.013	0.015	0.04	0.04
Percent Sulfur.....				
Gasoline Composition:	29.2	41.3	33.7	41.3
Percent Aromatics.....	13.8	15.0	25.2	41.7
Percent Olefins.....	57.0	43.7	41.1	17.0
Percent Saturates.....	52.5	49.7	57.4	54.0
Gravity, ° API.....				

Although the reactivation treatments normally carried out in the pretreater 18 are treatments which will not materially alter the alumina support or change the platinum content on the catalyst significantly, it is possible in another modification of this invention to use the pretreater to vary the platinum concentration on the catalyst when this is desirable. This can be done preferably by increasing the acid concentrations used in acid treating to extract the desired amount of platinum when the lower platinum content catalysts are needed. On the other hand, when higher platinum content catalysts are needed, the enriched acid solution (obtained from extracting platinum in the previous case) or acid solution enriched with outside platinum can be used to treat the catalyst. Changing the platinum concentration of the catalyst is a desirable way to modify hydroforming and/or hydrocracking to change the volatility of the gasoline produced.

Lower platinum content catalysts give gasolines of higher volatility for a given octane number than higher platinum content catalysts.

In another modification of this invention which is useful when metallic contamination of the catalyst occurs, the platinum is extracted in the pretreater 18 from a por-

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tion of the catalyst which is circulating through the system. The spent alumina is withdrawn from the system through line 134 and is discarded to reworking and residual platinum recovery. The acid solution which has been enriched with platinum and contains some of the metallic impurities, is purified by any of the methods known in the art and a purified aqueous or acidic platinum enriched solution is recycled to the pretreater 18 through line 125, to treat the next aliquot of catalyst in one pretreater. This portion of enriched platinum catalyst is diluted to the average platinum content desired with fresh eta alumina which is introduced into the system through line 94. Likewise if it is desired to dilute the normal platinum catalyst for volatility control, eta alumina is introduced into the system through line 94. This method is especially valuable in fluid operation because of the intimate mixing of catalyst with unimpregnated alumina possible in such a system. Pure eta alumina is the preferred alumina diluent.

Referring now to the combination of steps shown diagrammatically in the drawing gas oil feed is introduced through line 22 and is heated to a temperature of about 700° to 900° F. and introduced into hydrocracking vessel 14 maintained at a temperature of about 975° to 1035° F. and maintained under pressure of about 800 to 700 p.s.i.g. The catalyst in the hydrocracking vessel 14 is made of platinum on eta alumina prepared as described in Example 1 above. The space velocity is between about 0.1 and 20 W./Hr./W. The hydrocracked products are introduced into the fractionating tower 32 to separate a gasoline which is withdrawn through line 38.

In a specific example the hydrocracking vessel was maintained at a temperature of about 1015° F., the pressure was about 400 p.s.i.g. and the space velocity was about 3.7 W./Hr./W. The amount of C₄ to 430° F. gasoline yield was 49 volume percent. The research octane number was 89.5 and the motor octane number plus 3 cc. of lead was 88.3. In the gasoline (C₅-430° F.) the volume percent of olefins was 5.2, the volume percent of aromatics was 47.6 and the weight percent of sulfur was 0.023 before caustic wash and 0.0044 after caustic wash. The amount of sulfur in the gas oil feed to the hydrocracking vessel 14 was about 0.23% by weight.

The hydrofining or desulfurizing vessel 12 was maintained at a temperature of about 700° F. and a pressure of about 350-400 p.s.i.g. The amount of hydrogen recycled to the vessel 12 or the hydrogen fed to the vessel 12 was about 700 cubic feet per barrel of naphtha feed. The feed rate was 9 W./Hr./W. The amount of sulfur in the naphtha feed which was a 250-370° F. West Texas naphtha was about 0.13% sulfur by weight and the desulfurized product contained only 10 parts per million of sulfur.

The hydroforming vessel 10 was maintained at a temperature of about 940° F. and the pressure was about 400 p.s.i.g. The feed to the hydroformer 10 was desulfurized 250° to 370° F. West Texas naphtha having an API gravity of 51.5° and a characterization factor of 11.82. The C₅ plus gasoline product yield withdrawn through line 104 was 84 volume percent. The amount of polymer boiling above 380° F. was equal to about 1 volume percent. The research octane number (clear) of the gasoline was 94 and the motor octane number plus 3 cc. of lead was equal to 92.

The catalyst introduced into the regeneration vessel 16 was regenerated with air introduced through line 118 and the regeneration zone was maintained at a temperature of about 1050° F. at a pressure of 400 p.s.i.g. Following regeneration, the regenerated catalyst was pretreated by soaking in air at 400 p.s.i.g. at a temperature of 950° F. for 4 hours. Following this rejuvenation, the catalyst was recycled through lines 123 and 92 and 132 to line 86. In line 86, the catalyst was reduced with hydrogen from line 56 at 400 p.s.i.g. The catalyst

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was then introduced into the hydrocracking vessel 14 for another hydrocracking cycle in this case.

As seen in some of the data above given in the tables, the gasoline product produced by hydrocracking according to the present invention has a lower sulfur content than that obtained on cracking with silica-alumina catalyst. In addition the sulfur which does remain in the gasoline after hydrocracking is easily removed by caustic washing which differs from the gasoline obtained on catalytic cracking. Gasoline obtained on hydrocracking with the platinum catalyst of this invention had a motor plus 3 cc. of lead octane number of 86.7 and a sulfur content of 0.036 wt. percent. This is compared to two gasolines obtained on catalytic cracking with silica-alumina in which the weight percent of sulfur was 0.041 and 0.063, respectively. The cracked gasolines when given a potassium hydroxide wash contained respectively 0.042 and 0.062 sulfur so that substantially no sulfur could be removed by the caustic wash. In contrast to this the gasoline obtained on hydrocracking had its sulfur content reduced from 0.036 to 0.012 by using the same type of potassium hydroxide wash as used for the cracking gasolines and thus it will be apparent that the sulfur in the hydrocracked gasoline is easily removed whereas it is not removed by a similar treatment in cracked gasolines.

As will be evident from the foregoing description to make this process and modifications of the process as indicated above feasible requires a very specific type of catalyst. The catalyst must give optimum performance in hydroforming, hydrofining, as well as in hydrocracking. In addition the catalyst must be regenerable and be amenable to resurrection in the pretreater. The present process results in savings such as conservation of heat and hydrogen, catalyst inventory, etc. A long catalyst life and stability are prerequisites for economic utilization of precious metal catalysts. As can be seen from the data presented above, practically indefinite life for the catalyst specified here is possible. Even when metallic contamination occurs which is possible from unit corrosion or from the presence of metals in high boiling petroleum fractions, provisions have been made for the removal of the effect of these contaminants from the system continuously, if desired. Other catalysts, and especially other platinum containing catalysts, have been proposed for these conversions. One such catalyst which has been proposed is platinum on carbon or platinum on carbon used in conjunction with cracking catalysts in homogeneous phase with the hydrocarbons. Such a catalyst is unsuitable in this process for the following reasons: (a) platinum on carbon is relatively inactive in hydroforming and especially in isomerization which is an important reaction in hydroforming; (b) platinum on carbon plus a cracking catalyst causes excessive degradation to gas in hydroforming since the cracking catalyst degrades naphthenes excessively; (c) a catalyst of this type is extremely difficult to regenerate and hence would have a limited life especially when processing high boiling refractory feeds in hydrocracking, and (d) the necessity for an oxidizing treatment before the platinum crystallites, which grow as platinum is kept at high temperatures for long periods of time, can be reformed the contracted lattice platinum, which is formed when platinum is kept in the presence of hydrogen at high temperatures for long periods of time, can be reactivated by any of the methods disclosed above, would rule out a carbon based catalyst since the carbon would be destroyed in such treatment. Other platinum on alumina catalysts have been proposed for hydroforming or hydrocracking gasoline stocks boiling below about 425° F. As has been pointed out above, the preferred type of platinum-alumina catalyst for the present process and its modifications is platinum on eta alumina because of its superior activity and stability, and its regenerability. Less active catalysts require a higher temperature in hydroforming for a given octane number.

Less active catalysts, especially those activated with fluoride, are octane limited because of the excessive volatility of the gasoline produced in hydroforming at the required conditions. Raising temperature in hydroforming to increase octane number tends to increase undesirable hydrocracking of naphthenes and hence gasoline yield is reduced. Therefore, it is desirable to have a catalyst which is very active and selective at low temperature. On the other hand, hydrocracking for high octane of feeds boiling above 425° F. requires relatively high temperatures. Hence a catalyst of superior stability in high temperature operation is necessary. For this reason the catalyst specified here is made of extremely pure alumina since it has been found that most metals tend to decrease stability of platinum containing catalysts. Hydrocracking of heavy gas oils produces carbon on the catalyst. Hence a regenerable catalyst is necessary. This also requires a heat stable catalyst. As has been shown, eta alumina is decidedly superior to other aluminas in this respect. It can be seen, therefore, that platinum on pure eta alumina is a catalyst which fulfills all the requirements of the presently visualized process and its modifications and that other platinum containing catalysts known in the art are decidedly inferior and probably could not be used effectively in this process.

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

What is claimed is:

1. A method of converting higher boiling hydrocarbons to lower boiling gasoline hydrocarbons of low sulfur and low olefin content which comprises hydrocracking gas oil boiling in the range of about 450° to 910° F. at a temperature between about 975° and 1035° F. under a pressure between about 200 p.s.i.g. and 700 p.s.i.g. in the presence of platinum on eta alumina catalyst and at a feed rate between about 0.5 and 8 W./Hr./W. and in the presence of between about 3000 and 15,000 SCF of hydrogen per barrel of gas oil feed, the eta alumina being produced from an aluminum alcoholate.

2. A method of producing high yields of high octane number gasoline of low sulfur and olefin content from relatively poor cracking feed stocks containing relatively large amounts of sulfur which comprises hydrocracking hydrocarbon gas oil boiling from about 450° to 910° F. in the presence of a stable catalyst comprising less than about 1% of platinum on eta alumina produced from an aluminum alcoholate and in the presence of added hydrogen while maintaining a total pressure between about 200 and 400 p.s.i.g. and a temperature of about 1015° F.

3. A method according to claim 2 wherein catalyst during the hydrocracking step accumulates carbonaceous deposit, regenerating the catalyst by burning off the carbonaceous deposit and then treating the regenerated catalyst with a halogen-containing compound and an oxidizing agent and then carrying out another hydrocracking step using the regenerated and treated catalyst.

4. A method of converting higher sulfur-containing boiling hydrocarbons to gasoline of low sulfur and low olefin content which comprises hydrocracking a hydrocarbon gas oil boiling from about 450° to 910° F. and containing at least 0.3% sulfur at a temperature between about 975° and 1035° F. under a pressure between about 200 p.s.i.g. and 700 p.s.i.g. in the presence of added hydro-

gen and in the presence of a catalyst containing less than 1% of platinum carried on a support consisting essentially of eta alumina produced from an aluminum alcoholate.

5. A method according to claim 4 wherein the catalyst becomes partially inactivated by the deposit of carbonaceous material thereon and the catalyst is then regenerated with air to burn off the carbonaceous material in the presence of an added halogen containing compound.

6. A method of cracking in the presence of added hydrogen which comprises hydrocracking a relatively high boiling gas oil feed stock boiling in the range of about 450° to 910° F. and having a high content of sulfur at a temperature between about 975° and 1035° F. at a pressure between about 200 and 700 p.s.i.g. and in the presence of a platinum on eta alumina catalyst to produce high octane gasoline low in sulfur, subjecting the hydrocracked gasoline to a hydroforming operation under pressure using the same type platinum on eta alumina catalyst at a temperature between about 850° and 1000° F. and in the presence of added hydrogen and recovering a higher octane number gasoline from the hydroformate, the eta alumina being produced from an aluminum alcoholate.

7. A method of cracking in the presence of added hydrogen which comprises hydrocracking a relatively high sulfur-containing gas oil feed stock boiling in the range of about 450° to 910° F. at a temperature between about 975° and 1035° F. at a pressure between about 200 and 700 p.s.i.g. and in the presence of a catalyst containing less than about 1% platinum on a base consisting essentially of eta alumina to produce high octane gasoline low in sulfur, the catalyst being prepared from eta alumina impregnated with a sufficient amount of chloroplatinic acid solution to produce a catalyst containing about 0.6% of platinum, aging the impregnated eta alumina, then drying the impregnated alumina for an extended period, then calcining the dried catalyst at a temperature of at least 1100° F. for at least 1 hour, then treating the calcined catalyst with a dilute aqueous solution containing HCl and HNO₃, heating the acid treated catalyst for an extended period at about 180° F. then washing and drying the treated catalyst and calcining the washed and dried catalyst at a temperature of about 1 hour at about 1100° F., the eta alumina being produced from an aluminum alcoholate.

8. A method as defined in claim 4 wherein a small amount of an added non-metallic halogen-containing compound is present during the hydrocracking step.

9. A method as defined in claim 8 wherein the non-metallic halogen-containing compound comprises carbon tetrachloride.

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