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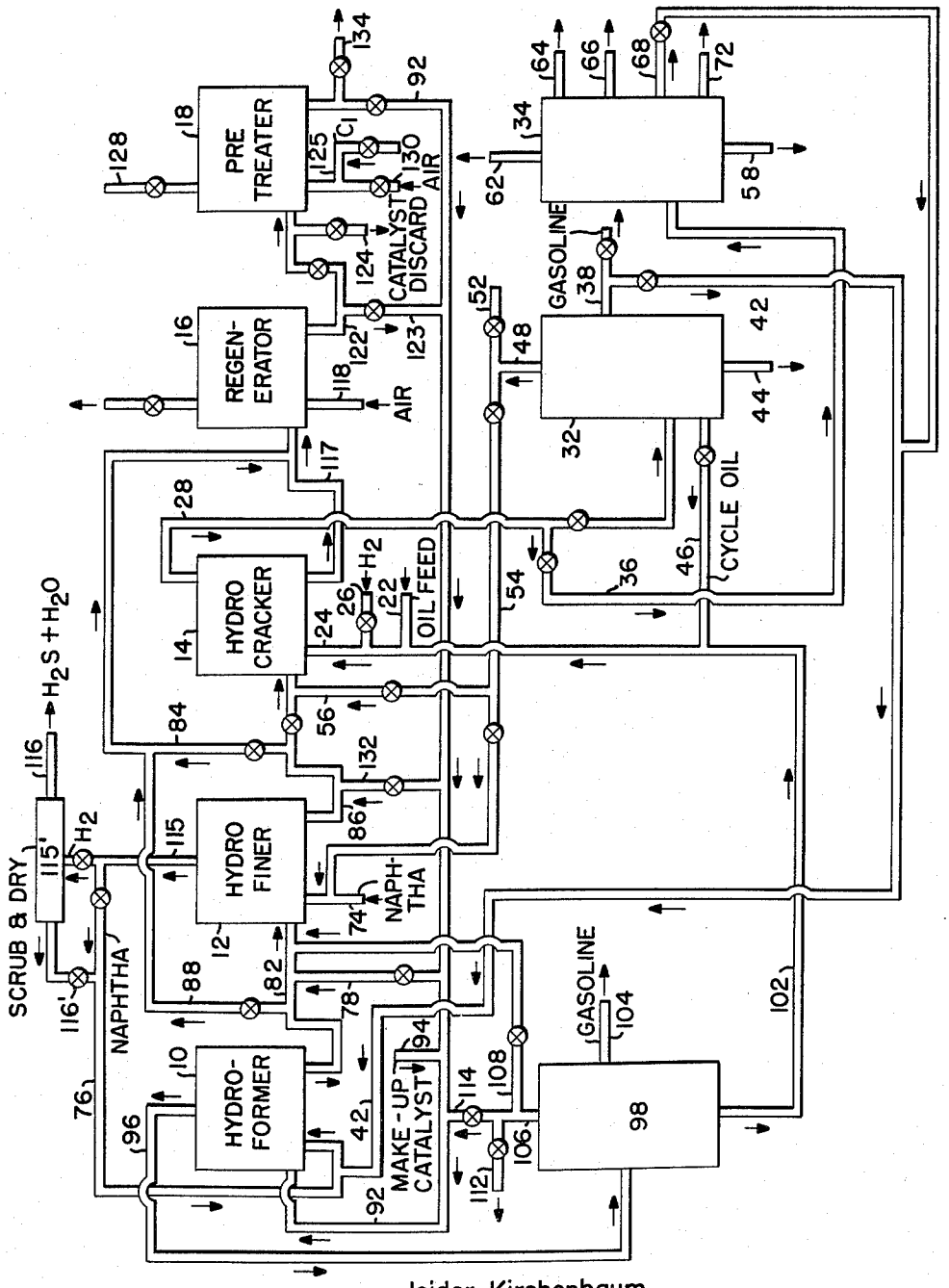


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# HYDROCRACKING OF SHALE OILS WITH A PLATINUM - ON - ETA - ALUMINA CATALYST COMPOSITE

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The present invention relates to the conversion of higher boiling hydrocarbons to lower boiling hydrocarbons and more particularly relates to hydrocracking of shale oil to produce high yields of gasolines of high octane number and low sulfur and nitrogen content.

This application is a continuation-in-part of Serial No. 538,722 filed October 5, 1955, which relates to hydrocracking of sulfur containing gas oil.

Raw shale oil is obtained by retorting oil shale and contains hydrocarbons and organic material consisting of hydrocarbons in combination with sulfur, nitrogen and oxygen. The shale oil has an extremely high content of nitrogen compounds which distinguishes it from crude petroleum oil. Various refining procedures have been suggested for shale oil or various fractions separated from shale oil. Conventional methods of refining or conversion are not applicable to the catalytic cracking of raw shale oil. Carbon or coke formation is excessive, presumably because of the nitrogen, sulfur and/or oxygen compounds present in the raw shale oil. In addition, the gasoline product contains sulfur and nitrogen and needs further refining. In order to eliminate these undesirable compounds and prepare a stock suitable for cracking or further refining, it has been felt necessary to resort to coking or hydrogenation of the shale oil. Hydrogenation is an expensive process and, accordingly, this method of processing shale oil is not competitive with processing of crude petroleum oil because it requires large amounts of hydrogen.

It has now been found that raw shale oil or a fraction thereof can be cracked directly in the presence of hydrogen and a catalyst comprising a small amount of platinum on eta alumina and may be used as finely-divided fluidized catalyst, as a moving bed catalyst or as a fixed bed catalyst. The cracking is carried out in the presence of hydrogen, under a pressure between about 100 and 1500 p.s.i.g., preferably about 200–1000 p.s.i.g. (pounds per square inch gage) and at a temperature between about 900° and 1050° F., preferably between about 950° and 1025° F. The amount of hydrogen introduced into the cracking zone is between about 100 cu. ft. and 10,000 cu. ft., preferably about 2000 and 6000 cu. ft. (measured at standard atmospheric pressure and temperature) per barrel of shale oil feed. Hydrogen is consumed during the reaction and therefore hydrogen must be supplied to the reaction from an external source of hydrogen or a hydrogen-rich gas.

In one form of the invention, the extraneous hydrogen is obtained from a hydroforming unit operated in conjunction with the hydrocracking unit, but extraneous hydrogen from any other source may be used.

With the present process, the raw shale oil is simultaneously cracked and hydrogenated to give a high yield of high octane number motor fuel. At the same time, a small amount of coke or carbonaceous material is produced which is much less than the amount of coke produced by other processes, such as catalytic cracking.

In addition to producing less carbon or coke than conventional catalytic cracking of the same kind of feed stock, the process of the present invention produces significantly more $C_4+$ and $C_5+$ gasoline of high octane number.

In one form of the invention, relatively high boiling oil feed stocks are hydrocracked to produce high yields of gasoline of high leaded octane number and low sulfur and nitrogen 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 hydrocracked 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 such as shale oil is hydrocracked in the presence of a catalyst and hydrogen and the gasoline separated 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 aluminum 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, in a suspensoid operation, as moving bed pill catalyst or as a fixed bed catalyst.

In another form of the invention, a naphtha fraction is hydrofined and then hydroformed, gas oil or other heavy oil feed which is low in nitrogen but high in sulfur content is hydrofined and then hydrocracked in the presence of a catalyst and hydrogen. The catalyst for this form of the invention is circulated as described above. The gasoline from the hydrocracked products is passed to the hydroforming zone if further upgrading is desired or to the gasoline pool directly. The gas oil may be hydrofined in a blocked operation or may be desulfurized concurrently with the naphtha fraction, separated from the naphtha, and sent to the hydrocracker. In a modification of this form of the invention, shale oil may be hydrocracked together with the gas oil. However, the shale oil is sent directly to the hydrocracker without prior hydrofining because of its high nitrogen content.

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 or tar sand bitumen high in nitrogen and sulfur to produce a gasoline of acceptable octane number without having to use a hydrogenating step prior to 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 nitrogen content of shale oil may vary between about 1 and 3 weight percent. The sulfur content of shale oil may vary between about 0.2 and 1.5 weight percent. The gasoline product recovered on hydrocracking according to the present invention has a relatively low sulfur and nitrogen content and further the small amount of residual sulfur and nitrogen are easily

removed from the gasoline product by simple acid washing 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 unsaturated 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 1000 lbs. per square inch gage (p.s.i.g.) and the temperature is preferably between about 950° and 1025° F. Generally, decreasing the pressure to about 200 p.s.i.g. increases octane number of the gasoline when using light gas oil, i.e. a feed boiling in the range of 500° to 700° F. Hydrocracking at a temperature of about 1000° to 1015° F. at about 200 to 400 p.s.i.g. gives the highest octane number gasoline without excessive degradation to gas.

On the other hand, when using a heavy gas oil, i.e. a feed boiling in the range of 600° to 900° F., increasing the pressure to about 700 p.s.i.g. increases yield and octane of the gasoline. Hydrocracking at a temperature of about 950°–1000° F. at about 700 p.s.i.g. gives the highest octane number gasoline in the greatest yield. When the product or fractions thereof are recycled to the hydroformer, that pressure is used for a given feed stock which gives 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 to 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 or move 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, raw or treated shale oil, shale oil fractions, or blended residuum, or blends of these fractions are passed through line **22** and into the hydrocracking vessel **14** through line **24**. The oil feed is preheated in any suitable manner to a temperature of about 500° to 700° F. and is then contacted with hydrocracking catalyst in the hydrocracking vessel **14** which is preferably maintained at a pressure of about 200 to 1000 lbs. per square inch and a temperature between about 950° and 1025° F. The catalyst used in the different vessels is the same and preferably comprises platinum on predominantly eta alumina. The alumina is in the eta form of alumina produced by heating the beta trihydrate of alumina to about 500°–1400° F. To make a stronger catalyst, less than 50% or 49% or less of the alumina is preferably in the gamma phase obtained by heating the alpha monohydrate of alumina. The amount of platinum may vary in the range between about 0.001–5% platinum, preferably about 0.05–1% platinum.

One method of preparing high eta alumina content 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 #2,636,865. Aluminum alcoholate is hydrolyzed with good agitation with from about 1 to 10 volumes of ammonium hydroxide solution per volume of aluminum alcoholate, preferably two to three volumes of ammonium hydroxide solution per volume of aluminum alcoholate, the concentration of $NH_3$ being preferably in the range of about 0.3 to 3.4 weight percent. The temperature of hydrolysis is preferably kept within a range of about 70° to 175° F. Upon hydrolysis an alumina slurry is obtained and this slurry is aged for a period of ½ to 48 hours, preferably 1 to 8 hours at room temperature. The aging is preferably carried out in the range of about 50°–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 high eta alumina content 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 $H_2PtCl_6.xH_2O$ (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 1150° F., preferably about 1100° F. The calcining step is preferably carried out for about 1 to 24 hours.

Before impregnating the high eta alumina content alumina base with the platinum compound, it is also within the contemplation of this invention to calcine the alumina and this can be done at a temperature between about 800° and 1450° F. for 1 to 24 hours.

In some cases, it is also desirable to treat the platinum catalyst or the high eta alumina content 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 on the total catalyst 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 to 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 1150° 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 pilled. The pilled catalyst was calcined for 1 hour at about 1100° F.

The pilled 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 about 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, pilled 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 1000 to 10,000 cubic feet per barrel of oil, preferably 2000 to 6000 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. The cycle oil boiling above about 430° F. is withdrawn as a sidestream through line **46** and at least partly withdrawn from the process and/or at least partly 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 such as shale oil and contains a relatively high percentage of sulfur and nitrogen, 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 comprise 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 high eta alumina content alumina catalyst as 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 and 700 p.s.i.g. and the temperature is maintained between about 800° and 1050° 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 high eta alumina content 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 where 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 well 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 most of the particles have an average size between about 20 and 80 microns. To maintain the finely divided catalyst in a fluidized condition, the superficial 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 or cracked naphtha or it may be a full boiling range straight run or cracked naphtha or it may be a blend of virgin and coker naphtha or it may be a naphtha produced from shale oil, 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 high eta alumina content 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. $C_5+$ 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 main-

tained 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 800 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 950° to 1025° F. and the pressure is maintained between about 200 and 1000 p.s.i.g. At low pressures there is a loss of selectivity to gasoline, whereas at pressures above about 1000 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 1–4 W./Hr./W. region.

The regeneration vessel **16** is maintained between a temperature of about 800° and 1050° F. and a pressure between about 0 and 1000 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°–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 1000 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 high eta alumina content 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 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 and less nitrogen 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 0.4% 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). 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, pilled, 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. This mixture was put on a steam bath and held for 1 hour at about 180° F. The pills were than 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 on eta alumina.

*Table 1*

| Catalyst | Pt on $Al_2O_3$ | $SiO_2$—$Al_2O_3$ | |
|---|---|---|---|
| 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 SCF $H_2$/BBL. OF OIL

[4 W./Hr./W. for one-hour period]

| Process | 400 p.s.i.g. Pt Hydrocracking | | |
|---|---|---|---|
| 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 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 $Al_2O_3$ | Acid Treated 0.6% Pt on $Al_2O_3$ | |
|---|---|---|---|
| $CCl_4$ (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*

Hydrocracking a 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 |
| 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: | |
| Motor+3 cc. | 83 |
| Research clear | 85 |

## EXAMPLE 5

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 feedstock 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. $H_2O$. 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. ETLGO (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 950°–1025° F., the catalyst is regenerated and pretreated. In general, increasing the temperature increases conversion and reduces carbon make.

## EXAMPLE 6

A Colorado shale oil containing 2% nitrogen and 0.6% sulfur (20.3° API; I.B.P. 363° F.; F.B.P. around 1015° F.) was hydrocracked over the same type of platinum on eta alumina catalyst used in Example 1 except that the acid treating was omitted and the data are given in the following Table 6.

*Table 6*

Hydrocracking Shale Oil

| | |
|---|---|
| Pressure, p.s.i.g. | 700 |
| Temperature, ° F. | 1000 |
| W./hr./w. | 1 |
| $H_2$ dilution, s.c.f./b. | 4000 |
| Product distribution, wt. percent: | |
| Hydrogen (i.e. 1650 s.c.f./b. consumed) | —2.6 |
| Dry gas | 19 |
| $C_4$ | 10.5 |
| $C_5$/430° F. gasoline | 44 |
| Coke | 7 |
| 430° F. conversion, wt. percent | 78 |
| $C_5$/430° F. gasoline,[1] vol. percent | 54.5 |
| Research octane number+3 cc. TEL | 93 |
| Sulfur, wt. percent | 0.02 |
| Nitrogen, wt. percent | 0.003 |

[1] Acid washed gasoline.

As can be seen, good yields of gasoline with low sulfur and extremely low nitrogen can be made in this one-step conversion.

In studies of hydrogenation of shale oil, results indicate that at least 3000 p.s.i.g. hydrogenation is required to remove about 90% of the nitrogen compounds from a raw shale oil. The overall nitrogen removal in the hydrocracking run above was about 95%. Furthermore, in catalytic cracking studies, results show that catalytic cracking of raw shale oil leads to a very poor product distribution with excessive coke make. These results are summarized in Table 7 in a comparison with the hydrocracking run. This comparison indicates that hydrocracking can be considered as a useful and valuable shale oil refining scheme.

*Table 7*

COMPARISON OF PROCESSES FOR REFINING SHALE OIL

| | Hydrocracking | Catalytic Cracking | 3,000 p.s.i.g. Hydrogenation plus Cat. Cracking |
|---|---|---|---|
| $C_4$/430° F. Gasoline: | | | |
| Yield, Vol. percent | 71.5 | 53 | 74 |
| Nitrogen, wt. percent | 0.003 | 0.01 | 0.01 |
| Coke, wt. percent | 7 | 25 | 10 |
| Dry Gas, wt. percent | 19 | 20 | 18 |
| $H_2$ Consumption, s.c.f./b | 1,650 | | 1,500 |
| 430° F. Conversion, wt. percent | 78 | 75 | 75 |

The bulk of the nitrogen removed during hydrocracking appears as $NH_3$ and $N_2$, with some low boiling amines.

## EXAMPLE 7

Although it is generally most desirable to use as wide a feed boiling range in hydrocracking as possible, in certain cases it may be advantageous to process shale oil from which a small amount of heavy ends and of light ends has been removed. To determine the effect of feed boiling range, a 530°/930° F. shale oil cut was processed under conditions comparable to those for the total (ca. 400°/1050+° F.) shale oil. The nitrogen content of both feeds was 2 wt. percent. As is indicated by the data in Table 8, this fraction, representing the 10–80% portion of the total shale oil, gave less coke and a higher yield of a better gasoline.

*Table 8*

HYDROCRACKING OF SHALE OIL FRACTION

| | |
|---|---|
| Process conditions: | |
| Pressure, p.s.i.g | 700 |
| Temperature, ° F | 1,000 |
| Feed rate, W./Hr./W | 1 |
| $H_2$ dilution, s.c.f./b | 4,000 |
| Run length, hr | 1 |
| Catalyst | [1] 0.6 |

| | 530°/930° F. Fraction | Total Shale Oil |
|---|---|---|
| Product Distribution, wt. percent: | | |
| $H_2$ (Consumption) | −2.8 (1,750 s.c.f./b.) | −2.6 (1,650 s.c.f./b.) |
| Dry Gas | 17.5 | 19 |
| $C_4$ | 11 | 10.5 |
| $C_5$/430° F. Gasoline | 46 | 44 |
| Coke | 5.3 | 7 |
| 430° F. Conversion, Wt. Percent | 77 | 78 |
| $C_5$/430° F. Gasoline: | | |
| Vol. Percent | 60 | 54.5 |
| Res. Oct. No. (+3 ml. TEL) | 98 | 93 |
| Sulfur, Wt. Percent | 0.015 | 0.02 |
| Nitrogen, Wt. Percent | 0.01 | 0.003 |

[1] Percent Pt on eta alumina prepared as above set forth.

Hydrogen consumption, dry gas yield, and $C_4$ production were comparable for the two cases. Coke make is appreciably lower for the 530°/930° F. fraction, presumably due to the elimination of coke precursors ("asphaltenes") in the heavy end of the feed. Nitrogen and sulfur are at about the same level for both cases.

Although the conversion for the two cases is approximately the same, the 530°/930° F. fraction gives a higher yield of a better quality gasoline. The difference in yield is even greater when it is considered that the total shale oil contains about 5 vol. percent material boiling below 430° F. The presence of this material could account for the lower octane observed. However, the lower octane might also be explained by the presence of catalyst deactivators in the high boiling fraction of the shale oil.

## EXAMPLE 8

An acidic substance such as HCl was added during the hydrocracking operation in an attempt to neutralize the basic nitrogen compounds adsorbed on the catalyst surface. Although it is not possible to prove whether



HCl acted in this fashion, data obtained and shown in Table 9 indicate that an increase in gasoline selectivity is obtained when 1 mole percent HCl is used in the hydrogen.

*Table 9*

Feed: Colorado shale oil 530°/930° F. fraction.
Catalyst: 0.6% Pt on eta alumina prepared as above set forth.
Process conditions: Pressure, 700 p.s.i.g.; temperature, 1,000° F.; feed rate, 1 w./hr./w.; $H_2$ dilution, 4,000 s.c.f./b.; one hour cycle.

| | 1% HCl in $H_2$ | $H_2$ |
|---|---|---|
| Selectivity, Wt. Percent: | | |
| $C_5$/430° F. Gasoline | 65 | 59 |
| Dry Gas | 21.5 | 23 |
| $C_4$ | 9 | 14.5 |
| Coke | 8 | 7 |
| $H_2$ (Consumption) | −3.5 (2,100 s.c.f./b.) | −3.5 (2,100 s.c.f./b.) |
| 430° F. Conversion, Wt. Percent | 82.5 | 77 |
| $C_5$/430° F. Gasoline: | | |
| Vol. Percent | 74 | 60 |
| Res. Oct. No. (+3 ml. TEL) | 96 | 98 |
| Sulfur, Wt. Percent | 0.008 | 0.015 |
| Nitrogen, Wt. Percent | 0.004 | 0.010 |

A fixed bed containing 500 cc. of catalyst was used to obtain the data in the above Table 9 and the run continued for about one hour. The increased gasoline selectivity shows about a 14 vol. percent gasoline yield advantage since the two runs were at roughly comparable conversions. The increased gasoline yield is associated with a lower sulfur and nitrogen content. The difference in Res. leaded octanes of 96 and 98 is almost within the limits of experimental error of the octane determination. It appears, therefore, that HCl addition is an economically feasible way of improving product distribution in shale oil hydrocracking. Instead of HCl, chlorine gas, HF or other similar halogen compounds or halogens may be used.

## EXAMPLE 9

There is considerable incentive in reducing the coke make in hydrocracking, since this increases cycle length and reduces the need for many expensive regenerations. The data in Table 10 shows the advantage of increasing hydrogen dilution (i.e. hydrogen partial pressure at constant total pressure) in reducing coke make.

*Table 10*

Feed: Colorado shale oil.
Boiling range, ° F.: 400°–1,050° F.
Wt. Percent $N_2$: 2.0.

| Catalyst | Pt on $Al_2O_3$ | Pt on $Al_2O_3$ |
|---|---|---|
| Temp., ° F | 980 | 980 |
| Pressure, p.s.i.g | 700 | 700 |
| Feed Rate, w./hr./w | 1.0 | 1.0 |
| S.c.f./b. $H_2$ | 4,000 | 8,000 |
| 430° F. Conversion, Wt. Percent | 78 | 80 |
| Product Distribution, Wt. Percent Selectivity: | | |
| $H_2$ (Consumption) | −2.6 (1,650 s.c.f./b.) | −4.2 (2,500 s.c.f./b.) |
| Dry Gas | 19 | 24.5 |
| $C_4$ | 10.5 | 7 |
| $C_5$–430° F | 44 | 50 |
| Coke | 7 | 2.5 |
| $C_5$–430° F. Gasoline: | | |
| Vol. Percent | 54.5 | 61 |
| Res. Oct. No. (+3 ml. TEL) | 93 | 90 |
| Sulfur, Wt. Percent | 0.022 | 0.015 |
| Nitrogen, Wt. Percent | 0.003 | 0.002 |
| Aromatics, Vol. Percent | 34.5 | 33 |
| Olefins, Vol. Percent | 3 | 0 |

In Table 10, using more hydrogen reduces coke but also results in increased hydrogen consumption. Also, the octane number is lower for the more saturated gasoline.

## EXAMPLE 10

The catalyst can be regenerated and there is no permanent poisoning of the catalyst when hydrocracking total shale oil as will be seen from the data in the following

Table 11 showing three cycles. The runs were made at 700 p.s.i.g, 980° F., 1.0 W./Hr./W., 4000 s.c.f./b. $H_2$ dilution, the catalyst comprised 0.6% Pt by weight on 99.4% by weight eta alumina made as above described in Example 1, and the feed was total shale oil boiling between 400° and 1050° +F.

*Table 11*

| No. of Regeneration | 0 | 1 | 2 |
|---|---|---|---|
| Chlorine on Cat., Wt. Percent | 0.6 | 1.2+$Cl_2$ treat. | 0.7+ No $Cl_2$ treat. |
| Product Distribution, Wt. Percent: | | | |
| $H_2$ (Consumption) | −3.1 | −3.2 | −4.3. |
| Dry Gas | 25.0 | 25.0 | 29.0. |
| $C_4$ | 9 | 16 | 8. |
| $C_5$–430° F | 42 | 34.5 | 43. |
| Coke | 3 | 8 | 5. |
| 430° F. Conversion, Wt. Percent | 76 | 81 | 80. |
| $C_5$–430° F. Gasoline: | | | |
| Vol. Percent | 51.5 | 41.5 | 52.5. |
| Res. Oct. No. (+3 ml. TEL) | 90 | 89 | 93. |
| Sulfur, Wt. Percent | 0.02 | 0.04 | 0.09. |
| Nitrogen, Wt. Percent | 0.025 | 0.035 | 0.016. |

The activity maintenance for the first and third cycle in Table 11 is evidenced by comparable gasoline yields and octane numbers at about the same conversion. The general product distribution for the first and third cycle is also about the same.

After the first regeneration, the catalyst was acid treated with a mixture of HCl and $HNO_3$. In the acid treatment, the catalyst was treated with a solution containing 7 wt. percent on catalyst of concentrated HCl and 4 wt. percent on catalyst of concentrated $HNO_3$ in 200 wt. percent on catalyst of distilled water. The catalyst pills were slurried in the acid solution and then placed on a steam bath in a covered container for one hour. Temperature of the solution was about 180° F. The acid solution was then drained off, and the catalyst was washed twice with 400 wt. percent on catalyst of distilled water. The washed catalyst was then dried at 250° F. for 16 hours in a drying oven, and finally calcined one hour at 1100° F.

As seen in the second column of Table 11, the activity of the catalyst was greatly increased, resulting in increased $C_4$ and coke production at the expense of gasoline. The activity of the catalyst was evidently too high for the process conditions used and more favorable results would be expected at a lower temperature.

While the data above were obtained using a fixed bed, the process is not restricted thereto but may also be carried out as a fluidized or moving bed or as a slurry to utilize relatively short cracking cycles followed by regeneration in a cyclic process.

The gasoline as produced by the present process is acid washed to reduce the nitrogen which appears as $NH_3$, and low-boiling amines or other basic nitrogen compounds. The raw gasoline contained about 0.3 wt. percent nitrogen and this was reduced to about 0.02 wt. percent nitrogen by washing the raw gasoline with dilute hydrochloric acid of about 10% concentration using about one part by weight of acid solution to one part by weight of raw gasoline.

Instead of hydrochloric acid, other mineral acids such as sulfuric acid may be used for washing the raw gasoline.

## EXAMPLE 11

A heavy gas oil (Boiling Range 600°–900° F.) was first hydrofined and the sulfur content was reduced from 1.33 wt. percent to 0.17. This desulfurized gas oil was then hydrocracked at both 200 and 700 p.s.i.g. Another portion of the same gas oil feed was hydrocracked directly at 400 p.s.i.g. The results, given in Table 12 below, show that it is advantageous to desulfurize heavy gas oil before hydrocracking, although good results are obtained on the desulfurized feed.

*Table 12*

[Feed: West Texas gas oil (600°–900° F.)]

| | Hydrofined and Hydrocracked | | Hydrocracked Directly |
|---|---|---|---|
| Sulfur, Wt. Percent | 0.17 | 0.17 | 1.33 |
| Pressure, p.s.i.g. | 200 | 700 | 400 |
| Temperature, ° F. | 945 | 1015 | 1015 |
| 430° F. Conversion, Wt. Percent | 55.5 | 80 | 59 |
| $C_5$–430° F. Gasoline: | | | |
| Yield, Vol. Percent | 38 | 41.5 | 42 |
| Res. Oct. No. (+3 cc. TEL) | 95.5 | 103.5 | 93.5 |
| Motor Oct. No. (+3 cc. TEL) | 87 | 93.5 | 83 |
| Aromatics in Gasoline, Vol. Percent | 47.5 | 75 | 38 |
| Olefins in Gasoline, Vol. Percent | 5.5 | 6 | 24 |
| Saturates in Gasoline, Vol. Percent | 47 | 19 | 38 |
| Yield of Aromatics on Feed, Vol. Percent | 18 | 32 | 15 |

It appears from the data in Table 12 that the sulfur inhibits the formation of aromatics in hydrocracking. The data in the first and third columns show a lower aromatic yield and a much more olefinic gasoline for the undesulfurized gas oil compared to the desulfurized gas oil at about the same conversion. As shown by the second column, a higher yield of aromatics is obtained when increasing temperature and pressure. The gasoline octanes obtained with desulfurized feed are higher than those obtained with undesulfurized feed. However, the gasoline yield is slightly higher for the undesulfurized feed, suggesting that sulfur promotes hydrocracking.

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.

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 portion of the catalyst which is circulating through the system. The spent alumina is withdrawn from the system through line **124** 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. High eta alumina content alumina is the preferred alumina diluent.

Referring now to the combination of steps shown diagrammatically in the drawing, shale oil feed is introduced through line 22 and is preheated to a temperature of about 500° to 700° F. and introduced into hydrocracking vessel 14 maintained at a temperature of about 950° to 1025° F. and maintained under pressure of about 200 to 1000 p.s.i.g. The catalyst in the hydrocracking vessel 14 is made of platinum on high eta alumina content 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 using shale oil feed boiling between about 363° F. and 1015+° F. to be hydrocracked, the hydrocracking vessel 14 was maintained at a temperature of about 990° F., the pressure was about 700 p.s.i.g., and the space velocity was about 1.2 W./Hr./W. The amount of $C_5$ to 430° F. gasoline yield was 54.5 volume percent. The Research Octane Number plus 3 cc. of lead was 93 and the Motor Octane Number plus 3 cc. of lead was 85.1. In the gasoline ($C_5$–430° F.) the volume percent of olefins was 3.0, the volume percent of aromatics was 34.6, and the weight percent of sulfur was 0.022 after caustic wash, and the weight percent of nitrogen before acid wash was about 0.3 and after the acid wash was 0.003. The amount of sulfur in the shale oil feed to the hydrocracking vessel 14 was about 0.66 by weight and the amount of nitrogen was about 1.9 wt. percent.

From the above it is apparent that hydrocracking a shale oil with the present process produces a high octane gasoline in one step without a further processing step such as hydroforming. The hydrocracked gasoline need only be acid washed to remove nitrogen compounds to produce high octane gasoline.

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 about 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 920° F. and the pressure was about 400 p.s.i.g. The naphtha feed in line 74 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 $C_5$ 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 700 p.s.i.g. The catalyst 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 gas oil with the platinum catalyst of this invention had 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.

The nitrogen is easily removed from the cracked gasoline obtained from shale oil by an acid wash as shown in the data of certain of the above tables.

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 fractions, provisions have been made for the removal of the effect of these contaminants from the system continuously, if desired.

Obviously, 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 hydrocarbons which comprises hydrocracking raw shale oil boiling above about 350° F. at a temperature between about 900° F. and 1025° F. under a pressure between about 200 p.s.i.g. and 1000 p.s.i.g. in the presence of platinum on high eta alumina content catalyst, said eta alumina being produced from an aluminum alcoholate, and at a feed rate between about 0.5 and 4 W./Hr./W. and in the presence of between about 1000 and 6000 s.c.f. of hydrogen per barrel of shale oil feed thereby converting a major proportion of said shale oil feed to lower boiling products low in nitrogen and sulfur.

2. A method of producing high yields of high octane number gasoline of low sulfur and low nitrogen content from raw shale oil containing relatively large amounts of sulfur and nitrogen which comprises hydrocracking shale oil boiling in the rang of about 600° to 900° F. in the presence of a stable catalyst comprising less than about 1% of platinum on high eta alumina content alumina produced from an aluminum alcoholate and in the presence of added hydrogen while maintaining a total pres-

sure between about 600 and 800 p.s.i.g. and a temperature between about 975° F. and 1000° F. thereby converting a major proportion of said shale oil feed to lower boiling products low in nitrogen and sulfur.

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

4. A method according to claim 2 wherein the catalyst contains coke following the hydrocracking step and the catalyst is regenerated by burning off coke with air and the regenerated catalyst is returned to another hydrocracking step.

5. A method of converting higher boiling hydrocarbons to gasoline of low sulfur and low nitrogen content which comprises hydrocracking a raw shale oil boiling above about 350° F. at a temperature between about 900° F. and 1025° F. under a pressure between about 200 p.s.i.g. and 1000 p.s.i.g. at a feed rate of between 0.5 and 4 W./Hr./W. in the presence of added hydrogen and adding 1 to 4 moles of HCl in the hydrogen or about 1.3% by weight of the catalyst of HCl and in the presence of a catalyst containing less than 1% of platinum carried on a support consisting essentially of eta alumina produced from aluminum alcoholate thereby converting a major proportion of said shale oil feed to lower boiling products low in nitrogen and sulfur.

6. A method according to claim 5 wherein the hydrocracked gasoline is treated with an inorganic acid solution to remove nitrogen compounds.

7. A method according to claim 5 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 a halogen containing compound.

8. A method of cracking in the presence of added hydrogen which comprises hydrocracking a raw shale oil feed stock boiling above about 350° F. and having a high content of sulfur and nitrogen at a temperature between about 900° F. and 1000° F. at a pressure between about 200 and 700 p.s.i.g. at a feed rate of between 0.5 and 4 W./Hr./W. and in the presence of hydrogen and a platinum on high eta alumina content alumina catalyst, said eta alumina being produced from an aluminum alcoholate, to produce high octane gasoline, low in sulfur and nitrogen, subjecting the hydrocracked gasoline to a caustic wash to remove sulfur and to an acid wash to remove nitrogen compounds.

9. A method of producing high yields of high octane number gasoline of low sulfur and low nitrogen content from raw shale oil containing relatively large amounts of sulfur and nitrogen which comprises hydrocracking shale oil boiling in the range of from about 500 to 700° F. in contact with a stable catalyst comprising less than about 1% of platinum on high eta alumina content alumina produced from an aluminum alcoholate at a feed rate of between about 0.5 and 4 W./Hr./W. and in the presence of between about 1000 and 6000 s.c.f. of hydrogen per barrel of shale oil feed while maintaining a total pressure between about 200 and 400 p.s.i.g. and a temperature between about 1000 and 1015° F. thereby converting a major proportion of said shale oil feed to high octane number gasoline of low sulfur and nitrogen content.

10. A method according to claim 9 wherein the catalyst contains coke following the hydrocracking step and the catalyst is regenerated by burning off coke with air and the regenerated catalyst is returned to another hydrocracking step.

11. A method according to claim 9 wherein catalyst during the hydrocracking step accumulates carbonaceous deposit, the catalyst is regenerated by burning off the carbonaceous deposit, and then the regenerated catalyst is treated with a halogen-containing compound and an oxidizing agent and then another hydrocracking step is carried out using the regenerated and treated catalyst.

12. A method of producing high yields of high octane number gasoline having low sulfur and low nitrogen content from raw shale oil boiling in the range of about 530° F. and 930° F. which comprises hydrocracking the shale oil at a temperature between about 900° F. and 1025° F. in the presence of hydrogen under a pressure of about 200 p.s.i.g. to 1000 p.s.i.g. in contact with a platinum-on-alumina catalyst in which the alumina is high in eta alumina produced from an aluminum alcoholate for a period to convert about 77 to 82.5 wt. percent of the shale oil to gaseous and gasoline hydrocarbons boiling up to 430° F. while forming less than about 8 wt. percent coke.

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