

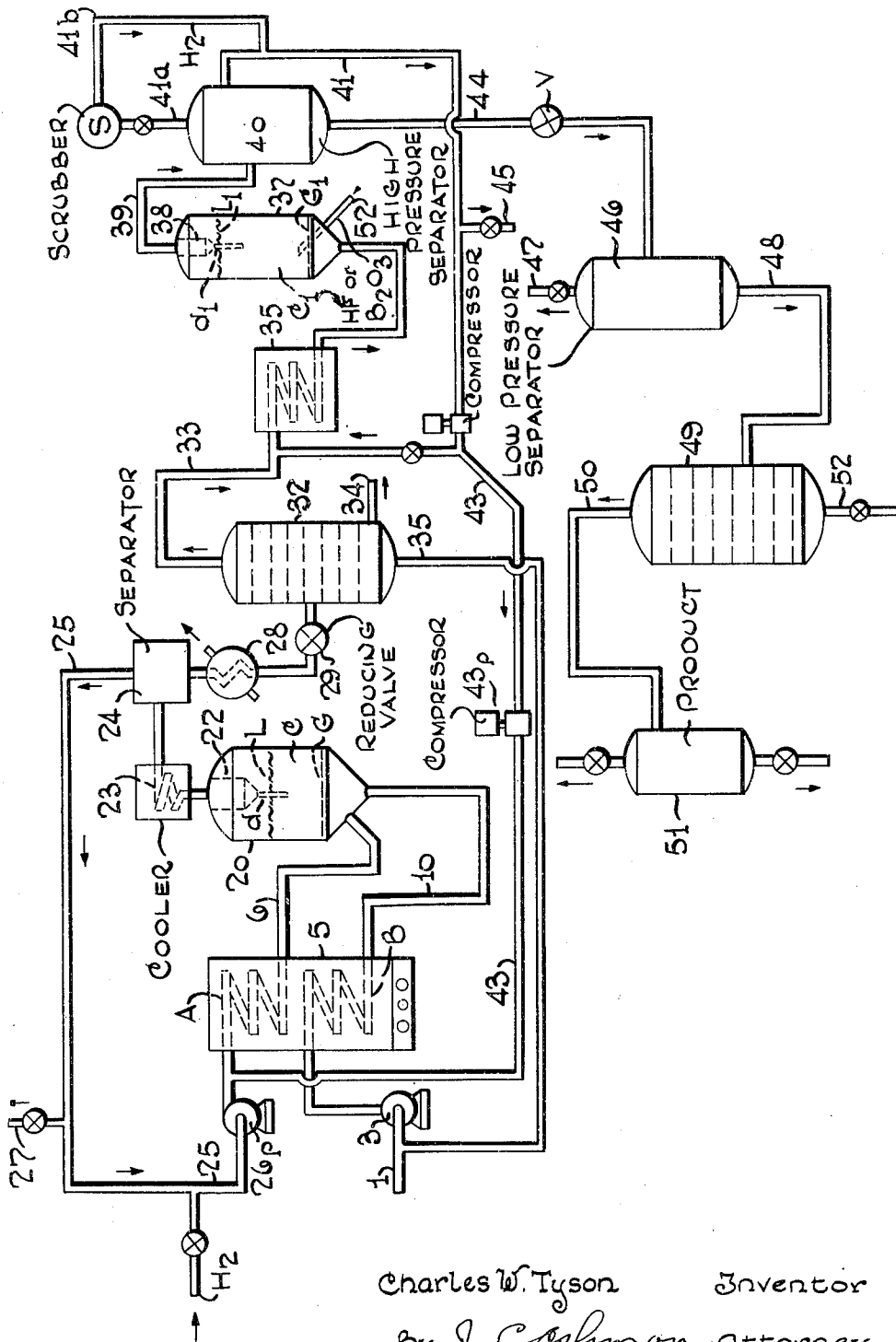
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TWO STAGE HIGH OCTANE GASOLINE PRODUCT

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TWO STAGE HIGH OCTANE GASOLINE PRODUCT

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3 Claims. (Cl. 196—49)

The present invention relates to the novel features hereinafter disclosed in the specification and claims.

Heretofore and prior to the present invention, catalytic cracking of hydrocarbon oils in the presence of hydrogen, coupled with the concept of hydroforming the resultant naphtha is a matter of record. These operations have been previously described in connection with a fixed bed of catalyst, a moving bed of catalyst and also in connection with a powdered catalyst in the form of a fluidized bed thereof.

The present improvements include any of the known methods of hydrocatalytic cracking gas oil, or the like, coupled with the concept of subjecting the cracked gasoline to a hydroforming operation in the presence of added hydrogen for the purpose of improving its octane rating by causing aromatization of cyclic olefins, naphthenes and the like, and also isomerizing paraffins present in the mixture undergoing hydroforming. As it will appear more fully hereinafter, the present improvements are characterized by the following specific features, among others:

(1) Utilization of boron oxide in connection with a supported hydroforming catalyst, the active component of which may be a noble metal such as one of the platinum group, or a sixth group metal oxide such as molybdenum or chromium oxide, the latter preferably being supported on active alumina;

(2) Recycling of the hydrogen present in the crude product from the hydroforming stage back to the hydrocracking stage;

(3) The continuous feeding of boron oxide to the hydroforming stage to replace that lost by volatilization.

The main object of the present invention, therefore, is to produce a high octane gasoline in maximum yields through the manipulation of a process which is efficient and economical.

A more specific object of the invention is to isomerize paraffins in the hydroforming stage while the naphthenes, cyclo-olefins and the like are undergoing dehydrogenation to form aromatics so that the final product in the second stage will predominate in aromatics and isoparaffins, and at the same time will possess a relatively low acid heat.

Another object of the present invention is to saturate non-cyclic olefins produced during the hydrocracking stage, in the hydroforming stage, and because these olefinic hydrocarbons are usually of the branch chain type, saturation of the said olefins will result in the formation of isoparaffins which, of course, are known to possess good octane quality.

To the accomplishment of the foregoing and related ends, a suitable feed stock, such as an East Texas gas oil boiling within the range of, say, from 400°–800° F. or higher is subjected to hydrocracking, the cracked products are then subjected to fractional distillation and thereafter a fraction boiling in the motor fuel boiling range and/or the aviation gasoline range is contacted with an effective hydroforming catalyst, such as a group VI metal

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oxide or a platinum group metal, supported on a suitable base or spacing agent, at elevated temperature and pressures in the presence of added hydrogen whereby a gasoline is eventually produced of high anti-detonation quality.

In the accompanying drawing there is shown a flow plan in which is illustrated diagrammatically, a preferred modification of the invention.

Referring in detail to the drawing a suitable gas oil is introduced into the system through line 1 and thence forced through a pump 3 into a suitable heating means, such as a furnace 5, containing a fired coil B, and after suitable heating, the oil is withdrawn through line 10 and passed into a cracking case 20 containing a suitable catalyst C in the form of a fluidized bed having an upper dense phase level at L. As indicated in the drawing, the oil vapors enter the bottom of case 20 and pass upwardly through a foraminous member G, which may be a grid, utilized for the purpose of effecting good vapor distribution. The catalyst itself may be a mineral clay such as montmorillonite or other bentonitic material which preferably has been acid treated, and to which a suitable hydrogenation catalyst has been added. However, a more suitable catalyst is one which consists of a synthetic gel containing silica and alumina or silica and magnesia containing a suitable hydrogenation catalyst. These hydrogenation catalysts include nickel, tungsten, molybdenum, cobalt, chromium, iron in sulfide or oxide form, or mixtures of such sulfides or oxides. The method of preparing these sulfide catalysts is well known, as is their preferred composition of ingredients and, therefore, it is not necessary to describe these hydrocracking catalysts in greater detail, for it will be sufficient to state that any suitable hydrocracking catalyst may be employed.

Since the cracking is to be performed in the presence of added hydrogen, a gas rich and/or predominating in hydrogen is fed to the reactor 20 from the product recovery system via line 25, through coil A of furnace 5. The heated hydrogen passes via line 6 into the cracking vessel 20. The gases and/or vapors passing upwardly through the fluidized bed of catalyst are controlled as to superficial velocity within the limits of, say, from 0.1 to 3 ft. per second where the powdered catalyst has a size of from 200–400 mesh or even finer so as to form within the cracking case 20 a dense, fluidized bed of catalyst in gases and/or vapors. The conditions for hydrocracking are well known. The cracking operation is carried out at relatively high pressures, namely, at pressures of from about 2000–3000 p. s. i. g. The temperature is maintained in the cracking zone within the range of from about 800°–925° F., and the feed rate to the cracking case is such that the feed is resident in the cracking zone for a period of from 20–120 seconds with 60–80 seconds giving good results. The cracked products pass from the dense fluidized bed upwardly and pass through, at the top of the reactor, one or more cyclone separators 22 wherein entrained catalyst is separated from the effluent vapors and returned to the dense bed via one or more dip pipes d. It will be understood, of course, that there is a light phase in the space above L in case 20 which comprises a dilute suspension of catalyst and vapor or gas which decreases in concentration upwardly. The cracked vapors substantially freed of catalyst are withdrawn from the reactor 20, cooled in coil 23 and charged to high pressure separator 24. A gas containing hydrogen is separated from the liquid and fed by line 25 and pump 26 to coil A, and after heating therein is returned to reactor 20 by line 6. A portion of this gas is bled from the system through line 27. This gas contains about 75–85% hydrogen. The liquid products are withdrawn from separator 24, heated in heat ex-

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changer 28 and thence passed through a pressure reducing valve 29 and thereafter charged into a fractionating column 32 wherein they are separated into three fractions as follows:

(1) A naphtha fraction is withdrawn through line 33 and processed as hereinbefore indicated in the hydroforming zone;

(2) A heavier fraction is withdrawn through line 34 and this fraction may be used as desired, for example, as a domestic heating oil;

(3) The heavy bottoms are withdrawn through line 35 and recycled to line 1 for further treatment.

The stream withdrawn through line 33 containing, as stated, the naphtha fraction, is passed through a heater 35 and thence into the bottom of a second reactor 37 which contains a hydroforming catalyst C₁. As usual, the hydroforming reactor 37 is provided with a grid G₁ and the powdered catalyst is formed into a dense fluidized turbulent mass having an upper dense phase level at L₁. The catalyst has a particle size of from 200-400 mesh or finer and the gas and/or vapor superficial velocity through the reactor is from 1/2-3 ft. per second. Under conditions more fully set forth hereinafter, the naphtha in reactor 37 undergoes hydroforming wherein naphthenes are converted to aromatics, branch chain olefins are hydrogenated to the corresponding isoparaffin and straight chain paraffins present, undergo at least partial isomerization to form branch chain paraffins. Also, as in the case of the reactor 20, there is disposed above the dense phase catalyst bed, a light phase in which the concentration of catalyst in the vapors decreases upwardly. The effluent from the dense phase passes upwardly through one or more "cyclone" separators 38 wherein entrained catalyst is removed from the vapors and returned to the dense phase through one or more dip pipes d₁. The effluent vapors are withdrawn from the reactor through line 39 and pass into a high pressure separator 40 wherein the hydrogen-containing gases are withdrawn through line 41. If desired, these gases may be passed via line 41a to a scrubber S wherein light hydrocarbons are removed by treatment of the gases with a hydrocarbon solvent, or with a solid adsorbent to remove said normally gaseous hydrocarbons, and thereafter the purified hydrogen gas is charged via line 41b to line 41. A portion of the hydrogen in line 41 is charged to line 33 for use in the hydroforming stage. Another portion of this hydrogen gas in line 41 is passed via line 43 and compressor 43p to line 25 for use in the hydrocracking stage. A bleed line 45 is provided for withdrawing excess hydrogen containing gas from the system. It is usually desirable to provide such a bleed line 45 also to remove from the system, sulfur bodies which may be contained in the original feed stock.

Referring again to high pressure separator 40, the liquid product is withdrawn through line 44, passed through a reducing valve V and thence discharged into a low pressure separator 46. From low pressure separator 46, light ends are withdrawn through line 47, while the higher boiling material is withdrawn through line 48 and discharged into a finishing still 49, wherein it is subjected to fractional distillation. The naphtha product is recovered from the still 49 through line 50 and collected in a product receiving drum 51. Higher boiling material is withdrawn from the finishing still 49 through line 52. This latter material, which is formed in relatively small quantity (2% or less by volume), may be mixed with the material from line 34 of fractionator 32 and used as a domestic heating oil, as a solvent or thinner, or otherwise utilized.

Since HF and B₂O₃ may be contained in the hydroforming catalyst composition and may be lost by volatilization during the process, they may be added separately or jointly as needed to reactor 37 via line 52.

In order to provide a better understanding of the present improvements, there is set forth below operating con-

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ditions in both the hydrocracking stage and the hydroforming stage:

Hydrocracking conditions

5	Temperature-----	800°-950° F.
	Pressure-----	2000-3000 p. s. i. g.
	Feed rate-----	0.2-2.0 lbs. of feed per lb. of catalyst per hour.
	Hydrogen recycle (standard conditions),	2000-4000 cu. ft. of hydrogen per barrel of oil.
	Catalyst composition----	Silica-alumina gel containing a mixture of nickel and tungsten sulfides, (10% by weight of 2NiS. WSA based on weight of gel.)

Hydroforming conditions

15	Temperature-----	875°-975° F.
	Pressure-----	100-500 p. s. i. g.
	Feed rate-----	0.2-5.0 lbs. of feed per lb. of oil per hour.
	Hydrogen recycle (standard conditions),	1000-6000 cu. ft. per barrel of oil.
	Catalyst composition by weight.	Pt 0.5%, HF* 1%, B ₂ O ₃ 1%, Al ₂ O ₃ ** 97.5%, MoO ₃ (10 wt. %) on Al ₂ O ₃ (90 wt. %).
20	Catalyst/oil weight ratio--	0.5-5.0.

* Optional.

** 5% of Al₂O₃ may be replaced by SiO₂.

The foregoing range of operating conditions, of course, may be varied depending on the nature of the stock and other variables. The operator familiar with the art is to consider them as representative of conditions giving good results. For example, in connection with the use of hydrogen fluoride or boron oxide, these may vary in amount present on the catalyst within rather wide limits. Also, the amount of platinum may vary when that material is used as a catalyst. Thus, for example, the boron oxide may vary from 0.1-10% of the total catalyst composition, and the same is true for the hydrogen fluoride. The platinum also may vary from 0.2-0.3 to 2% based on the total weight of the catalyst. It is also advisable to include in the molybdena-alumina catalyst quantities of either or both of boron oxide and the hydrogen fluoride within the limits set forth immediately above. The molybdena may, in some cases, be replaced by other metal oxides of the VI group of the periodic system, such as chromium, or by a II group of metal oxide, such as beryllium oxide.

EXAMPLE

An East Texas gas oil was cracked in the presence of hydrogen and a conventional synthetic gel catalyst containing alumina and silica and also containing a mixture of nickel and tungsten sulfides, the amount of hydrogen being 2500 cu. ft. of hydrogen containing gas (75% hydrogen) at a temperature of about 900° F., while operating under a pressure of about 2500 p. s. i. g. A 65% conversion of gas oil to gasoline was obtained. After separation of the cracked gasoline from the heavier material, the former was subjected to hydroforming in the presence of a catalyst consisting of 10% by weight (MnO₃) and 90% alumina, the catalyst also containing 1% boron oxide and 1% HF, both based on the total weights of the molybdena and the alumina. A temperature of about 900° F. and a pressure of about 250 p. s. i. g. was maintained during this hydroforming reaction and 2500 cu. ft. of hydrogen containing gas (75% hydrogen) was fed to the hydroforming zone with each barrel of oil. In the table below there is set forth the octane number of the hydrocracked gasoline and the subsequently hydroformed product.

Research clear octane number

After hydrocracking-----	66
After hydroforming-----	93

Results comparable to those set forth in the above example are obtainable using a platinum catalyst carried on active alumina and also containing boron oxide and hydrogen fluoride. This catalyst contained 0.5% HF, 0.5% Pt., 0.5% B₂O₃, and 98.5% Al₂O₃ (active), the foregoing percentages being by weight. In this process a pressure of about 750 p. s. i. g. was maintained

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whereby the process is operable continuously for several months without interruption to reactivate the catalyst.

In describing the present invention, a showing of many conventional devices and accessory apparatus which are commonly used and well known to petroleum engineers has been omitted in order to simplify the explanation and direct attention to the present improvements. Also omitted are descriptions of ways and means the petroleum engineer would recognize as necessary in the regeneration of the reformer catalysts. As is well known, the regeneration of these catalysts is usually accomplished by treatment at elevated temperatures of the catalyst with a free oxygen-containing gas. This regeneration of catalyst has been described in the prior literature and patents, and it is unnecessary to set forth herein a description of the method of regenerating the catalyst. It will be sufficient to say that any known safe and rapid method for regenerating the catalyst may be employed when necessary.

It is also well known that when operating under pressure of, say, 750 p. s. i. g., it is not necessary to regenerate the platinum catalyst at frequent intervals, for the same may be employed on-stream during an extended period of, say, several months without having to discontinue the productive phase to regenerate the catalyst. Similarly, the hydrocracking catalyst may remain continuously on-stream for several months without requiring interruption of the productive phase. To regenerate either catalyst when it finally loses activity to the point where it is no longer practical to use it, it is desirable to remove it from the system and rework in the catalyst manufacturing plant.

With respect to the regeneration of the catalyst, that is to say, the platinum catalyst when operating at pressures of, say, 200 p. s. i. g. or less, the catalyst acquires deposits which must be removed. One way to remove them is by means of an oxygen-containing gas which is contacted with the catalyst at elevated temperatures for a sufficient period of time to burn off such deposits. Another method is to treat the fouled catalyst with hydrogen or hydrogen-containing gas. In the latter case, the cycle is usually arranged so that the catalyst is on-stream for, say, 1-3 hours while it undergoes regeneration with hydrogen during a period of two or three times as long as the on-stream period.

While the use of a fluid system has been stressed in the present disclosure, it will be appreciated that a fixed bed of hydrocracking catalyst may be used in place of the fluid bed, and in the same manner a fixed bed of hydroforming catalyst may be used instead of the fluidized bed of catalyst.

To recapitulate briefly, the present invention relates, as indicated, to a method of forming high octane gasoline from a suitable feed stock. The invention is performed in two stages. In the first stage, the feed stock is subjected to hydrocracking in the presence of added hydrogen and a suitable hydrocracking catalyst, preferably a synthetic plural gel catalyst of the alumina-silica, or the alumina-magnesia type containing oxides or sulfides of the VI and VIII groups of the periodic system. Mixtures of these hydrogenation catalysts such as a mixture of nickel and tungsten sulfide may be used.

The hydrocarbons boiling within the gasoline boiling range are separated from the effluent of the first stage and subjected to hydroforming in the second stage, the catalyst used in the second stage being molybdenum oxide on alumina or platinum on alumina and/or silica. The catalyst also may contain a relatively small amount of boron oxide, which is useful in isomerizing paraffins, as well as a small amount of hydrogen fluoride. The normal product of the hydroforming operation is a mixture of aromatics and paraffins. Since straight chain paraffins

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ing to the present invention, these straight chain paraffins undergo at least some isomerization, thereby converting them to the more valuable isoparaffins. Since the hydroforming operation functions so as to result in the production of hydrogen as a result of the dehydrogenation of the naphthenes present, the hydroforming operation gives a net production of hydrogen. The added and produced hydrogen is recycled, according to the present invention, to the first stage so that the system may be self-sustaining with respect to the hydrogen requirements.

Many modifications of the present invention will suggest themselves to those who are familiar with the art without departing from the spirit thereof.

What is claimed is:

1. The method of producing high octane gasoline in a system comprising a hydrocracking zone and a hydroforming zone which comprises feeding gas oil to the hydrocracking zone containing a bed of hydrocracking catalyst consisting essentially of nickel sulfide and tungsten sulfide, in which the weight ratio of nickel sulfide to tungsten sulfide is 2:1, which sulfides are carried on a silica-alumina gel and which sulfides constitute about 10 weight percent of the said gel, simultaneously feeding to said reactor a hydrogen-containing gas produced in the system, maintaining the hydrocracking zone at a temperature from about 800°-950° F., a pressure of from about 2,000-3,000 p. s. i. g., and a feed rate of from about 0.2-2 lbs. of feed oil per lb. of catalyst in the reactor per hour, withdrawing a crude product from the hydrocracking zone, separating a fraction boiling up to about 400° F., charging the separated fraction to the hydroforming zone, contacting said fraction in said hydroforming zone with a hydroforming catalyst consisting essentially of platinum carried on active alumina, the amount of platinum being about 0.2-2.0 weight percent, the catalyst also containing from 0.1 to 10 weight percent of boron oxide and an amount of hydrogen fluoride within the range of from about 0.1 to 10 weight percent, the foregoing percentages being based on the total weight of the catalyst, and feeding a hydrogen-containing gas to said hydroforming zone in an amount of from about 1,000-6,000 s. c. f. of hydrogen per barrel of oil feed, maintaining said hydroforming zone under a temperature of from about 875-975° F., a pressure of from about 100-500 p. s. i. g. and an oil feed rate of from about 0.2-5.0 lbs. of feed oil per hour per lb. of catalyst in the reactor, maintaining boron oxide and hydrogen fluoride on the catalyst in the said hydroforming zone by adding boron oxide and hydrogen fluoride to the catalyst in amounts required to replace these materials lost by volatilization, withdrawing crude product from the said hydroforming zone, recovering hydrogen from the crude product in a separation zone and recycling the latter to the hydrocracking zone and recovering a gasoline product of high octane value from said hydroforming zone.

2. The method set forth in claim 1, in which the catalyst in the feed zones is in the form of fluidized beds.

3. The method set forth in claim 1, in which the catalyst in the feed zones is in the form of fixed beds.

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