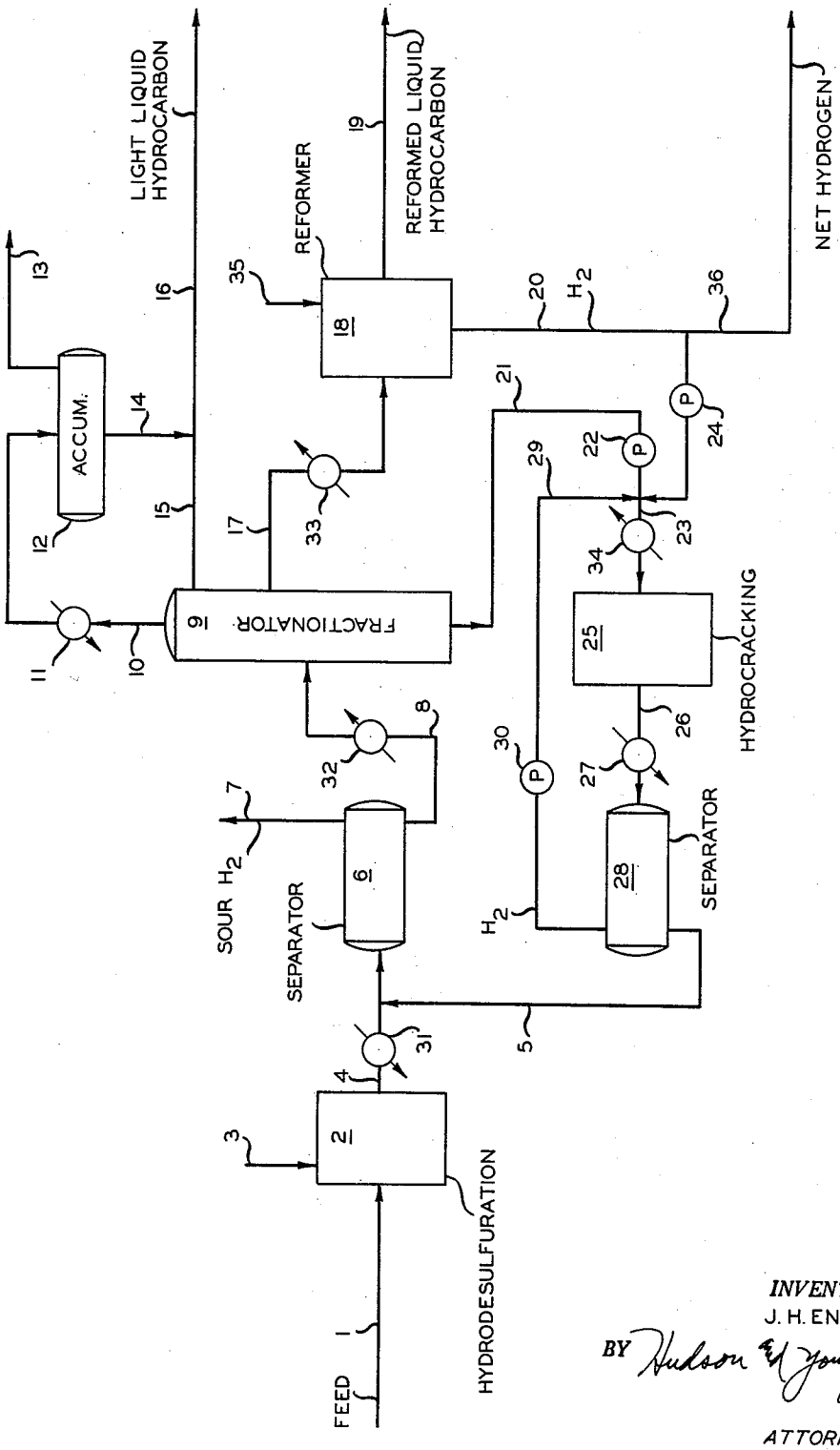
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COMBINED DESULFURIZATION, HYDROCRACKING AND REFORMING OPERATION

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COMBINED DESULFURIZATION, HYDROCRACKING, AND REFORMING OPERATION

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This invention relates to upgrading of motor fuel stocks. In one aspect it relates to upgrading of motor fuel stocks as regards yields and antiknock value. In another aspect it relates to an operation utilizing less costly equipment and therefore a lower capital investment than required by known processes.

Catalytic and noncatalytic conversion processes have been devised in attempts to increase motor fuel yields and to improve such other properties as antiknock value. In one prior art process, over which the present invention is an improvement, an entire hydrodesulfurization effluent liquid, along with the high boiling end fraction of a hydrocracking operation, is charged to the hydrocracking operation for conversion. The present invention is a marked improvement over this prior art process because in place of hydrocracking a hydrodesulfurized naphtha of full boiling range, only the high boiling end fraction of the naphtha, along with the high boiling end fraction of a hydrocracking operation, is charged to the hydrocracking operation. In this manner the more or less free-riding, gasoline boiling range portion of the naphtha, which is usually not markedly improved in antiknock value, is not passed through the hydrocracking portion of the operation. Thus, by eliminating the portion of the feed stock which is improved slightly or even not at all, I am able to employ a hydrocracking unit of markedly reduced capacity and therefore much less costly than larger units.

An object of this invention is to devise a process for upgrading motor fuel stocks as regards antiknock values. Another object of this invention is to provide an operation which can produce increased yield of motor fuel stocks of at least equal or greater antiknock values than prior art processes. Still another object of this invention is to provide an operation which can be carried out in less costly apparatus and equipment than conventional. Still other objects and advantages of this invention will be realized upon reading the following description which, taken with the attached drawing, forms a part of this specification.

Specifically, this invention comprises a process for increasing the production of valuable hydrocarbons comprising mixing a hydrocarbon naphtha and a cycle oil with an effluent of a hydrocracking operation as subsequently produced, separating the mixture into a gas phase and a first liquid phase, from this liquid phase separating by distillation a bottoms material, hydrocracking this bottoms material in the presence of added hydrogen, separating the effluent of the hydrocracking operation into a hydrogen gas rich phase and a second liquid phase, said second liquid phase being the aforementioned effluent of a hydrocracking operation as subsequently produced, and from the aforesaid distillation separating an intermediate boiling range product of increased yield as a product of the process.

The drawing illustrates in diagrammatic form one arrangement of apparatus parts for carrying out the process of this invention.

In the drawing, feed material which is a full boiling range naphtha, a light cycle oil, or a mixture of these two materials, is introduced from a source, not shown, through a conduit 1 into a hydrodesulfurization zone 2. The catalyst vessel of the hydrodesulfurization zone is provided with a cobalt-molybdena containing catalyst

alone or supported on suitable carriers. A suitable cobalt-molybdena catalyst is prepared by adding two parts of ammonium hydroxide to one molar part of ethylenediamine tetraacetic acid slurried in water. One molar part of cobaltous hydroxide or cobaltous carbonate is added to the mixture just prepared with gentle warming to speed the chelation reaction. Upon concentration of this solution, a salt is obtained having the formula

$$(NH_4)_2Co(Y)\cdot 4H_2O$$

in which the symbol Y is used to designate the completely ionized form of ethylenediamine tetraacetic acid with the formula as follows:

$$[(CH_2COO)_2NCH_2CH_2N(CH_2COO)_2]^{-4}+4H^+$$

White beads of a commercial silica-alumina cracking catalyst containing 10 percent by weight of alumina, and 8 to 14 mesh, are used as a support for the above-produced cobalt-containing material. The cobalt-chelate solution concentration is adjusted so that the volume of chelate solution absorbed by the support material contains a quantity of dissolved cobalt metal equal to 0.5 percent by weight of the finished catalyst. Sufficient ammonium molybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ is then dissolved in the cobalt-chelate solution so that the volume of the solution absorbed by the support material contains a quantity of molybdenum metal equal to 2 percent of the finished catalyst by weight. Since the cobalt has been prepared as a chelate compound, it is not necessary to add ammonia in great excess, as is required to maintain cobalt and molybdenum in the conventional impregnating solution where the cobalt is not chelated. The support is covered with the cobalt-molybdenum solution and allowed to stand for 24 hours to assure thorough impregnation. The support material is then removed from the solution and kept at 250° F. until dry. It is then calcined for two hours at 830° F., two hours at 930° F. and for twelve hours at 1030° F.

Full details of the preparation of this cobalt-molybdenum catalyst are given in U.S. Patent 2,889,287.

However, if desired, the hydrodesulfurization vessel can employ a platinum containing catalyst in place of the cobalt-molybdenum catalyst described above. If platinum supported catalyst is desired, it may be prepared by adding, for example, ammonium hydroxide to a salt of aluminum, as, for example, aluminum chloride, aluminum sulfate, aluminum nitrate, or other suitable, soluble aluminum salt in an amount to form aluminum hydroxide. Upon drying this so-formed aluminum hydroxide, it is converted to alumina, this term being intended to be sufficiently broad to include aluminum hydroxide as produced by the ammonium hydroxide reaction. Thus, after this alumina has been formed, it is washed to remove such soluble impurities as chloride. Washing is usually carried out with water either by filtration or by decantation. Washing is expedited in case the wash water is made alkaline with ammonium hydroxide. After the alumina is free from soluble impurities halogen ion such as fluoride, preferably, or chloride is added in the form of, for example, the corresponding acid. Sufficient concentration of halogen ion in the finished catalyst will be within the range of from about 0.1 percent to about 8 percent by weight of the alumina on a dry basis. In case fluoride is added, the concentration of the fluoride is generally within the range of about 0.1 to about 3 percent by weight of the alumina on a dry basis. In case the halogen ion is chloride, it will be added to the alumina in an amount to provide chloride from about 0.2 percent to about 8 percent and preferably from about 0.5 percent to about 5 percent by weight of the alumina on a dry basis.

After halogenating the alumina catalyst, as just described, a separate solution of chloroplatinic acid in water is saturated with hydrogen sulfide at room temperature

until the solution reaches a constant dark coloration. It is preferable to add the hydrogen sulfide to the chloroplatinic acid solution at room temperature. The platinum is added in an amount to produce a final catalyst containing from about 0.01 percent to about 1 percent by weight of platinum on the alumina on a dry basis. After addition of the platinum the mixture is preferably dried at a temperature of from about 200° to about 400° F. for a period of from about 4 to 24 hours or more to form a cake. If desired, the cake can be pilled to form pills ranging in size from about ⅛" by ⅛" to about ¼" by ¼". Pills also can be made by extrusion methods if desired. Also, if desired, the catalyst can be used as a powder or granules of irregular size and shape.

After pilling, extruding, or forming as a powder or granules, the catalyst is calcined at a temperature of from about 800° to about 1200° F. for a period of from about 2 to 8 hours or more

Full details of the preparation of such a platinum catalyst are given in U.S. Patent 2,479,110.

The boiling range of the combined naphtha (100° to 500° F.) and light cycle oil (460° to 660° F.) fed through conduit **1** to the hydrodesulfurization zone **2**, when employing a cobalt-molybdenum catalyst prepared as mentioned hereinabove, is from about 100° to about 700° F. The feed material is heated to a temperature within the range of about 500° to about 900° F. and passed at this temperature into the cobalt-molybdenum catalyst at a space velocity of about 0.5 to 4 volumes of feed material per volume of catalyst per hour. At a space velocity of 3 the catalyst is maintained at a temperature of about 700° F. under a pressure of about 425 p.s.i.g. (pounds per square inch gauge). Hydrogen, from a source, not shown, is passed through a conduit **3** into the hydrodesulfurization zone **2** at a rate of about 500–5000 s.c.f. per barrel of hydrocarbon feed. Pressure in the zone can be varied between approximately 350 and 1000 p.s.i.g. (S.c.f. is standard cubic feet.)

Effluent from the hydrodesulfurization zone is removed therefrom and passed through a conduit **4** and is cooled to a heat exchanger **31**. After cooling in exchanger **31** a liquid hydrocarbon hydrocracking effluent, subsequently produced, is passed through a conduit **5** and added thereto and the combined feed material is passed into a phase separator **6**. In this phase separator maintained at a temperature within the range of about 95° to about 115° F., and at a pressure of about 275 to 325 p.s.i.g., the gaseous material is withdrawn through a conduit **7** for such disposal as desired. This gaseous material is rich in hydrogen and contains hydrogen sulfide in proportion to the sulfur content of the naphtha in the feed in conduit **1**. The liquid phase separated in separator **6** is withdrawn therefrom and is passed through a conduit **8**, and is heated in a heat exchanger **32** and introduced into a fractionator **9**. This fractionator is operated under such fractional distillation conditions as to produce a light hydrocarbon overhead product, and a difficultly condensible overhead gas. Also, an intermediate boiling range sidestream is withdrawn through a conduit **17** while a bottoms liquid material is withdrawn through a conduit **21**. The overhead vapors from fractionator **9** are withdrawn therefrom by way of a conduit **10**, condensate is produced in condenser **11** and phase separation takes place in an accumulator vessel **12**. Uncondensed gases are removed through a conduit **13** for such disposal as desired. Condensate passes through a conduit **14** and that portion thereof required for refluxing the fractionator is passed through a conduit **15** to the upper portion of the vessel. The portion of condensate, not required for refluxing is withdrawn from the system through a conduit **16** for such disposal as desired.

The sidestream taken through conduit **17** boiling in the range of about 150–400° F. can, if desired, be improved in antiknock value by conversion in a reforming operation. For reforming the sidestream from conduit **17** is heated in a heat exchanger **33**, which can be a furnace, to such a temperature as required for conversion in a reforming unit **18**. In the reforming unit **18** a platinum-containing catalyst such as that mentioned hereinbefore can, if desired, be used. Gaseous hydrogen, from a source not shown, is introduced into the reforming unit **18** through a conduit **35**.

In general, a reforming operation employing the platinum catalyst involves subjecting the sidestream from conduit **17** in the reforming unit to contact with the catalyst at a temperature of from about 800° to about 1000° F., at a pressure from about 200 to about 800 p.s.i.g., at a weight hourly space velocity of from about 0.5 to about 10, in the presence of from about 0.5 to about 10 mols of hydrogen per mol of hydrocarbon. The catalyst in this particular case comprises support alumina containing from about 0.01 percent to about 1 percent of platinum by weight of the catalyst and halogen ions in an amount of from about 0.1 percent to about 8 percent by weight of the catalyst.

This reformer **18** includes the actual catalyst-containing vessels with furnaces for reheating in between the vessels, reformer effluent condensing means and liquid-gas separator. The reformed liquid hydrocarbon is withdrawn through a conduit **19** for such disposal as desired while the gas from the separator is withdrawn through a conduit **20**. In such a reforming operation the gas in conduit **20** is largely hydrogen. In case more hydrogen is produced in the reforming operation than is required in the reforming operation and in a subsequent operation, to be hereinafter described, the net hydrogen produced is withdrawn from the system through a conduit **36** for such disposal as desired. A portion of the hydrogen from the reformed can be recycled from the conduit **20** to conduit **35**, and the remainder used for other purposes, as herein disclosed.

The liquid bottoms fraction passing through conduit **21** from fractionator **9** has a boiling range in general higher than the end boiling point of the desired gasoline fraction. This material, I find, is susceptible to further improvement as regards production of gasoline boiling range hydrocarbons of improved octane number or antiknock value. Thus, I pass this high boiling bottoms fraction through conduit **21** by pump **22**, through a conduit **23** to a heater or heat exchanger **34**. This heat exchanger heats this material to a temperature within the range of about 400° to about 900° F. After passing through heat exchanger **34** the heated material is passed into a hydrocracking zone **25** maintained at a pressure within the limits of about 500 to 2000 p.s.i.g., and which is provided preferably with a cobalt-molybdenum-containing catalyst hereinabove described. Along with the bottoms from fractionator **9** free hydrogen gas is also heated in heater **34** and passed into the hydrocracking zone. At least a portion of the hydrogen entering conduit **23** can, if desired, originate in the reforming unit **18** and, after being separated from the reformed liquid hydrocarbon in zone **18**, is passed through conduit **20**, compressor **24**, for addition to the hydrocarbon in conduit **23**. The hydrocracked effluent material is passed from zone **25** through a conduit **26** and is cooled in a heat exchanger **27**.

From the cooler or heat exchanger **27** the hydrocracked material is passed on into a separator vessel **28** in which difficultly condensible gases are separated from a liquid phase. The difficultly condensible gases separated in separator **28** comprise largely unused or newly produced free hydrogen gas. This gas is passed through a conduit **29** by a compressor **30** and is added to the charge liquid passing through conduit **23**. Liquid separated in separator **28** is passed through a conduit **5** and is added to the hydrodesulfurization zone effluent flowing through conduit **4** prior to its entry into the phase separator **6**. The separator **28** is maintained at a temperature within the range of about 105° to about 125° F. at a pressure within the range of about 500 to about 2000 p.s.i.g. The

pressure in this separator is usually about 20 p.s.i.g. less than in the conversion zone **25**.

As mentioned hereinabove, a preferable catalyst for use in the hydrocracking operation in zone **25** is a cobalt-molybdena catalyst as previously described. New hydrogen for introduction into the hydrocracking zone and originating from the reforming operation comprises about 2 to 9 pounds per barrel of charge, while the total recycle hydrogen, that is, that hydrogen separated in separator **28** and passed through conduit **29**, comprises from about 4 to 35 pounds per barrel of charge to zone **25**. The space velocity of the charge liquid entering the hydrocracking zone **25** is from 3 to 4 volumes of hydrocarbon per volume of catalyst per hour.

The fractionator **9** is provided with efficient vapor-liquid contact promoting apparatus such as bubble cap trays which are conventional in the fractional distillation art. Reboiling heat is provided as required.

In the following tabulation are given the broad operating conditions of the several process steps of this invention.

	Range	Specific Example
(a) Hydrodesulfurization Zone:		
Pressure, p.s.i.g.	350–1,000	425.
Temperature, ° F.	500–900	700.
Catalyst Used	CoMo	CoMo.
Hydrogen, s.c.f./bbl.	500–5,000 (2.5 to 27 lbs./bbl.)	3,200.
Feed, b./h.		Naphtha 600; 51.1° API. Light cycle oil 200; 28° API.
(Light Cycle Oil) API at 60/60° F.	24 to 32	28.
Boiling Range	350° F. to 700° F. (ASTM).	460° F. to 660° F.
Aniline No.	100–120° F.	110° F.
Space Velocity, Vol./Hr./Vol.	0.5 to 4.0	3.0.
(b) Hydrocracking Separator Liquid:		
Quantity to HDS Separator, b./h.		344.
API at 60/60° F.	55.0–65.0	61.9.
Boiling Range	—60° F. to 700° F. TBP.[1]	—44° F. to 650° F. (TBP.)[1]
(c) HDS Separator Zone:		
Temperature, ° F.	90–120	105.
Pressure, p.s.i.g.	200–500	300.
H_2 (foul) removed, Lbs./hr.		2,500.
Liquid to Fractionator, b./h.		1,140.
API at 60/60° F.	44–55	49.7.
Boiling Range	100° F. to 700° F. (ASTM).	160° to 656° F. (ASTM).
(d) Fractionation Zone:		
Top pressure, p.s.i.g.	30–40	35.
Top temperature, ° F.	190–220	200.
Bottom pressure, p.s.i.g.	35–45	40.
Bottom temperature, ° F.	530–560	550.
Yields:		
Vapor (composition), s.c.f./Hr.		18,600.
Light H/C, b./h.		133.
API at 60/60° F.		87.3.
Boiling Range		—44° F. to 190° F. TBP [1] Distillation.
To Reformer, b./h.		698.
API at 60/60° F.		47.8.
Boiling Range		195° F. to 400° F. (ASTM).
Reformed Gasoline, RON w./3 cc. TEL.[2]		99.2.
Bottoms, b./h.		288.
API at 60/60° F.		30.3.
Boiling Range		373° F. to 650° F. (ASTM).
(e) Hydrocracking Zone:		
Pressure, p.s.i.g.	500–2,000	1,520.
Temperature, ° F.	400–900	450.
H_2 from Reforming, #/barrel of charge.	2–9	5.9.
Recycle H_2, #/barrel of charge.	2–26	18.3.
Space Velocity, Vol./Hr./Vol.	3–4	3.5.
(f) Hydrocracking Zone Separator:		
Pressure, p.s.i.g.	500–2,000	1,500.
Temperature, ° F.	105–125	115.

[1] True boiling point.
[2] Research Octane Number with 3 cc. tetraethyl lead.

While certain embodiments of the invention have been described for illustrative purposes, the invention obviously is not limited thereto.

That which is claimed is:

1. A process for increasing the production of valuble hydrocarbons comprising hydrodesulfurizing a hydrocarbon feed liquid comprising a full boiling range naphtha and a light cycle gas oil, said feed liquid boiling within the range of about 100° to about 700° F. at a temperature within the range of about 500° to about 900° F. at a pressure within the range of about 350 to 1000 p.s.i.g. in the presence of a hydrogenation catalyst and from about 2.5 to about 27 pounds free hydrogen per barrel of said feed liquid, mixing with the effluent of the hydrodesulfurizing operation an entire liquid phase effluent of a hydrocracking operation as subsequently produced, separating the mixture into a gas phase and a first liquid phase at a temperature within the range of about 90° to 120° F. and at a pressure within the range of about 200 p.s.i.g. to about 500 p.s.i.g., from this first liquid phase separating by distillation a bottoms material boiling within the range of about 350° and about 700° F., hydrocracking only this bottoms material at a temperature within the range of about 400° to about 900° F. at a pressure of within the range of about 500 to 2000 p.s.i.g. in the presence of added hydrogen within the range of about 2 mols to about 10 mols per mol of bottoms hydrocarbon and in the presence of a hydrogenation catalyst comprising cobalt oxide and molybdenum oxide on an alumina containing catalyst, cooling the effluent of the hydrocracking operation and separating therefrom a hydrogen gas rich phase and a second liquid phase at a temperature within the range of about 105° to 125° F. at a pressure within the range of about 500 to 2000 p.s.i.g., said second liquid phase being said entire liquid phase effluent of a hydrocracking operation as subsequently produced, said hydrogen gas rich phase being at least a portion of said added hydrogen, and from the aforesaid distillation separating an intermediate boiling range product of increased yield and suitable as a charge stock for a reforming operation.

2. In the process of claim 1, reforming said intermediate boiling range product thereby producing a final product of improved antiknock value and of increased yield.

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