

April 28, 1959

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HYDROCRACKING SHALE OIL

2,884,371

Filed Dec. 30, 1954

2 Sheets-Sheet 1

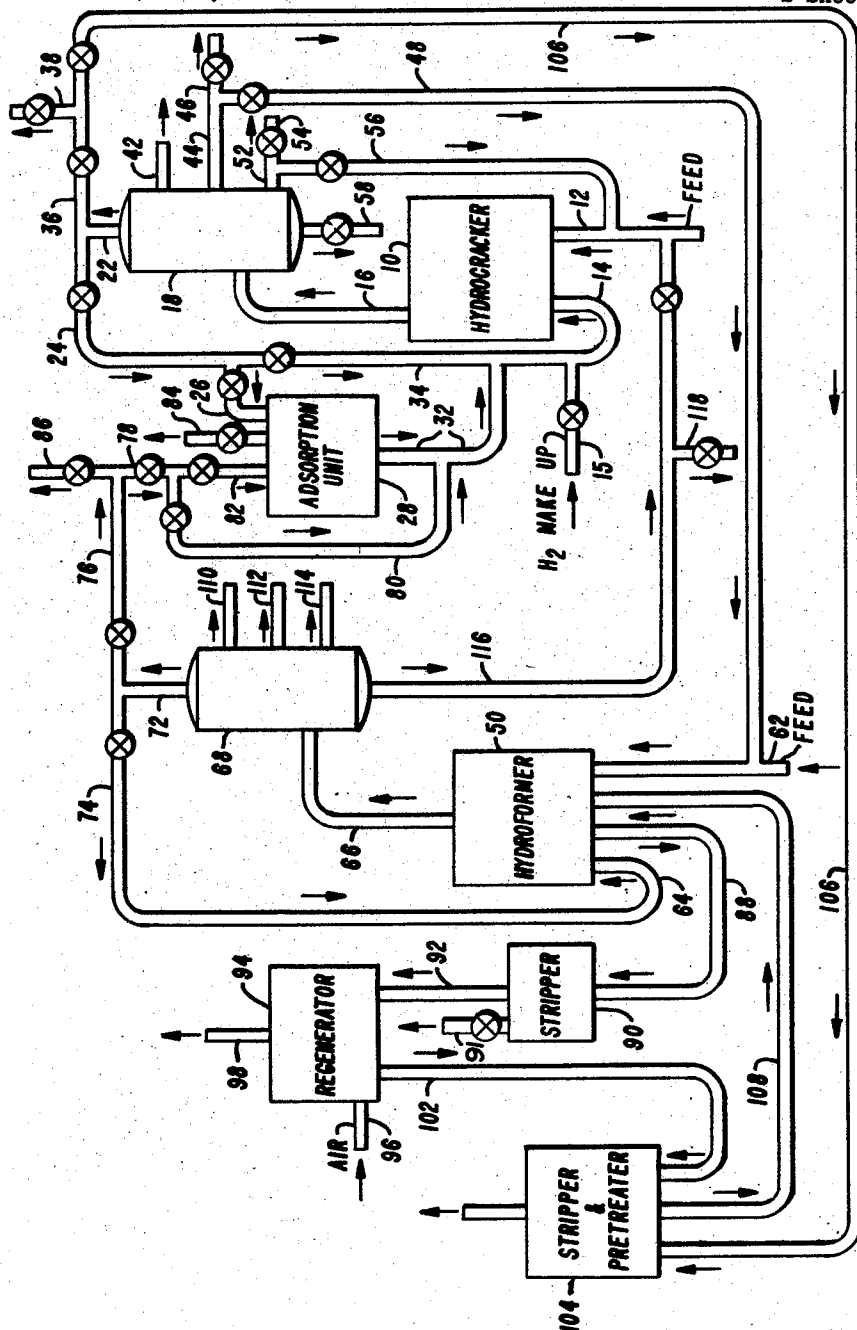


FIG. 1

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2 Sheets-Sheet 2

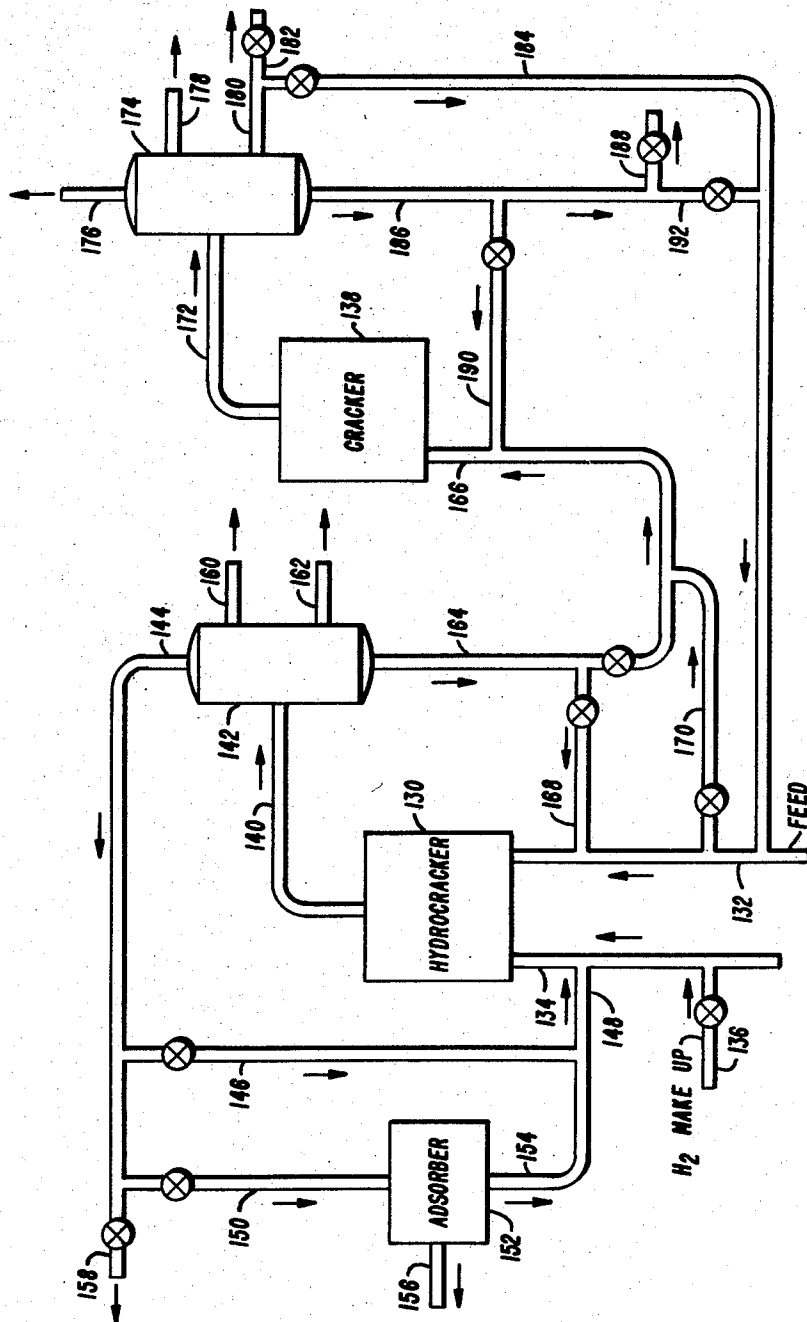


**FIG. - 2**

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## HYDROCRACKING SHALE OIL

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Application December 30, 1954, Serial No. 478,682

10 Claims. (Cl. 208—111)

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 olefinic and aromatic gasolines of high octane number and low sulfur content.

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 oil shale 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 an excessive amount of sulfur 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 excessive amounts of hydrogen.

It has now been found that raw shale oil can be cracked directly over cracking catalysts containing an added hydrogenation component such as molybdenum oxide, platinum, etc. The cracking is carried out in the presence of hydrogen, under a pressure between about 100 and 700 p.s.i.g., preferably 200–500 (pounds per square inch gage) and at a temperature between about 950° and 1100° F. The amount of hydrogen introduced into the cracking zone is between about 2,000 cu. ft. and 10,000 cu. ft., preferably 3,500–6,000 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 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. In another form of the invention the hydrocracking process is used in combination with a catalytic cracking process and in this case the hydrocracking process lowers the nitrogen and sulfur contents of the shale oil and produces an improved shale oil feed for catalytic cracking.

A catalyst which is particularly effective in the present hydrocracking process consists of a conventional cracking catalyst such as a silica-alumina catalyst containing about 87% silica and 13% alumina, to which is added from about 8 to 16%, preferably around 10 to 12% by weight, based on the total catalyst composition, of molybdenum

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oxide. Other silica containing cracking catalysts such as silica-magnesia, silica-alumina magnesia, silica-alumina-zirconia etc. may be used as the cracking catalyst base. Although the molybdenum oxide catalyst is preferred for the treatment of shale oil, under some conditions, platinum may be used as the hydrogenation component in which case about 0.1 to 5% by weight of the total catalyst composition is platinum, preferably 0.5–1 wt. percent. Instead of using fresh silica-alumina cracking catalyst, used catalyst removed from a commercial catalytic cracking unit 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.

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<sub>4</sub>+ and C<sub>5</sub>+ gasoline of high octane number.

The molybdenum oxide or other hydrogenation component may be added to the silica-alumina base or support by merely mixing the dry ingredients together or by impregnating the silica-alumina catalyst or support with ammonium molybdate and drying and calcining. Or the molybdenum oxide may be sublimed to coat or be deposited on the cracking catalyst. The amount of the silica-alumina catalyst component may vary between about 84 and 92 parts by weight of the total catalyst so that there will be between about 8 and 16 parts by weight of the molybdenum oxide or its equivalent.

The process may be carried out using the fluid solids technique but fixed bed and moving bed catalysts or other conventional types may be used.

In the drawings:

Fig. 1 represents a system including a hydrocracking unit and a hydroforming unit; and

Fig. 2 represents another system including a hydrocracking unit and a catalytic cracking unit.

Referring now to Fig. 1 of the drawings, the reference character 10 designates a hydrocracking unit into which raw shale oil to be cracked is introduced through line 12. Also introduced into the hydrocracking unit 10 is a hydrogen-rich gas introduced through line 14. In the hydrocracking unit the shale oil is heated to a temperature of about 950° to 1100° F., preferably between about 1035° and 1060° F. The pressure in the hydrocracking unit 10 is maintained between about 100 and 700 p.s.i.g. pressure, preferably about 200 to 500 p.s.i.g. The hydrogen-rich gas supplied through line 14 is introduced at the rate of preferably about 3500 to 6000 cubic feet of hydrogen per barrel of shale oil feed to the hydrocracking unit 10. The catalyst in the hydrocracking unit 10 comprises about 90% of a silica-alumina cracking catalyst base containing about 13% alumina and about 10% molybdenum oxide. In the hydrocracking process hydrogen is consumed and it is therefore necessary to supply hydrogen to the process. Part of the hydrogen is recovered from the gaseous products of hydrocracking and the rest of the hydrogen is supplied from an external source. In the particular combination shown in Fig. 1 excess hydrogen from a hydroforming unit is supplied to the hydrocracking step. The hydrogen from any external source is supplied to the line 14 through line 15.

The hot hydrocracked vaporous products are withdrawn overhead from the hydrocracking unit 10 and passed through line 16 to a fractionating tower 18 for

separating the hydrocracked products into desired fractions. The gaseous fraction is taken overhead from the fractionating tower through line 22 and all or a portion of this gas is passed through line 24 and line 26 to an adsorption unit 28 for removing hydrocarbon gases and providing a hydrogen-rich gas. The tail gas in line 22 contains up to about 50%  $C_1$ - $C_3$  hydrocarbons with the rest being hydrogen. The amount of hydrogen in the tail gas depends upon the  $H_2$  dilution introduced with the recycle gas and upon the severity of operation. With a 5000 c.f.  $H_2$ /bbl. of shale oil recycle rate and cracking to about a 70% conversion, the tail gas contains about 55%  $H_2$ . The hydrogen-rich gas is withdrawn from the adsorption unit through line 32 and recycled to the line 14 for introduction into the hydrocracking unit. In some cases, especially when hydrocracking mildly, the gaseous products passing through line 24 may be directly recycled in whole or part to the hydrocracking unit 10 through line 34. The adsorption unit may utilize the fluid char adsorption process, an oil absorption process or low temperature fractionation or any other well known separation process. The adsorption process is conventional and no further detailed description is considered necessary. The main purpose of the adsorption unit is to concentrate hydrogen in the gas to be recycled.

Another portion of the gas from line 22 may be passed through line 36 and withdrawn from the system through line 38 and used as a source of hydrogen, as for example in the hydrogenation of residual fuels, catalytically cracked stocks, etc. Returning to the fractionating tower 18 any number of side streams may be withdrawn and in the drawing there are shown three withdrawal lines. A light fraction is withdrawn through top line 42 and consists primarily of  $C_4$  hydrocarbons with a little  $C_3$  and  $C_5$  hydrocarbon. The middle withdrawal line 44 comprises the  $C_5$  to 430° F. motor fuel fraction and this fraction is withdrawn as product through line 46. If desired, a portion or fraction of this motor fuel fraction may be recycled through line 48 to a hydroforming unit 50 to be described hereinafter.

The lower withdrawal line 52 contains hydrocarbons higher boiling than the motor fuel fraction and this fraction may be withdrawn from the system through line 54 or all or part of this fraction may be recycled through line 56 to the feed line 12 for recycle cracking in the hydrocracking unit 10. A bottoms fraction boiling above about 800 or 900° F. is withdrawn from the bottom of the tower 18 through line 58.

Turning now to the hydroforming unit 50, line 62 comprises a feed line for introducing a virgin naphtha boiling between about 200° and 430° F. preferably 225-380° F. The hydroforming unit 50 is maintained under a pressure of about 100-750 lbs. per square inch gauge, temperature of about 750-1050° F. and about 2,000 to 10,000 cubic feet of hydrogen recycle gas are used per barrel of oil. The hydrogen-rich gas is introduced into the hydroforming unit 50 through line 64. The hydroformed products in vapor form pass overhead from the hydroforming unit 50 through line 66 and are introduced into a second fractionating tower 68 for fractionating the hydroformed products into desired fractions. The separated gaseous fraction passes overhead through line 72. The tail gas in line 72 normally contains less than about 40%  $C_1$ - $C_3$  hydrocarbons with the rest being hydrogen. A portion of this gas is recycled to the hydroforming unit 50 through lines 74 and 64.

During the hydroforming reaction there is a net production of hydrogen and some of this excess hydrogen in the gaseous product withdrawn overhead from the tower 68 is passed through line 76 and line 78 for recycle to the hydrocracking unit 10 through lines 80 and 32. If it is desired to concentrate further the hydrogen in this gaseous stream the gas from line 78 may be passed through line 82 into the adsorption unit 28 and the more concentrated hydrogen-containing gas withdrawn through

line 32 for passage to the hydrocracking unit 10. The gaseous hydrocarbons removed from the hydrogen in the adsorption unit 28 are withdrawn overhead from the adsorption unit 28 through line 84. A portion of the gaseous stream from line 76 may be withdrawn from the system through line 86.

The hydroforming reaction in the hydroforming unit 50 can be carried out in the presence of any well known hydroforming catalyst such as alumina-molybdena, alumina-chromia, or alumina-platinum type catalysts. During the hydroforming reaction some carbon or coke may be deposited on the catalyst and in a fluid solids type process or in a moving bed process the partially spent or coked catalyst is withdrawn from the hydroforming unit 50 through line 38 and passed to a stripping zone 90 where the catalyst is treated with an inert gas such as recycle gas, flue gas or steam for removing volatilizable and/or entrained hydrocarbons. The stripped vapors may bypass the regenerator through line 91 and when steam stripping is used, stripped hydrocarbons may be separated from the condensate and recovered. If recycle gas is used for stripping it may be returned to the reactor 50. Tail gas from the hydrocracker 10 or desorbed gases leaving unit 28 through 84 may be used for stripping. The stripped catalyst is passed through a line 92 to a regenerator 94 into which air or other oxidizing gas is introduced through line 96. The combustion gases are passed overhead through line 98. The temperature during regeneration is between about 900° and 1200° F.

The hot regenerated catalyst is withdrawn from the regenerator through line 102 and passed to a stripping and pretreating zone 104 where the catalyst may be treated with a hydrogen-containing gas at a temperature between about 800 and 1000° F. to remove any retained combustion gases and also to reduce the valence of the molybdenum component on the catalyst. During regeneration the molybdenum oxide is believed to be oxidized to a different form which is not as active as the partially reduced molybdenum oxide and the treatment and stripping in treating zone 104 reduces the molybdenum compound to the active valence state. As the hydrogen-containing gas for treatment in the stripping or pretreating zone 104, a part of the overhead gases from the first fractionating tower 18 may be used. A part of the gas from line 36 may be passed through line 106 and used as the treating gas in zone 104. The hot regenerated catalyst is withdrawn from the stripping zone 104 and returned to the hydroforming unit 50 through line 108.

Returning to the second fractionating tower 68 there are shown three side stream withdrawal lines but any number of such streams may be withdrawn. The top withdrawal line 110 is used for withdrawing  $C_3$  and  $C_4$  hydrocarbons. The second withdrawal line 112 is used for withdrawing a  $C_5$ -430° F. motor fuel fraction. The bottom withdrawal line 114 may be used to withdraw a hydrocarbon fraction boiling above the gasoline or motor fuel boiling range and having an end boiling point below about 600° F. The motor fuel from hydrocracking line 46 and the motor fuel from hydroforming line 112 may be utilized separately, or they are blended to form a high octane gasoline of low sulfur content. Blending of the two gasolines gives a more balanced fuel containing both aromatics and olefins.

The bottoms from the fractionating tower 68 containing the higher boiling polymers boiling above 430° F. are withdrawn from the bottom of the tower 68 through line 116 and may be withdrawn from the system through line 118 but are preferably recycled to the feed line 12 for hydrocracking in the hydrocracking unit 10. The products from line 114 may be combined with this stream (line 116), if they are not used for special purposes, for example, as aromatic solvents.

The motor fuel produced by hydrocracking raw shale oil is more olefinic than that produced by hydroforming naphtha and to adjust the olefin-aromatic ratio of

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the motor fuel obtained by blending hydroformed product (line 112) and hydrocracked motor fuel (46), a portion of the hydrocracked motor fuel from line 44 may be recycled to hydroformer feed line 62 through line 48 as part of the feed to hydroformer reactor 50. This reduces the olefin content and increases the leaded motor octane number obtainable at a given Research Motor Octane Number. This is of advantage when the gasoline is used in engines having compression ratios of about 8 or higher.

During hydrocracking in the hydrocracking unit 10 coke or carbonaceous material is deposited on the catalyst and it is necessary to regenerate the catalyst. In a fluid solids system the catalyst is withdrawn from the hydrocracking unit, stripped with steam or other inert gas to remove volatile hydrocarbons and the stripped catalyst is then regenerated in a regeneration zone (not shown in the drawing but similar to vessel 94) by air or other oxygen-containing gas. The temperature during regeneration is between about 900° and 1200° F. Following regeneration the catalyst may be then pretreated with a hydrogen-containing gas similar to the treatment given to the hydroforming catalyst in zone 104 and the so-treated regenerated catalyst is then returned to the hydrocracking unit 10. In either case the pretreating step is optional and with some feedstocks may be omitted.

Referring now to Fig. 2 of the drawings, the reference character 130 designates a hydrocracking unit into which the raw shale oil is introduced through line 132. Hydrogen-rich gas is introduced into the hydrocracking unit 130 through line 134. Line 136 is used for introducing extraneous hydrogen to line 134 and hydrocracking unit 130. The catalyst in the hydrocracking unit is the same type of catalyst described in connection with the hydrocracking unit 10 in Fig. 1 and preferably comprises about 90% of a silica-alumina cracking catalyst base and 10% of molybdenum oxide.

In Fig. 2 the hydrocracking unit is used to modify the characteristics of the raw shale oil and to prepare a clean gas oil feedstock for the catalytic cracking unit 138. As above pointed out the raw shale oil contains nitrogen, sulfur and oxygen compounds which are deleterious to cracking catalysts. Further, if raw shale oil were used as a feed for catalytic cracking the gasoline produced would contain excessive amounts of sulfur and further treatment of the gasoline would be required to make an acceptable product.

The pressure in the hydrocracking unit 130 is maintained between about 100 and 700 p.s.i.g., the temperature is maintained between about 950 and 1100° F. and the amount of hydrogen used is about 2,000 to 10,000 cubic feet per barrel of shale oil fed to the hydrocracking unit 130. Feed rates are sufficiently high to maintain mild hydrocracking conditions and to maximize the yield of product boiling above 430° F.

The vaporous hydrocracked products are passed overhead through line 140 to a fractionating tower 142 for separating the cracked products into desired fractions. The gaseous fraction is taken overhead through line 144 and may be recycled in whole or in part through line 146 and line 148 to hydrogen inlet line 134 to the hydrocracking unit. In cases where there is no net production of hydrogen, the gaseous overhead stream is passed through line 150 to an adsorption unit 152 for removing hydrocarbons from the gaseous stream and to produce a hydrogen-rich stream which is withdrawn through line 154 and recycled through line 148 and line 134 to the hydrocracking unit 130. The separated hydrocarbon gases are removed from the adsorption unit through line 156. If desired, a portion of the gaseous stream passing through line 144 may be withdrawn from the system through line 158.

Returning now to the fractionating tower 142 the cracked products are fractionated and a lighter fraction comprising relatively light (C<sub>4</sub> and lower) hydrocarbons

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is withdrawn through top withdrawal line 160. A motor fuel fraction comprising a C<sub>5</sub>—430° F. motor fuel is withdrawn through the bottom withdrawal line 162. Bottoms from the fractionating tower 142 are withdrawn through line 164 and all or a part thereof passed through line 166 as feed to the catalytic cracking unit 138. This bottoms fraction has an initial boiling point of about 430° F. and a mid-boiling point of about 600–700° F. Another portion of the bottoms from line 164 may be recycled to the hydrocracking unit 130 through line 168. In some cases a portion of the shale oil feed from line 132 may be passed through line 170 to feed line 166 to the catalytic cracking unit 138.

The catalytic cracking unit 138 represents a conventional catalytic cracking unit utilizing silica-alumina catalyst which may be synthetically prepared or which may comprise acid treated bentonitic clays. The temperature during cracking is maintained between about 850° and 1000° F. The cracked products are taken overhead through line 172 and passed to a second fractionating tower 174 where the cracked products are separated into desired fractions. A gaseous fraction is taken overhead through line 176 and a C<sub>4</sub>—430° F. motor fuel fraction is withdrawn through top withdrawal line 178. A cycle oil fraction boiling above the motor fuel range is withdrawn through lower withdrawal line 180 and a portion of this stream may be withdrawn from the system through line 182. If desired, a portion of this cycle oil from line 180 may be recycled through line 184 to feed line 132 for recycling to the hydrocracking unit 130. This results in an overall smaller production of coke. The bottoms fraction from tower 174 is withdrawn through line 186 and all or a portion of this bottoms fraction can be removed from the system through line 188. If desired, a portion of the bottoms fraction from line 186 may be recycled through line 190 to the catalytic cracking unit 138 and/or another portion of the bottoms fraction passed through line 192 is preferably recycled to line 132 as feed to the hydrocracking unit 130 to reduce coke formation.

The motor fuel from catalytic cracking (line 178) and the motor fuel from hydrocracking (line 162) may be separately utilized, but preferably the two motor fuels are blended to form a high octane number gasoline of low sulfur content. When the hydrocracking unit is operated at conditions of mild severity blending balances the octane number of the two products.

Shale oil (designated NTU shale oil) produced from Colorado shale in a gas combustion pilot plant retort of the Bureau of Mines has the following physical properties:

|                              |      |
|------------------------------|------|
| Gravity, ° API, 60° F. ----- | 19.0 |
| Pour, ° F. -----             | 75.0 |
| Vis. SUS, 130° F. -----      | 153  |
| Vis. SUS, 210° F. -----      | 51   |

The analysis of the shale oil was as follows:

|                                 |      |
|---------------------------------|------|
| Total sulfur, wt. percent ----- | 0.74 |
| Nitrogen, wt. percent -----     | 2.06 |

The shale oil also contained tar acids and tar bases. The following is the ASTM distillation:

|                         |          |
|-------------------------|----------|
| I.B.P. -----            | ° F. 390 |
| 5 volume percent -----  | 486      |
| 50 volume percent ----- | 686      |

Shale oil of the above characteristics was hydrocracked in a fixed bed operation at a temperature of about 1050° F. and a pressure of 500 p. s. i. g. in the presence of 5000 standard cubic feet of hydrogen per barrel of shale oil. The fixed bed comprised 750 ccs. of catalyst in pill form comprising 3/16 inch x 3/16 inch cylinders. The feed rate of oil was 0.6 volume of liquid oil per volume of catalyst per hour and the crack-

ing cycle was carried out for a period of 2 hours. The results of this cracking test are as follows:

| Conversion                        | 78 Wt. percent                    | Feed, percent |
|-----------------------------------|-----------------------------------|---------------|
| Yields:                           |                                   |               |
| C <sub>5</sub> —430° F.           | 35.4                              | 42.9          |
| C <sub>4</sub> 's                 | 7.5                               |               |
| 430—464° F.                       |                                   | 3.4           |
| Dry gas                           |                                   | 27.3          |
| Carbon                            |                                   | 4.3           |
| 464+° F.                          |                                   | 22.1          |
| C <sub>5</sub> —430° F. Gasoline: |                                   |               |
| Research Octane No.               | 89.5                              |               |
| Aromatics                         | 40.4 Vol. percent.                |               |
| Olefins                           | 25.2 Vol. percent.                |               |
| % Sulfur, by weight               | 0.16                              |               |
| Hydrogen consumption              | 730 cubic feet per barrel of oil. |               |

Thus the shale oil was cracked to C<sub>5</sub>+ gasoline with a 45.5 weight percent selectivity and to C<sub>4</sub>+ gasoline with a 55.1 weight percent selectivity. The selectivity to carbon was 5.4%. The gasoline produced had a 42.4° F. aniline point and a 50.3° API gravity.

The following comparison with other processes is given to show the improved results obtained with the present invention. From these data it will be apparent that the process of the present invention produces higher yields of gasoline of high octane number and low sulfur with the production of less coke and less consumption of hydrogen.

| Process                         | Feed                   | Conversion, Wt. Percent |         | H <sub>2</sub> Consumed, s.c.f./b. | Yields, Wt. Percent       |        | Percent S in Gasoline |
|---------------------------------|------------------------|-------------------------|---------|------------------------------------|---------------------------|--------|-----------------------|
|                                 |                        | 430° F.                 | 400° F. |                                    | C <sub>4</sub> + Gasoline | Carbon |                       |
| Hydrocracking of this invention | Raw shale oil          | 74                      |         | 730                                | 143                       | 4      | 0.16                  |
|                                 | Raw shale oil          | 60                      |         |                                    |                           | 14     |                       |
| Catalytic Cracking              | Raw shale oil          |                         | 50      |                                    | 221                       | 23     | 0.48                  |
|                                 | Hydrogenated shale oil | 60                      |         | 600                                |                           | 13     |                       |
|                                 |                        |                         |         | 900                                |                           | 7      |                       |
| Recycle Coking                  | Raw shale oil          |                         | 39      |                                    | 220                       | 14     | 0.68                  |

<sup>1</sup> Research O.N.=89.5.

<sup>2</sup> Research O.N.=90.

<sup>3</sup> Research O.N.=65.

One example for carrying out a process according to Fig. 1 is as follows:

#### Hydroformer—

Catalyst: 90Al<sub>2</sub>O<sub>3</sub>—10MoO<sub>3</sub>

Feed: 20,000 bbls./day of a 225°—430° F. naphtha

Recycle: 89 million cu. ft./day of recycle gas containing 67% H<sub>2</sub>

Product:

16,000 bbls./day of C<sub>4</sub>—430° F. gasoline (98 Res. O.N.)

28 million cu. ft./day of tail gas (67% H<sub>2</sub>)

300 bbls./day of 430° F.+ polymer

Operating pressure: 200 p.s.i.g.

#### Hydrocracking unit—

Catalyst: 78SiO<sub>2</sub>—12Al<sub>2</sub>O<sub>3</sub>—10MoO<sub>3</sub>

Feed: 10,000 bbls./day of 686° F. midboiling point shale oil

Recycle: 83.5 million cu. ft./day of gas containing about 60% H<sub>2</sub>

Product: 4290 bbls. of C<sub>4</sub>—430° F. gasoline (90 Res. O.N. clear)

H<sub>2</sub> consumption: 7.3 million cu. ft./day

Operating pressure: 500 p.s.i.g.

#### Fluid char adsorption unit—

Operating conditions: 500 p.s.i.g.; 150° F. adsorption temp.; 0.3 lb. of char per cu. ft. of tail gas; 550° F. desorption temp.

Product: Enriched gas having an H<sub>2</sub> content of about 78 mol percent

In the operation of the process, the 300 bbls. of 430° F.+ polymer is cycled through line 116 to the hydrocrack-

ing unit 10 for further processing. Some of the tail gas from the hydroformer 50 which contains about 67% hydrogen is blended with some of the tail gas from the hydrocracker 10 containing about 51% hydrogen. This mixed stream is fed to the char adsorber 28 to produce gas containing about 78% H<sub>2</sub>. This stream from adsorber 28 is mixed in line 34 or in the hydrocracking unit 10 with additional hydrocracker tail gas containing 5% H<sub>2</sub> to give the 83.5 million cu. ft. of hydrocracker recycle gas containing 50 million cu. ft. of H<sub>2</sub>. This recycle gas is fed through line 14 with the shale oil into the hydrocracker 10. Part of the hydrocracker tail gas is fed via lines 36 and 106 to the stripping and/or pretreating section (104 and others not shown) of the various units.

The hydroforming reaction can be carried out under pressures between about 100 and 700 p.s.i.g., at a temperature between about 750° and 1050° F. and in the presence of about 2,000 to 10,000 cubic feet of hydrogen-rich recycle gas per barrel of feed. The hydrocracking reaction can be carried out at a pressure between about 100 and 700 p.s.i.g. at a temperature of about 950° and 1100° F. and in the presence preferably of about 3,500 to 10,000 cubic feet of hydrogen rich recycle gas per barrel of feed. The adsorption process using activated carbon or an alkali or alkaline earth metal aluminum silicate molecular sieve type adsorbent may be carried out at a pressure between 100 and 500 p.s.i.g. or greater, an adsorption temperature at the feed plate between about 100° and 200° F. and utilizing between about 0.15 and 1.0 lbs. of adsorbent per cubic foot of tail gas.

Varying the severity of operation of the hydrocracking and hydroforming units changes the hydrogen content of the tail gases from these units. In general, the less severe operations result in more hydrogen in the tail gases.

The shale oil feed contains nitrogen compounds and some of these nitrogen compounds or decomposition products thereof are carried over with the distillate fractions. The nitrogen compounds may be removed from the distillates by solvent extraction or other extraction processes to recover valuable chemicals. For example, amines of various types are present and these can be recovered by extraction with dilute acids or by suitable solvents or solid adsorbents.

What is claimed is:

1. A process for converting shale oil containing sulfur and nitrogen compounds as impurities to motor fuel of high octane number in the region of 90 with low carbon production which comprises contacting shale oil with a single solid catalyst consisting of silica-alumina cracking catalyst containing about 8–16% by weight of the total catalyst of molybdenum oxide at a temperature between about 950° F. and 1100° F., under a pressure between about 100 and 700 p.s.i.g. and in the presence of a hydrogen rich gas in an amount between about 2000 and 10,000 cubic feet per barrel of shale oil.

2. A process according to claim 1 wherein the amount of molybdenum oxide is 10% by weight.

3. A process according to claim 2 wherein the temperature is about 1050° F., the pressure is about 500

p.s.i.g., and the amount of hydrogen rich gas is about 5000 cubic feet per barrel of shale oil.

4. A process according to claim 1 wherein the silica-alumina cracking catalyst contains about 78% of silica and 12% of alumina and the high octane motor fuel contains low sulfur and easily removable compounds.

5. A process according to claim 1 wherein the products from the conversion step are fractionated into a motor fuel fraction and a gas and hydrogen is consumed during the conversion step, said gas is treated to produce a hydrogen-rich gas, said hydrogen-rich gas is recycled to said conversion step and hydrogen-rich gas is supplied from an extraneous source.

6. A process for hydrocracking raw shale oil to produce motor fuel which comprises feeding a raw shale oil to a hydrocracking reactor for contact with a single solid catalyst consisting of a silica-alumina cracking catalyst containing about 10% by weight of molybdenum oxide, said reactor being maintained at a temperature between about 950° and 1100° F., and at a pressure between about 100 and 700 p.s.i.g., introducing hydrogen into said reactor at a rate between about 2000 and 10,000 cubic feet per barrel of shale oil and consuming hydrogen during the hydrocracking step, recovering motor fuel from the hydrocracked products, simultaneously subjecting naphtha to a catalytic hydroforming operation under conditions to have a net production of hydrogen, utilizing some of the hydrogen from the hydroforming operation to supply hydrogen for the hydrocracking step, and recovering reformed naphtha from the hydroformed products.

7. A process according to claim 6 wherein the hydrocracked products are separated into a liquid fraction and a gaseous fraction, the gaseous fraction is treated to increase the hydrogen content thereof and the so-treated hydrogen-rich gaseous fraction is recycled to said hydrocracking reactor.

8. A process for converting raw shale oil to motor fuel of high octane number and with low production of coke, which comprises feeding such raw shale oil to a hydrocracking reactor containing a silica-alumina cracking

catalyst modified by the addition of about 10% of molybdenum oxide, under superatmospheric pressure between about 100 and 700 p.s.i.g., at a cracking temperature between about 950° F. and 1100° F. and in the presence of at least 2000 cubic feet of hydrogen per barrel of shale oil, removing hydrocracked products from said reactor, separating gas from a motor fuel fraction having a high octane number and a fraction higher boiling than the motor fuel fraction, passing said higher boiling fraction to a catalytic cracking unit, recovering an additional amount of motor fuel and a gas oil cycle fraction from the catalytically cracked products and recycling at least part of said gas oil cycle fraction to said hydrocracking reactor.

9. A process according to claim 6 wherein the hydrocracked motor fuel and reformed naphtha are blended to form a high octane gasoline.

10. A process according to claim 6 wherein the hydrocracked motor fuel is olefinic and is at least in part passed to said hydroforming step to reduce the olefin content and to increase the octane number of the motor fuel.

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