

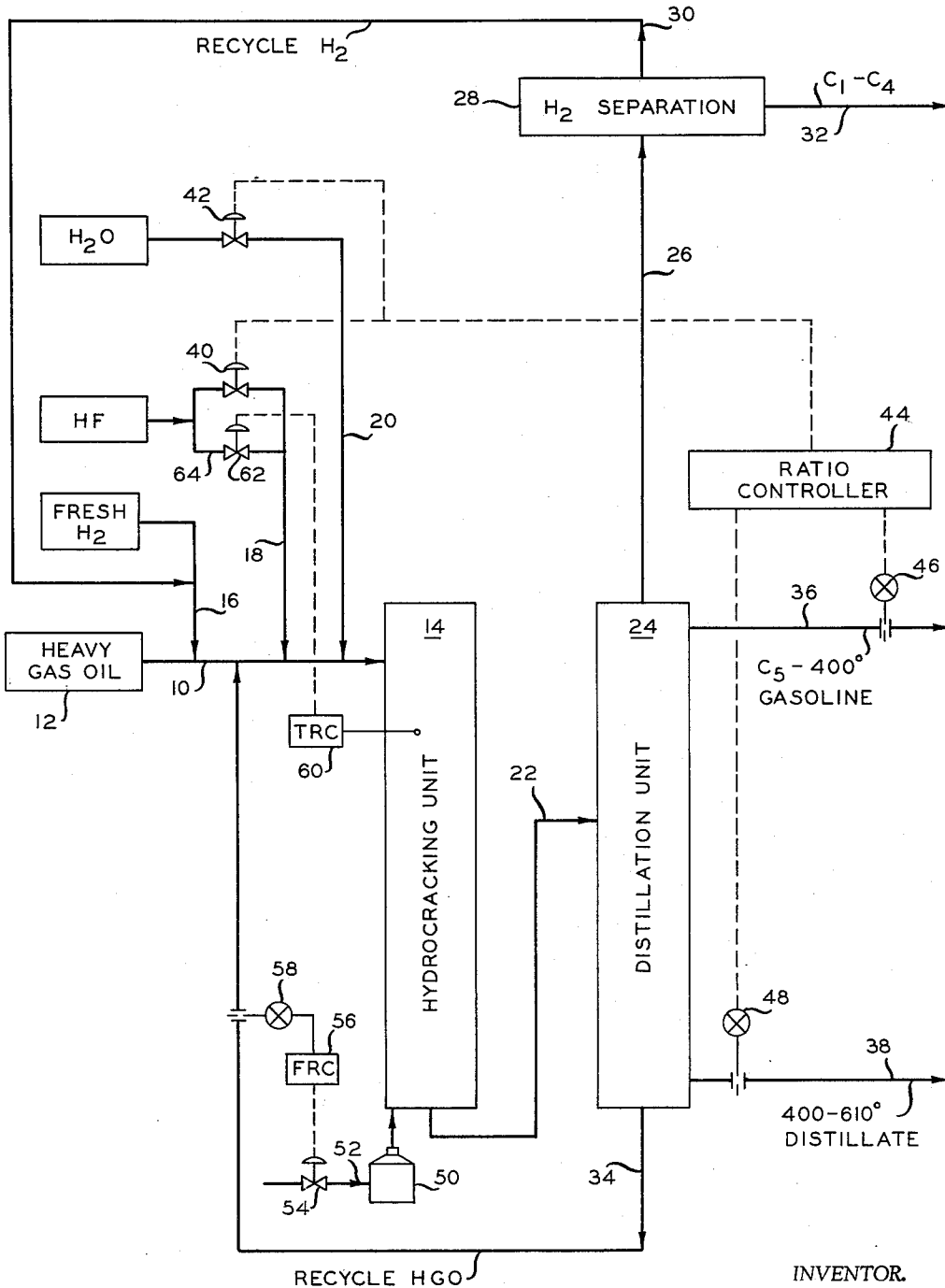
June 14, 1966

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3,256,176

HYDROCRACKING HEAVY HYDROCARBONS TO GASOLINE AND DISTILLATE

Filed Oct. 21, 1964



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3,256,176

## HYDROCRACKING HEAVY HYDROCARBONS TO GASOLINE AND DISTILLATE

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 Filed Oct. 21, 1964, Ser. No. 407,612  
 18 Claims. (Cl. 208—89)

This application is a continuation-in-part of application S.N. 243,231, filed December 10, 1962, now abandoned.

This invention relates to a process and apparatus for hydrocracking a heavy hydrocarbon feed stock, such as a gas oil, to gasoline and distillate in varying proportions.

Hydrocracking of high molecular weight petroleum stocks has a number of advantages over simple catalytic cracking of the same stocks: (1) it permits operation at considerably lower temperatures—e.g., 550–700° F. instead of 800–1100° F.; (2) it minimizes coke formation, thus permitting very long on-stream periods or even continuous operation—which results in considerably higher productivity from a given cracking unit; and (3) it minimizes light gas formation, which means that the light gas separation facilities can be considerably smaller and that excess C<sub>3</sub> and C<sub>4</sub> hydrocarbons are not produced to compete with the large amounts of those hydrocarbons available from natural gasoline. However, hydrocracking, as it has been practiced in the past, is not a completely flexible process responsive to the varying demands for the various liquid products. In an integrated refining operation charging crude oil or crude oil and natural gasoline, it is advantageous to have flexibility in the distillate-to-gasoline production ratio because of seasonal demand and sales limitations. Gasoline is produced from both natural gasoline and crude oil, and sales are limited by both seasonal demand and volatility requirements. In a company with large light hydrocarbon reserves, it is very frequently necessary to minimize gasoline production and maximize distillate production in response to these limitations to prevent backing natural gasoline out of the finished gasoline and to achieve a distillate-to-gasoline ratio more nearly in line with the industry average.

Accordingly, it is an object of the invention to provide a process and apparatus for hydrocracking a heavy hydrocarbon feed stock to gasoline and distillate in varying ratios to suit demands for these products. Another object is to provide flexibility in the hydrocracking of a gas oil which permits varying the ratio of gasoline to distillate to meet seasonal and industry demands. Other objects of the invention will become apparent to one skilled in the art upon consideration of the accompanying disclosure.

The invention comprises varying the distillate-to-gasoline ratio in the product from hydrocracking a heavy hydrocarbon feed stock containing not more than about 15 p.p.m. of nitrogen, such as a virgin or cracked heavy gas oil, by injecting a halogen-containing material, with or without steam, into the feed to the hydrocracking unit.

I have discovered a way to increase the flexibility of the hydrocracking process such that the distillate-to-gasoline ratio is cracking a heavy gas oil of low nitrogen content can be varied over the range of essentially all gasoline to about 80 to 90 percent distillate—thus overcoming the major objection to conventional hydrocracking. I propose to do this by selective hydrocracking with a catalyst consisting of a hydrocracking component on a support whose acidity can be varied by injection of a

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halogen-containing material (preferably fluorine-containing) into the feed, with or without steam addition. Injection of steam reduces the cracking activity of the catalyst and results in a higher distillate-to-gasoline ratio in the product. Injection of the halogen-containing material increases the cracking activity of the catalyst and results in a lower distillate-to-gasoline ratio in the product.

The process of my invention is carried out continuously in well-known types of equipment, within the following ranges of operating conditions:

	Broad	Preferred
Temperature, ° F.-----	500-850	550-700
Pressure, p.s.i.g.-----	500-5000	1,000-3,000
H <sub>2</sub> /gas oil, mol ratio-----	1/1 to 25/1	10/1 to 18/1
H <sub>2</sub> , s.c.f./bbl-----	500-10,000	4,500-7,500
Gas oil, LHSV-----	0.1-10.0	0.5-3.0

Catalysts for my process can be chosen from the Group VIA oxides and sulfides and from the Group VIII metals, oxides, and sulfides and are supported on materials whose acidity can be varied by treatment with either steam or a halogen-containing material, such as alumina or the so-called "activated clays" of commerce. My invention is based on the fact that alumina-halogen (e.g., alumina-fluorine) is a very strong acid with high hydrocracking activity. Admission of steam to a catalyst utilizing an alumina-halogen base during use of that catalyst at elevated temperatures results in thermal hydrolysis of a portion of the alumina with the halogen to form an inactive aluminum trihalogen (e.g., aluminum fluoride). Thus the acidity is varied during my process by varying the amount of active alumina-halogen present at a given time or by substantially completely eliminating the contribution of the halogen.

The Group VIA metals include chromium, molybdenum, tungsten, and uranium. These metals are utilized in the form of their oxides and/or sulfides. The Group VIII metals include iron, nickel, cobalt, ruthenium, rhodium, palladium, osmium, iridium, and platinum. These metals are used in metallic form and/or in the form of their oxides and sulfides. Cobalt, nickel and platinum are preferred metals in the group. The hydrocracking catalyst concentration on the carrier is usually in the range of about 0.5 to 1.0 or up to 15 weight percent of the carrier or support.

The required support in the process must contain porous active alumina. Active alumina, alone, or in admixture with silica, is suitable. The alumina may be synthetic or prepared in conventional manner from bauxite. Synthetic silica-alumina composites, containing a substantial amount of alumina, such as at least 10 percent, function well in the required catalyst. Another support consists of activated clays commercially available as supports for cracking catalysts. These consist of porous aluminum silicates of varying proportions of alumina and silica.

The halogen-supplying agent may be selected from the group consisting of organo-halogen compounds that decompose under reaction conditions to provide F or Cl (e.g., methyl fluoride, ethyl chloride, the butyl fluorides, etc.), and inorganic halogen-containing compounds that either decompose under reaction conditions to provide F or Cl or are capable of reacting with the catalyst base to incorporate F or Cl therein (e.g., F<sub>2</sub>, Cl<sub>2</sub>, HF, HCl, ammonium fluoride or chloride, interhalogens of F and Cl such as chlorine monofluoride, etc.).

A more complete understanding of the invention may

be had by reference to the accompanying schematic flow diagram illustrating one arrangement of apparatus and flow for effecting the process of the invention.

Referring to the drawing, a heavy gas oil or other heavy hydrocarbon feed stock of not more than 15 p.p.m. of nitrogen is passed thru line 10 from supply source 12 into hydrocracking unit 14 in admixture with hydrogen from line 16. Halogen, as such, or in the form of a halogen supplying agent, is introduced thru line 18 to feed line 10 as required and steam is injected into line 10 thru line 20 as required and hereinafter described.

The feed in admixture with hydrogen is hydrocracked in unit 14 to produce gasoline and distillate. Hydrocracking unit 14 may comprise conventional hydrocracking equipment utilizing either a fluidized catalyst bed, a fixed bed, or a gravitating bed of particulate catalyst. The hydrocracked effluent from unit 14 is passed via line 22 to distillation unit 24 for separation into the desired fractions. A light fraction containing  $C_1-C_4$  and hydrogen is passed thru line 26 to a hydrogen separation column 28 to recover hydrogen which is passed thru line 30 as recycle to line 16. The  $C_1-C_4$  fraction is recovered thru line 32 and passed to other refinery operations conventional in the art. Unconverted heavy gas-oil is recovered and passed thru line 34 as recycle to feed line 10.  $C_5-400^\circ$  F. gasoline is recovered as product thru line 36 and distillate boiling in the range of  $400^\circ$  to  $610^\circ$  F. is recovered thru line 38.

Motor valves 40 and 42 in lines 18 and 20, respectively, control the injection of halogen-supplying agent and water into the hydrocracking unit. A ratio controller 44 receives signals from flow transmitters 46 and 48 in lines 36 and 38, respectively, and puts out a signal, depending upon the set point of the controller, to valves 40 and 42 which maintains the desired ratio of gasoline to distillate by controlling the hydrocracking activity of the catalyst in unit 14. Valves 40 and 42 are split range valves, one valve being held open over a certain range of instrument air pressure and the other being held open over another range of instrument air pressure. To illustrate, valve 40 may be made to open in the range of 3 to 9 pounds instrument air pressure, closing at 9 pounds. Valve 42 is then designed to be closed in the range of 3-9 pounds and open at 9 pounds with increasing flow up to 15 pounds. As the ratio of gasoline to distillate falls below the set ratio, the signal from ratio controller increases the flow thru valve 40 to increase the activity of the catalyst in the manner described hereinbefore. When the ratio of gasoline to distillate is higher than the set ratio, the signal from ratio controller 44 cuts back on the injection of halogen by pinching down on valve 40 to decrease the activity of the catalyst and produce more distillate and less gasoline. When necessary to further decrease the activity of the catalyst, the signal from ratio controller 44 exceeds 9 pounds and valve 42 is opened part way to admit steam to unit 14 and reduce the activity of the catalyst therein. It is usually desirable to inject at least about 0.1 weight percent of halogen based upon the weight of the feed under the conditions in unit 14 in order to maintain some hydrocracking activity as well as to compensate for the natural aging of the catalyst base. This may be accomplished thru a small by-pass line around valve 40 or by utilizing a flow control valve which is cracked to pass the required amount of halogen even when in its lowest setting. This is also accomplished by means of bypass line 64 and valve 62 which can be cracked enough at all times to admit a minimum of halogen to line 10.

Although hydrocracking is exothermic, some heat must be supplied to unit 14 to maintain the desired operating temperature. This is accomplished by a furnace or burner 50 to which fuel gas is fed thru line 52 containing motor valve 54. Flow-recorder-controller 56 is actuated by flow transmitter 58 in recycle line 34 and actuates motor valve 54 to increase the fuel supply when the flow

of recycle gas oil is high and decrease the flow of fuel and the heating in unit 14 when recycle is low. The flow of recycled distillate is an indication of the amount of hydrocracking in unit 14, the flow rate being high at low hydrocracking and low at high hydrocracking rates.

Temperature-recorder-controller 60 senses the temperature in unit 14 and actuates motor valve 62 in a by-pass line 64 around valve 40 in line 18. When the temperature in the hydrocracking unit tends to rise above a selected maximum temperature such as  $700^\circ$  F., instrument 60 opens valve 62. The conversion level decreases as the catalyst in reactor 14 ages and becomes less active over a longer period of time. This results in higher flow rate of recycled unconverted oil in line 34 with FRC 46 increasing heat input by opening valve 54 in fuel line 52 in response to the flow transmitter 58. As the temperature sensed by instrument 60 reaches a selected maximum, such as  $700^\circ$  F. for example, this instrument further opens valve 62 so as to increase the flow rate of HF (or other halogen) into the feed line 10 to increase the activity of the catalyst in reactor 14. This results in a decrease in the flow rate in line 34 and cutting back in the flow rate of fuel in line 52. This assumes that valve 62 is cracked at all times to allow a selected minimum flow of HF into the feed in line 10, such as 0.1 weight percent of the feed.

The following examples are presented to illustrate the invention and are not to be construed as unnecessarily limiting the invention.

#### Example I

A hydrotreated heavy cycle oil containing 13 p.p.m. of nitrogen and boiling above  $610^\circ$  F. is charged to the hydrocracking unit of my process at a liquid hourly space velocity of 0.5, a pressure of 2000 p.s.i.g., with 7500 cubic feet of combined recycle and fresh hydrogen per barrel of combined recycle and fresh feed, and with a 1.3 percent nickel on activated clay catalyst. The temperature controller is set to give a total conversion of 25 weight percent of the feed and the ratio controller is set to give a distillate-to-gasoline ratio of 4. The temperature lines out at  $582^\circ$  F., a very small amount of HF and some steam are injected as demanded by the ratio controller, and the gasoline and distillate yields line out at 4.7 and 18.9 weight percent of the feed, respectively. In response to an increased demand for gasoline relative to distillate, the ratio controller is set to give a distillate-to-gasoline ratio of 0.7 at the same total conversion. The injection of HF is increased, that of water is decreased, the temperature lines out at  $574^\circ$  F., and the gasoline and distillate yields line out at 14.2 and 9.9 weight percent of the feed, respectively.

#### Example II

In response to an increased demand for distillate at about the same gasoline demand, with the same charge stock and operating given in Example I, the flow-rate-controller is set to give a total conversion of 50 weight percent of the feed, and the ratio-controller is set to give a distillate-to-gasoline ratio of 3. Over-all injection of HF decreases, steam is injected to decrease gasoline production, the temperature lines out at  $629^\circ$  F., and the gasoline and distillate yields line out at 12.1 and 36.3 weight percent of the feed, respectively. In response to a large increase in gasoline demand, with a continued relatively high demand for distillate, the ratio-controller is set to give a distillate-to-gasoline ratio of 0.7 at the same total conversion. Steam injection stops completely, HF injection increases, the temperature lines out at  $638^\circ$  F., and the gasoline and distillate yields line out at 27.1 and 19.0 weight percent of the feed, respectively.

In both these examples, a widely varying total conversion levels, the distillate-to-gasoline ratio is changed by a factor of about 500 percent by controlled injection of a halogen-containing material or steam.

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## Example III

At Sweeny, Texas heavy cycle oil containing 490 p.p.m. of nitrogen was hydrotreated in two passes under the conditions set forth below.

	First Pass	Second Pass
Pressure, p.s.i.g.	1,000	1,000
Temperature, ° F.	750	750
LHSV	1.0	0.5
H <sub>2</sub> /bbl. feed, S. ft. <sup>3</sup>	5,000	5,000
Catalyst	Ni-Mo-Al <sub>2</sub> O <sub>3</sub>	Ni-Mo-Al <sub>2</sub> O <sub>3</sub>

The heavy oil effluent from the first pass had a nitrogen concentration of 63 p.p.m. and this was further reduced to 13 p.p.m. in the second pass. It is to be understood that the nitrogen is in the form of unknown compounds in the feed.

## Example IV

The hydrotreated oil from the second pass of Example III, containing 13 p.p.m. of nitrogen was hydrocracked over a catalyst consisting essentially of 1.3 weight percent nickel on Filtrol 62 (commercial aluminum silicate) treated with 10 percent HF. The pressure was 2000 p.s.i.g., the space velocity 0.5 LHSV, and the H<sub>2</sub> feed was 6000-8000 S. ft.<sup>3</sup> per barrel of oil feed. Data obtained from the run are presented below.

Hours on Stream	0-12	13-25	26-38	38-51	52-57½	60-66	67-72
Temperature, ° F.	575	600	650	700	700	700	650
Yields, Wt. Percent Feed:							
Gas	1.1	1.2	3.3	9.7	7.5	9.7	3.7
C <sub>5</sub> -400° F.	10.3	14.3	35.6	69.7	68.7	82.0	39.2
400-500° F.	4.5	5.6	10.6	8.0	9.9	4.4	10.7
500-610° F.	9.8	9.3	8.6	3.9	4.2		7.1
610° F. +	74.3	69.6	41.9	8.7	9.7	3.9	39.2
Coke							
Conversion, Wt. Percent of 610° F. + in Feed	25.7	30.4	58.1	91.3	90.3	~100	60.8
API of Total Product	37.6	39.3	46.6	60.1	58.9	65.6	47.8

These data demonstrate that a temperature of 650° F. is necessary for practical conversion. Note that conversion and API of product were essentially the same at 650° F. after operation for 38 hours and 72 hours. Also, there was no deactivation of the catalyst at 700° F. for 28-30 hours of operation.

Another run with the same feed as used in Example IV was made under similar conditions but using a feed rate of 1.8 LHSV. A temperature of 700° F. was required to effect a conversion of 63 percent during the initial part of the run. After 190 hours on stream the temperature required to obtain 63 percent conversion of the heavy oil was 720° F.

The heavy cycle oil treated in Examples I and II was taken from the effluent of the second pass of Example III.

Since raw heavy oils such as gas oils and cycle oils frequently have substantial nitrogen content as high as 400 to more than 5000 p.p.m., it is considered that a hydrotreated heavy oil containing not more than about 15 p.p.m. of nitrogen is substantially nitrogen free for the purposes of the claimed process. Evidence supporting this fact is found in the data in Example IV, demonstrating the lack of any material deactivation of the catalyst in the hydrocracking operation when the nitrogen content of the feed is about 13 p.p.m.

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

I claim:

1. A process for hydrocracking a high molecular weight petroleum feed stock containing a minor concentration but not more than 15 p.p.m. of nitrogen to produce distillate and gasoline which comprises the steps of:

(a) contacting said stock, containing said minor con-

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centration of nitrogen, in a reactor in admixture with hydrogen with a hydrocracking catalyst on a porous support selected from the group consisting of alumina, silica-alumina, and aluminum silicate containing 0.1 to 15 weight percent halogen under hydrocracking conditions;

(b) feeding steam to said reactor in an amount in the range 0 to 3 weight percent of the petroleum feed;

(c) feeding a halogen supplying agent to said reactor in an amount in the range of 0.1 to 3 weight percent of said feed;

(d) maintaining hydrocracking conditions in said reactor to effect from 15 to 80 percent conversion of said feed, the production of gasoline in C<sub>5</sub> to 400° F. boiling range being higher at higher conversions and the production of distillate being higher at lower conversions in said range;

(e) during one period, controlling the proportions of produced gasoline and distillate by increasing the halogen addition rate and decreasing the steam addition rate within said ranges to increase gasoline production; and

(f) during another period increasing the steam addition rate and decreasing the halogen addition rate within said ranges to increase distillate production.

2. The process of claim 1 wherein said halogen supplying agent is HF.

3. The process of claim 1 wherein said catalyst consists essentially of at least one member of the group consisting of metals, oxides, and sulfides of Group VIA and Group VIII.

4. The process of claim 1 wherein said catalyst consists essentially of Ni deposited on an activated clay and said halogen supplying agent is HF.

5. The process of claim 1 wherein said catalyst consists essentially of platinum on active alumina and said halogen supplying agent is HF.

6. The process of claim 1 wherein the effluent from the reactor is fractionated to recover separate streams of C<sub>4</sub>'s and lighter, C<sub>5</sub>-400° F. gasoline, distillate, and heavier hydrocarbons; said heavier hydrocarbon stream is recycled to said reactor; and the temperature in said reactor is increased when the flow rate of recycled heavier hydrocarbons reaches a selected maximum and is decreased when said flow rate reaches a selected minimum.

7. The process of claim 6 wherein the temperature in said reactor is sensed and halogen flow is increased when said temperature reaches a selected maximum so as to effect a decrease in operating temperature for a given level of conversion.

8. A process for producing gasoline and distillate from a high molecular weight petroleum stock containing nitrogen substantially in excess of 15 p.p.m. which comprises the steps of:

(a) hydrotreating said stock so as to reduce the nitrogen content to a small amount but not more than 15 p.p.m.;

(b) hydrocracking the hydrotreated stock of step (a), containing said small amount of nitrogen, in admixture with hydrogen and in contact with a hydrocracking catalyst consisting essentially of a member selected from the group consisting of the oxides and

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sulfides of Group VIA, the metals, oxides, and sulfides of Group VIII, and mixtures thereof deposited on a porous support selected from the group consisting of alumina, silica-alumina, and aluminum silicate containing 0.1 to 15 weight percent halogen under hydrocracking conditions;

- (c) feeding steam to said reactor in an amount in the range 0 to 3 weight percent of the petroleum feed;
- (d) feeding a halogen supplying agent to said reactor in an amount in the range of 0.1 to 3 weight percent of said feed;
- (e) maintaining hydrocracking conditions in said reactor to effect from 15 to 80 percent conversion of said feed, the production of gasoline in C<sub>5</sub> to 400° F. boiling range being higher at higher conversions and the production of distillate being higher at lower conversions in said range;
- (f) during one period, controlling the proportions of gasoline and distillate by increasing the halogen addition rate and decreasing the steam addition rate within said ranges to increase gasoline production; and
- (g) during another period, increasing the steam addition rate and decreasing the halogen addition rate within said ranges to increase distillate production.

9. The process of claim 8 wherein said catalyst consists essentially of Ni deposited on an activated clay and said halogen supplying agent is HF.

10. The process of claim 8 wherein said catalyst consists essentially of platinum on active alumina and said halogen supplying agent is HF.

11. A process for hydrocracking a high molecular weight nitrogen-containing petroleum feed stock containing not more than 15 p.p.m. of nitrogen to produce distillate and gasoline which comprises the steps of:

- (a) contacting said nitrogen-containing stock in a reactor in admixture with hydrogen with a hydrocracking catalyst on a porous support selected from the group consisting of alumina, silica-alumina, and aluminum silicate containing 0.1 to 15 weight percent halogen under hydrocracking conditions;
- (b) feeding steam to said reactor in an amount in the range 0 to 3 weight percent of the petroleum feed;
- (c) feeding a halogen supplying agent to said reactor in an amount in the range of 0.1 to 3 weight percent of said feed;
- (d) maintaining hydrocracking conditions in said reactor to effect from 15 to 80 percent conversion of said feed, the production of gasoline in C<sub>5</sub> to 400° F. boiling range being higher at higher conversions and the production of distillate being higher at lower conversions in said range;
- (e) fractionating the hydrocracked effluent to recover separate streams of hydrogen, C<sub>1</sub> to C<sub>4</sub> hydrocarbons, C<sub>5</sub>-400° F. gasoline, 400-610° F. distillate, and unconverted feed stock;
- (f) sensing the ratio of gasoline to distillate in the separate streams of (e); and
- (g) controlling the ratio of gasoline to distillate by increasing the rate of halogen addition and decreasing the rate of steam addition in response to the

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sensed ratio of step (f) to increase said ratio during one period and by decreasing the rate of halogen addition and increasing the rate of steam addition in response to said sensed ratio to decrease said ratio.

12. The process of claim 11 including the steps of:
- (h) sensing the temperature of the hydrocracking of step (d); and
- (i) separately controlling halogen addition to maintain a selected conversion level in the range of 15 to 80 percent of the feed.
13. The process of claim 12 including the steps of:
- (j) recycling the stream of unconverted feed stock of step (e) to said reactor;
- (k) sensing the flow rate of the stream of step (j); and
- (l) regulating the heat input to said reactor in response to the sensed flow rate of step (k), increasing the heat input as said flow rate increases and decreasing the heat input as said flow rate decreases from a selected level.

14. Apparatus comprising in combination a hydrocracking reactor having a hydrocarbon feed line, halogen feed line, a steam feed line, a hydrogen feed line, an effluent line, and burner heating means for heating said reactor; a distillation unit connected with said effluent line having a gasoline product line, a distillate product line, a recycle line for unreacted heavy hydrocarbons connected with said reactor, and a line for light ends removal; a pair of split range motor valves, one in said steam feed line and one in said halogen feed line; flow transmitters on each said gasoline and distillate lines; and a ratio controller sensitive to the flow transmitters on said gasoline and distillate product lines and in actuating control of said split range motor valves.

15. The apparatus of claim 14 including a fuel line leading to said burner having a motor valve therein; a flow transmitter on said recycle line; a flow controller sensitive to said transmitter in actuating control of last said motor valve.

16. The apparatus of claim 14 including a bypass line in said halogen feed line around the motor valve therein provided with a motor valve; and a temperature controller sensitive to temperature in said reactor in actuating control of the motor valve in said feed line.

17. The process of claim 8 wherein the steam addition rate in step (f) is reduced to zero.

18. The process of claim 1 wherein the steam addition rate in step (e) is reduced to zero.

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