

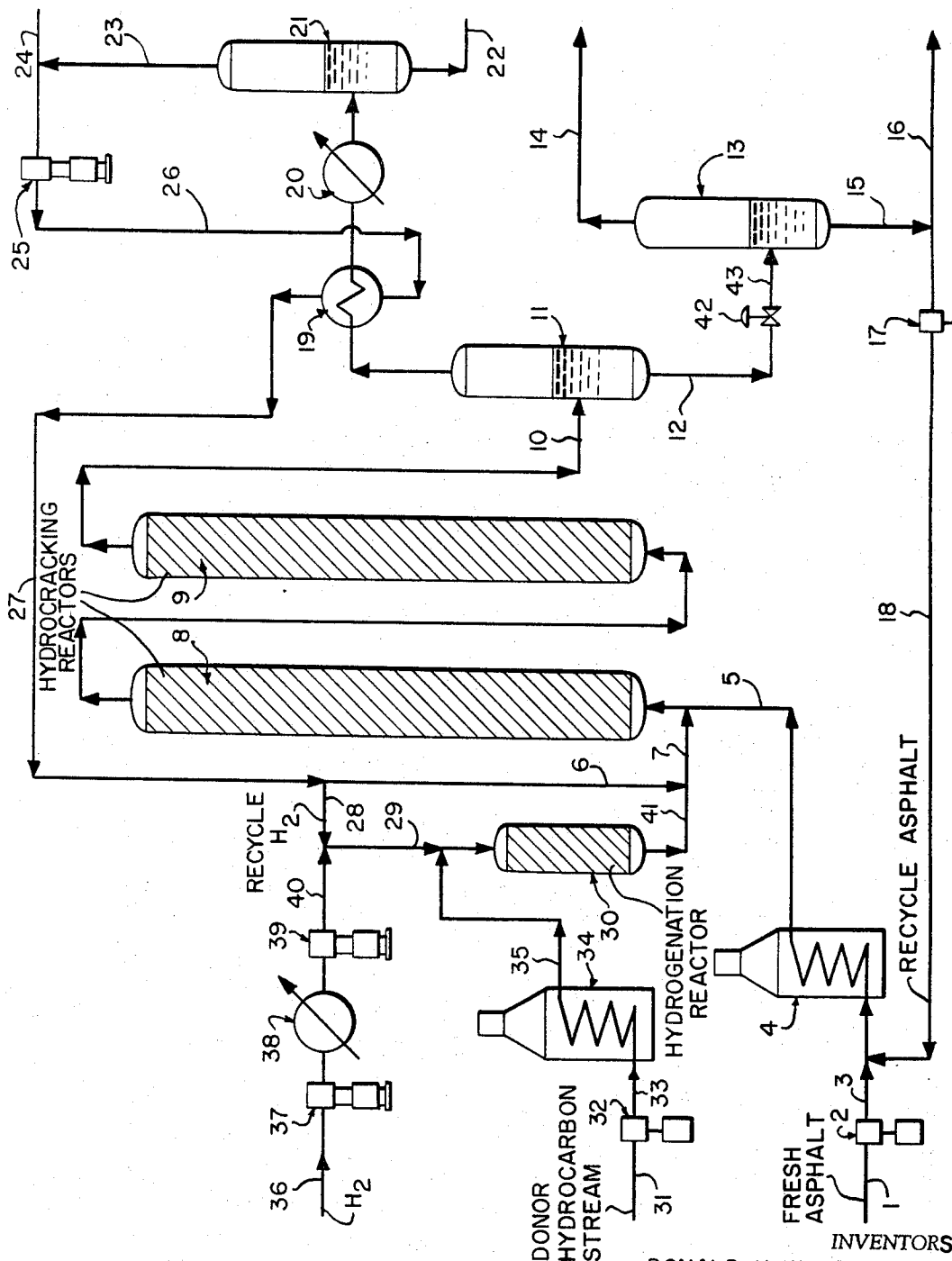
Oct. 22, 1968

D. K. WUNDERLICH ET AL

3,407,134

PROCESS FOR HYDROCRACKING AN ASPHALTIC HYDROCARBON
FEED STOCK IN THE PRESENCE OF A HYDROGENATED
HYDROCARBON AND HYDROCRACKING CATALYST

Filed Aug. 9, 1966



INVENTORS
DONALD K. WUNDERLICH &
WILLIAM MURRAY

BY *McLean, Morton & Boustead*
ATTORNEYS

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PROCESS FOR HYDROCRACKING AN ASPHALTIC HYDROCARBON FEED STOCK IN THE PRESENCE OF A HYDROGENATED HYDROCARBON AND HYDROCRACKING CATALYST

Donald K. Wunderlich, Chicago, and William Murray, Olympia Fields, Ill., assignors to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

Filed Aug. 9, 1966, Ser. No. 571,237

10 Claims. (Cl. 208—111)

ABSTRACT OF THE DISCLOSURE

A process for hydrocracking a residual, penetration grade asphaltic hydrocarbon stock which comprises hydrogenating a heavy aromatic hydrocarbon boiling primarily above about 500° F., e.g. clarified oil, passing an at least partially liquid phase mixture of the residual, penetration grade asphaltic stock and about 10 to 75 percent by weight of the hydrogenated heavy aromatic hydrocarbon boiling primarily above about 500° F., and hydrogen, upflow, in contact with a fixed bed of macrosized hydrocracking catalyst under hydrocracking conditions at a temperature of about 750 to 850° F.

The present invention relates to an improved process for hydrocracking an asphaltic petroleum residual stock. More particularly, the invention concerns the extension of catalyst life by hydrocracking at reduced temperatures while maintaining catalyst activity and conversion normally associated with higher hydrocracking temperatures.

It is well known that the cycle length in catalytic fixed bed hydrocracking processes is strongly influenced by the temperature of the operation, i.e. higher temperatures more readily cause catalyst deactivation and catalyst bed coking, necessitating frequent shut downs for regeneration. Existing processes utilize conventional downflow, processing methods which require high operating temperatures causing rapid catalyst deactivation and thus reduced cycle length. Downflow methods also tend to cause channeling of the feedstock in the catalyst bed resulting in poor catalyst-feed contact which adversely affects product recovery and the overall efficiency of the system.

In accordance with the present invention, an improved process for hydrocracking asphaltic petroleum residual stocks has been discovered which comprises passing, for instance, a residual asphaltic stock to be hydrocracked with a hydrogenated aromatic stream, at least partially in the liquid phase, and hydrogen, upflow through a fixed bed of macrosized hydrocracking catalyst under hydrocracking conditions. The upflow liquid phase processing method produces good feed-catalyst contact and substantially eliminates channeling thus rendering the catalyst system more effective relative to conventional downflow processing. This permits a substantial reduction in reaction temperatures, thereby increasing catalyst activity and catalyst life, when maintaining the conversion to materials lighter than the feed at a constant value. Alternatively, improved results can be achieved if the reaction temperatures are not lowered.

The hydrogenated aromatic stream which is present with the residual asphalt prior to cracking serves to release hydrogen to the asphalt during the hydrocracking reaction and further serves as a heat sink which aids in reducing temperature rise in the reactor. The hydrogenated stream may be produced by treating a heavy aromatic stream, for instance, a clarified oil boiling primarily above about 500° F., preferably above about 600° F., and having an aromatic content of about 35 to 100%, with hydrogen under hydrogenation conditions including a temperature of about 650 to 800° F., preferably about 700 to 750° F., and a

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hydrogen partial pressure of about 500 to 3000 p.s.i.g., preferably about 1000 to 2000 p.s.i.g. The amount of free hydrogen employed is generally about 1000 to 6000 standard cubic feet per barrel of feed, preferably about 1000 to 3000 standard cubic feet per barrel, with the amount of hydrogen consumption varying from about 250–1500 s.c.f./bbl., preferably about 600–900 s.c.f./bbl. The weight hourly space velocity (WHSV), weight units of feed introduced into the reaction zone per weight unit catalyst per hour, will usually be within the range of about 0.2 to 5, preferably about 0.5 to 2.

Clarified oils can be produced by catalytically cracking gas oils and cycle oils boiling primarily in the range of about 400 to 1000° F., and then distilling the cracking unit effluent to produce gas, gasoline, cycle oils and a bottom product. The latter material is settled to separate the clarified oil and a heavier bottom materials containing catalyst fines which can be recycled back to the cracking unit.

Various hydrogenation catalysts may be employed in producing the hydrogenated clarified oil stream used in the process of the present invention. The catalyst is of macro-size and thus can be made by tableting, extruding or other convenient method. The macrosized catalysts often have diameters of about $\frac{1}{32}$ to $\frac{1}{2}$ ", preferably about $\frac{1}{16}$ to $\frac{1}{4}$ ", and may be about $\frac{1}{16}$ to 1" or more in length, preferably about $\frac{1}{8}$ to $\frac{1}{2}$ ".

Some specific examples of satisfactory catalysts include nickel oxide or sulfide, tungsten oxide or sulfide, molybdenum oxide or sulfide, vanadium oxide or sulfide, etc. Particularly desirable is a mixture of nickel oxide and/or sulfide with tungsten oxide and/or sulfide, or a mixture of cobalt or nickel oxide and/or sulfide with molybdenum oxide and/or sulfide. These catalysts can be deposited upon porous carriers such as alumina, alumina containing a small amount of silica, pumice, silica-alumina cracking catalyst, etc. An often used catalyst is cobalt molybdate on alumina.

The residual asphalt stock to be hydrocracked is generally a heavy residual crude material that contains asphaltenes and maltenes, as for example, penetration range vacuum asphalts having a penetration from about 10 to 200 at 77° F. The asphalt can be used with about 10 to 75% by weight of the hydrogenated stream, preferably about 20 to 50% by weight based on the asphaltic feed plus the hydrogenated stream.

The residual asphalt and hydrogenated stream can be hydrocracked under hydrocracking conditions including a temperature of about 750 to 850° F., preferably about 780 to 830° F. and at a hydrogen partial pressure of about 300 to 3000 p.s.i.g., preferably about 500 to 1500 p.s.i.g. The amount of free hydrogen employed is generally about 1000 to 10,000 standard cubic feet per barrel of feed, preferably about 2000 to 6000 standard cubic feet per barrel, with the amount of hydrogen consumptions varying from about 200 to 1500 s.c.f./bbl. of the blended feed, preferably about 400 to 900 s.c.f./bbl. The weight hourly space velocity (WHSV), weight units of hydrocarbon feed introduced into the reaction zone per weight unit catalyst per hour, will usually be within the range of about 0.2 to 5, preferably about 0.5 to 1.

Various hydrocracking catalysts are applicable in the hydrocracking step of the present invention. Often used catalysts may contain about 0.05 to 10 weight percent of a Group VIII metal, such as, for example, platinum, palladium, rhodium, iridium, nickel, and cobalt, deposited on a solid inorganic metal oxide cracking component, such as, for instance, silica-alumina. Other examples of applicable highly acidic catalysts are those disclosed in U.S. Patent 2,478,916, such as, for example, platinum or palladium deposited on, e.g. silica-alumina, silica-

zirconia, silica magnesia, silica-thoria, silica-alumina-zirconia, alumina-boria, etc.

The accompanying drawing is a schematic of the general flow process illustrating the present invention. A vacuum residual asphalt stock to be hydrocracked enters the system through line 1, is directed through line 3 by pump 2, mixed with a recycle stream from line 18, and passed through a fired heater 4 in which the combined stream is brought to a temperature somewhat in excess of the required hydrocracking reactor inlet temperature. The heated feed passes through line 5 and is mixed with a "donor" (hydrogenated aromatic) hydrocarbon stream and a recycle hydrogen-rich gas stream from line 7. The mixture then passes upflow through fixed bed catalyst-containing reactors 8 and 9 which are arranged in series. The reactor effluent overhead from reactor 9 passes through line 10 to a flash separation drum 11 where the vapor and liquid portions of the reactor effluent are separated at the pressure and temperature of the reactor effluent. The flash bottoms (liquid) are passed through line 12 to pressure release valve 42 where an isenthalpic flash vaporization occurs which regulates the initial boiling point of the recycle material. The vaporized products pass through line 43 to flash separation drum 13 where the flashed vapor passes through line 14 to further fractionation in conventional equipment to yield products such as gasoline, light gas oil, and heavy oil. The liquid from the flash separator 13 passes through line 15 where a part of the stream passes to line 16 and is drawn off as a net product (normally requiring additional fractionation in conventional equipment), while the remainder passes to the recycle pump 17 which directs the liquid through line 18 and to admixture with fresh feed in line 3.

The overhead vapor from flash drum 11 passes to cooler 19 in which heat is exchanged with the recycle hydrogen stream, partially cooling the vapor stream. The stream is further cooled in heat exchanger 20 and passes to flash drum 21. The liquid from flash drum 21 passes through line 22 to a conventional fractionator for the recovery of gasoline and gas oils. The overhead vapor from vessel 21 passes through line 23 and is split with a small portion going to a gas plant through line 24 for the recovery of light gasoline components and fuel gas, and the bulk of the stream passing to recycle compressor 25 which transfers the gas through line 26 to heat exchanger 19 where the stream is warmed. The warmed gas passes through line 27 and is split into a stream which goes directly through line 6 to the bottom of reactor 8 and into a stream which passes through line 28 and mixes with incoming make-up hydrogen.

The "donor" hydrocarbon-stream or clarified oil enters through line 31 and is pumped by pump 32 through line 33 to fired heater 34 where the stream is preheated to a somewhat higher temperature than the desired hydrogenation reactor inlet temperature. The heated oil passes through line 35 to the top of the hydrogenation reactor 30. Make-up hydrogen for both the "donor" hydrogenation and the hydrocracking reactions enters through line 36. The hydrogen, which may come from catalytic reforming or a hydrogen-production process, is compressed by a first stage compressor 37, passes through cooler 38 and is finally compressed to the system pressure by compressor 39. The compressed gas passes through line 40 and is mixed with recycle hydrogen-rich gas from line 28. The combined gas stream passes through line 29 and enters the downflow hydrogenation reactor 30. In this reactor, the "donor" stock picks up hydrogen, some of which is released to the asphalt in the hydrocracking reactions. The reactor effluent from reactor 30 passes through line 41 and enters the hydrocracking reactors along with additional recycle hydrogen and the fresh and recycle asphalt stream.

The following example illustrates the present invention, but is not to be considered as limiting.

EXAMPLE I

Clarified oil having an API gravity of 13.5 and an aromatic content of about 75% was hydrogenated at 0.5 WHSV and 730° F., with 3000 s.c.f./bbl. of hydrogen at a hydrogen partial pressure of 1000 p.s.i.g. (650 s.c.f./H₂/bbl. consumption) for use as the donor diluent. The hydrogenated product had an API gravity of 21.8. The catalyst used contained 2.5% cobalt and 12.4% molybdenum oxide on an alumina carrier. The hydrogenated material was blended with 10.4° API residual asphalt in the proportion 1 part diluent per 3 parts asphalt (weight basis). Using the same catalyst composition the mixture, which has an API gravity of 12.9, and contains 11.06 weight percent hydrogen and 1.23 weight percent sulfur was processed upflow once-through at 806° F., 1000 p.s.i.g., 0.66 WHSV (0.50 WHSV on asphalt contained, with 2250 s.c.f. hydrogen per barrel of feed 3000 s.c.f./bbl. on asphalt contained) with there being a hydrogen consumption of 450 s.c.f./bbl. of blend. The hydrogenated clarified oil-asphalt blend was analyzed and the results are listed in Run No. 1 of Table 1. The liquid yield was about 94 weight percent based on the blended feedstock. For comparison, results for a downflow run on straight asphalt at 0.51 WHSV and 820° F. are also shown in Table 1. As can be seen, the conversion and bottoms properties are essentially identical, indicating a 14° F. temperature advantage of the upflow, donor system over the downflow straight asphalt system.

TABLE I

	Run No.	
	(1) Upflow Donor ¹	(2) Downflow— No Donor
API Gravity.....	19.5	21.5
Percent Sulfur.....	0.415	0.485
Percent Hydrogen.....	11.33	11.51
	On Asphalt Plus Donor	On Asphalt ²
TBP Distillation:		
IBP-180° F., Wt. Percent.....	0.6	0.6
180-370° F., Wt. Percent.....	5.6	5.9
370-650° F., Wt. Percent.....	21.7	22.7
650-950° F., Wt. Percent.....	45.4	35.2
950° F.+, Wt. Percent.....	26.7	35.6
Inspections on TBP Cuts:		
180-370° F., API Gravity.....	54.9	55.0
370-650° F.:		
API Gravity.....	32.8	35.3
Pour Point, ° F.....	0	-----
650-950° F.:		
API Gravity.....	18.6	19.8
Percent Carbon Residue (Rams).....	0.817	1.275
Percent Sulfur.....	0.285	0.358
KV at 210° F.....	7.974	9.923
950° F.+::		
API Gravity.....	3.0	3.2
Percent Carbon Residue (Con).....	29.68	30.11
Percent Sulfur.....	0.935	0.961
P.p.m. Ni.....	20	20
P.p.m. V.....	14	17
Penetration at 77° F.....	21	20

¹ Donor run product contains clarified oil.

² Contribution of clarified oil deducted; total prorated to 100%.

It is claimed:

1. A process for hydrocracking a residual, penetration grade asphaltic hydrocarbon stock, which comprises hydrogenating a heavy aromatic hydrocarbon boiling primarily above about 500° F. to produce a hydrogen donor stock, passing an at least partially liquid phase mixture of said residual, penetration grade asphaltic hydrocarbon stock and about 10-75 percent by weight of said hydrogen donor stock, with hydrogen, upflow through a catalytic hydrocracking reaction zone in contact with a fixed bed of macrosized hydrocracking catalyst therein and under catalytic hydrocracking conditions, including a temperature of about 750-850° F., to transfer hydrogen from said hydrogen donor stock to said residual, penetration grade asphaltic hydrocarbon stock, said hydrogen transfer taking place substantially during said catalytic

hydrocracking reaction within said catalytic hydrocracking reaction zone containing said hydrocracking catalyst.

2. The process of claim 1 wherein the heavy aromatic stream hydrogenated is a petroleum clarified oil with an aromatic content of about 35 to 100%.

3. The process of claim 2 wherein the hydrogenated heavy aromatic stream is formed by contacting the clarified oil with a hydrogen-containing gas under hydrogenating conditions including a temperature of about 650 to 800° F.

4. The process of claim 1 in which the hydrocracking catalyst is comprised of molybdenum and cobalt or nickel on alumina.

5. A process for hydrocracking a mixture of residual, asphaltic hydrocarbon stock having a penetration of about 10–200 at 77° F. and hydrogenated heavy aromatic hydrocarbon, which comprises contacting a heavy aromatic hydrocarbon boiling primarily above about 500° F. and having about 35 to 100 percent aromatics, with hydrogen in the presence of a hydrogenation catalyst and at a temperature of about 650–800° F., a hydrogen partial pressure of about 500–3000 p.s.i.g., a hydrogen rate of about 1000–6000 standard cubic feet per barrel of hydrocarbon, and a space velocity of about 0.2–5 WHSV, to effect a hydrogen consumption of about 250–1500 standard cubic feet of hydrogen per barrel of hydrocarbon feed and to produce a hydrogen donor stock, passing an at least partially liquid phase mixture of said residual, asphaltic hydrocarbon stock and about 10–75 percent by weight of said hydrogen donor stock, with hydrogen, upflow through a catalytic hydrocracking reaction zone in contact with a fixed bed of macrosized hydrocracking catalyst therein and under catalytic hydrocracking conditions, including a temperature of about 750–850° F., a hydrogen partial pressure of about 300–3000 p.s.i.g., a hydrogen rate of about 1000–10,000 standard cubic feet per barrel of said mixture, and a space velocity of about 0.2–5 WHSV, to effect in said catalytic hydrocracking reaction zone a hydrogen consumption of about 200–1500 standard cubic feet of hydrogen per barrel of said mixture, and to transfer hydrogen from said hydrogen donor stock to said residual, asphaltic hydrocarbon stock, said hydrogen transfer taking place substantially during said catalytic hydrocracking reaction within said catalytic hydrocracking reaction zone containing said hydrocracking catalyst.

6. The process of claim 5 in which the heavy aromatic hydrocarbon is a petroleum clarified oil.

7. The process of claim 6 in which both the hydro-

genation and hydrocracking catalysts are comprised of molybdenum and cobalt or nickel on alumina.

8. A process for hydrocracking a mixture of residual, asphaltic hydrocarbon stock having a penetration of about 10–200 at 77° F. and hydrogenated heavy aromatic hydrocarbon, which comprises contacting a heavy aromatic hydrocarbon boiling primarily above about 600° F. and having about 35 to 100 percent aromatics, with hydrogen in the presence of a hydrogenation catalyst and at a temperature of about 700–750° F., a hydrogen partial pressure of about 1000–2000 p.s.i.g., a hydrogen rate of about 1000–3000 standard cubic feet per barrel of hydrocarbon, and a space velocity of about 0.5–2 WHSV, to effect a hydrogen consumption of about 600–900 standard cubic feet of hydrogen per barrel of hydrocarbon feed and to produce a hydrogen donor stock, passing an at least partially liquid phase mixture of said residual asphaltic hydrocarbon stock and about 20–50 percent by weight of said hydrogen donor stock, with hydrogen, upflow through a catalytic hydrocracking reaction zone in contact with a fixed bed of macrosized hydrocracking catalyst therein and under catalytic hydrocracking conditions, including a temperature of about 780 to 830° F., a hydrogen partial pressure of about 500 to 1500 p.s.i.g., a hydrogen rate of about 2000 to 6000 standard cubic feet per barrel of said mixture, and a space velocity of about 0.5–1 WHSV, to effect in said catalytic hydrocracking reaction zone a hydrogen consumption of about 400 to 900 standard cubic feet of hydrogen per barrel of said mixture, and to transfer hydrogen from said hydrogen donor stock to said residual, asphaltic hydrocarbon stock, said hydrogen transfer taking place substantially during said catalytic hydrocracking reaction within said catalytic hydrocracking reaction zone containing said hydrocracking catalyst.

9. The process of claim 8 in which the heavy aromatic hydrocarbon is a petroleum clarified oil.

10. The process of claim 9 in which both the hydrogenation and hydrocracking catalysts are comprised of molybdenum and cobalt or nickel on alumina.

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DELBERT E. GANTZ, *Primary Examiner*.

A. RIMENS, *Assistant Examiner*.