

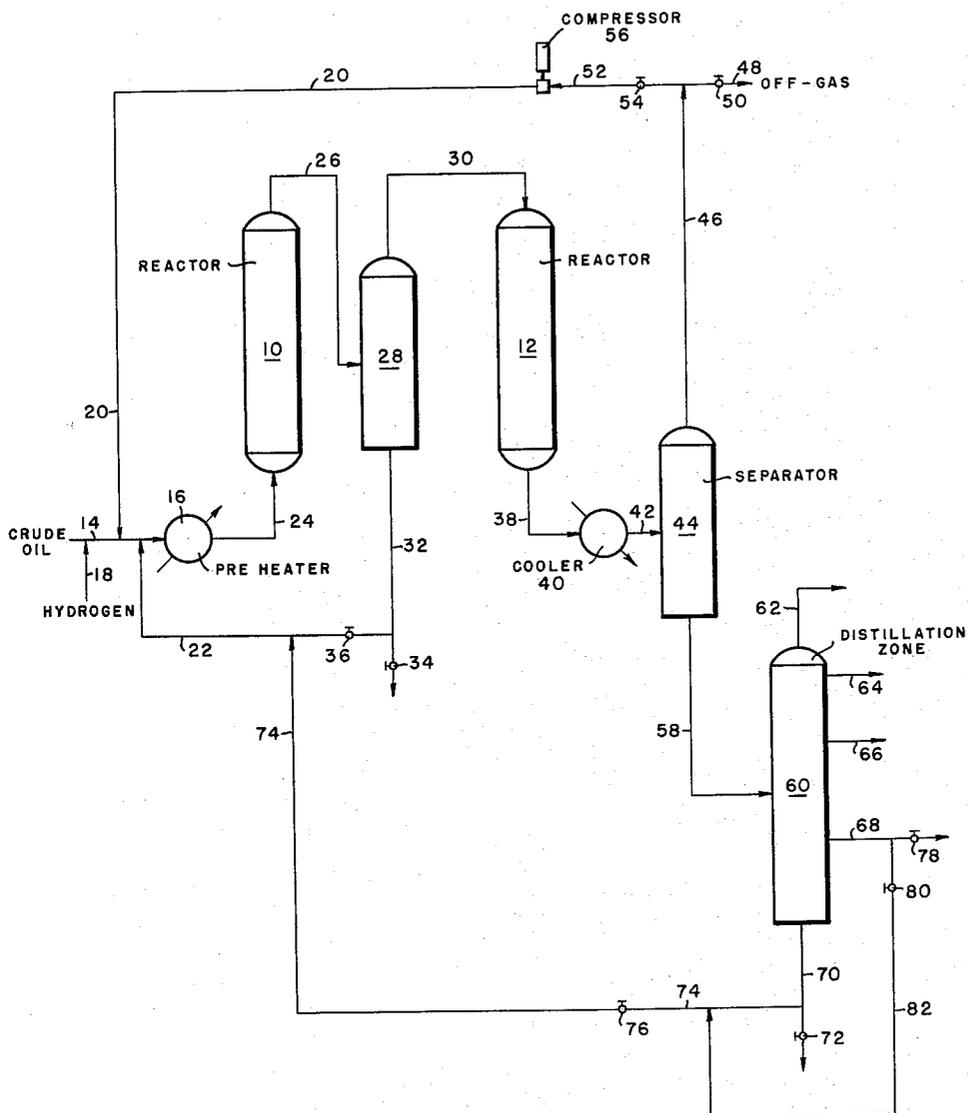
Jan. 28, 1964

H. G. CORNEIL ET AL

3,119,765

CATALYTIC TREATMENT OF CRUDE OILS

Filed Oct. 19, 1959



INVENTORS.
HAMPTON G. CORNEIL,
RICHARD S. MANNE,
GEORGE R. L. SHEPHERD,
ARMAND M. SOUBY,
BY *Carl G. Ries*
ATTORNEY.

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CATALYTIC TREATMENT OF CRUDE OILS

Hampton G. Cornell, Richard S. Manne, George R. L. Shepherd, and Armand M. Souby, Baytown, Tex., assignors, by mesne assignments, to Esso Research and Engineering Company, Elizabeth, N.J., a corporation of Delaware

Filed Oct. 19, 1959, Ser. No. 847,298

3 Claims. (Cl. 208—210)

This invention relates to a method for the catalytic treatment of petroleum hydrocarbon crude oils.

More particularly, this invention relates to a catalytic hydrotreating process for the upgrading of hydrocarbon crude oils.

Petroleum hydrocarbon crude oils are comprised of a wide variety of components boiling over a wide range. Accordingly, it is the customary practice to fractionate the crude oil and to separately treat the various fractions that are obtained.

In accordance with the present invention, however, a method is provided wherein the crude oil is treated in a manner to convert selectively the higher boiling fractions thereof and in order to provide for a substantially desulfurized product.

Briefly, in accordance with the present invention, a petroleum hydrocarbon crude oil is passed upwardly through a fixed bed of a supported cobalt molybdate catalyst in the presence of controlled amounts of added hydrogen in order to desulfurize partially the crude oil and in order to at least partially convert the heavier components of the crude oil. The total effluent is separated into a vapor phase fraction which is further treated with hydrogen in the presence of a supported cobalt molybdate catalyst in order to provide a substantially desulfurized product and a liquid phase which is preferably recycled.

The feed stocks for the present invention are petroleum hydrocarbon crude oils which contain residuum components such as total crudes, topped crudes, residua, etc. and which are further characterized by containing about 50 to 100 volume percent of components boiling above about 800° F.

The catalyst that is utilized in accordance with the present invention is a supported cobalt molybdate catalyst such as a catalyst comprising from about 5 to 20 weight percent of cobalt molybdate supported on a high surface area carrier such as synthetic gamma alumina, bauxite, etc.

The conversion conditions to be utilized in both the first and second stage include a pressure within the range of about 200 to 1000 p.s.i.g., a temperature within the range of about 700° to 800° F., a space velocity within the range of about 0.5 to 5 v./v./hr., and a hydrogen charge rate within the range of 700 to 7000 standard cubic feet of hydrogen per barrel of feed. The first stage reaction is conducted upflow, the second stage reaction being conducted either upflow or downflow, as desired.

The reaction conditions may be the same or different in the second stage as compared with the first stage within the above-described limits. Thus, the second stage may be operated at the same pressure or a lower pressure if not less than about 200 p.s.i.g.

Numerous advantages are obtained in accordance with the present invention. Thus, at least a portion of the residuum components of the crude oil (those boiling above about 1000° F.) are converted to lower boiling desulfurized products. When appropriate recycle operations are employed, substantially all of the residuum compo-

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nents may be thus converted. In addition a high yield of substantially sulfur-free heavy and light gas oil fractions are obtainable, together with a good yield of low sulfur naphtha fractions containing reduced quantities of olefins.

The invention will be further illustrated with reference to the accompanying drawing wherein the single figure is a schematic flow sheet illustrating a preferred form of the present invention.

Turning now to the drawing, there is shown a first stage reactor 10 and a second stage reactor 12. A bed of particulate supported cobalt molybdate such as gamma alumina supported cobalt molybdate is provided in each of the reactors 10 and 12.

A crude oil from any suitable source (not shown) may be charged by way of a line 14 to a preheater 16 wherein the charge is heated to reaction temperature. Make-up hydrogen from an extraneous source may be added to the crude in the line 14 by way of a line 18, recycle off-gas rich in hydrogen may be charged to the crude line 14 by way of a recycle line 20, and heavy conversion components may be charged to the line 14 by way of a liquids recycle line 22.

The thus-prepared mixture of feed components is heated in the preheater 16 to a desired conversion temperature and discharged from thence by way of a charge line 24 leading to the bottom of the first stage reaction zone 10. The feed mixture is passed upflow through the first stage reactor 10 under conversion conditions as above set forth. As a consequence, the liquid components of the feed stock are partially desulfurized and, in addition, partial conversion of heavier components of the feed stock occurs. The total effluent from the reaction zone 10 is discharged from the top thereof by way of a discharge line 26 leading to a separator 28 wherein the total effluent is separated into a gas phase and a liquid phase. The gas phase, which will contain a substantial portion of the charge components, is charged to the second stage reactor 12 by way of a line 30 for further treatment under the above-described conversion conditions. As a consequence of the second stage, the sulfur content of the vapor phase fraction 30 is materially reduced and, in addition, olefins that may be present in the conversion products are at least partially saturated with hydrogen.

The liquid fraction from the separator 28 is discharged by way of a bottoms draw-off line 32 controlled by a valve 34. All or a selected portion of the bottoms fraction may be discharged from the system for further treatment. However, in accordance with a preferred embodiment of the present invention, the liquid fraction is recycled by closing the valve 34 and by opening the valve 36 in the above-mentioned recycle line 22.

The total effluent from the second stage reactor 12 is discharged by a line 38 leading to a cooler 40 wherein liquefiable hydrocarbons are condensed. From cooler 40, the total effluent is charged by a line 42 to a second separator 44. A gas phase consisting principally of hydrogen and containing normally gaseous hydrocarbons is taken overhead by way of a line 46. Normally, at least a portion of the off-gas will be discharged from the system by a discharge line 48 controlled by a valve 50. All or a selected portion of the off-gas may be charged by way of a line 52 controlled by a valve 54 to a compressor 56 discharging into the above-described recycle line 20.

The liquid phase from the second separator 44 is discharged by way of a line 58 leading to further treating facilities. Thus, for example, the liquid fraction may be

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charged by way of a line 58 to a distillation column 60 wherein the liquid fraction may be separated into a naphtha fraction 62, a kerosene fraction 64, a light gas oil fraction 66, a heavy gas oil fraction 68, and a residuum fraction 70.

The residuum fraction may be discharged from the system by opening the valve 72 in the bottoms discharge line 70. Alternately, it may be returned by way of a branch line 74 controlled by a valve 76 to the recycle line 22.

Similarly, all of the heavy gas oil may be discharged from the system for further treatment (e.g., catalytic cracking) by opening the valve 78 in the discharge line 68. Alternately, a valve 80 in a recycle line 82 leading to the recycle line 74 may be opened whereby at least a portion of the heavy gas oil may be returned to the recycle line 22.

The invention will be further illustrated by the following specific examples which are given by way of illustration and not intended as limitations on the scope of this invention.

EXAMPLE I

In order to illustrate the necessity for operating the first stage in an upflow phase, a crude oil is processed under superficially identical reaction conditions in two separate reactors, one reactor being operated on a downflow basis and the other being operated on an upflow basis.

The composition of the feed stock is set forth in Table I, the reaction conditions employed and the results obtainable are set forth in Table II.

Table I
INSPECTIONS ON CRUDE OIL CHARGED

Gravity, °API	25.9
Sulfur, wt. percent	2.70
Viscosity at 80° F., SSU	270
Viscosity at 100° F., SSU	195
Ash, p.p.m.	94
ASTM distillation: ¹	
IBP, °F	181
5% off at, °F	257
10% off at, °F	301
20% off at, °F	398
30% off at, °F	544
40% off at, °F	647
60% off at, °F	790
70% off at, °F	923

¹ Duplicate ASTM D-158 gas oil distillations to 600° F., followed by ASTM D-1160 10 mm. distillation on combined bottoms. Temperatures at 10 mm. converted to the equivalent temperatures at atmospheric pressure shown above by means of the chart on page 42 of Maxwell, "Data Book on Hydrocarbons," Von Nostrand (New York, 1950).

Table II
FIRST-STAGE HYDRODESULFURIZATION
[800 p.s.i.g., 745° F. inlet, 0.9 v./v./hour, 1700 s.c.f. H₂/B]

Type of Operation	Crude Charged		Downflow		Upflow	
	Vol. Per-cent ¹	Wt. Per-cent S	Vol. Per-cent ¹	Wt. Per-cent S	Vol. Per-cent ¹	Wt. Per-cent S
Overall Desulfurization, Percent			67		63	
Distillation Fractions						
C ₅ -375° F. Naphtha	18.1	0.03	17.8	0.02	23.6	0.02
375°-530° F. Kerosene	12.1	0.22	14.3	0.04	17.4	0.07
530°-600° F. Light Gas Oil	5.6	0.75	7.3	0.07	7.9	0.23
600°-1,040° F. Gas Oil	33.5	2.3	38.1	0.31	37.2	0.84
1,040° F.+Residuum	30.2	3.8	22.1	2.9	14.8	3.1
Total C ₃ and Heavier	99.5	2.7	99.6	0.89	100.9	1.00

¹ Based on original crude charged.

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From Table II, it will be observed that there is a significant conversion of the 1040° F.+ residuum fraction in the upflow reactor and that a much lesser conversion is obtained with respect to the downflow reactor. It will be noted, moreover, that although enhanced yields of kerosene and naphtha are obtained by the upflow reaction conducted in accordance with the present invention, substantially the same quantities of heavy and light gas oil are obtained in both instances.

As is seen by the analysis of sulfur, however, the first stage reaction is not satisfactory from the point of sulfur removal in that significantly larger amounts of sulfur are present in the gas oil fractions from the upflow reaction as compared with the sulfur removal obtained by the downflow reaction.

However, further treatment of the vapor phase from the first stage reaction here illustrated significantly reduces the sulfur content of the distillate materials.

EXAMPLE II

In order to illustrate the effects obtainable by the two stage process of the present invention, a separate hydrocarbon feed stock is treated in stages.

The feed stock that is utilized is a West Texas vacuum residuum fraction having the composition set forth in Table III.

Table III

INSPECTION ON WEST TEXAS VACUUM RESIDUUM	
West Texas vacuum residuum	
Gravity, °API	8.8
Sulfur, weight percent	3.86
Conradson carbon, weight percent	17.2
ASTM distillation, ¹ percent off at 1040° F.	9.0

¹ Method of ASTM D-1160, but run at 1 mm. pressure instead of 10 mm. Temperature converted to the equivalent at atmospheric pressure by means of the chart on page 42 of Maxwell, "Data Book on Hydrocarbons," Von Nostrand (New York, 1950).

Treat the above-identified feed stock in the presence of a commercial catalyst consisting of about 15 weight percent of cobalt molybdate supported on gamma alumina under upflow conversion conditions including a pressure of about 800 p.s.i.g., an average reactor temperature of about 785° F., a space velocity of about 0.55 v./v./hr. and a hydrogen charge rate from about 2950 cubic feet of hydrogen per barrel. As a result of the first stage reaction, about 57 percent desulfurization is obtained and about 60 percent of the 1040° F.+ material is converted to lighter products.

Separately collect the vapor and liquid products from the first stage. The mol percent of each component or fraction in the total reactor product and the percentage of that component or fraction in the vapor phase at the reactor outlet are set forth in Table IV.

Table IV

Component	Mol Percent in Product Stream	Percent Component Vaporized
CO	1.3	100
H ₂	71.9	98.8
H ₂ S	3.7	97.1
C ₁ and C ₂	13.8	97.9
C ₃ and C ₄	4.1	97.0
C ₅	0.5	100
IBP-360° F.	0.3	100
360°-440° F.	1.2	91.6
440°-530° F.	1.1	83.3
530°-650° F.	0.9	75
650°-740° F.	0.2	67
740°-870° F.	0.7	47.8
870°-1,004° F.	0.3	20
Total	100.0	

Treat two portions of the vapor phase in accordance with the present invention in separate runs. Conduct one second-stage run at a pressure of about 400 p.s.i.g. and an average reaction temperature of about 766° F. Conduct the other second-stage higher pressure of 575 p.s.i.g. and a high reaction temperature of about 787° F.

The reaction conditions employed and the gross results obtained are set forth in Table V.

Table V

HYDRODESULFURIZATION OF VAPOR PHASE FRACTION OF PRODUCT FROM HYDRODESULFURIZATION OF CRUDE RESIDUUM

Run No., HDS	2002	2008
Pressure p.s.i.g.	400	575
Avg. Catalyst Temp., ° F	766	787
Feed Rate, v/v./hr.	2.0	1.9
H ₂ Rate, s.c.f./b.	2,970	2,870
H ₂ Consumption, s.c.f./b.	305	290
Percent Desulfurization	89	96
Liquid Product Yield, Vol. Percent of Feed	99.6	95.7
	Feed	
Inspections on Liquid Product:		
Gravity, ° API	29.4	30.9
Sulfur, Wt. Percent	0.66	0.05
Distillation Data—		
IBP, ° F	345	162
FBP, ° F	1,004	1,004
IBP-430° F. Fraction, Vol. Percent	20.2	23.0
430°-650° F. Fraction, Vol. Percent	37.1	42.4
650°-1,004° F. Fraction, Vol. Percent	42.7	34.6

From Table V, it will be noted that substantially complete desulfurization is obtained and that the total product is much improved in quality as compared with the material charged.

Each of the fractions from the second stage operation is substantially improved as compared with the corresponding fraction from the first stage. This is shown, for example, by the inspections of each of the three major fractions of the first stage and of the two second stage products, as set forth in Table VI.

Table VI

INSPECTIONS ON PRODUCTS FROM HYDRODESULFURIZATION OF VAPOR PHASE PRODUCT FROM HYDRODESULFURIZATION OF CRUDE RESIDUUM

Run No., HDS	Feed	2002	2008
Naphtha Fraction (IBP-430° F.):			
Gravity, ° API	49.3	47.3	46.8
Sulfur, Wt. Percent	0.07	0.01	0.02
Res. Oct. No. (+1.5 cc. TEL)	68.3	64.0	66.6
Aromatics, Percent	23.4	24.6	26.6
Bromine No., Mg./gm.	9.7	2.1	1.5
Heating Oil Fraction (430°-650° F.):			
Gravity, ° API	30.1	30.4	29.9
Sulfur, Wt. Percent	0.36	0.05	0.01
Aniline Point, ° F	124		129
Neut. Value, mg. KOH/gm.	0.20	0.04	0.01
Aromatics, Percent	55.6	55.0	56.3
Phenol Content, Wt. Percent	0.10	0.01	0.01
Thiophenol Content, Wt. Percent	0.006	0.002	0.001
Bromine No., mg./gm.	11.0	3.0	3.1

Table VI—Continued

Run No., HDS	Feed	2002	2008
5 Gas Oil Fraction (650°-1,004° F.):			
Gravity, ° API	19.1	21.9	22.3
Sulfur, Wt. Percent	0.83	0.07	0.04
Nitrogen, Wt. Percent	0.28	0.22	0.20
Bromine No., mg./gm.	13.1	9.9	11.2
Comradson Carbon, Wt. Percent	10.2	0.73	0.44
Refractive Index at 67° C., n _D ⁶⁷	1.5166	1.5062	1.5080
ASTM D-1160 Distillation—			
5% off at, ° F	754	734	737
20%	804	754	747
50%	908	807	795
80%	984	890	883
95%	1,047		968
Aromatic Rings, Wt. Percent	20.9	19.5	21.2

15 Having described our invention, what is claimed is:

1. A method which comprises the steps of passing a crude petroleum hydrocarbon feed stock containing at least about 50 volume percent of components boiling above about 800° F. in an upflow direction through a first reaction zone containing a fixed bed of a supported cobalt molybdate catalyst under conversion conditions including a temperature of 700° to 800° F. and a pressure of 200 to 1000 p.s.i.g. at a space velocity of about 0.5 to 5 volumes of feed stock per volume of catalyst per hour in the presence of 700 to 7000 cubic feet of hydrogen per barrel of feed stock, separating the total effluent from said first reaction zone without substantial cooling thereof into a vaporized fraction and a liquid fraction, recycling at least a portion of liquid fraction to said first reaction zone, passing said vaporized fraction directly after said separation through a second reaction zone containing a fixed bed of supported cobalt molybdate catalyst under conversion conditions similar to those in the first reaction zone and recovering a desulfurized product from the effluent from said second reaction zone.

2. A method as in claim 1 wherein the effluent from the second reaction zone is fractionated to separate components boiling above about 800° F. from the remaining components of said effluent, wherein the normally liquid components of said effluent boiling below 800° F. are recovered and wherein the components of said effluent boiling above 800° F. are recycled to said first reaction zone.

3. A method as in claim 2 wherein a hydrogen containing normally gaseous off-gas product is recovered from the effluent from said second reaction zone and wherein at least a portion of said off-gas is recycled to said first reaction zone to provide at least a portion of the hydrogen.

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