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[54] **SPLIT FLOW HYDRODESULFURIZATION OF PETROLEUM FRACTION**

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[58] **Field of Search** 208/210, 89, 218, 58, 59, 208/108, 109, 110, 111, 112

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[57] **ABSTRACT**

Heavy hydrocarbon oils are desulfurized in a split flow catalytic process in which the upper catalyst bed temperature is at least 875°F. and the lower catalyst bed temperature is below 850°F.

10 Claims, No Drawings

SPLIT FLOW HYDRODESULFURIZATION OF PETROLEUM FRACTION

This invention relates to the treatment of petroleum oils. More particularly, it is concerned with the production of hydrocarbon oils of reduced sulfur content from heavy hydrocarbon oils containing tar and asphalt.

Motor fuel, jet fuel and diesel fuel are, for the most part, the more valuable of the products obtained from crude petroleum. As a result, the petroleum refining industry is geared to produce maximum amounts of these products. To this end, a crude petroleum oil is distilled to obtain these fractions as distillates and the materials boiling above the desired products such as the heavier gas oils are subjected to cracking and/or hydrocracking to convert them to lighter products. For ecological reasons, it is now important that these fuels also contain a minimum amount of sulfur. If the crude petroleum oil has been distilled under atmospheric pressure up to a temperature at which incipient cracking begins, usually between about 650° and 750°F., there remains in the still a residue generally referred to as atmospheric residuum containing relatively large amounts of tar and asphalt. This atmospheric residuum may be further distilled under reduced pressure to produce as distillate vacuum gas oils leaving a still residue generally referred to as vacuum residuum. Attempts to convert still residues into more valuable products by means of catalytic processes have not been particularly successful as tar and asphalt tend to settle on the catalyst and over a period of time form a layer of coke which prevents the oil from coming into contact with the catalyst thereby reducing the catalyst activity.

Because of the many legal requirements restricting the amount of sulfur present in fuels, it has become necessary to treat more and more hydrocarbon oils for the removal of sulfur. Conventionally this is done by contacting the hydrocarbon oil at elevated temperature and pressure in the presence of hydrogen with a desulfurization catalyst whereby the sulfur present in the oil is converted to hydrogen sulfide and may be separated with relative ease from the hydrogen which can then be recycled to the reaction zone. Because of the greater volumes of oils which must be treated the amount of hydrogen required has greatly increased and it has been necessary to augment refinery facilities with hydrogen-producing plants. Hydrogen consumption will vary depending on the charge stock and the amount of desulfurization required but generally it will amount to between 400 and 500 standard cubic feet per barrel of oil. It would therefore be a great saving if the amount of hydrogen consumed in a hydro-desulfurization process could be reduced. For example a reduction in the hydrogen consumption of 100 cubic feet per barrel would amount to a saving of 1,000,000 cubic feet of hydrogen a day for a 10,000 barrel per day unit which, according to today's standards is a unit of modest size.

It is therefore an object of this invention to provide a process for the catalytic conversion of residue-containing petroleum oils into lighter, more valuable products. Our invention contemplates a process which comprises charging the heavy hydrocarbon oil together with hydrogen at elevated temperature and pressure into a bed of catalyst particles. That portion of the petroleum oil which is still liquid at reaction conditions passes downwardly through the catalyst bed and is met by an upwardly flowing stream of hydrogen. The hydrogen passes upwardly through the catalyst bed while contacting the oil and catalyst and becomes mixed with vaporous hydrocarbon materials formed either by the catalytic reaction which takes place as the liquid oil flows downwardly through the bed or vaporous hydrocarbons which have been formed during the heating of the oil feed. The mixture of hydrogen and vaporous hydrocarbons is then passed to a separate catalytic zone where the vaporous materials are subjected to desulfurization conditions. According to a preferred embodiment of our invention, the oil optionally with a portion of the hydrogen is introduced into a fixed bed of particulate catalyst to permit the liquid portion of the oil to flow downwardly through the catalyst bed at a temperature below 850°F. and the vaporous material formed during the heating of the charge oil and/or produced by the catalytic reaction during the downward flow of the liquid oil through the catalyst bed is passed in vapor phase with hydrogen introduced at the bottom of the bed into a catalyst bed maintained at a temperature above 875°F. By following the procedure of our invention good yields of oils of reduced sulfur content and lower boiling range are obtained with lower hydrogen consumption.

The oil used as charge to the process of our invention is a heavy oil ordinarily having an initial boiling point between about 550° and 750°F. with at least 80 percent boiling above 650°F. and preferably at least about 90 percent boiling above 650°F. Typically, it has a Conradson Carbon Residue of at least 1 percent by weight and usually at least 5 percent by weight. Examples of such charge stocks are atmospheric residua, vacuum residua and heavy distillates such as vacuum gas oils obtained from crude petroleum, shale oil, tar sand oil and the like.

The hydrogen used in our process need not necessarily be pure. Hydrogen having a purity of at least 50 percent and preferably at least 65 percent may be used. Suitable sources of hydrogen are catalytic reformer by-product hydrogen, electrolytic hydrogen and hydrogen produced by partial oxidation of a carbonaceous or hydrocarbonaceous material followed by shift conversion and CO_2 removal. In a preferred embodiment, hydrogen at a rate of between 500 and 5000 standard cubic feet per barrel is introduced into the catalyst bed with the oil feed and hydrogen is introduced into the bottom of the catalyst bed to flow upwardly therethrough at a rate between 3,000 and 20,000 scfb preferably between 8,000 and 15,000 scfb.

The catalyst used in our process comprises a Group VIII metal and/or compound thereof optionally composited with a Group VI metal or compound thereof on a support comprising a refractory inorganic oxide. The Group VIII metal is preferably an iron group metal such as nickel or cobalt or a mixture thereof. Suitable Group VI metals are molybdenum and tungsten. Preferred hydrogenating components are mixtures of the metal oxides or sulfides such as cobalt oxide and molybdenum oxide, nickel sulfide and tungsten sulfide, nickel oxide, cobalt oxide and molybdenum oxide. Suitable supports for the hydrogenating components of the catalyst comprise inorganic oxides such as alumina, silica, magnesia, titania, beryllia, zirconia and the like and mixtures thereof. A preferred support comprises alumina stabilized with a minor amount, for example, less than 15 percent silica based by weight on the catalyst composite. The catalyst is used as a fixed bed with

catalyst particles. The particles may have spheroidical or cylindrical shapes. In a preferred embodiment the catalyst bed is made up of cylindrical particles having a maximum dimension of between one-half inch and one-sixteenth inch.

The Group VIII metal may be present in an amount between about 1 and 15 percent by weight preferably between about 1.5 and 10 percent by weight of the catalyst composite. When present, the Group VI metal may comprise between about 3 and 30 percent preferably between about 5 and 20 percent by weight of the catalyst composite. Particularly suitable catalysts comprise about 2 percent iron group metal such as nickel or cobalt and about 18 percent Group VI metal such as molybdenum or tungsten. Advantageously the catalyst contains a minor amount of silica e.g., less than about 10 percent such as 2–4 weight percent of the catalyst composite.

In carrying out the process of this invention, the heavy hydrocarbon oil charge stock is introduced into a desulfurization catalyst zone herein defined to include a first catalyst zone in downflow relationship to the downward flow of the heavy hydrocarbon stock and a second catalyst zone above the point of entry of the heavy hydrocarbon charge stock and in upflow relationship to the lower boiling hydrocarbons which proceed from the first catalyst zone into the second catalyst zone. By the use of the term "downward flow" is meant that the heavy hydrocarbon charge stock proceeds in downflow relationship to the first catalyst zone. By the use of the term "above" in reference to the second catalyst zone is meant only that the second catalyst zone is in upflow relationship to the flow of the hydrogen containing gas and in upflow relationship to the volatile hydrocarbon and any entrained liquid hydrocarbon proceeding from the first catalyst zone into a second catalyst zone. The word "above" is used to define a flow relationship with the first catalyst zone, which relationship provides for the flow of hydrogen, volatile hydrocarbons and entrained lower boiling hydrocarbons from the first catalyst zone in countercurrent relationship with the downward flow of the heavy hydrocarbon charge stock into a second catalyst zone. Thus the second catalyst zone can be located directly in a space dimension above the first catalyst zone such as when the first and second catalyst zones are present in a single reactor vessel with an intermediate point of entry for the heavy hydrocarbon charge stock. However, this invention contemplates that the second catalyst zone can be present in a separate reactor vessel which is connected to a first reactor by conduit means, although it is preferred in carrying out the process of this invention to use a vertical reactor wherein the first catalyst zone and second catalyst zone are present in the same reactor vessel. Within the first and second catalyst zone is a catalyst which has hydrodesulfurization activity under process conditions of temperature, pressure and space velocity which are utilized during the process. In addition, the catalyst in the first catalyst zone can be either the same or different than the catalyst present in the second catalyst zone.

The heavy hydrocarbon charge stock upon entry to the catalyst zone proceeds downwardly in downflow relationship to the first catalyst zone. Hydrogen is introduced into the first catalyst zone at or near the lower extremity and, if desired, at intermediate points in said first catalyst zone in countercurrent relationship to the hydrocarbon charge flow through the first catalyst zone and in upflow relationship to the second catalyst zone. Volatile hydrocarbons and the lower boiling entrained hydrocarbons proceed with the hydrogen into the second catalyst zone. The volatile hydrocarbons and the entrained liquids after contact with the catalyst leave the second catalyst zone and are recovered by conventional means such as by cooling of the hydrocarbon vapors and liquid. The hydrogen which proceeds from the second catalyst zone may then be recycled together with fresh make-up hydrogen into the first catalyst zone. In addition, hydrogen optionally can be blended with the heavy hydrocarbon charge stock and introduced at ambient temperature or higher such as temperatures up to desulfurization temperatures into the catalyst zone.

The temperature in the first desulfurization catalyst zone may range between about 550° and 850°F. preferably between 700° and 850°F. The temperature in the second catalyst zone should be at least 875°F. but not more than about 1,000°F. A preferred temperature range is from 880° to 950°F. Pressures in both of the reaction zones may range between about 500 and 5,000 psig, a preferred pressure range being from 1,000 to 2,500 psig. The residue-containing petroleum fraction may be introduced into the catalytic zone at a space velocity of between about 0.1 and 5 volumes of oil per volume of catalyst per hour based on the total volume of catalyst in both desulfurization zones, a preferred range being from 0.25 to 2 v/v/hr.

By following our novel procedure it is possible to convert heavy oils into products of reduced sulfur content while incurring a hydrogen consumption of between about 100 and 300 scfb whereas, by following known procedures an equivalent amount of sulfur reduction would incur a hydrogen consumption in excess of 400 scfb.

The following examples are submitted for illustrative purposes only and it should not be construed that the invention is limited thereto.

EXAMPLE I

The charge in this example is an atmospheric reduced crude derived from West Texas-New Mexico sour crude. It has the following characteristics:

TABLE I

API Gravity	17.7
Sulfur wt. %	2.63
Metals-ppm. Ni-V-Fe	6–16–10
Carbon Residue-wt. %	6.5
Tests on Fractions	
550–650°F. Fraction-wt. %	7.8
API Gravity	29.9
Sulfur-wt. %	1.50
650–850°F. Fraction-wt. %	28.2
API Gravity	25.6
Sulfur-wt. %	1.84
850–1000°F. Fraction-wt. %	3.4
API Gravity	23.0
Sulfur-wt. %	2.44
1000°F. Residuum-wt. %	60.6
API Gravity	13.0
Sulfur-wt. %	2.94
Metals-ppm. Ni-V-Fe	12–4–21
Carbon Residue-wt. %	9.7

The charge is introduced into the catalytic zone in a single reactor vessel at a point where 45 percent of the catalyst is above and 55 percent below the point of introduction. The catalyst, in pellet form, contains 3 wt.

percent cobalt oxide and 11 wt. percent molybdenum oxide supported on alumina. Hydrogen is introduced with the charge at a rate of 4000 scfb. and is also introduced at the bottom of the lower catalyst bed at a rate of 11,000 scfb. Charge rate is 0.41 weight of oil per total weight of catalyst per hour and pressure in the reaction zone is 1500 psig. Data on the run are tabulated below. The temperature designation "mid" is the temperature at the point of introduction of the feed and "upper" and "lower" is the average temperature of the respective desulfurization catalyst beds.

TABLE II

Period		A	B	C	D
Temp. °F.	Upper	825	875	900	950
	Mid.	800	800	825	825
	Lower	800	800	800	800
Time on Stream-Hrs.		112	220	286	508
IBP–400°F. Fraction-wt.%		7.5	13.1	16.6	14.8
API Gravity		51.1	48.7	50.0	47.7
Sulfur-wt. %		<0.002	0.0011	0.007	0.002
H.C. Type Anal.	Paraffins	44.0	44.6	44.6	48.2
	Naphthenes	34.4	28.0	29.7	18.9
	Aromatics	21.5	27.5	28.8	32.9
400–500°F. Fraction-wt.%		7.5	11.2	11.8	7.3
API Gravity		39.2	36.7	37.1	30.5
Sulfur-wt. %		0.007	0.008	0.011	0.013
Smoke Point mm		13	13	13	11
Aniline Point °F.		113.7	116.7	107.6	55.8
500–650°F. Fraction-wt. %		15.2	6.9	9.5	4.4
API gravity		32.6	32.0	30.5	20.5
Sulfur-wt. %		0.039	0.045	0.071	0.085
650–850°F. Fraction-wt. %		20.8	20.8	17.7	7.7
API Gravity		28.4	27.4	24.6	19.7
Sulfur-wt. %		0.38	0.36	0.68	0.59
850–1000°F. Fraction-wt. %		20.5	—	13.5	18.3
API Gravity		22.2	—	20.7	22.0
Sulfur-wt. %		1.02	—	1.06	0.99
1000°F. + Residuum-wt. %		28.0	48.0**	30.8	33.2
API Gravity		7.8	14.8	9.4	9.8
Sulfur-wt. %		2.56	1.76	2.34	2.26
H_2 Consumption-SCF/BBL.		430	450	220	150

*includes 850–1000°F. Fraction

EXAMPLE II

This example is similar to Example I, the principal differences being that 50 percent of the catalyst is above and 50 percent below the point of feed introduction, the composition of the catalyst in the upper bed is 10 percent cobalt oxide on alumina and the composition of the catalyst in the lower bed is 3 percent nickel oxide and 13.6 percent molybdenum oxide on alumina, the charge feed rate is 0.45 w/w/hr. Hydrogen is introduced with the charge at a rate of 8800 scfb and also at the bottom of the lower catalyst bed at a rate of 13,000 scfb. Experimental data appear below:

TABLE III

Period		A	B	C	D
Temp.°F.	Upper	925	925	950	950
	Mid.	825	825	825	825
	Lower	800	800	800	800
Time on Stream-Hrs.		144	329	634	814
IBP 400°F. Fraction-wt. %		19.4	16.1	15.9	20.7
API Gravity		54.1	53.9	53.4	53.7
Sulfur-wt. %		0.010	0.03		
H.C. Type Anal.	Paraffins	41.1	41.4		
	Naphthenes	39.5	40.1		
	Aromatics	19.3	18.4		
400–500°F. Fraction-wt. %		13.1	12.4	7.1	7.2
API Gravity		36.0	35.6	32.2	34.5
Sulfur-wt. %		0.009	0.015	0.023	
Smoke Point-mm		10	10	9	11
Aniline Point °F.		102.8	98.4	64.7	75.1
500–650°F. Fraction-wt. %		13.8	12.1	7.5	10.4
API Gravity		28.6	28.0	23.0	24.9
Sulfur-wt. %		0.016	0.031	0.057	
650–850°F. Fraction-wt.%		11.3	13.1	13.4	16.8
API Gravity		23.2	23.6	22.7	
Sulfur-wt. %		0.11	0.20	0.33	
850–1000°F. Fraction-wt. %		7.1	11.8	15.6	10.5
API Gravity		21.1	22.3	22.0	20.7
Sulfur-wt. %		0.26	0.43	0.62	0.6
1000°F. + Residuum-wt.%		23.4	23.0	24.5	22.0
API Gravity		14.5	11.7	10.3	9.7
Sulfur-wt. %		0.90	1.56	1.7	1.8
H_2 Consumption SCF/BBL		200	200	210	240

These examples show that as the upper section temperatures were increased, the measured hydrogen consumption decreased from 430–450 SCF/bbl. at the lower temperatures to 220 SCF/bbl. at the 900°F. upper section temperature, and to 150 SCF/bbl. at the 950°F. upper temperature. Sulfur contents, and other properties, of the fractions boiling above 500°F. did not greatly change as the overhead temperature was raised but the lighter naphtha and kerosene fraction did show a significant response. Aromatic content of the naphtha

increased from 21.5 percent at the lowest overhead section temperature to 32.9 at the 95°F. temperature.

Obviously, various modifications of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be made as are indicated in the appended claims.

We claim:

1. A process for the conversion of a residue-containing petroleum fraction into lighter products of reduced sulfur content in which the hydrogen consumption is between 100 and 300 scfb which comprises introducing said petroleum fraction through a point of entry into a desulfurization reactor comprising a first hydrodesulfurization catalyst zone below and a second hydrodesulfurization catalyst zone above said point of entry to flow downwardly through said first catalyst zone in countercurrent flow relationship to hydrogen passing upwardly through said first catalytic zone, passing said hydrogen upwardly with volatile hydrocarbons and entrained liquids into and through said second catalyst zone and recovering said products of reduced sulfur content from the reaction effluent of said first and second catalyst zones, the temperature in said first catalyst zone being maintained between 550° and 850°F. and the temperature in said second catalyst zone being maintained between 875° and 1000°F.

2. The process of claim **1** in which the temperature of the first catalyst zone is between 700° and 850°F.

3. The process of claim **1** in which said hydrogen consumption is between 150 and 220 scfb.

4. The process of claim **1** in which hydrogen is introduced into said desulfurization reactor with said residue-containing petroleum fraction at a rate between 500 and 5,000 scfb.

5. The process of claim **1** in which said hydrogen is introduced into said first catalytic zone at a rate of at least 3,000 scfb.

6. The process of claim **5** in which hydrogen is introduced into said desulfurization reactor with said residue-containing petroleum fraction at a rate between 500 and 5000 scfb.

7. The process of claim **5** in which said hydrogen is introduced at a rate between 8,000 and 15,000 scfb.

8. The process of claim **1** in which said residue-containing petroleum fraction is a vacuum gas oil.

9. The process of claim **1** in which said residue-containing petroleum fraction is an atmospheric residuum.

10. The process of claim **1** in which said residue-containing petroleum fraction is a vacuum residuum.

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