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DESULFURIZATION OF HEAVY PETROLEUM OILS

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The present invention relates to the treatment of sulfur-containing organic materials, in particular, sulfur-bearing hydrocarbon material, to desulfurize the same. More particularly, the present invention relates to the desulfurization of sulfur-containing petroleum fractions, particularly heavy fractions as residua.

The problem of sulfur removal from petroleum fractions and crudes is as old as the petroleum industry. For most purposes it is undesirable to have an appreciable amount of sulfur in any petroleum products. Gasoline should be relatively sulfur-free to make it compatible with lead. Motor fuels containing sulfur as mercaptans are undesirable because of odor and gum formation characteristics. Sulfur is objectionable in fuel oils of any kind because it burns to form SO₂ which is obnoxious and corrosive.

Sulfur occurs in petroleum stocks generally in two main forms, as mercaptans and as part of a more or less substituted ring, of which thiophene is the prototype. The former type is generally found in the lower boiling fractions, in the naphtha, kerosene, and light gas oil material, whereas the ring-sulfur compounds form the bulk of the sulfur-bearing material of the high boiling petroleum fractions. Numerous processes for sulfur removal from relatively low molecular and lower boiling fractions have been suggested such as "doctor" sweetening, wherein mercaptans are converted to disulfides, caustic treating, solvent extraction, copper chloride treating, etc., all of which give a more or less satisfactory decrease in sulfur or inactivation of mercaptans by their conversion into disulfides. The latter remain in the treated product, and must be removed if it is desired to obtain a sulfur-free product.

Sulfur removal from higher boiling fractions however, has been a much more difficult operation. As pointed out, here the sulfur is present for the most part, as a part of a ring. Such sulfur is, of course, not susceptible to chemical operations satisfactory with mercaptan sulfur. Also, extraction processes are unsatisfactory, for solvents specific for sulfur compounds, for instance, boron fluoride complexes or liquid hydrogen fluoride-boron fluoride mixtures, or liquid SO₂, no longer are of much use when possibly every molecule of the oil contains a sulfur ring. Thus, a high boiling product, such as a residuum that contains about 3% of sulfur is estimated to consist extensively of molecules containing sulfur, and so extraction of sulfur-containing material is no longer feasible, inasmuch as the bulk of the extracted material is in the extract and

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lost, unless a means is present for removing sulfur from this extract.

One satisfactory method for removing sulfur from products wherein it is present as a ring type compound, has been by hydrogenation in the presence of a so-called sulfactive catalyst. Thus, it has been found that certain catalysts, such as cobalt molybdate, tungsten sulfide, nickel sulfide, molybdenum sulfide, etc., are good hydrogenation catalysts and that when these catalyst substances are employed in the hydrogenation of petroleum stocks containing sulfur, these catalysts are not poisoned by sulfur, but on the contrary, tend to reduce the sulfur content of the material being hydrogenated, the sulfur being removed as H₂S. However, though this process is quite satisfactory for the hydrogenation, or hydrodesulfurization of low and medium boiling petroleum fractions, the process is completely unsatisfactory for sulfur removal from high boiling stocks, such as cycle stock and residua. The latter, which are the bottoms product after the 1050° F. gas oil is taken overhead, are notorious carbonizers. When they are passed over a fixed bed of a sulfactive catalyst of the type described above in order to remove a portion of the sulfur content by catalytic hydrodesulfurization, carbonization of the catalyst proceeds at once, and in an extremely short time, the catalyst is covered by deposition of carbonaceous material and is inactivated. Regeneration is expensive, and since the period of activity is so short, it is economically unfeasible to operate with such a process.

It is, therefore, an object of the present invention to provide an improved method of desulfurizing sulfur-bearing organic hydrocarbon material, in particular desulfurizing high boiling stocks such as residua.

A further object of the invention is to provide an improved means of refining petroleum fractions to separate therefrom, sulfur and undesirable sulfur compounds.

A still further object of the present invention is to provide a cheap method for upgrading heavy stocks such as residua.

A still further object of the present invention is to disclose a novel means of hydrodesulfurizing in the absence of a fixed catalyst bed whereby inactivation of catalyst is substantially avoided.

Other objects and advantages of the present invention will become apparent from the following description, read in conjunction with the accompanying drawing describing one embodiment of the present invention.

It has now been found that these objects and advantages may be realized by subjecting sulfur-containing high boiling hydrocarbon material, such as reduced crudes and residua, to a hydrodesulfurization reaction employing, instead of a fixed catalyst bed, a homogeneous catalyst which is not fouled and inactivated by the large quantities of asphaltenes and ash present in such so-called "dirty" feed stocks, thereby making it possible to dispense with the expensive and easily fouled heterogeneous catalysts, such as molybdenum sulfide, tungsten sulfide, etc.

By a homogeneous catalyst system is meant a system wherein the catalyst is always presenting a fresh "surface" to the reactants, i. e., any system having a self-generating surface. Thus, such a system is realized when the catalyst is miscible in the material being treated, or it is completely dispersed therethrough, and reaction products being precipitated, fresh surface is constantly provided.

It has now been found that boron halide complexes are particularly useful as homogeneous catalysts in reducing the sulfur content of reduced crudes and residua in the presence of hydrogen, and in upgrading such residua. Residua are of little commercial value per se, because of their high coking characteristics and sulfur content, and because of their high ash and asphaltene content. In accordance with the present invention, they may readily and economically be converted into useful products, such as feed stock for catalytic cracking, or for bunker and marine fuel, neither of which can tolerate high sulfur content.

It is, of course, known to the art to treat sulfur-containing oil stocks with boron fluoride complexes, in order to extract or precipitate sulfur-containing molecules from non-sulfur bearing product. But, as has been pointed out, though this is quite feasible where the sulfur molecules are a relatively small fraction of the total number of molecules, it is no longer feasible when the bulk of the molecules contain ring-bound sulfur atoms. Similarly, though "treating" a hydrocarbon feed stock with a boron fluoride to remove sulfur is known, this also is but a form of selective extraction of sulfur-containing hydrocarbon molecules, and is not feasible in the case of, say, reduced crudes and residua, wherein the sulfur content may be as high as 6%, corresponding to a mixture wherein the vast bulk of the molecules contain sulfur and are, of course, of high molecular weight.

In accordance with the invention, high boiling high molecular weight petroleum fractions, particularly reduced crudes and residua, are treated in a hydrogenation zone with hydrogen at pressures from about 500-5000 p. s. i. g. and temperatures of 300°-900° F., though preferably below 800° F., in the presence of one of the halides of boron, particularly boron fluoride-alcohol complexes, boron fluoride-ether complexes, boron fluoride-water complexes, etc. Boron fluoride may be employed in the ratio of 100 to 2.5 parts hydrocarbon feed per part boron fluoride, and the complexing material may be present in the ratio of 0.25 to 6 parts boron fluoride per part complexing compound.

The boron fluoride complex is readily prepared by bubbling an excess of boron fluoride through the complexing material, such as water, at about 35 to 100° F. until a stoichiometric amount has been absorbed, and then subjecting the mix-

ture to reduced pressure to remove the excess boron fluoride.

The invention will best be understood when read in conjunction with the accompanying drawing, which is a diagrammatic representation of a preferred embodiment of the present invention.

Turning now to the figure, wherein is shown a procedure for hydrodesulfurizing and upgrading a heavy residuum, such as Kuwait bottoms, in the presence of a boron-fluoride-water complex catalyst, the petroleum stock is introduced through lines 2 and 6 into reactor 10, together with catalyst either from storage through lines 4 and 6, or in part from recycled catalyst as shown. The mixture is contacted countercurrently with a hydrogen-containing gas introduced through line 8. The hydrogenator 10 is suitably a packed tower, though other known means of obtaining intimate contact between liquids and gases may be employed.

Within vessel 10 there is maintained a pressure of from about 500 to 5000 p. s. i. g., depending upon the nature of the material being treated, and temperatures in the range of 300° to 900° F. may be employed, though temperatures under 800° F. are preferred since above 800° F. cracking occurs to a certain extent. The quantity of complex used may vary from 5 to 50% by weight of the feed, and the ratio of boron fluoride to the complex-forming material may be in the range of 0.25 to 6. The latter ratio depends considerably upon the molecular weight of the complexing material. Mol ratios of boron fluoride to complexing materials of 1/1 and 2/1 and 0.5/1 are preferred. The feed rates of 0.25 to 4 v./v./hr. may be employed, together with hydrogen feed rates of about 500 to 5000 standard cubic feet per barrel of liquid feed. Though commercial hydrogen is preferable, even hydrogen containing appreciable quantities of carbon monoxide may be employed.

Product streams containing in suspension considerable amounts of carbonaceous solids, asphaltenes, ash, etc., as well as boron fluoride distributed both through the liquid and the solid residue, is withdrawn from the reactor 10 through lines 12 and passed to settling vessels 14, wherein sludge and carbonaceous solids are allowed to settle. Liquid product is drawn off through lines 28 and passed via line 30 to water scrubber 32, wherein boron fluoride dissolved or dispersed in the liquid is recovered for recycle to the process via lines 34, catalyst concentrator 36, and line 40.

Catalyst dispersed in the solid residue may advantageously be recovered by treating the solid with HF introduced through line 16. The volatilized boron fluoride is withdrawn overhead through line 18 and passed through lines 20, 5 and 6, back to the reactor.

The overhead from reactor 10, which may contain, besides hydrogen, also a certain amount of liquid hydrocarbons occurring as a result of cracking, and also, gases such as H₂S and a small amount of boron fluoride, may be passed to separator 24. Overhead therefrom, gas may be withdrawn and, if desired, recycled via lines 26 and 8 to the reactor. Any known means for removing H₂S from this gas stream may be employed, when it is desired to free recycle gases from this material.

Liquid product from separator 24 may be withdrawn through line 26 and passed to scrubber 32, wherein it is combined with the main liquid

fraction. The scrubbed oil is passed via line 42 to fractionating system 44 equipped with suitable heating means. Overhead through line 46, there is recovered a substantially sulfur-free naphtha, while through line 48 there are withdrawn gas and heating oils with very low sulfur content. Residue is withdrawn through line 49, and this may be recovered as such, as when it is desired to recover bunker fuel, or it may be recycled in part or in total to the process via line 52.

Make-up boron fluoride or water or both, may be introduced as needed through line 4. Coke free of boron halide may be withdrawn from settlers 14 through line 17.

The above description and exemplary operation admit of many variations obvious to those skilled in the art. Thus, the catalyst, instead of being the fluoride of boron, may be another halide. Recovery of boron fluoride from the deposited solids need not take place in the settler, but may take place in auxiliary vessels. Under certain circumstances it may be desirable to pretreat the residua or reduced crude with hydrogen in the absence of a catalyst prior to homogeneously catalytically hydrodesulfurizing the same; appreciable reduction in amount of catalyst required may sometimes thus be realized. Furthermore, though the present invention has its greatest area of utility in upgrading reduced crudes and residua, boron halide catalyzed hydrodesulfurizing is advantageously employed in desulfurizing and upgrading other materials, such as gas oils, cycle oils, and heating oils, particularly these boiling above about 650° F.

The effectiveness of the boron fluoride complex as a homogeneous catalytic agent in the hydrodesulfurizing of heavy feed stocks is clearly demonstrated by the following data showing the results obtained when a $\text{BF}_3\text{-H}_2\text{O}$ complex was employed in desulfurizing a 78% Kuwait residuum in bottoms fractions.

Hydrodesulfurizing of 78% Kuwait bottoms

Run	Feed	A	B
Catalyst.....		None	$\text{BF}_3/\text{H}_2\text{O}$
Wt. Ratio, $\text{BF}_3/\text{H}_2\text{O}$			2/1
Wt. Percent Catalyst, On Feed.....			30
Added Gas.....		H_2	H_2
Pressure, p. s. i. g.....		2,000	2,000
Temperature, °F.....		750	750
Sulfur, Wt. Percent.....	3.07	2.23	0.45
Desulfurization, Wt. Percent.....		27.3	85.5
Product Distribution:			
Naphtha, 400° F—			
Wt. Percent of product.....	0	20.5	14.4
Wt. Percent sulfur.....		0.11	0.04
Gas Oil, 850° F. (600° F. @ 3 mm.)—			
Wt. Percent of product.....	50.2	60.8	80.8
Wt. Percent of sulfur.....	1.70	2.08	0.45
Gas Oil Bottoms—			
Wt. Percent product.....	49.8	18.7	4.8
Wt. Percent sulfur.....	4.41	5.04	1.67

It will be noted that not only is the sulfur reduction extremely large, but also, the product, as a result of the treatment in accordance with the present invention, has been upgraded into a form readily utilizable as feed to the catalytic cracking process.

While the foregoing description and exemplary

operations have served to illustrate specific applications and results, the invention is not limited thereto. Other modifications may appear to those skilled in the art without departing from the spirit of the invention.

What is claimed is:

1. The process of desulfurizing and upgrading sulfur-containing petroleum residua which comprises converting said residua into a product of lower boiling range, which product contains a major proportion of gas oil and a minor proportion of naphtha, and at the same time removing the major proportion of the sulfur contained in the said residua by contacting said residua feed in a hydrogenation zone with hydrogen in the presence of a catalyst comprising a boron fluoride addition product represented by the formula BX_3Y , where X is a halide, and Y is an oxygenated material selected from the group consisting of water, alcohols, and ethers in which the ratio of BX_3 to Y is from 0.5 to 1 to 2 to 1, maintaining within said zone reaction conditions of temperature pressure and through-put rates avoiding substantial cracking to products boiling in the naphtha range maintaining within said zone a pressure in the range of 500–5000 p. s. i. g. and a temperature in the range of 300°–900° F., maintaining a feed rate of 0.25 to 4 v./v./hr. and recovering a product containing substantially less sulfur than said feed.

2. The process of claim 1 wherein said temperature is below about 800° F.

3. The process of claim 1 wherein said pressure is about 2000 p. s. i. g.

4. The process of claim 1 wherein said compound is represented by the formula $2\text{BF}_3\cdot 1\text{H}_2\text{O}$.

5. The process of claim 1 wherein said feed is contacted with hydrogen and partially desulfurized prior to catalytic hydrodesulfurization.

6. The process of claim 1 wherein said additional product and said feed form substantially a single phase.

7. The process of claim 1 wherein said catalyst is added to the extent of about 5 to 50% by weight as boron fluoride on the feed.

8. An improved process for preparing feed stock for a catalytic cracking process from high sulfur petroleum residua, which comprises contacting said residua feed in a hydrogenation zone with hydrogen under conditions avoiding substantial cracking of said feed to naphtha, maintaining within said zone elevated pressures, a temperature above about 300° F., but less than about 800° F., a feed rate sufficient to avoid substantial cracking of said residua, contacting said residua with a homogeneous hydrosulfurization catalyst comprising an addition product of boron fluoride and water, and recovering a catalytic cracking feed stock containing substantially less sulfur than said initial feed.

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References Cited in the file of this patent

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