

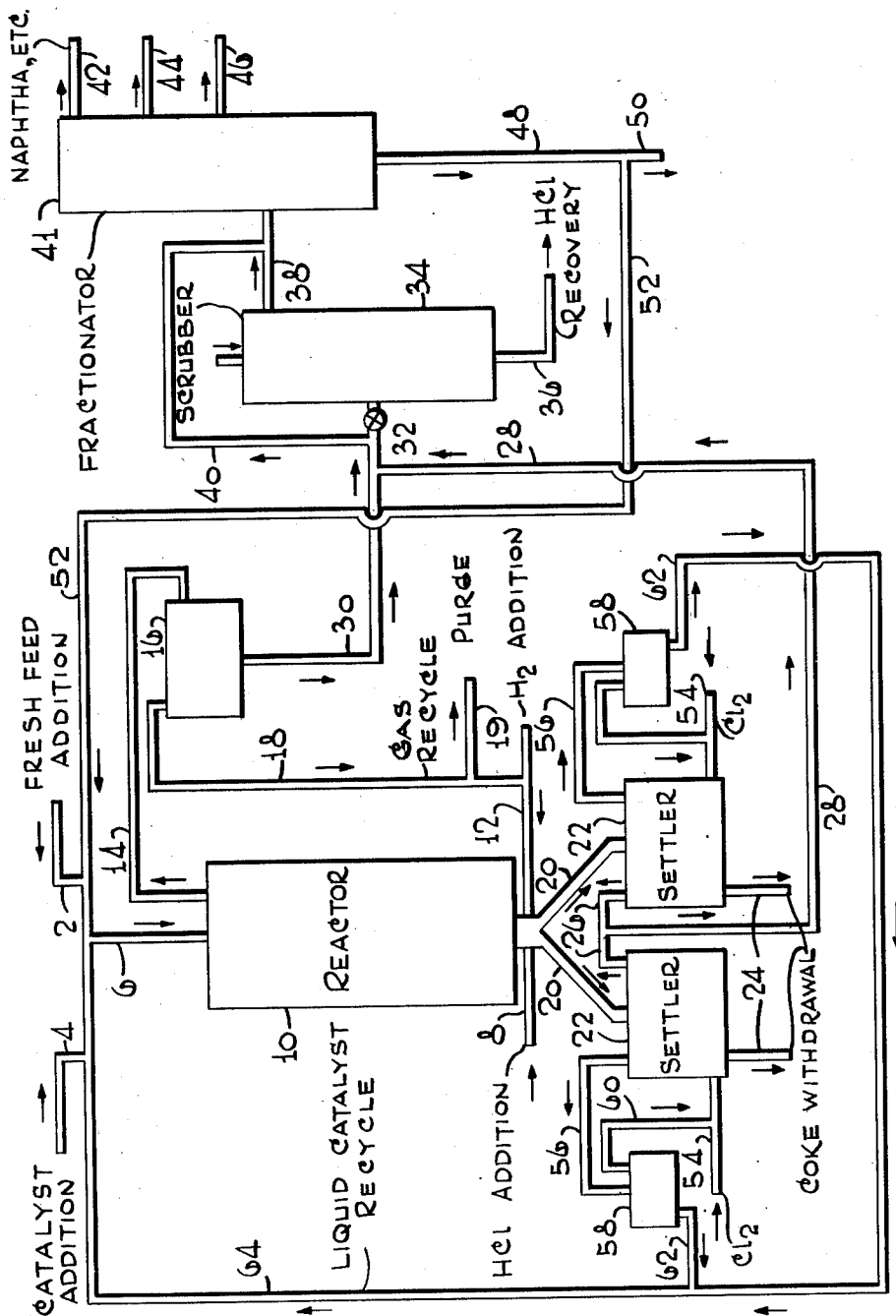
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DESULFURIZATION OF HEAVY PETROLEUM OILS

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DESULFURIZATION OF HEAVY
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1

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, such as residua and reduced crudes.

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 SO_2 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, or liquid SO_2 , 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

2

is no longer feasible, inasmuch as the bulk of the extracted material is in the extract and 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 catalyst, 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 H_2S . However, though this process is quite satisfactory for the hydrogenation, or hydrosulfurization 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 hydrosulfurization, 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 hydrosulfurizing 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 follow-

ing 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., a system having a self-generating surface. Such a system is fully realized when the catalyst is completely miscible in the material being treated, and to a less extent when the catalyst is completely dispersed therethrough and the reaction products comprise a separate phase; reaction product precipitating, fresh surface is constantly provided.

It has now been found that the higher valent halides of the amphoteric metals, in particular, stannic chloride and titanium tetrachloride, are particularly useful as homogeneous catalysts in reducing the sulfur content of reduced crudes and residua in the presence of hydrogen. Residua have little commercial value, because of their high coking characteristics and sulfur content, besides containing large amounts of ash and asphaltenes. In accordance with the present invention, residua and reduced crudes may be readily and economically converted into useful products, such as feed stock for catalytic cracking, or for bunker and marine fuel, none of which products can tolerate high sulfur content.

It is known in the art to treat sulfur-containing oil stocks with salts of heavy metals to polymerize olefinic material and to precipitate asphaltenes. This treatment cannot, however, remove sulfur when the sulfur is firmly attached to the ring of the oil molecule, and these sulfur-containing molecules comprise substantially the whole of the oil being treated, as where a reduced crude, for example, contains 3% or more of sulfur; this corresponds to a mixture wherein the vast bulk of the molecules contain sulfur and are, of course, of high molecular weight.

The halides of tin and titanium are excellent homogeneous catalysts for the hydrodesulfurization of these heavy stocks, because such halides are to a considerable extent, soluble in the hydrocarbon as a result of the hydrogenation, the solid sulfides are formed which do not inactivate the catalyst as they would tend to if the latter were a solid, by forming a coat of the respective sulfide about the catalyst. The catalyst is readily regeneratable from the reaction products and may be re-used.

It has further been found that the activity of these homogeneous hydrodesulfurization catalysts may be substantially enhanced and promoted by carrying out the hydrodesulfurization in the presence of a hydro-halide, such as HCl.

In accordance with the present 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 100-5000 p. s. i. g. and at temperatures in the range of 300°-900° F., preferably between 400° and 800° F. in the presence of tin or titanium tetrachloride, and prefer-

ably, though not of necessity, in the further presence of a hydrogen halide promoter such as HCl.

Because the liquid catalyst is dissolved in and dispersed through the sulfur-containing feed, the deposition of carbonaceous solids, as asphaltenes, and of ash, does not inactivate the catalyst as a fixed catalyst bed of sulfactive catalyst would have been inactivated.

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 invention.

Turning now to the figure, wherein there is shown diagrammatically, a procedure for hydrodesulfurizing and upgrading a heavy residuum, such as Kuwait bottoms in the presence of the liquid catalyst of the present invention, 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 or regenerated catalyst, as shown hereinafter. The liquid mixture is contacted counter-currently with a hydrogen-containing gas introduced through line 12. 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 100 to 5000 p. s. i. g., preferably 1500 to 3000 p. s. i. g., depending upon the nature of the material being treated, and temperatures in the range of 300° to 900° F., preferably between 400°-800° F. are employed. Feed rates of 0.25 to 4 v./v./hr. may be used, together with hydrogen feed rates of about 500 to 5000 standard cubic feet per barrel of liquid feed. Though commercial hydrogen is to be preferred, even hydrogen containing appreciable amounts of CO may be used.

The amount of catalyst employed in the hydrogenation may vary from 2 to 20% by weight on the feed, depending in part upon the amount of promoter, if any, added to the reaction system. In accordance with the present invention, hydrogen chloride is introduced into reactor 10 through line 8. This material is most effective in promoting the hydrodesulfurization reaction within 10, and may be added continuously or intermittently to the extent of 1 to 15% by weight of the hydrocarbon feed.

Product streams containing in suspension, considerable amounts of carbonaceous solids, asphaltenes, ash, as well as precipitated metal sulfides, and catalyst metal compounds distributed both through the liquid and the solid residue, are withdrawn from reactor 10 through lines 20 and passed to settling vessels 22, wherein sludge and solids are allowed to settle. Liquid products are drawn off through lines 26 and 28 and may, if desired, be passed to scrubber 34, via line 32. In scrubber 34, the product may be scrubbed with an alkaline material, as dilute caustic, etc. to remove residual HCl. If desired, however, liquid product may by-pass scrubber 34 by by-pass line 40, and pass directly to fractionator 41. Overhead there is recovered through line 42, a substantially sulfur-free naphtha, while through lines 44 and 46, low sulfur gas and heating oils may be withdrawn. Residue is withdrawn through line 48; and this may be recovered as such, as when it is desired to recover bunker fuel, or it may be recycled in part or as a whole to the process via line 52.

Returning to hydrogenator 10, gaseous products comprising unreacted hydrogen, HCl, H₂S, and some hydrocarbon liquids and gases result.

ing from decomposition within the reaction zone, of petroleum stock feed, may be passed overhead and, after cooling (not shown) passed via line 14 to separator 16. The liquid condensate may be withdrawn through line 30 and be added to the hydrodesulfurized liquid product in scrubber 34. The gaseous portion may be withdrawn from separator 16 through line 18. A portion may, if desired, be purged to prevent accumulation of inert gases and H_2S , the inert gases resulting from product decomposition and cracking. The balance of the gas may be recycled to

Furthermore, though the present invention finds its greatest utility in upgrading reduced crudes and residua, the invention may also be employed in the upgrading and desulfurizing of other material, such as shale oil, petrolatum, etc., in particular, those boiling above about $650^\circ F$.

The effectiveness of the halides of tin and titanium as homogeneous catalytic agents in the hydrodesulfurizing of heavy feed stocks is clearly demonstrated in the following example. The material desulfurized was a 78% Kuwait bottoms fraction.

Hydrodesulfurizing of 78% Kuwait bottoms

Run	Feed	A	B	C	D	E	F
Catalyst		None	$SnCl_4$	$SnCl_4$	$TiCl_4$	$SnCl_2$	$SnCl_2$
Wt. Percent Catalyst			5	5	10	5	5
Wt. Percent HCl promoter			0	0	6	0	6
Added Gas		H_2	H_2	H_2	H_2	H_2	H_2
Pressure, p. s. i. g.		2,000	2,000	2,000	2,000	2,000	2,000
Temperature		750	750	750	750	750	750
Sulfur, Wt. Percent	3.07	2.23	1.36	1.0	0.79	1.59	1.36
Desulfurization, Wt. Percent		27.3	56	67.5	74	48.2	55.7
Product Distribution:							
Naphtha, $400^\circ F$ —							
Wt. Percent of product	0	20.5	3.2	3.5	6.2	1.5	1.7
Gravity, $^\circ API$			72.4	69.8	69.8	72.1	69.2
Sulfur, Wt. Percent		0.11	0.07	0.06	0.21	0.10	0.07
Gas Oil, $850^\circ F$ —							
Wt. Percent of product	50.2	60.8	76.9	81.3	84.7	75.0	77.4
Gravity, $^\circ API$	32.1		33.5	32.7	34.8	32.9	33.1
Sulfur, Wt. Percent	1.70	2.08	1.20	0.83	0.72	1.33	1.21
Gas Oil Bottoms—							
Wt. Percent of product	49.8	18.7	19.9	15.2	9.1	23.5	20.9
Sulfur, Wt. Percent	4.41	5.04	2.22	2.14	1.8	2.49	2.07

reactor 10, with or without prior removal of H_2S by any conventional method.

The settled solids in settlers 22, which consist in large proportions of tin or titanium sulfide, as well as Sn or Ti compounds dispersed or occluded in the carbonaceous solids and ash, are advantageously treated with a halogen, preferably chlorine, to recover the catalyst. This may advantageously be accomplished by injecting Cl_2 through lines 54 into settlers 22. As a result of the ensuing reaction, preferably aided by a suitable heating process, the sulfides, etc. are reconverted into the respective high valent halides. The regenerated catalyst and unreacted chlorine may be withdrawn overhead from 22 via line 56 and, after cooling, allowed to separate into a liquid and gas phase respectively in separators 58. The chlorine may be recycled for further conversion in settlers 22, while the liquid $SnCl_4$ or $TiCl_4$ may be passed downwardly through line 62, and thence through lines 64 and 6, back to the reaction system.

The above description and exemplary operation admit of many variations obvious to those skilled in the art. Thus, mention has not been made of various accessory equipment which normally would be used in a commercial plant. Thus, in the interest of good heat economy, various heat exchangers and economizers would be employed to utilize whatever heat is available in the most efficient manner and, in order to control the process, pumps, compressors, agitators, valves, flow meters, etc., would be included in the equipment. Also, it may be desirable to withdraw coke and precipitated sulfides from settlers 22 and to treat the solids for catalyst recovery in suitable auxiliary equipment. Under certain circumstances it may be desirable to pretreat the residua or reduced crude with hydrogen in the absence of a catalyst or promoter prior to homogeneously catalytically hydrodesulfurizing the same; appreciable reduction in amount of catalyst required may sometimes thus be realized.

The above data clearly show the effective desulfurization to be obtained by the use of stannic or titanium tetrachloride in accordance with the hydrodesulfurization process of the present invention. It will be noted that the beneficial effects of the metal halides, are considerably enhanced by the addition of the hydrogen halide promoter. Even stannous chloride which, being a solid, and thus not a homogeneous catalyst and which did not show particularly high desulfurization characteristics, had its efficiency enhanced by the presence of added HCl promoter.

It is also of interest to note that the bottoms 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, and that the halides themselves, particularly when promoted with HCl, show good cracking characteristics, as shown by the increased yields of the distillate fractions when HCl is employed. Furthermore, it will also be noted that desulfurization in the lower boiling fractions resulting from the treatment is practically complete.

While the foregoing description and exemplary operations have served to illustrate specific applications and results of the invention, it is not limited thereto. Other modifications obvious to those skilled in the art are within its scope.

What is claimed is:

1. The process of desulfurizing and upgrading sulfur-containing petroleum residua which comprises contacting said residua feed in a hydrogenation zone with hydrogen in the presence of a catalyst comprising the tetrachloride of a metal selected from the group consisting of tin and titanium, maintaining within said zone, a pressure in the range of 100 to 5000 p. s. i. g. and a temperature in the range of 300° – $900^\circ F$, and recovering a hydrocarbon product containing substantially less sulfur than said feed.

2. The process of claim 1 wherein a hydrogen halide promoter is added to said hydrogenation zone.

7

3. The process of claim 2 wherein said promoter is HCl.
4. The process of claim 1 wherein said catalyst is SnCl_4 .
5. The process of claim 1 wherein said catalyst is TiCl_4 .
6. The process of claim 1 wherein said catalyst and said feed form substantially a single phase.
7. The process of claim 1 wherein 2 to 20% by weight of catalyst is added to said zone.
8. The process of claim 1 wherein said feed is contacted with hydrogen and partially desulfurized before addition of catalyst to said zone.
9. The process of desulfurizing and upgrading sulfur-containing petroleum residua which comprises contacting said residua feed in a hydrogenation zone with hydrogen in the presence of a catalyst comprising the tetrachloride of a metal selected from the group consisting of tin and titanium, maintaining within said zone a pressure in the range of 100-5000 p. s. i. g. and a temper-

8

ature in the range of 300°-900° F., adding 1 to about 15% of HCl promoter based on petroleum feed to said zone, and recovering a hydrocarbon product containing substantially less sulfur than said feed.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,814,410	Richter et al.	July 14, 1931

FOREIGN PATENTS

Number	Country	Date
3,318	Great Britain	1873
421,858	Germany	Nov. 19, 1925

OTHER REFERENCES

20. Torossian, Ind. and Eng. Chem., vol. 13, p. 903, Oct. 1921.