

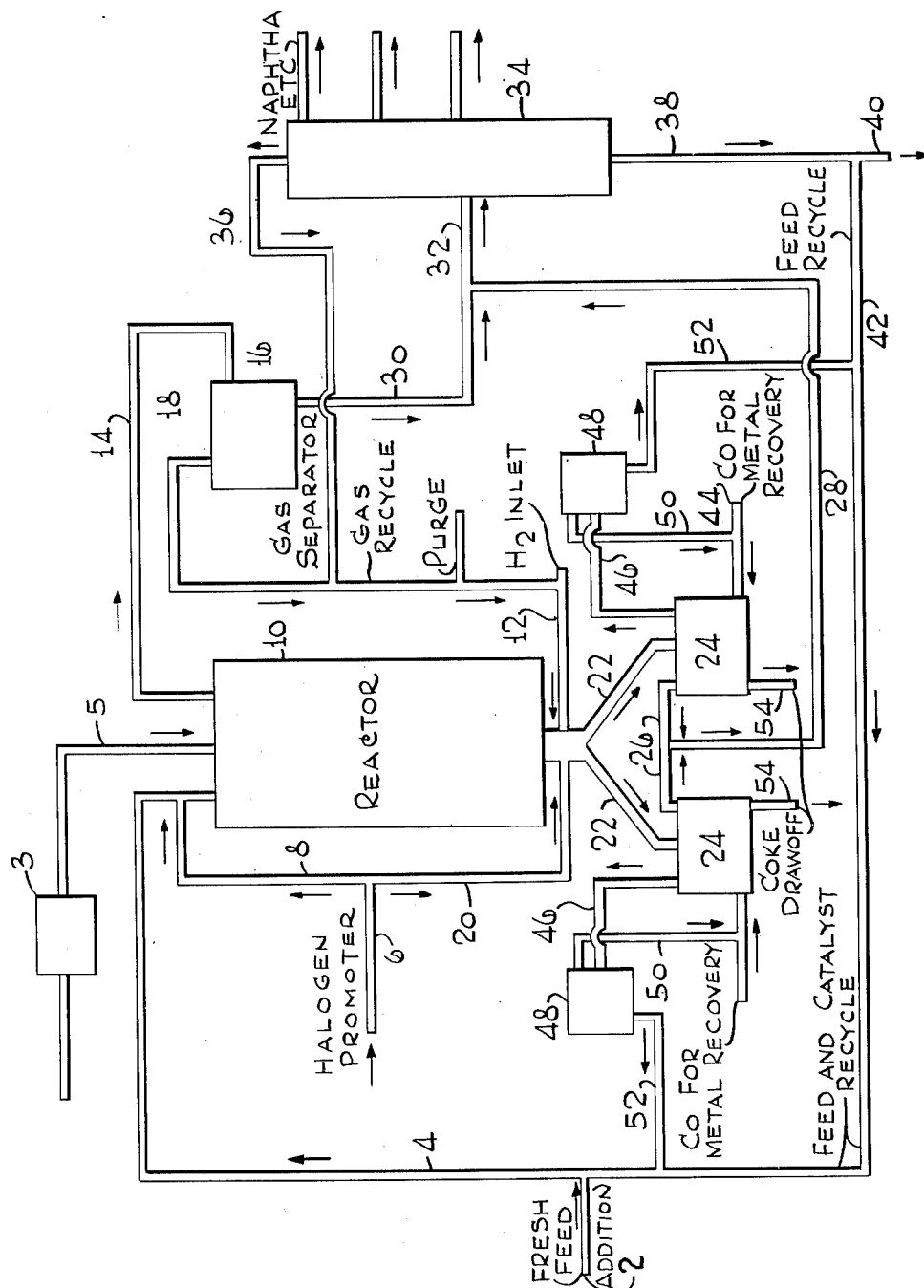
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DESULFURIZATION OF HEAVY PETROLEUM OILS

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DESULFURIZATION OF HEAVY
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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 reduced crudes and 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, and decreased sulfur content means increased lead susceptibility. 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 problem and 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 which are satisfactory with mercaptan sulfur. Also, extraction processes are unsatisfactory, for solvents specific for sulfur compounds, such as, for instance, boron fluoride complexes, or liquid hydrogen fluoride-boron fluoride mixtures, or liquid SO_2 , no longer are of much

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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 almost entirely, 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 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 H_2S . 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, reduced crudes 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 and reduced crudes.

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 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 hydrosulfurization 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 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. Such a system is most readily realized, of course, when the catalyst is completely miscible in the material being treated. Thus, solid reaction products, formed as a result of the catalytic treatment, would exist in a separate phase, and can not inactivate such catalyst by forming a layer or surface coating, as is the case in heterogeneous catalysis.

It has now been found that suitably promoted iron group metal carbonyls, such as $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_8$, $\text{Fe}(\text{CO})_5$, etc. are particularly useful and desirable as homogeneous catalysts in reducing the sulfur content of reduced crudes and residua and upgrading such residua. Petroleum residua, which is the term generally applied to the bottoms product after petroleum stock has been topped and the gas oil removed, i. e., that fraction boiling above 650°F . at atmospheric pressure, are of little value per se, because of their high content of sulfur, ash, and asphaltenes, and their tendency to coke on heating. 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, none of which uses can tolerate high sulfur content.

In accordance with the present invention, high boiling high molecular weight petroleum fractions, such as reduced crudes and residua, are treated in a hydrogenation zone with hydrogen at pressures from about 500-5000 p. s. i. g. and at temperatures of about $300^\circ\text{--}900^\circ\text{F}$., though preferably below 800°F ., in the presence of a carbonyl of a metal of the iron group, preferably promoted with a halogen or a hydro-halide promoter. Suitable are chlorine, bromine, iodine, and the corresponding hydro-halides. The catalyst may be present up to 30% of the feed, preferably 5 to 20% by weight, while the promoter may be added in amounts of from 0.5 to 5% by weight of the petroleum feed.

The employment of the promoted carbonyls is particularly advantageous, for not only are the metal carbonyls completely miscible in the feed stock, but also, one may employ for the hydrogenation, a gas containing substantial amounts of carbon monoxide. Commercial hydrogen contains small amounts of carbon monoxide, and the

cheap and readily available hydrocarbon synthesis gas consisting of 1 to 2 parts H_2 per part CO is particularly suited to this purpose, because not only does the relatively high CO partial pressure tend to keep the metal carbonyl from decomposing, but also, decomposed metal or metal sulfide will be reconverted into the carbonyl in situ.

Metal carbonyl is readily prepared by passing a carbon monoxide-containing gas over or through a solid or liquid dispersion or solution of the metal or metal compound.

The invention will be best 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 is shown diagrammatically a procedure for hydrosulfurizing and upgrading a heavy residuum, such as Kuwait bottoms, in the presence of a nickel carbonyl catalyst promoted with iodine, the petroleum stock is pumped through lines 2 and 4 into hydrosulfurization reactor 10, preferably after preheating the stock to make pumping feasible. Nickel carbonyl, prepared in any convenient manner, is passed from storage 3 via line 5 to reactor 10. Likewise, the halogen promoter, such as iodine, dissolved, if desired, in a small amount of hydrocarbon solvent, is introduced into reactor 10 via lines 8 and 20. The mixture is contacted countercurrently with a hydrogen-containing gas introduced through line 12. The gas may be either commercial hydrogen or one containing substantial quantities of CO , such as 1/1 H_2/CO hydrocarbon synthesis gas. Hydrogenator 10 is suitably a packed tower, though other means of obtaining intimate contact between liquids and gases may be employed.

Within vessel 10 there is maintained a pressure from about 500 to 5000 p. s. i. g., preferably 1500 to 3000 p. s. i. g., depending in part, upon the nature of the material being treated, and temperatures in the range of $300^\circ\text{--}900^\circ\text{F}$. may be employed, though temperatures under 800°F . are preferred since above 800°F ., cracking is favored. The essence of desulfurizing ring type sulfur molecules involves, probably, fracture of the molecule, and thus, some cracking will occur regardless of temperature.

The amount of catalyst is preferably 10 to 20% by weight of the feed, and the promoter is added preferably to the extent of 1 to 2% by weight of the hydrocarbon feed. Feed rates (liquid), of 0.25 to 4 V./V./hr. may be employed, in conjunction with hydrogen feed rates of about 500 to 2500 standard cubic feet per barrel. Hydrogen consumption is generally low, inasmuch as it is consumed for the most part, in the conversion of the sulfur to H_2S .

Product streams containing in suspension, considerable amounts of carbonaceous solids, asphaltenes, ash, nickel sulfide, etc. as well as $\text{Ni}(\text{CO})_4$ and I_2 distributed both through the liquid and the solids residue, is withdrawn from reactor 10 through lines 22 and conveyed to settling vessels 24, wherein sludge and coke, etc., are allowed to settle. Liquid product is drawn off through lines 26 and passed via lines 28 and 32 to fractionating equipment 34 equipped with suitable heating means. Overhead is recovered dissolved nickel carbonyl and iodine, and these volatilized materials are preferably recycled via lines 36 and 18 to the hydrogenation stage. After the removal of the catalytic constituents, fractionation may proceed at atmospheric or reduced pressures, and suitable fractions, as

naphtha, gas oil, heating oil, etc., may be withdrawn and recovered, all in a manner known per

amount of I_2 was employed in desulfurizing a 78% Kuwait residuum bottoms fraction.

Hydrodesulfurizing of 78% Kuwait bottoms

Run.....	Feed	A	B	C	D
Catalyst.....		None	$Ni(CO)_4$	$Ni(CO)_4$	$Ni(CO)_4$
Wt. Percent Catalyst.....			10	20	20
Wt. Percent I_2 promoter.....			0	2	2
Added Gas.....		H_2	$1/1 H_2/CO$	$1/1 H_2/CO$	H_2
Pressure, p. s. i. g.....		2,000	2,000	2,000	2,000
Temperature, °F.....		750	750	750	750
Sulfur, Wt. Percent.....	3.07	2.23	2.2	0.89	0.44
Desulfurization, Wt. Percent.....		27.3	27	71.0	85.9
Product Distribution:					
Naphtha, 400° F.—					
Wt. Percent of product.....	0	20.5	7.3	8.4	4.6
Wt. Percent sulfur.....		0.11	0	0.04	0.05
Gas Oil, 850° F.—					
Wt. Percent of product.....	50.2	60.8	63.6	85.9	83.0
Wt. Percent sulfur.....	1.70	2.08	1.61	0.87	0.37
Gas Oil Bottoms—					
Wt. Percent of product.....	49.8	18.7	29.1	5.7	12.4
Wt. Percent sulfur.....	4.41	5.04	4.07	2.64	1.03

se, all these fractions having very low sulfur content. Residue may be withdrawn through line 38 and this may be recovered as such, as when a low sulfur bunker fuel is required, or it may be recycled in part or in toto to the process' via line 42.

Returning to reactor 10, overhead there is withdrawn through line 14 a gaseous mixture comprising hydrogen, oxides of carbon, nickel carbonyl, H_2S , iodine, hydrocarbon gases and low boiling liquids formed as a result of ring rupture, etc. After cooling (not shown), the overhead product may be passed to a gas-liquid separation zone 16. Overhead gas stream may be recycled through line 18 to hydrogenator 10 while liquid product, comprising hydrocarbons and probably some dissolved $Ni(CO)_4$ and I_2 , may be passed via lines 30 and 32 to the fractionation zone for separation of catalyst and recovery of product.

After withdrawal of the oil product streams from settlers 24, it may be desirable to recover catalyst and promoter from the solid residue. Accordingly, a carbon monoxide-containing gas, which may be synthesis gas, is passed into 24 through lines 44. Suitable conditions for good $Ni(CO)_4$ recovery within settler 24 are temperatures of about 300° F. and pressures of about 2000 p. s. i. g. The volatilized carbonyl and iodine are withdrawn upwardly through lines 46, passed into separator 48, and the excess CO recycled to the settler via line 50. The recovered catalyst and promoter are withdrawn through line 52 and preferably recycled to the catalyst system via lines 42 and 4, together with the recycle feed. Coke and ash may be withdrawn through lines 54 for further processing.

The above description and exemplary operation admits of numerous variations obvious to those skilled in the art. Thus, under certain circumstances it may be desirable to pretreat the reduced crude or residua with hydrogen in the absence of catalyst prior to the homogeneous desulfurizing process; appreciable reduction in catalyst and promoter requirements may be realized.

The effectiveness of the halogen promoted metal carbonyl catalyzed hydrosulfurizing of heavy feed stocks is clearly demonstrated by the following autoclave data showing results obtained when $Ni(CO)_4$ promoted with a small

It will be noted that not only is the sulfur reduction exceptionally high, but also, the product, as a result of the hydrodesulfurizing treatment in accordance with the present invention, has been upgraded into a form readily utilizable as feed to the catalytic cracking process or as a marine fuel, (gas oil bottoms).

While the foregoing description and exemplary operations have served to illustrate specific applications and results of the invention, the latter is not limited thereto, and other modifications which may appear to those skilled in the art are within its scope.

What is claimed is:

1. The process of desulfurizing and upgrading sulfur-containing high boiling petroleum fractions which comprises contacting said fractions in a hydrogenation zone with a hydrogen-containing gas in the presence of an iron group metal carbonyl catalyst and a halogen promoter, maintaining within said zone, a pressure in the range of about 500-5000 p. s. i. g. and a temperature in the range of about 300°-900° F. and recovering a product containing substantially less sulfur than said first-named fraction.

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

3. The process of claim 1 wherein said petroleum fraction is a petroleum residuum.

4. The process of claim 1 wherein said catalyst is nickel carbonyl.

5. The process of claim 1 wherein said catalytic reaction is promoted with iodine.

6. The process of claim 1 wherein said catalyst and promoter are dissolved in said petroleum fraction.

7. The process of claim 1 wherein said hydrogen-containing gas also contains substantial amounts of carbon monoxide.

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