

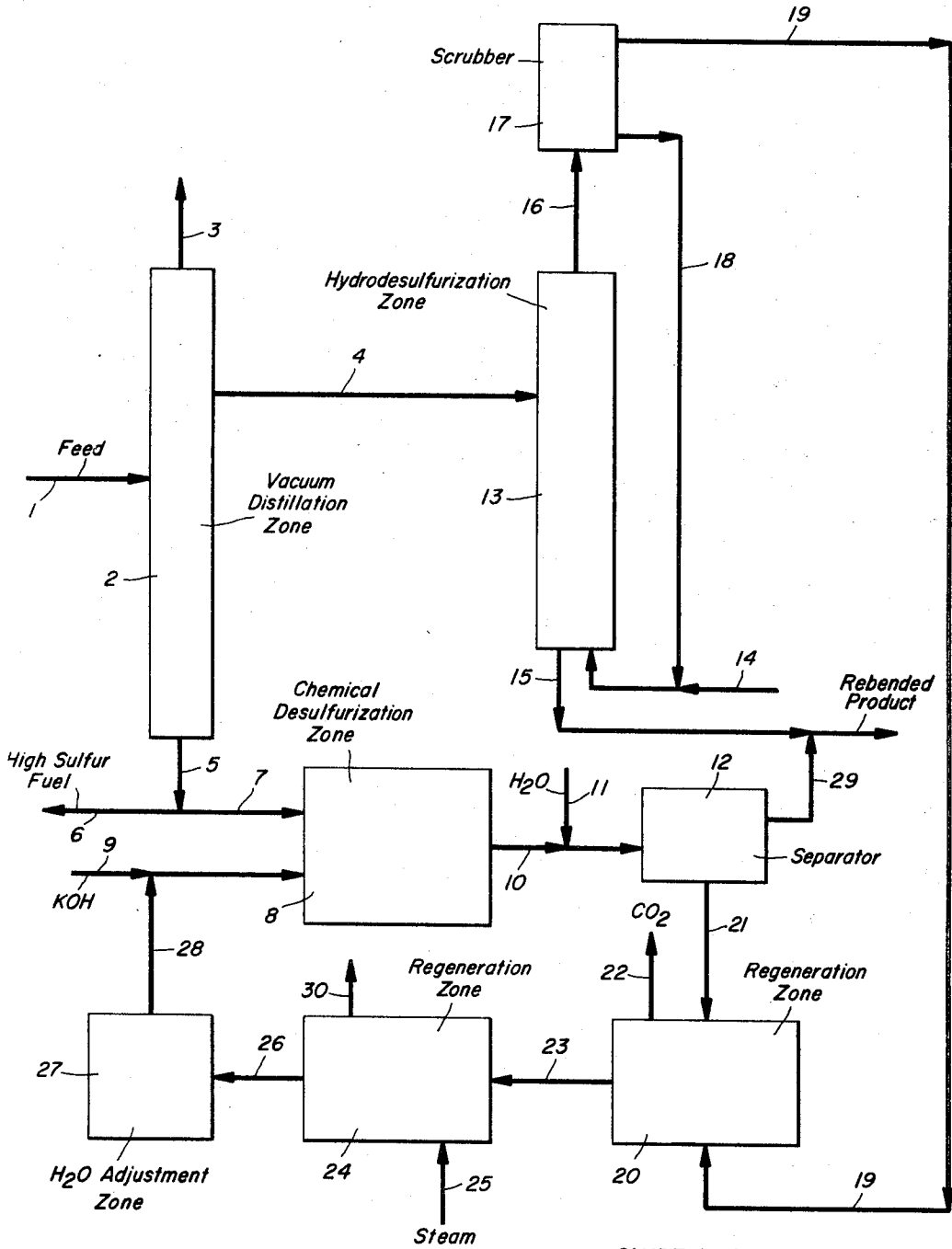
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PROCESS FOR DESULFURIZING VACUUM DISTILLED FRACTIONS

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PROCESS FOR DESULFURIZING VACUUM DISTILLED FRACTIONS

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1 Claim

ABSTRACT OF THE DISCLOSURE

An atmospheric residuum is split by vacuum distillation to provide a gas oil fraction and a bottoms fraction; the gas oil fraction is desulfurized by catalytic hydrodesulfurization and the bottoms fraction is desulfurized by contacting with molten KOH, an oxygen-containing gas, and 5–30 wt. percent water based on the total reagent. The recovered products are then blended together to produce a low sulfur content oil. The H_2S formed in the hydrodesulfurization step is used to regenerate the KOH treating agent.

This invention relates to a process for the removal of sulfur from liquid hydrocarbon streams, particularly hydrocarbon residuums. More specifically the invention relates to an integrated two-phase desulfurization process involving split treatment of a residuum.

Generally, sulfur occurs in petroleum stocks in one of the following forms: mercaptans, sulfides, disulfides and as part of a more or less substituted ring, of which thiophene, benzothiophene and dibenzothiophene are the prototypes. The mercaptans are generally found in the lower boiling fractions, e.g., the naphtha, kerosene, and light gas oil. Numerous processes for sulfur removal from these 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. When the process results in the later effect, the disulfides generally remain in the treated product and must be removed by another step if it is desired to obtain a sulfur-free product.

Sulfur removal from higher boiling fractions, however, has been a much more difficult operation. Here the sulfur is present for the most part in the less reactive forms as sulfides, disulfides and as a part of a ring compound, such as thiophenes, benzothiophenes or dibenzothiophenes. Such sulfur is, of course, not susceptible to chemical operations satisfactory for removal of mercaptans. Extraction processes employing sulfur-selective solvents are also unsatisfactory because the high boiling petroleum fractions contain such a high percentage of sulfur-containing molecules. For example, even if a residuum contains only about 3% sulfur it is estimated that substantially all of the molecules may contain sulfur. Thus, if such a residuum were extracted with a solvent selective to sulfur compounds the bulk of the residuum would be extracted and lost.

Metallic contaminants, such as nickel and vanadium compounds, are found as innate constituents in practically all crude oils. These contaminants present another problem. Upon fractionation of the crudes, the metallic contaminants are concentrated in the residua which normally have initial boiling points of about 1000° F. Such residua are conventionally used as heavy fuels, and it has been found that the metal contaminants therein adversely affect the combustion equipment in which the residua are burned. The contaminants not only form ash, which leads to sludging and the formation of deposits upon boiler

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tubes, combustion chamber walls, the gas turbine blades, but also attack the refractories which are used to line boilers and combustion chambers and severely corrode boiler tubes and other metallic surfaces with which they come into contact at high temperatures.

The nitrogenous compounds are found in many crude oils to a varying extent depending on the source. These compounds are objectionable primarily due to (1) their tendency to promote instability in the finished, marketable products, such as gasoline, kerosene, heating oil, jet fuels and the like regardless of whether these are obtained by simple distillation procedures or by cracking heavier fractions and (2) due to their adverse effects on the activity of catalytic materials used in cracking reactions, etc.

A process for the chemical desulfurization of residuum stocks employing fused alkali metal hydroxides has been disclosed by Mattox in U.S. Patent 3,164,545, issued Jan. 5, 1965. The disclosed process is also effective in removing nitrogen compounds and metallic contaminants. While contaminant removal is excellent using fused alkali metal hydroxides, the process suffers from the inherent defect that the treating agent becomes spent and it must be regenerated.

Processes for hydrodesulfurizing oils in the presence of a catalyst are well known in the petroleum refining art. It is also well known that most of the present processes are limited to feeds which contain low amounts of sulfur, and nitrogen compounds and metal contaminants. Such pretreatments as solvent deasphalting and vacuum distillation are used to reduce sulfur, nitrogen and metals to a level so that the hydrodesulfurization catalyst is not rapidly poisoned.

The object of this invention is to provide a process for the desulfurization of heavy oils which does not require extensive feed conditioning or expensive and complicated pretreating steps. It is another object of this invention to provide a combined chemical desulfurization-hydrodesulfurization process in which the disadvantages of each type of treatment are alleviated by coordinating the two treatments.

I have found that heavy oils such as whole crude oils, topped crude oils, atmospheric residuums and the like can be split by vacuum distillation to provide a vacuum gas oil fraction and a vacuum residuum fraction which can be separately treated. The vacuum gas oil is treated by conventional hydrosulfurization. The vacuum residuum is treated by chemical desulfurization with an alkali metal hydroxide. Furthermore, I have found that the H_2S formed in hydrodesulfurization can be used to regenerate the spent alkali metal hydroxide treating agent.

The invention will be further illustrated by the accompanying drawing which is a schematic flow sheet showing a preferred method for practicing the process of the invention.

Reference numeral 1 denotes a line carrying a petroleum feed to vacuum distillation tower 2. The tower is operated at a temperature ranging from 600–800° F. and a pressure in the range of from about 10 mm. to about 200 mm. of Hg. A typical feed comprises an atmospheric residuum having an initial boiling point of 350–650° F. Light materials are carried overhead by line 3. Vacuum gas oil having an initial boiling point ranging from 350–650° F. and an end point of 1000–1200° F. is removed by line 4. Vacuum residuum boiling above about 1000–1200° F. is removed by line 5. This material can be divided into a high sulfur fuel fraction removed by line 6 and a fraction to be desulfurized carried by line 7 to treating zone 8. The fused alkali metal hydroxide treating agent, KOH for example, is added to zone 8 by line 9. The quantity of KOH will range from 5–100 wt. per-

cent based on the feed. The preferred quantity of KOH ranges from 5-30 wt. percent.

The amount of water in the molten alkali metal hydroxide is important for the improved results of the instant invention. The water content should be within the range of about 5-30 wt. percent based on total reagent, preferably 7-25 wt. percent, and more preferably 10-20 wt. percent. The most preferred water content is about 15 wt. percent, based on molten alkali metal hydroxide. Temperature conditions during the contacting step should be maintained within the range of 400-800° F., preferably 450-750° F., more preferably 500-700° F. Treating time may be as little as 1/10 hour to 16 hours, generally the longer the time of contact, the greater the impurity removal. Generally, treating times within the range of 1/4 to 6 hours are used. The preferred treating time per stage will be 1/2 to about 2 hours. The pressure may vary from 0-500 p.s.i.g., depending on the hydrocarbon feedstock, and is not critical to the desulfurization reaction.

The mixture of KOH and treated residuum bottoms leaves the treating zone through line 10 and is mixed with about 50-300 wt. percent water based on the treating agent introduced through line 11 and passes to separator 12. The separator can be a conventional settler in which the mixture of molten alkali metal hydroxide, the reaction products of the feed impurities with the treating agent and the water separate as a distinct phase from the treated residuum.

The treatment with KOH removes from 10-60 percent of the sulfur and a major amount of the nitrogen and metal contaminants from the oil. A Kuwait vacuum residuum was treated with 100 wt. percent KOH at 650° F. for 4 hours resulting in a decrease of sulfur content from 5.2 wt. percent to 1.9 wt. percent and vanadium content was reduced from 75 p.p.m. to 1.0 p.p.m. It is the consensus of experts that it is the metals, especially the vanadium found in many crude oils which severely limit catalyst life in treating residuum and thereby makes hydrodesulfurization of whole vacuum residuums impractical. The process of the invention provides an accommodation of the problem by concentrating sulfur, nitrogen and metals in the vacuum bottoms and removing these contaminants without using a catalyst.

The gas oil fraction is passed by line 4 to hydrodesulfurization zone 13. This fraction contains from 0.5-3.0 wt. percent sulfur but metals and nitrogen compounds have been left in the vacuum bottoms. Hydrogen is added to zone 13 by line 14. The hydrodesulfurization treatment is carried out in the conventional manner with known catalysts. Desulfurized product is removed by line 15 for reblending with product from line 29. Suitable process conditions are:

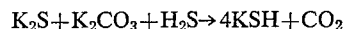
Feed rate	-----v./v./hr.	0.2-3.0
Hydrogen rate	-----s.c.f./bbl.	500-6000
Pressure	-----p.s.i.g.	300-3000
Temperature	-----° F.	550-850

Preferred catalysts are 5-15 wt. percent molybdena on porous alumina and mixtures of cobalt oxide (3-6 wt. percent) with molybdenum oxide (6-12 wt. percent) on adsorptive alumina. Catalysts containing nickel, chromia, platinum, and tungsten in the form of metals, oxides and sulfides on alumina, charcoal, kieselguhr and bauxite can be used as well.

A gas comprising H₂ and H₂S is carried overhead from the hydrodesulfurization zone by line 16 and the H₂S is removed by a conventional gas separation process such as amine scrubbing in scrubber 17. Hydrogen is recycled by lines 18 and 14.

H₂S from the gas scrubber 17 is passed by line 19 to zone 20 for use in regeneration of the spent alkali metal treating agent from the chemical treating step. When KOH is used as the treating agent, the spent material contains unreacted KOH, K₂CO₃, K₂S and water. Considering the

KOH, K₂S and K₂CO₃ as a basis, the K₂CO₃ constitutes from 10-65 wt. percent of these materials. It is the most difficult material to regenerate. The spent material is passed by line 21 to regeneration zone 20 and contacted with H₂S at a temperature ranging from 190-400° F., and at atmospheric, subatmospheric, or elevated pressures, preferably 1-500 p.s.i.a., employing an excess of H₂S based on the K₂CO₃ and K₂S. The carbonate and the K₂S are converted to KSH by this regeneration treatment according to the following reaction:



CO₂ is removed by line 22. A 35 wt. percent aqueous solution of K₂CO₃ was contacted by bubbling H₂S through the solution at 217° F. and atmospheric pressure. The off gas contained 50% CO₂ demonstrating a conversion of 78%. This result was unexpected because H₂S is a weaker acid than CO₂ (aq.).

In the aforementioned regeneration step, K₂S is converted to KSH.

A stream containing KSH, and water is passed by line 23 to a second regeneration zone 24 in which the KSH is converted to KOH, the desired alkali metal hydroxide chemical desulfurization agent. This conversion can be accomplished by a number of methods, however the preferred embodiment is by treating with steam at a temperature ranging from 400-1000° F. Steam is introduced to zone 24 by line 25. Unreacted steam is removed by line 30. Regenerated KOH is passed by line 26 to H₂O adjustment zone 27. In zone 27, the water content of the KOH treating agent is adjusted, by stripping for example, to a range of about 5-30 wt. percent based on the total reagent used in zone 8. Frequently it is desirable to follow the steaming step with a treatment of the caustic solution by a metal or metal oxide such as Cu or CuO, Fe or Fe₂O₃, etc., to insure good removal of the sulfur and to complete caustic regeneration. Regenerated KOH treating agent is recycled to zone 8 by lines 28 and 9.

Thus, it can be seen that the present invention discloses a two-phase desulfurization system in which the material containing catalyst poisons is treated in a non-catalytic chemical desulfurization step and the gas oil containing essentially only sulfur contaminants is hydrodesulfurized in the presence of a catalyst. In addition, the hydrodesulfurization phase benefits the chemical desulfurization phase by providing H₂S for regeneration of the molten alkali metal treating agent.

The products of the present invention can be used as industrial fuels, as feed to catalytic cracking processes, and as feed to hydrocracking processes or in any other area of utility where it is mandatory that the stock being used or treated be low in sulfur, nitrogen and metals content.

The molten alkali metal hydroxides suitable for use in carrying out the process of the invention include molten sodium hydroxide, potassium hydroxide, lithium hydroxide, cesium hydroxide and the like. KOH is the preferred treating agent and it can be promoted with any of the aforementioned alkali metal hydroxides in a eutectic mixture.

In a particularly preferred embodiment of the invention, the molten alkali metal having the aforementioned water content of 5-30 wt. percent is employed in the presence of an oxygen containing gas. It has been found that the addition of oxygen during the chemical desulfurization stage results in a surprising increase in the amount of contaminants removed from the residuum. Generally it is preferred to supply the oxygen by bubbling air or a similar oxygen-containing gas through the feed during treatment with the fused hydroxide. When air is used, air rates of from about 1-1500 standard cubic feet per barrel of residuum can be used. Spargers, distribution plates or other conventional means, not shown in the drawing can be used to promote contacting of the oxygen and the oil.

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In a further modification of the present invention, the alkali metal bisulfide treated in zone 24 is converted to the alkali metal hydroxide phase by contacting the alkali metal bisulfide with a finely-divided metal, metal oxide or metal hydroxide. The metal sulfides can be converted back to the metals, metal oxides or hydroxides by known methods. Suitable metals include copper, nickel, iron, manganese, cobalt, calcium, magnesium, molybdenum, lead, tin and zinc. Oxides or hydroxides of these metals would also be suitable. Copper and iron and the oxides and hydroxides of these metals are preferred.

Where their use is deemed advisable solvents, diluents and solutizers can be used to thin the residuum so that contacting will be more complete.

The molten alkali metal treating stage and the hydrodesulfurization stage of the process can be carried out in a batchwise or in a continuous manner. A continuous process is preferred. Recycle of process streams of treating agents to the various treating or regeneration steps is to be considered within the scope of the invention.

Other obvious variations of the process which would occur to those skilled in the art are intended to be included in the scope of the disclosure and the claim.

What is claimed is:

1. A process for desulfurizing an atmospheric residuum comprising the steps of subjecting the residuum to vacuum distillation at a temperature in the range of 600–800° F. and a pressure of from about 10 mm. to about 200 mm.

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of Hg. to produce a gas oil fraction boiling in the range of 350–1000° F. and a bottoms fraction boiling above 1000° F., hydrodesulfurizing the gas oil fraction in the presence of hydrogen and a cobalt molybdate on alumina catalyst, desulfurizing the vacuum bottoms fraction in the presence of molten KOH, an oxygen containing gas and 5–30 wt. percent water based on the total reagent, recovering desulfurized products from each stage and blending the products to produce a low sulfur content oil, recovering H₂S from said hydrodesulfurization step and employing said H₂S as a regeneration treating agent in treating K₂S and K₂CO₃ formed in the KOH desulfurization step.

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