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ALKALI-DESULFURIZATION PROCESS

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ABSTRACT OF THE DISCLOSURE

The present disclosure relates to the desulfurization of petroleum fractions with chemical desulfurization agents in the presence of added oxygen.

The present invention concerns an improved process for removing sulfur from hydrocarbon fractions. More particularly, the present invention concerns an improved process for removing sulfur from various petroleum fractions. This sulfur removal is effected by treating the fractions at high temperatures in the presence of oxygen with a chemical desulfurization agent. Particularly acceptable chemical reagents are alkali metals, alkali metal hydroxides and alkali metal salts. The agents are well-known; thus, it is the use of these agents in the presence of oxygen in conjunction with the use of high temperatures which distinquishes this invention.

The problem of sulfur removal from petroleum fractions and crudes goes back to the inception of the petroleum industry. For most purposes, it is undesirable to have an appreciable amount of sulfur in any petroleum product. Gasoline should be relatively sulfur free to make it compatible with lead. Motor fuels containing sulfur and mercaptans are undesirable because of odor and gum formation characteristics. Sulfur is objectionable in fuel oils because upon combustion sulfur dioxide, a corrosive gas having a noxious odor, is formed. Metropolitan areas have been particularly conscious of the air polution problems caused by sulfur-containing fuels and in certain instances, have restricted by law the amount of sulfur permissible in the fuel oils utilized in the locale.

Generally, sulfur appears in feedstocks in one of the following forms: mercaptans, sulfides, disulfides, and as part of complex ring compounds of which thiophene is a prototype. The mercaptans are more reactive and are generally found in the lower boiling fractions, e.g. gasoline, naphtha, kerosene and other light gas oil fractions. Well-known treating processes for these lower boiling fractions have been employed such as "Doctor" Sweetening (wherein mercaptans are converted to disulfides). However, these disulfides remain in the hydrocarbon so that no overall sulfur reduction is effected. The instant invention does not pertain to the oxidation of mercaptans to disulfides; it is conceived with desulfurization agents only. In the well-known caustic treating process, aqueous solutions of sodium hydroxide are used to aid in the removal of sulfur. Other processes, such as solvent extraction and copper chloride treating, have given satisfactory results to some degree. However, they have produced some drawbacks; these include the fact that another step is needed to remove the disulfides.

In the past, methods to chemically remove sulfur have been ineffective to remove large amounts of sulfur and furthermore, had little or no effect on the nitrogenous or metallic impurities, these materials requiring other methods for their removal.

Sulfur removal from higher boiling fractions has presented the most difficult problem. That is to say, the removal of sulfur from residuum is the most difficult to solve problem with respect to sulfur removal. In these residua, sulfur is present for the most part in the less

reactive forms such as sulfides and as part of the complex ring compounds of which the thiophene structure is representative. Such sulfur compounds are not susceptible to conventional chemical treatment found satisfactory for the removal of mercaptans and hydrogen sulfides. Extraction processes employing sulfur-selective solvents are usually not satisfactory because the high boiling petroleum fractions contain such a high percentage of sulfur-containing molecules. For example, even if a residuum contains only a small amount of sulfur, it is possible 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 also and lost for any future use.

These shortcomings have been recognized by the prior art and a variety of attempts have been made recently to get around them. However, none of these methods have produced a high level of sulfur removal particularly in the heavier fractions.

According to this invention, the problems previously encountered in obtaining maximum desulfurization have been eliminated. It has unexpectedly been discovered that the chemical desulfurization of hydrocarbons, is promoted markedly by the presence of free or combined oxygen at high temperatures. More particularly, temperatures of 500° to 800° F. may be utilized, the most preferred range of temperatures being 600° to 750° F. Sufficient oxygen must be added so that the hydrocarbon fraction contains from 0.1 to 2.0% by weight of oxygen. The oxygen may be added in free or combined form. However, no matter which form is utilized it is preferred to have the oxygen within the range of 0.1 to 2.0 wt. percent; this is the preferred range and additonal oxygen could be added and, in fact, might be required in certain circumstances. Up to 5.0 wt. percent and higher of oxygen may, under proper conditions, produce the desired result. It should be emphasized that this invention pertains to desulfurization and not to the oxidation of mercaptans to disulfides.

The invention may be used to remove sulfur from all sulfur-containing hydrocarbon fractions. This would include naphthas, kerosenes, gas oils of all weights, lubricating oils and residua.

Various petroleum fractions such as distillate and residual oils and other hydrocarbons have been desulfurized in the past by treatment with known chemical reagents. However, the use of elevated temperatures in conjunction with oxygen as proposed in the instant invention is a unique process. The oxygen to be utilized may be bubbled in directly by introducing air into the sulfur-containing feedstock or the oxygen may be added or combined in suitable organic or inorganic forms. The oxygen may be employed simultaneously with the desulfurization treating agent or be added separately to the oil preceding contact with the various chemical desulfurization agents. Alternatively, one may both preoxidize and simultaneously treat with oxygen. The level of oxygen addition or utilization may vary widely from about 0.1 to 2 or more wt. percent preferably or even up to 5 wt. percent or higher based on oil and may be approximately equal to or 2 to 5 times greater than the sulfur content of the oil. Various known oxidation promoters or catalytic materials may be employed to facilitate the addition of oxygen to the oil.

A great variety of chemical treating agents are known which facilitate the desulfurization of the various hydrocarbon fractions. A mere cataloging of these desulfurization agents does not appear to be in order since they are well-known to those skilled in the art.

However, in the interest of clarity, some of the more widely known chemical treating agents which may be

utilized to facilitate desulfurization will be mentioned. It should be noted that books such as "Chemical Refining of Petroleum," by Stagner and Kalichevsky, 2nd edition, Rheinhold Publishing Corp., 1942, pages 217, 220–222, 229, 234 and 237 contain an extensive discussion of the various chemical desulfurization agents. These pages are herein incorporated by reference.

Included in these chemical treating agents are alkali metals and their oxides, hydroxides and salts, especially alkali metal salts of weak, non-volatile acids. Further, various acidic agents, such as hypochlorous acid, may also be utilized. The alkali metal family includes lithium, sodium, potassium, rubidium and cesium. Sulfur acceptors may also be employed within the scope of this invention. They include various metals such as iron, copper, manganese, nickel, cobalt, zinc, sodium and antimony. The oxides of these metals and their hydrated oxides are also effective in the removal of sulfur. Various halogenated compounds such as $AlCl_3$ may also be used. The alkali metals along with their oxides and hydroxides are particularly well-known for this purpose and will be used as examples to demonstrate the entire group of desulfurization agents which may be utilized in the process of this invention. However, there is no intention to be bound by any particular mechanism or category of desulfurization agent. Specific examples of the chemical desulfurization agents to be utilized with the process of the instant invention include the following: molten potassium hydroxide with a water content of about 10 to 15 wt. percent having the formula: $KOH \cdot \frac{1}{2}H_2O$, $KSbO_3$, $NaSbO_3$, MnO(OH). All of these desulfurization agents must be used under reaction conditions with respect to catalysts, pressures, etc. These are well-known to those skilled in the art. Excellent results can be achieved with an alkaline chemical reagent such as potassium hydroxide.

The invention is particularly applicable to treating heavy sulfur bearing residua. Residuum is that portion of a crude oil which remains after naphtha and gas oil have been removed by atmospheric or vacuum distillation. These residual fractions usually have initial boiling points of about 600° to 650° F. if obtained from distillation at atmospheric pressure and about 900° to 1100° F., if obtained from vacuum distillation. Included among the various residua which may be treated by the instant invention are the resids obtained from Safaniya, Kuwait, Bachaquero and Arabian crudes. In essence, the instant invention applies to the treatment of all hydrocarbon oils in which a substantial proportion of the component molecules contain sulfur atoms.

Oxygen may be added directly by passing it in intimate contact through the oil until the oil contains 0.1 to 2 wt. percent up to about 5 wt. percent or higher of oxygen. The optimum oxygen content will vary with the particular oil and the type of treat employed, that is whether the oil is preoxidized or whether oxygen is added continuously. If added continuously, the above higher levels of oxygen content may not necessarily be required. The oxygen may also be added directly to the oil in the form of oxygen-containing oil-soluble compounds. Examples of these compounds include the following: organic acids and salts, ketones, aldehydes, oxides, peroxides and epoxides. The oxygen which enters into combination with the oil molecule is not combined with the sulfur atom as sulfoxide or sulfone but rather is present as carbonyl oxygen. The presence of this carbonyl oxygen serves to increase the effectiveness of the chemical desulfurization of resids and other hydrocarbon fractions in some manner that is not fully understood. However, maximum effectiveness is obtained with the desulfurization agent when the oxygen is present in the carbonyl form.

Temperatures are critical in the oxygen promotion of chemical desulfurization. Temperatures utilized during the actual desulfurization may vary from 500° to 800° F. but should be most preferably 600° to 700° F. This high temperature greatly facilitates the removal of sulfur.

The complete desulfurization technique to be utilized in the instant invention would proceed as follows. A sulfur bearing hydrocarbon fraction which may be a naphtha, gas oil, kerosene or a residua is to be treated for maximum sulfur removal. Most effective results are obtained by treating the residua but it is readily apparent to one skilled in the art that the other sulfur bearing fractions may be treated in a similar fashion. The residuum boiling at a temperature of about 600° F. and above is pretreated with oxygen. Oxygen (air) is bubbled into the residua for a period of about ½ to 4 hours until a level of about .1 to 2.0 wt. percent of oxygen is obtained within the residua. The residua is then subjected to contact with molten potassium hydroxide, preferably $KOH \cdot \frac{1}{2}H_2O$, a highly effective chemical desulfurization agent. Contacting approximately equal weights of oil and KOH at 500° to 700° F. for about 15 to 200 minutes will remove about 56–60% of the sulfur. Further reductions in sulfur content are effected by repeating the treat or by separating the oil phase and recontacting it with additional KOH in a separate vessel. Caustic-oil separation is readily accomplished by diluting the KOH to about 50% with water followed by settling at a temperature of 300–350° F. Any remaining caustic is removed by water washing at approximately the same temperature. Alternative methods, which are equally effective within the scope of this invention, other than the alkali treating described above, include the use of high melting point, solid desulfurization reagents, such as manganese hydroxides or hydrated oxides, alkali metal salts of weak, non-volatile acids, such as $KSbO_3$, etc., in fixed bed or in slurry type operations.

During the time when the oxygenated resid is contacted with the KOH, the temperature in the contacting zone is maintained at about 500° to 700° F. After a period of 15 to 200 minutes, the desulfurization is substantially complete and about 40 to 60% of the sulfur is removed. The sulfur removed includes mercaptans, thiophenes, etc., for as mentioned above, the process of the instant invention is equally applicable to removing all types of organic sulfur. As a suitable alternative to the preoxidation, oxygen may be added to the oil by means of a compound such as potassium oleate which is oxygen-containing and soluble in oil. Similar results are achieved no matter how the oxygen is added to the sulfur-containing hydrocarbon fraction.

EXAMPLES

TABLE I.—Desulfurization of Safaniya Residuum

[1/1 KOH/oil ratio; 4-hr. treats]

Test No.	Temp., °F.	Oxygen Source	Wt. percent Oxygen in Oil			Percent Desulfurization
			Initial	Added	Total	
1	600	None	0.2	0	0.2	29
2	625	do	0.2	0	0.2	48
3	650	do	0.2	0	0.2	51
4	600	Preoxidation	0.2	0.4	0.6	51
5	600	K-oleate	0.2	1.0	1.2	39
6	625	do	0.2	1.0	1.2	57
7	650	do	0.2	1.0	1.2	59

The above table, Table I, indicates the results which are obtained when desulfurizing a Safaniya residuum which boils above about 500° F. In Runs 1, 2 and 3 there was no additional oxygen added to the system. In Run 4, preoxidation was utilized to increase the oxygen present. This preoxidation was effected by bubbling oxygen into the residuum for a period of about 2 hours. The desulfurization obtained was 51%. This compares to 29% desulfurization which was obtained with no oxygen added at a similar temperature, i.e., 600° F. in Run 1. In Runs 5, 6 and 7, potassium oleate was added as the oxygen source. About 0.25 mole of potassium oleate was added per atom of sulfur in the oil. As a result, the oxygen present was raised by about 1.0 wt. percent. When treating at 600° F. in Run 5, the percent desulfurization was 39. In Run 1 when treating at 600° F. the percent desulfurization was only 29% since there had been no additional oxygen added. Run 6 at 625° F. resulted in 57% of the sulfur removed. This is a considerable increase from the 48% removal effected in Run 2 where there was no additional oxygen utilized at the same temperature of 625° F. Run 7 produced a sulfur removal of 59%. This again compares favorably with Run 3 where the removal was only 51% at the identical temperature. The extent of sulfur removal was determined by analysis of the treated oil after separation from the caustic. Thus, from the above it is apparent that the Safaniya Residuum may be more effectively desulfurized in the presence of oxygen when appropriate high temperature levels are reached.

A West Texas deasphalted oil having an initial boiling point of 745° F., an API gravity of 17.6 and a sulfur content of 1.3% was also subjected to KOH desulfurization. This was done in the presence of continuous air blowing.

TABLE II

	Percent Desulfurization		
Temperature of Treat., ° F.	400	500	600
Oxygen Contact:			
None (0.3% O in Feed)		10	15
Preoxidized to 0.8% Oxygen			39
Continuous Air Addition	19	39–41	49

The above table, Table II, indicates the improvement in desulfurization which was found as temperature increased. At 400° F. continuous air addition produced

19% desulfurization; at 500° F. this increased to 39 to 41%, whereas at 600° F. 49% was obtained in 4 hour treats. These tests indicate substantial desulfurization at 400° F. with a marked increase in desulfurization with rising temperatures.

Combining the two tables, it is readily apparent that higher temperatures in the range of 500° to 800° F. produce a far more satisfactory desulfurization. As indicated in Table II, 600° F. produces markedly superior results with respect to 400° and 500° F. Thus, it is apparent that the mere use of oxygen without increased temperatures is not sufficient to produce the desired desulfurization. The upper limit of suitable desulfurization temperatures will usually be determined by the extent of sulfur removal desired, the type of feedstock employed and the proportion of cracked products produced in the desulfurized oil.

Although this invention has been described with some degree of particularity, it is intended to be limited only by the attached claims.

What is claimed is:

1. An improved process for removing sulfur from a hydrocarbon fraction which comprises increasing the carbonyl oxygen content of said fraction to about 0.1 to 2.0% by weight by contacting said fraction with an oxygen containing gas, contacting said oxygen-containing fraction with an alkali metal hydroxide at a temperature of 500° to 800° F. for a period of 15 to 300 minutes whereby a substantial portion of said sulfur is removed.

2. The process of claim 1 wherein an oxygen-containing compound is bubbled into said fraction directly.

3. The process of claim 1 wherein said alkali metal hydroxide is potassium hydroxide.

4. The process of claim 1 wherein said temperature is maintained at 600° to 750° F.

5. The process of claim 1 wherein said sulfur is present in at least one form selected from the group consisting of mercaptans, sulfides, disulfides and thiophene type structures.

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