United States Patent Office

3,505,210

Patented Apr. 7, 1970

1

3,505,210

DESULFURIZATION OF PETROLEUM RESIDUA

Thomas J. Wallace, Whippany, and Barry N. Heimlich, Union, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Continuation-in-part of abandoned application Ser. No. 434,643, Feb. 23, 1965. This application June 4, 1968, Ser. No. 734,228

Int. Cl. C10g 31/14, 27/06, 19/02

U.S. Cl. 208—228 15 Claims

ABSTRACT OF THE DISCLOSURE

Heavy petroleum hydrocarbon fractions and particularly residua containing bivalent sulfur are desulfurized in a two-step process in which the heavy hydrocarbon is first contacted with hydrogen peroxide or other suitable peroxy compound in an acidic medium, oxidizing bivalent sulfur to the sulfone state, and then treating the hydrocarbon fraction with a molten alkali metal hydroxide to cleave the sulfone ring and form a hydrocarbon fraction of reduced sulfur content.

CROSS-REFERENCE TO EARLIER APPLICATIONS

This application is a continuation-in-part of our copending applications Ser. No. 434,643, filed Feb. 23, 1965, now abandoned; Ser. No. 454,693, filed May 10, 1965, now Patent No. 3,413,307, issued Nov. 26, 1968; Ser. No. 543,061, filed Apr. 18, 1966, now abandoned; and Ser. No. 557,633, filed June 15, 1966, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to processes for the desulfurization of heavy petroleum hydrocarbon fractions, and particularly to processes for desulfurization residua.

Air pollution is becoming an increasingly important problem to the entire world. Residual fuel oils that contain significant quantities of sulfur form sulfur dioxide combustion. Recent studies substantiating this indicate that the amount of sulfur dioxide in the atmosphere is continually growing. The presence of sulfur in this form, aside from lending to a generally high level of discomfort for those who are forced to live in areas where it is present, also constitutes an extremely dangerous health hazard and has contributed greatly to the growing presence of respiratory diseases such as emphysema.

In the past, a great deal of time was spent trying to improve this situation. The conventional process for the desulfurization of petroleum fractions is catalytic hydrosulfurization. This technique is economically employed for the removal of sulfur from petroleum distillates such as naphtha, kerosene, and diesel fuels. However, heavy stocks such as crude oil, gas oil, and residua cannot be hydrodesulfurized as readily as the lighter hydrocarbon fractions. Hydrotreating of heavy stocks is not selective, and therefore consumes hydrogen in quantities in considerable excess of the stoichiometric requirement for sulfur removal. Hydrodesulfurization of heavy stocks must be conducted at high temperatures such as 650° to 850° F. and at very high pressures such as 800 to 2000 p.s.i.g. Since current processes for the manufacture of hydrogen have high investment and operating costs, operate at low pressure, and would require large and costly compression equipment in order to charge the hydrogen to the hydrodesulfurization process, hydrodesulfurization of heavy stocks such as residua is a costly process. In addition, because the sulfur compounds in heavy stocks are primarily the very refractory thiophene type, low space velocities are required for substantial sulfur removal. As a result, the investment for the hydrodesulfurization reactor is excessive. The presence of naphthenic hydrocarbons hinders sulfur removal. Furthermore, because residua and gas oils contain significant quantities of organometallic compounds such as vanadium, nickel, and iron porphyrins, which are poisons for desulfurization catalysts, and because of the high tendency for coke formation of the high molecular weight hydrocarbons and asphaltenes found in residua and gas oil, severe catalyst deactivation is unavoidable. For the above-mentioned reasons, sulfur removal from heavy petroleum fractions such as gas oils, reduced crudes, and residua by hydrodesulfurization is costly and not fully satisfactory.

Other methods of desulfurization involve the use of acid- or base-catalyzed techniques. Large amounts of resinous material and coke have been observed in many previous acid-catalyzed desulfurization studies. Desulfurization using alkaline reagents, such as metallic sodium, under alkaline conditions would appear to be a more attractive route. Polymerization problems are not as severe as in the case of acid catalysis. The major problem in utilizing an alkali metal is that the regeneration of the alkali metal is an extremely difficult and costly task. The only feasible regeneration technique thus far is electrochemical reduction.

A more recent approach is described in Webster et al. Patent No. 3,163,593, issued Dec. 29, 1964. According to the Webster et al. patent, a heavy hydrocarbon oil is treated with an oxidizing agent such as hydrogen peroxide in the presence of formic or acetic acid, forming compounds containing both oxygen and sulfur, and the hydrocarbon is then subjected to a thermal treatment at about 350° to 450° C. (662° to 842° F.). At these high temperatures some thermal degradation of the residuum takes place. Furthermore, substantial quantities of sulfur remain in the residuum even after treatment.

SUMMARY OF THE INVENTION

Heavy petroleum hydrocarbon fractions, and particularly petroleum residua, are desulfurized according to the present invention by (1) contacting the hydrocarbon fraction with an oxidizing agent in a aqueous acidic medium, thereby oxidizing bivalent sulfur compounds such as thiophene to sulfur-oxygen compounds such as sulfoxides and sulfones, (2) contacting the oxidized hydrocarbon fraction containing the sulfur-oxygen compounds with a molten alkali metal hydroxide, thereby rupturing the carbon-sulfur bond and forming water soluble sulfur compounds, and (3) recovering a hydrocarbon fraction of reduced sulfur content.

DETAILED DESCRIPTION OF THE INVENTION

This invention is useful in the treatment of heavy petroleum derived hydrocarbon fractions containing bivalent sulfur compounds, and especially thiophenes. The heavy petroleum fractions treated according to this invention include higher boiling range petroleum fractions such as topped crudes, gas oils, and residua. These fractions may be characterized generally as petroleum hydrocarbon fractions over 30% of which boil at a temperature above 900° F. This invention is particularly applicable to the treatment of residua of high sulfur crudes. A residuum is the heavy fraction which remains in crude oil after the lighter fractions, including naphtha and gas oil, have been removed. The atmospheric residuum of Safaniya crude oil is representative of the high sulfur materials which may be benefited by this invention. A typical analysis of Safaniya atmospheric residuum is as follows:

TABLE I

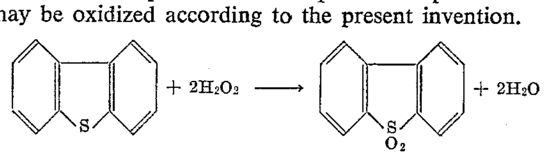
API gravity	11.4
S, wt. percent	4.21
Conradson C, wt. percent	14.09
Naphtha insolubles	7.8
Elemental analysis:	
C, wt. percent	84.28
H, wt. percent	10.79
S, wt. percent	4.21
Ni, p.p.m.	26
V, p.p.m.	93
Fe, p.p.m.	2
Viscosity, furol seconds at 122° F.	1408
Viscosity, furol seconds at 140° F.	670
Flash point (open cup) ° F.	392
Pour point ° F.	62
ASTM distillation D-1160 at 1 mm. (atmospheric equivalent B.P.'s):	
Initial B.P. ° F.	555
5% ° F.	683
10% ° F.	747
20% ° F.	839
30% ° F.	910
40% ° F.	968
50% ° F.	—
60% ° F.	—
Final B.P. ° F.	1047
Recovery percent	50.5
Residue do	49.5

The first step in the instant process is to oxidize the thiophene content to the sulfoxide or sulfone state. This is done by contacting the heavy hydrocarbon fraction with a suitable oxidizing agent. Before proceeding with this step, it is desirable to dissolve materials of high viscosity such as residua in an inert hydrocarbon medium such as benzene.

It is desirable to dissolve materials of high viscosity such as residua in an inert hydrocarbon medium such as benzene before treating according to this invention.

The oxidizing agent utilized for this invention may be any of the several well-known oxidizing agents. However, the preferred agent is hydrogen peroxide in a liquid acidic medium, e.g., acetic acid. A variety of reagents may be substituted for hydrogen peroxide. These include the alkali metal periodates, perchlorates, chromates, and permanganates; metal oxides such as manganese dioxide and chromic oxide; perchloric and hypochlorous acids; metal peroxides, especially barium peroxide; peracids such as performic, peracetic, pertrichloroacetic, perbenzoic, and perphthalic acids; and organic peroxides and hydroperoxides such as tert-butyl hydroperoxide.

About 2 to 10 moles of hydrogen peroxide are used for each mole of bivalent sulfur to be oxidized. The stoichiometric quantity of hydrogen peroxide is 2 moles for each mole of bivalent sulfur to be oxidized. This is illustrated by the following equation, in which benzothiophene is chosen as a representative thiophene compound which may be oxidized according to the present invention.



Dibenzothiophene has been used simply for purposes of illustration in the above equation; it will be understood that other thiophenes react in the same way. Also, hydrogen peroxide has been chosen for purposes of illustration only. Equivalent amounts of other oxidizing agents may be substituted for hydrogen peroxide. Thus, sodium periodate may be substituted mole for mole in place of hydrogen peroxide. While the oxidation step can be carried out using the stoichiometric quantity of oxidizing agent, desulfurization is usually more nearly complete if an excess of oxidizing agent is used.

The acidic medium, which appears to act as a catalyst, may be a water soluble organic carboxylic acid such as formic acid, acetic acid, chloroacetic acid, dichloroacetic acid, or trichloroacetic acid; a sulfonic acid such as benzenesulfonic acid or carbobenzoxysulfonic acid; an oxymineral acid such as sulfuric, nitric, or chloric acid; or mixtures of two or more of the above acids. Ordinarily, the acidic medium is an aqueous solution of the acid, although the presence of water is not essential if the anhydrous acid is a liquid. A particularly effective catalyst is acetic acid. The acid concentration is generally from about 10% to about 100% by volume. Excellent results have been obtained in concentrations of about 50% by volume of acetic acid in water, and other concentrations in the range of 10% to 100% by volume of acetic acid are quite effective. Mixed acid systems, such as aqueous solutions of acetic and sulfuric acids, are highly effective catalysts. Such a system may contain, for example, about 1 to 50 volume percent acetic acid, about 1 to 50 volume percent of sulfuric acid, and up to about 90 volume percent of water. When a haloacetic acid is used, the amount may be from about 1 to about 30 moles per liter of petroleum fraction being disulfurized.

The oxidation reaction of this invention may be carried out by mixing the hydrocarbon fraction, preferably dissolved in an inert hydrocarbon solvent such as benzene, with the aqueous acidic solution. The reaction mixture is agitated vigorously by stirring, for example, throughout the reaction in order to assure a good contact between the hydrocarbon and the aqueous phase. Hydrogen peroxide or other oxidizing agents is added to the reaction medium incrementally throughout the reaction. Alternatively, the entire amount of oxidizing agent may be charged to the aqueous medium prior to admixture with the hydrocarbon, but best results are obtained when the oxidizing agent is added incrementally as the reaction progresses.

The reaction may be carried out at either subatmospheric, atmospheric, or superatmospheric pressures, and at elevated temperatures ranging from about 100° to about 300° F. In general, the results obtained at atmospheric pressure are just as good as those obtained at either subatmospheric or superatmospheric pressure, and hence atmospheric pressure is preferred. Excellent results may be obtained when operating at the reflux temperature of the hydrocarbon diluents; in the case of benzene, this is about 167° F. The oxidation reaction may be carried out over periods of time ranging from about 10 minutes up to about 4 hours or more. Complete oxidation can generally be obtained in periods ranging from about 30 minutes to about 2 hours.

The oxidation conditions utilized in the present invention oxidize the bivalent sulfur compounds to the sulfone state. A part of the bivalent sulfur may be oxidized only to the sulfoxide state. However, sulfone formation is preferred because the sulfones are more easily cleaned than sulfoxides in the second step of the reaction according to this invention.

Upon completion of the reaction, the aqueous and hydrocarbon phases are separated, and the oxidized hydrocarbon fraction (i.e., the hydrocarbon fraction containing an oxidized sulfur compound such as a sulfone or sulfoxide) is then treated according to the second step of the process of this invention. Benzene or other diluent used in the first step of the reaction may be distilled off prior to the second step; this is a preferred procedure, since the hydrocarbon diluent would be instantly volatilized at the reaction temperatures prevailing in the second step.

In the second step, the hydrocarbon fraction containing the oxidized sulfur compound is contacted with an alkali metal hydroxide in the molten state. The preferred base is sodium hydroxide, but equally successful results have been achieved with potassium hydroxide. Excellent results have been obtained at temperatures in the range of about 572° to about 752° F. (about 300° to about 400° C.); generally, the reaction may be conducted at temperatures ranging from about 482° to about 842° F. (about 250° to about 450° C.). The reaction is most advantageously carried out at pressures of about 0 to about 100 p.s.i.g., although higher or lower pressures may be used. In a preferred mode of operation, the reaction is carried out in a corrosion resistant autoclave, either glass lined or made of a corrosion resistant alloy such as "Inconel," for example, under autogenous pressure at desired temperature. The reaction requires at least 5 moles of alkali metal hydroxide for every mole of sulfone to be treated. When treating residua, the preferred amounts of metal hydroxide will be from about 0.5 to about 1.5 parts by weight of alkali metal hydroxide on the anhydrous basis for each part by weight of residuum. (This corresponds to about 10 to 30 moles of NaOH per mole of sulfur, assuming the residuum contains 4.2% by weight S.) These ratios have been found suitable in treating a high sulfur residuum such as the atmospheric residuum from Safaniya crude; it will be understood that the amount of alkali metal hydroxide will be proportionately less when the sulfur content of the hydrocarbon fraction being treated is lower.

The reaction mechanism for the cleavage of sulfones by alkali metal hydroxides is not clear cut. A slight amount of the hydrocarbon residuum may enter the reaction. The principal reaction products are a desulfurized hydrocarbon fraction having significantly lower sulfur content than the original hydrocarbon fraction, and various inorganic sulfur and carbon compounds such as sulfides, sulfites, sulfates, thiosulfates, and carbonates. The use of potassium hydroxide as the base favors the formation of carbonate to a much greater extent than does the use of sodium hydroxide. Sulfide is the preponderant sulfur-bearing ion in the reaction product mixture. It will be noted that the greater part of the sulfur present in the hydrocarbon fraction after the first stage is transformed in the second step into water soluble inorganic sulfur compounds.

Alkali metal hydroxides are the only bases which have been found to be effective according to the present invention. Other bases such as calcium hydroxide, sodium carbonate, potassium carbonate, and cupric oxide are not effective.

Upon completion of the alkali metal hydroxide treatment, the reaction mixture is cooled and water is added in order to dissolve the inorganic reaction products. The sulfur compound, as well as excess unreacted alkali, go into the aqueous phase. The aqueous phase can be separated from the hydrocarbon phase by allowing the reaction mixture to settle. The heavy hydrocarbon fraction having considerably reduced sulfur content as compared to the initial or untreated heavy hydrocarbon fraction is recovered. Generally, sulfur removals of about 75 to 90% can be obtained according to this invention.

This invention will now be described further with respect to specific embodiments thereof, as illustrated by the following examples.

EXAMPLES

Examples 1 to 3 illustrate desulfurization of an atmospheric residuum of a high sulfur crude oil, showing the effect of varying the oxidizing agent to feed ratio and of using different reaction media in the oxidation step, and the effect of varying the caustic to hydrocarbon ratio in the desulfurization step.

Example 1

This example describes the desulfurization of a high sulfur residuum obtained by atmospheric distillation of Safaniya crude oil. The residuum was desulfurized in a two-step process comprising oxidation followed by caustic treatment. The residuum contained 4.2% by weight S, mostly in the form of thiophenes.

Four 100-cc. portions of residuum, each diluted with 450 cc. of benzene, were added to solutions of 50 cc. of glacial acetic acid and 50 cc. of water. Predetermined amounts of 30% aqueous hydrogen peroxide, corresponding to 2, 4, 6, and 8 moles of H_2O_2, respectively, per mole of S, were added to the systems at the reflux temperature of the hydrocarbon phase (167° F.) over a period of one hour. The systems were refluxed for an additional two hours. The reaction mixtures were allowed to cool, the aqueous and benzene phases separated, and the benzene distilled off to yield the residuum samples, each having a volume of about 100 cc. Recovery of acid in the aqueous phase was nearly complete (about 97% to more than 99%) in each run, so that little caustic was required for neutralizing acid in the ensuing desulfurization step. The sulfur content of the residuum from each run was determined.

Two 50 cc. aliquots of each of the oxidized residuum samples were desulfurized with molten sodium hydroxide. These runs were carried out at 572° F. (300° C.) in an Inconel autoclave under autogenous pressure for about 4.5 hours, using 20 g. (0.5 mole) of molten sodium hydroxide. The weight ratio of residuum to NaOH in each run was 2.5. Upon termination of the reaction, the autoclave was allowed to cool, benzene was added to dilute the residuum, water was added to dissolve the base and inorganic products, the mixture was heated at 212° F. for one hour, cooled, allowed to settle, and the benzene phase was removed. The desulfurized residuum was obtained by distilling off the benzene diluent. The sulfur content of each residuum sample was determined. The desulfurization procedure was also carried out on two 50 ml. aliquots of unoxidized residuum.

Results are given in Table II below.

TABLE II

Run	Oxidation		Desulfurization	
	Moles H_2O_2/Mole S	Percent S	Percent S	Percent S Removed
A	2	4.10	3.53, 3.28	20
B	4	3.97	2.03, 2.24	50
C	6	4.08, 4.19	1.39, 1.84	62
D	8	2.56, 2.89	0.68, 0.77	82
Blank	0	4.2	3.68, 3.68	13

Example 2

This example illustrates desulfurization of a high sulfur residuum in a process comprising oxidation with hydrogen peroxide followed by caustic desulfurization, using sulfuric acid as a catalyst in the oxidation step.

In each oxidation run, a 250-cc. sample of Safaniya residuum as described in Example 1 was added to a solution made by combining 125 cc. of glacial acetic acid, 25 cc. of concentrated sulfuric acid, and 125 cc. of water. This solution was heated to 167° F. and refluxed at that temperature for 7 hours. During this time 284 cc. (2.78 moles) of 30% aqueous hydrogen peroxide was added. The system was then allowed to cool and the aqueous and residuum phases were separated.

Two 50-cc. aliquots of each sample of oxidized residuum were desulfurized with molten sodium hydroxide in an Inconel autoclave at autogenous pressure for 5 hours. The amounts of NaOH and the temperatures, as well as the weight percentage of sulfur in the product and the percentage of sulfur in the product and the percentage of sulfur removed, are recorded in Table III below.

TABLE III

Run	Temp., ° F.	Wt. Ratio, NaOH to Residuum	Wt. percent S	Percent S Removed
E	572	1.2	1.06	75
F	662	0.8	1.21	72

Example 3

This example illustrates the effects of the base-to-residuum ratio and of temperatures on desulfurization.

Four 100-cc. samples of Safaniya residuum were oxidized with hydrogen peroxide in the presence of aqueous acetic acid as described in Example 1. Two 50-cc. aliquots of each oxidized sample were desulfurized using either sodium hydroxide or potassium hydroxide as indicated in Table IV below. Also indicated in Table IV are base/residuum weight ratio, temperature, time, weight percentage of sulfur in the product, and percentage sulfur removal.

TABLE IV

Run	Base	Wt. Ratio, Base to Residuum	Temp., °F.	Time, hrs.	Wt. percent S	Percent S Removed
G	NaOH	0.8	572	4.5	2.33 2.22	46
H	NaOH	1.2	572	5	1.58 1.59	63
J	NaOH	0.8	662	5	1.44 1.59	64
K	KOH	1.1	572	5	1.68 1.70	60

The behavior of a sulfur-containing residuum can be predicted in large measure in laboratory tests using a refined heavy hydrocarbon oil to which a specific sulfur compound has been added. Examples 4 to 9 illustrate such tests, using a white oil to which dibenzothiophene was added.

Examples 4 through 9 show the use of various oxidizing agents and reaction media in the oxidation step.

Example 4

About 0.1 mole of dibenzothiophene was contacted with an oxidizing agent. The oxidizing agent was 0.2 mole of H_2O_2 in 200 cc. of acetic acid. The two were contacted in a glass vessel at a temperature of 212° F. for about one hour. The reaction mixture was well agitated. At the end of this time, a 90% yield of dibenzothiophene sulfone was obtained. This is determined by melting point and gas chromatographic data. Following this, the dibenzothiophene sulfone was dissolved in 750 cc. of mineral oil and about 0.5 mole of NaOH was mixed with the solution. The mixture was heated at 392° F. for a period of about three hours in a glass vessel. Pressures utilized were ambient. At the end of this time, complete conversion of the sulfone was observed and about an equimolar mixture of sodium 2-phenylbenzene sulfonate and sodium 2-phenylphenolate was obtained. The sulfonate was identified by conversion to a sulfonyl chloride by PCl_5 and the phenolate was substantiated by infrared. The phenolate and sulfonate mixture was treated next with a 5-mole excess of NaOH at 572° F. for five hours. At the end of this time a 90% yield of dibenzofuran was obtained. The furan was identified by gas chromatography and mass spectrography.

Example 5

The following example indicates the relative success in converting dibenzothiophene which is attained with various oxidizing mixtures. In all instances, the dibenzothiophene was treated under identical conditions. About 5.14 g. of dibenzothiophene in a solution made up of 100 cc. of highly refined white oil, to which 5 cc. of n-hexadecane was added to serve as a chromatographic standard, was

contacted with 16.6 cc. of 30% H_2O_2 in various aqueous acidic reaction media for a period of 120 minutes in a glass vessel. The temperature utilized for all runs was 212° F. Atmospheric pressure was used in all runs. The white oil solution of the dibenzothiophene and the oxidizing mixtures were separately heated to reaction temperature and then brought into reaction in a well agitated flask. Aliquot samples of the oil were taken initially and periodically as the run progressed and were analyzed by gas chromatography. The conversion of dibenzothiophene was determined by measuring its peak area on the chromatograph relative to the peak area of the n-hexadecane. The reaction products were isolated and found to be dibenzothiophene sulfone by gas chromatography, infrared and by melting point. Table V below indicates the conversions obtained.

TABLE V

Run	30% H_2O_2, cc.	Glacial Acetic Acid, cc.	Water, cc.	Conc. H_2SO_4, cc.	k min.$^{-1}$	Percent DBT Conversion
1	16.6	10	90	----	.0032	30 (120 min.).
2	16.6	10	80	10	.0189	68 (80 min.).
3	16.6	50	50	----	.0255	80 (60 min.).
4	16.6	50	50	----	.0202	82 (100 min.).
5	16.6	50	49	1	.296	98 (15 min.).
6	16.6	50	40	10	.547	94 (5 min.).
7	16.6	75	25	----	.0941	90 (24 min.).
8	16.6	100	----	----	.346	90 (7 min.).
9	16.6	10	65	25	.0866	90 (27 min.).
10	16.6	25	65	10	.100	90 (23 min.).
11	16.6	----	75	25	Nil	No conversion.
12	16.6	----	50	50	.0156	85 (120 min.).

The oxidation products of this example may be reacted with caustic alkali according to any of the procedures in Examples 1 to 4 in order to obtain a hydrocarbon fraction (in this case white oil) of reduced sulfur content.

These data clearly show that the addition of sulfuric acid to the aqueous acetic acid-hydrogen peroxide oxidation medium greatly increases the rate of oxidation of dibenzothiophene despite the fact that sulfuric acid alone is a very poor oxidation catalyst, as shown in Runs 11 and 12. The addition of 10 cc. of H_2SO_4 to the mixture containing 10 cc. of acetic acid in Run 2 brought about an increase in the oxidation rate comparable to increasing the amount of acetic acid to 50 cc. in Run 4. The addition of 1 cc. of sulfuric acid in Run 5 and 10 cc. of sulfuric acid in Run 6 brought about very marked improvement. The addition of the 1 cc. of sulfuric acid, with 50 cc. of glacial acetic acid, resulted in a 98% conversion in 15 minutes. This rate is almost as good as that which was effected in Run 8 with 100 cc. of glacial acetic acid and no H_2SO_4. Furthermore, the presence of only 10 cc. of sulfuric acid in Run 6 brought about a result which was markedly superior to the use of 100 cc. of glacial acetic acid alone. Of more practical importance, the presence of 25 cc. of sulfuric acid and 10 cc. of acetic acid in Run 9 brought about a rate that is comparable to that with 75 cc. of acetic acid and no H_2SO_4 in Run 7. Also, 10 cc. of sulfuric acid and 25 cc. of acetic acid in Run 10 was superior to the use of 75 cc. of acetic acid alone. Thus, it is possible to use relatively dilute acid media and still accomplish high rates of oxidation.

The presence of an acid catalyst is essential to the obtaining of a reaction between dibenzothiophene and hydrogen peroxide. This is shown by the following Comparison Run A, which was conducted under conditions similar to those of Example 5, except for the omission of the acid catalyst.

Comparison Run A.—About 100 cc. of water was added to a solution of 5.14 g. of dibenzothiophene in a mixture of 100 cc. of white oil and 5 cc. of n-hexadecane in a 300 cc. autoclave. To this mixture 16.6 cc. of 30% by weight aqueous hydrogen peroxide was added. The reaction mixture was maintained at 212° F. for 2 hours. No oxidation was observed.

From the above, it is apparent that this invention represents a significant improvement in the oxidation art. The addition of small quantities of sulfuric acid will greatly reduce the amount of acetic acid needed to maintain a high reaction rate and therefore permit the use of large amounts of water. Because acetic acid is more soluble in water than in oils, good recovery of the acetic acid will be possible. Furthermore, the use of dilute aqueous media reduces the possibility of emulsion formation, which would complicate acid recovery in a commercial process.

Since small amounts of sulfuric acid will greatly increase the oxidation rate, large volumes of water may be tolerated in the reaction mixture. The use of more dilute media will result in a considerable financial saving in process equipment and heat requirements. Most important of all, there is considerably less hazard in handling H_2O_2 when it is dilute rather than when it is concentrated. The sulfuric acid which is used in this reaction will also be dilute due to the large amounts of water which are present. It is well-known in the art that dilute sulfuric acid can be more readily recovered from a process that can be concentrated acid. Naturally, a great saving in the amount of glacial acetic acid needed will also ensue since sulfuric acid may be utilized as an effective substitute for large amounts of acetic acid. Since a dilute acid medium is employed, separation of the hydrocarbon from the aqueous phase is also easier, since emulsions tend to form in the presence of concentrated acid solutions.

It is also within the scope to utilize halogenated acetic acids such as mono-, di-, and tri-chloroacetic acids, as catalysts along with H_2O_2. In this instance, sulfuric acid will not be needed to speed up the reaction since it proceeds satisfactorily. This is further substantiation of the advantage of having strong acids in mixture with acetic acid in the oxidation medium, since the haloacetic acids have very much higher acid strengths than acetic acid itself. Furthermore, because the haloacetic acids are stronger acids and have higher polarities, they are much less oil soluble than acetic acid and would be more readily recovered. The advantages of using haloacetic acids are illustrated in the example below.

Example 6

These experiments were conducted in the same manner as those discussed in the previous example except that the indicated haloacetic acid was used in place of the sulfuric-acetic acid mixtures. Again, 5.14 g. of dibenzothiophene and 5 cc. of n-hexadecane (chromatographic standard) were dissolved in 100 cc. of white oil and heated to 212° F. This oil was then brought into reaction with oxidation mixtures made up of 0.435 mole of the acid catalyst indicated below in 75 cc. of water to which 16.6 cc. of 30 weight percent H_2O_2 was added. Again, aliquot samples of the oil were withdrawn and analyzed by gas chromatography to determine the extent of dibenzothiophene disappearance. The reaction product was found to be dibenzothiophene sulfone.

TABLE VI

Run	Acid Catalyst	k. min.$^{-1}$	Rate Relative to Acetic Acid
1	Acetic acid	0.0058	1.0
2	Chloroacetic acid	0.092	15.9
3	Dichloroacetic acid	0.329	56.7
4	Trichloroacetic acid	0.092	15.9
5	Trifluoroacetic acid	0.121	20.9

These runs clearly show the advantage of using haloacetic acids in place of acetic acid. The haloacetic acids are 16 to 57 times as effective as an equimolar quantity of acetic acid. Also, the oxidation rates with these very dilute aqueous solutions are comparable to the use of 75 volume percent acetic acid. The acetic acid used in Run 1 was 25 volume percent for comparison.

Examples 7 and 8 show that barium peroxide in an acidic reaction medium can be used instead of hydrogen peroxide as the oxidizing agent.

Example 7

In this example barium peroxide in an aqueous acetic acid reaction medium was utilized as the oxidizing agent for dibenzothiophene dissolved in a hydrocarbon oil. About 5.14 g. of dibenzothiophene (DBT) and 5 cc. of small n-hexadecane were dissolved in 100 cc. of heavy white oil. A mixture of 100 cc. of glacial acetic acid into 25 cc. of water was utilized as the reaction medium. The solution of dibenzothiophene and n-hexadecane in the white oil was added to the reaction medium. The resulting mixture was heated to 212° F. at ambient temperature in a flask which was agitated in conjunction with the heating, and was maintained at this temperature for four hours. During the first 160 minutes after the reaction mixture reached 212° F., barium peroxide was added incrementally at 20-minute intervals in amounts shown in Table VII below. Samples were taken at the times indicated in Table VII below to determine the effect of adding barium peroxide gradually to the reaction mixture. These tests were labeled 1 through 12 and are presented in Table VII.

TABLE VII

Test	Time, min.	Gms, BaO_2 Added	Total, Mole BaO_2/Mole DBT	Percent DBT Conv. by GC
1	0	4.8	.86	0
2	20	2.0	1.22	12.6
3	40	2.0	1.56	45.5
4	60	2.1	1.96	59.5
5	80	1.7	2.26	79.0
6	100	1.7	2.56	91.6
7	120	1.7	2.87	90.9
8	140	2.6	3.33	93.4
9	160	0.9	3.50	92.6
10	180		3.50	
11	210		3.50	95.7
12	240		3.50	96.3

Example 8

This example shows the effect of varying the ratio of acetic acid to water, and the effect of incremental addition of barium peroxide versus addition of the entire amount at the beginning of the reaction period. The reaction conditions were the same as in Example 7, except that the amounts of acetic acid in water present were varied as indicated in Table VIII.

TABLE VIII

Total, Moles BaO_2/Mole DBT	Acetic Acid, cc.	Water, cc.	Mode of BaO_2 Addition	Time, min.	Percent DBT Conv.
2	40	0	All initially	5–15	*20–25
2	40	10	do	5	*29
3.5	50	50	1 g./10 min	180	44
3.5	100	25	2 g./20 min	180	92
3.5	100	25	2 g./20 min	180	93
3.5	100	25	2 g./10 min	100	92

*No further conversion after 120 to 240 minutes.

When all of the barium peroxide was added rapidly at the outset, the maximum conversion of dibenzothiophene was only 29%. In the case of the slower incremental addition, far better conversions were obtained. When adding at a rate of 2 g. each 20 minutes a conversion of dibenzothiophene of 93% was obtained. This is determined in the same manner as in Example 7.

In view of the above, it is apparent that barium peroxide, when used in conjunction with water and acetic acid, produces an excellent conversion of dibenzothiophene. The preferred rate of addition of the barium peroxide, i.e., about 1 to 2 moles of BaO_2/mole S/hr., serves to enhance greatly the performance of the instant invention.

Barium peroxide does not react with dibenzothiophene in the absence of acid. This will be shown in comparison Runs B and C which follow.

Comparison Run B.—About 100 cc. of water was added to a solution of 5.14 g. of dibenzothiophene and 5 cc. of n-hexadecane in 100 cc. of white oil in a 300 cc. autoclave. Then 22.2 g. of 85% by weight barium peroxide was added, and the reaction mixture was heated to 212° F. at autogenous pressure with stirring. No reaction took place. Increasing the temperature up to 572° F. still did not produce any oxidation of dibenzothiophene to the sulfone state even after 21 hours.

Comparison Run C.—The procedure of Comparison Run B was followed except that the water was omitted from the reaction mixture. As in Comparison Run B, no reaction was observed.

Sodium periodate catalyzed by aqueous acetic acid is also an effective oxidizing agent for dibenzothiophene, as shown in Example 9.

Example 9

This example shows the effect of various conditions, i.e., temperature, acid concentration, and mole ratio of sodium periodate to sulfur compound, in oxidizing dibenzothiophene in white oil. In this example a series of runs was made in which 0.028 g. moles (about 5.14 g.) of dibenzothiophene was added to a mixture of 100 cc. of white oil and 5 cc. of hexadecane in a reaction flask. Sodium periodate in 100 cc. of aqueous acetic acid was added to this mixture, and the resulting mixture was heated with stirring. Reaction temperature and time, and the amounts of acetic acid, water, and sodium periodate used to make up the aqueous phase, as well as the results obtained, are shown in Table IX below.

converting a major portion of the bivalent sulfur content to the sulfone state,

(b) contacting the treated hydrocarbon fraction containing sulfones with a molten alkali metal hydroxide, thereby converting said sulfones into water soluble sulfur compounds, and

(c) recovering a heavy petroleum hydrocarbon fraction of reduced sulfur content.

2. A process according to claim **1** in which said hydrocarbon fraction is treated with said peroxy compound in the presence of an aqueous acidic medium.

3. A process according to claim **2** in which said heavy petroleum hydrocarbon fraction is a residuum.

4. A process according to claim **1** including the steps of adding water to the reaction mixture obtained on contacting said hydrocarbon fraction with said alkali metal hydroxide, thereby dissolving water soluble sulfur compounds and unreacted alkali metal hydroxide in the aqueous phase, and separating said aqueous phase from said hydrocarbon fraction.

5. A process according to claim **2** in which said aqueous acidic medium comprises a haloacetic acid.

6. A process according to claim **1** in which said peroxy compound is an alkali metal or alkaline earth metal peroxide.

7. A process according to claim **6** in which said peroxide is barium peroxide.

8. A process according to claim **1** in which said peroxy compound is an alkali metal periodate.

TABLE IX

[0.028 g. mole S compound, 5 cc. hexadecane, 100 cc. white oil]

Run	Temp., ° F.	Time, mins.	H_2O, cc.	Acetic Acid, cc.	$NaIO_4$, g.	Mole $NaIO_4$/mole S	Percent Conv.	Percent Yield of Sulfone
4	167	120	50	50	17.9	2	67	------------
5	167	120	50	50	23.86	4	80	88
6	167	120	50	50	47.72	8	81	72
7	167	120	25	75	23.86	4	94	90
8	212	20	50	50	47.72	8	75	100
9	212	50	50	50	23.88	4	94	90
10	212	120	75	25	23.88	4	81	75
11	212	30	25	75	23.88	4	99	100

These results as outlined in Table IX show that solutions of aqueous acetic acid and sodium periodate in combination are extremely effective for the oxidation of organic sulfur compounds in hydrocarbon solution to sulfones. The results of Runs 4, 5 and 6 show that the effectiveness of the system is relatively independent of the quantity of periodate used as long as a minimum of 2 mole $NaIO_4$ per mole of sulfur compound is present. The results of Runs 6, 7, 8 and 11 show the advantage of carrying the reaction out at 212° F. The results of Runs 9, 10 and 11 show that increased acetic acid concentration also has a beneficial effect on the extent of conversion. Extremely good results can be obtained at 212° F. using 4 moles of $NaIO_4$ per mole of S compound in aqueous solutions containing 25 to 75% by volume of acetic acid.

Sodium periodate is ineffective as an oxiding agent for dibenzothiophene in the absence of the acetic acid catalyst. An attempt was made to oxidize dibenzothiophene with sodium periodate in the absence of acetic acid, and no reaction took place.

It will be understood that the foregoing specification and examples are illustrative of preferred embodiments of the invention but that variations can be made by those skilled in the art without departing from the scope and spirit of this invention.

What is claimed is:

1. A process for reducing the sulfur content of a heavy petroleum hydrocarbon fraction, having an initial boiling point above about 600° F. and which contains bivalent sulfur in the form of thiophenes, which comprises:

(a) treating said heavy petroleum hydrocarbon fraction with a peroxy compound under conditions for

9. A process for treating a heavy petroleum hydrocarbon fraction in order to oxidize bivalent sulfur therein which comprises contacting the hydrocarbon fraction with an aqueous solution of an organic carboxylic acid and a peroxide selected from the group consisting of the alkali metal and alkaline earth metal peroxides under reaction conditions for oxidizing said bivalent sulfur.

10. A process according to claim **9** in which said peroxide is barium peroxide.

11. A process according to claim **9** in which said peroxide is added incrementally.

12. A process for treating a heavy hydrocarbon fraction containing bivalent sulfur in order to oxidize said sulfur, which comprises contacting said hydrocarbon fraction at reaction conditions with an aqueous solution of an organic carboxylic acid and a water-soluble periodate.

13. A process according to claim **2** in which said peroxy compound is hydrogen peroxide.

14. A process for reducing the sulfur content of a heavy petroleum hydrocarbon fraction having an initial boiling point above about 600° F. and which contains bivalent sulfur in the form of thiophenes, which comprises:

(a) treating said heavy petroleum hydrocarbon fraction with a peroxide compound in an acidic liquid medium under conditions for converting a major portion of the bivalent sulfur content to the sulfone state;

(b) contacting the treated hydrocarbon fraction containing sulfones with a molten alkali metal hydroxide, thereby converting said sulfones into water-soluble sulfur compounds; and

(c) recovering a heavy petroleum hydrocarbon fraction of reduced sulfur content.

15. A process according to claim **14** in which said acidic medium is an aqueous acidic medium.

References Cited

UNITED STATES PATENTS

3,341,448	9/1967	Ford et al.	208—211
3,284,342	11/1966	Nathan et al.	208—208
3,163,593	12/1964	Webster	208—219
2,744,054	5/1956	Peters	196—29
3,413,307	11/1968	Heimlich	260—329.3
607,017	7/1898	Colin	208—230

DELBERT E. GANTZ, Primary Examiner

J. M. NELSON, Assistant Examiner

U.S. Cl. X.R.

208—196