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DESULFURIZATION PROCESS INCLUDING AN OXIDATION STEP WITH OZONE AND A VANADIUM CATALYST

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9 Claims

ABSTRACT OF THE DISCLOSURE

A desulfurization process for the reduction of sulfur in a sulfur containing hydrocarbon oil by contacting the sulfur containing hydrocarbon oil with ozone in the presence of a Group IV-B, V-B or Group VI-B metal followed by sulfur reduction utilizing for example a base treatment, a thermal treatment or a hydrosulfurization treatment.

This invention relates to the desulfurization of a hydrocarbon material and more particularly to the desulfurization of hydrocarbon materials of petroleum origin and in particular petroleum fraction of high molecular weight.

In the past, numerous processes have been employed to eliminate undesirable sulfur compounds or to convert them into more innocuous forms. One type of process involves physical extraction with a liquid such as sulfuric acid, the sulfur dioxide or furfural. Another type of process removes the sulfur compounds by adsorption on suitable materials, for example activated bauxite, activated charcoal or an activated clay. A further type of process converts objectionable forms of sulfur compounds, such as mercaptans, into less harmful forms, such as disulfides and polysulfides by various chemical treatments, for example plumbite treatments, hydrochlorite treatments and copper chloride treatments. The above processes are particularly used for the treatment of gasoline fractions. With feedstocks of high molecular weight, a large proportion of the material is in the form of molecules containing at least one sulfur atom, including thiophene sulfur and, particularly in selective separation processes, would be removed only to a limited extent and with consequent low product yield.

In addition to the above methods for desulfurization of a hydrocarbon material, desulfurization of hydrocarbon materials has been attempted utilizing oxidation with oxygen as an oxidant followed by thermal treatment to remove sulfur from the oxidized material. The problem that arises utilizing the prior art methods is that heavy hydrocarbon materials such as vacuum residues contain sulfur in the form of thiophene sulfur which type of sulfur is particularly difficult to remove from such hydrocarbon material. In addition, the air oxidation of a sulfur containing hydrocarbon material is not selective towards sulfur oxidation of the hydrocarbon materials, and the formation of ketones and acids occurs.

Additional disadvantages of the prior art methods are the high product losses which occur using for example an air oxidation process as well as the length of time that is needed in order to effect even minimum sulfur removal. As is apparent from the foregoing, there exist the problems in a desulfurization process of obtaining low product losses, high percent sulfur reduction and in the case of an oxidation process selectivity as to what material is oxidized.

It is therefore an object of this invention to increase desulfurization of a hydrocarbon material at low product losses.

It has now been found that desulfurization of a hydrocarbon material can be accomplished by contacting a sulfur containing hydrocarbon material with ozone in the presence of a metal catalyst selected from the group consisting of Group IV-B metals, Group V-B metals and Group VI-B metals, and reducing the sulfur content of the hydrocarbon material utilizing a sulfur reducing process step. Thus it has been found that the use of certain Group IV-B, V-B and Group VI-B metal catalysts (hereinafter referred to as catalysts) in combination with ozone is selective toward the oxidation of sulfur, that is, undesirable oxidation products are not formed to any substantial degree. In addition, low product losses (e.g. high product yields) are obtained during the subsequent removal of sulfur using a sulfur reduction treatment. By the term desulfurization process is meant the process of treating a sulfur containing hydrocarbon material with ozone in the presence of a metal catalyst in conjunction with the process step of sulfur reduction. The sulfur reduction process step can be by way of example a base treatment process, a thermal treatment process, a solvent refining process or a hydrosulfurization process. Thus, the use of certain metal catalysts with ozone promotes the oxidation of sulfur in a hydrocarbon material whereby selectivity is accomplished without appreciably lowering product yield. A particularly preferred embodiment of this invention is the use of the oxidation step in combination with either a base treatment process or a thermal treatment process. These processes are preferred since it has been discovered that these two processes are capable of effecting excellent sulfur removal and reduction in combination with the ozone oxidation step with minimum losses of reduced sulfur containing hydrocarbon material.

In general the process of this invention is carried out by contacting the sulfur containing hydrocarbon material with ozone in the presence of a metal catalyst for a time sufficient to effect oxidation of at least a portion of the sulfur present in the hydrocarbon material (that is an oxidizing amount of ozone.) The catalyst is used at a concentration which is sufficient to promote the effectiveness of ozone. In general, however, it is preferred to use a catalyst concentration varying from about 0.0001 to about 10 wt. percent based upon the weight of the sulfur containing hydrocarbon oil and still more preferably from about 0.10 wt. percent to about 10 wt. percent. The concentration of ozone is usually dependent upon the weight percent sulfur present in the hydrocarbon material and in general the mole ratio of ozone to sulfur is from about 0.2 to about 10 mole of ozone per mole of sulfur, more preferably from about 0.5 to about 8 moles of ozone per mole of sulfur and still more preferably from about 1.5 to about 5 moles of ozone per mole of sulfur. The temperature utilized in carrying out the ozone oxidation step in general is from about 20° F. to about 125° F. preferably from about 30° F. to about 75° F. The process of this invention can be carried out at atmospheric pressure although pressures up to about 100 atmospheres or higher can be utilized.

The time which is utilized for carrying out the process of this invention can vary over a wide range and in general varies depending upon the rate of contact of moles of ozone per mole of sulfur present in the sulfur containing hydrocarbon material as a function of time. In general times varying from one-half hour to twenty-four hours preferably from about one hour to about twelve hours are utilized in carrying out the process of this invention. The mole ratios of ozone to sulfur which are set forth above relate to the total moles of ozone which are utilized within the time span as set forth above. In carrying out the process of this invention, solvents can be utilized in combination with the sulfur containing heavy

hydrocarbon material. Thus for example, solvents such as chloroform and fluorinated hydrocarbons can be mixed with the sulfur containing heavy hydrocarbon material in varying amounts such as volume of solvent to volume of sulfur containing hydrocarbon material of from about 0.1:1 to about 4:1. In addition, the ozone gas can be combined with other gases during contacting of the sulfur containing heavy hydrocarbon material with ozone. Thus ozone can be blended with gases such as nitrogen, oxygen and/or air and the use of such gases together with ozone is contemplated within the scope of this invention.

The ozone step as set forth above, can optionally include a stripping of the hydrocarbon material with a gas such as steam, hydrogen, carbon monoxide, carbon dioxide or nitrogen. This stripping step can accompany the oxidation step or can follow the oxidation step prior to the sulfur reducing step.

Many types of apparatus are suitable for carrying out the reaction including rocking autoclave, mechanically stirred tanks, etc. The reactions can be carried out batchwise semicontinuously or continuously.

In carrying out the process of this invention a sulfur reduction step is utilized in combination with the oxidation step. A brief description of the preferred sulfur reduction step that is the base treatment process and thermal treatment process are illustrated below together with a hydrodesulfurization step which can in addition be utilized.

In the base treatment step the oxidized sulfur containing hydrocarbon material is contacted with a base preferably an alkali metal hydroxide for a time sufficient to reduce the sulfur content of the hydrocarbon material, generally for about 10 minutes to about 24 hours preferably from about 1 hour to about 6 hours. The reaction temperature is generally from about 300° F. to about 800° F., preferably from about 400° F. to about 700° F. In addition, pressures above atmospheric can be utilized in carrying out the base treatment. Thus, for example pressures up to 100 atmospheres can be utilized in carry-out the base treatment. In general, it is preferred to use an alkali metal hydroxide preferably potassium or sodium hydroxide although alkaline earth metal hydroxides or oxides, calcined dolomitic materials and alkalinized aluminas can be utilized in carrying out the base treatment. In addition mixtures of different bases can be utilized. In general, an aqueous solution of the base hydroxide at a concentration on a mole bases of general from about 1 mole of base to 1 mole of sulfur up to about 4 moles of base per mole of sulfur is utilized.

In the thermal treatment step, sulfur reduction is accomplished by treating the oxidized sulfur containing hydrocarbon material at temperatures above 300° F., preferably above 500° F. and particularly in the temperature range of from about 550° F. to about 800° F. for a period sufficient to ensure that substantially all the gaseous sulfur decomposition products are removed. This period in general is within the range of about ½ to 5 hours, preferably between about ½ to 2 hours. Under these conditions, the oxidized sulfur compounds are decomposed and the sulfur is liberated mainly as SO₂ although at higher temperatures in the region of 550° F. and over, increasing quantities of H₂S are also liberated. The thermal decomposition step may be carried out in the presence of suitable promoting materials comprising porous solids having acidic or basic properties for example, ferric oxide on alumina, bauxite, thoria on pumice, silica alumina, soda-lime and acid sodium phosphate on carbon. Preferably, in the thermal, decomposition step, a small quantity of an inert carrier gas, for example nitrogen, is passed through the reaction mixture to avoid local overheating and also to remove the gaseous sulfur decomposition products.

The catalytic hydrodesulfurization stage may be carried out under relatively mild conditions in a fixed, moving, fluidized or ebullating bed of catalyst. Preferably a fixed

bed of catalyst is used under conditions such that relatively long periods elapse before regeneration becomes necessary, for example a temperature within the range of from about 500 to 900° F. preferably from about 650–800° F., and at a pressure within the range of from about 100 to 2300 p.s.i.g., preferably from about 500 to 1500 p.s.i.g.

This invention contemplates the treatment of various type hydrocarbon material, especially hydrocarbon oils of petroleum origin which contain sulfur. In general, the sulfur content of the oils is in excess of 1%. A particular problem that is encountered in heavy hydrocarbon oil is the presence of thiophene sulfur. Thus it has been found that hydrocarbon oils containing thiophene sulfur are extremely difficult to process as to sulfur reduction utilizing the prior art methods. The use of more drastic conditions utilizing the prior art methods such as air oxidation brings about many problems such as extensive oxidation of the hydrocarbon oil and the formation of extensive amounts of resinous material and coke. The process of this invention is particularly applicable to reducing the sulfur content of hydrocarbon oils which contain thiophene sulfur. Typical examples of hydrocarbon oils which are particularly adaptable to the process of this invention are those petroleum fractions containing a major portion of material boiling above 500° F. for example, crude oil and atmospheric and vacuum residues which contain usually 1% by weight or more of sulfur. Additional examples of hydrocarbon oils to which the present invention may be usefully applied are cracked gas oils, residual fuel oils, topped or reduced crudes, crude petroleum from which the lighter fractions are absent, vacuum residues, residues from cracking processes, oils from tar sands and oil shale. The invention is especially applicable to such of these and other, like materials as cannot be deeply flashed without extensive carry over of sulfur containing compounds. In general the thiophene containing materials which are found in the hydrocarbon oils which are extremely difficult to remove are by way of example tetraphenylthiophene, diacenaphtho [1,2-b,1',2'-d] thiophene and anthra [2,1,9-cde] thianaphthene.

The catalyst which is utilized to promote the oxidation of sulfur is a catalyst selected from Group IV–B, Group V–B and Group VI–B metals. This catalyst can be incorporated into the oxidation system by any means known to those skilled in the art, and can be either a homogeneous or heterogeneous catalyst system. The catalyst can be incorporated by a variety of means or and by the use of a variety of carriers. The particular catalyst carrier which is utilized is not critical with respect to the practice of this invention and can be for example, a support medium or an anion (including complex formation) which is attached to the metal (e.g. a ligand). The particularly preferred metals are titanium, zirconium, vanadium, tantalum, chromium, molybdenum and tungsten. Illustrative ligands include halides, organic acids, alcoholates, mercaptides, sulfonates, phenolates and oxides amongst others. These metals may be also bound by a variety of complexing agents including acetylacetonates, amines, ammonia, carbon monoxide and olefins, amongst others. The metals may also be introduced in the form of organometallics including "ferrocene" type structures. The various ligands illustrated above are utilized solely as carriers to incorporate the metal into the process system and in general have an organic radical attached to a functional group such as the carbonyl carbon of the acid, the oxygen of the alcohol, the sulfur of the mercaptan, the



of the sulfonate, the oxygen of the phenolic compound and the nitrogen of the amines. The organic radical attached to the afore-described functional groups can be

defined as a hydrocarbon radical and in general contains from 1 to about 30 carbon atoms. Typical examples of hydrocarbon radicals are alkyl such as methyl, ethyl, butyl, t-butyl, 3-methyl-1-pentyl, n-octyl and those aliphatic radicals which represent the hydrocarbon portion of a middle distillate or kerosene, cycloalkyl radicals such as cyclopentyl, alkylated cycloalkyl radicals such as mono and polymethylcyclopentyl radicals, aryl and cycloalkyl substituted alkyl radicals, such as phenyl and alkyl phenyl substituted alkyl radicals examples of which are benzyl, methylbenzyl, caprylbenzyl, phenylethyl, phenylpropyl, naphthylmethyl, naphthylethyl, aryl radicals such as phenyl, alkaryl radicals such as xylyl, alkylphenyl, alkylethyl.

The metals present in the heterogeneous catalyst can include one or more metals, the concentration of these metals upon their substrates in general being within the range from about 0.1 to about 10%. These metals may be distended on a suitable material, for example alumina, silica (or combinations of both) as well as activated clays or carbon, amongst others. The modes of contacting whereby the catalytic effect may be achieved may include slurry-bed reactions or continuous contacting over a stationary phase in a trickle-tube reactor. The particularly preferred catalyst for carrying out the process of this invention is molybdenum such as molybdenum hexacarbonyl.

The invention can be better appreciated by the following non-limiting examples.

EXAMPLE 1

To a glass reactor equipped with stirrer and addition means to charged 100 grams of reduced Arabian crude (550+ F. 2.6 wt. percent sulfur) and 100 grams of chloroform solvent. The temperature is reduced to 19° C. and ozone (3.9 percent by weight ozone in an oxygen stream) at 600 ml./min. is introduced into the reduced crude over a period of 2 hours. The ozone is introduced into the reaction mixture in order to produce an ozone to sulfur mole ratio of 1.8:1. After a period of 2 hours the solvent is stripped from the reaction mixture and the reaction mixture is charged to a static reactor for thermal treatment. The temperature of the reaction mix is increased to 650° F. and maintained for a period of 4 hours while bubbling nitrogen through the reaction mixture. The temperature is reduced to ambient temperature and the reduced crude has a percent sulfur of 2.1 wt. percent and the percent desulfurization obtained is found to be 20%.

EXAMPLE 2

To a glass reactor equipped with stir and addition means is charged 100 grams of reduced Arabian crude (550+ F. 2.6 wt. percent sulfur) together with 0.1% by weight based upon the weight of the Arabian crude of oxohydroxy-bis(8-hydroxyquinoline)vanadium and 100 grams of chloroform solvent. The temperature is reduced to 19° C. and ozone (2.1 percent by weight ozone in an oxygen stream at 600 ml./min.) is introduced into the reaction mixture over a period of 5 hours. The ozone is introduced into the reaction mixture in order to produce an ozone to sulfur mole ratio of 1.9:1. After a period of 2 hours the solvent is stripped from the reaction mixture and the reaction mixture is charged to a static reactor for thermal treatment. The temperature of the reaction mix is increased to 650° F. and maintained for a period of 4 hours while bubbling nitrogen through the reaction mixture. The temperature is reduced to ambient temperature and the reduced crude has a percent sulfur of 1.4 wt. percent and the percent desulfurization obtained is found to be 45%.

EXAMPLE 3

A 650° F.+ reduced Arabian crude containing 3.1 percent sulfur was air oxidized in a continuous manner at

300° F., 0.5 LHSV and 2000 s.c.f. barrel air throughput over a 1/8" extended V₂O₅-P₂O₅ catalyst on kieselguhr (11% P₂O₅-3.4% V₂O₅). A 400 gram portion of the oxidized oil was subsequently treated with 100 g. of 40 percent KOH solution at 650° F. for 1.5 hr. Upon work-up and analysis the treated oil fraction contained 3.0 percent sulfur or a 4 percent sulfur reduction with respect to the treated oil.

The preceding examples demonstrate the outstanding effectiveness of the ozone catalyzed oxidation step when combined with a sulfur reducing step as compared to either the ozone alone or to an air catalyzed oxidation step process. More particularly a large increase in sulfur removal was obtained utilizing an ozone catalyzed oxidation step as compared to the non-catalyzed ozone step. In addition the use of air plus catalyst gave little or no percent sulfur reduction when compared to the original sulfur content of the reduced crude oil and especially when compared to the process of this invention.

While this invention has been described with respect to various specific examples and embodiments it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

We claim:

1. In a desulfurization process wherein a sulfur containing hydrocarbon material is oxidized with an oxidant and oxidized sulfur compounds removed by a sulfur reducing process step, the improvement which comprises contacting the sulfur containing hydrocarbon material with a sulfur oxidizing amount of ozone in the presence of oxohydroxy-bis-(8-hydroxyquinolino) vanadium and removing oxidized sulfur compounds.

2. A process of claim 1 wherein the oxidizing amount of ozone is from 0.5 mole of ozone to 8 moles of ozone per mole of sulfur present in the sulfur containing hydrocarbon material.

3. A process of claim 2 wherein the ozone is present in a mole ratio of from about 1.5 moles to about 5 moles of ozone per mole of sulfur present in the sulfur containing hydrocarbon material.

4. A process of claim 1 wherein the oxidized sulfur compounds are removed by heating the oxidation product to 300-800° F.

5. A process of claim 1 wherein the oxidized compounds are removed by contacting the oxidized sulfur containing hydrocarbon material with a solution of a base at a temperature between about 300 and 800° F.

6. A process of claim 1 wherein the oxidized compounds are removed by contacting the oxidized sulfur containing hydrocarbon material with a desulfurization catalyst at a temperature between about 500 and 900° F. and a pressure between about 100 and 2300 p.s.i.g. in the presence of hydrogen.

7. A process of claim 1 wherein the sulfur containing hydrocarbon material is a reduced crude oil.

8. A process of claim 4 wherein the sulfur containing hydrocarbon material is a reduced crude oil.

9. A process of claim 3 wherein the sulfur containing hydrocarbon material is a reduced crude oil.

References Cited

UNITED STATES PATENTS

1,947,869	2/1934	Morrell et al.	208-208
1,969,302	8/1934	Egloff et al.	208-295
3,105,812	10/1963	Flinn et al.	208-295
3,284,342	11/1966	Nathan et al.	208-208
3,341,448	9/1967	Ford et al.	208-208

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