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[54] PROCESS FOR THE DESULFURIZATION OF HYDROCARBONS

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[58] **Field of Search** .... 208/196, 208 R, 240, 243

[56] **References Cited**

UNITED STATES PATENTS

3,565,793	2/1971	Herbstman et al.	208/208 R
3,719,589	3/1973	Herbstman et al.	208/208 R

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[57] ABSTRACT

A process for reducing the sulfur content of sulfur-containing hydrocarbon material by oxidizing at least a portion of the sulfur in the sulfur-containing hydrocarbon material with an oxidant in the presence of certain catalysts, for example, a molybdenum-containing catalyst. The oxidized sulfur-containing hydrocarbon material is further processed by means of a sulfur reducing step to remove sulfur from the hydrocarbon material. A hydrocarbon material having reduced sulfur content is thereafter recovered. The preferred oxidant is tertiary butyl hydroperoxide and the oxidation may occur in the presence of a solvent, preferably tertiary butyl alcohol. The tertiary butyl alcohol, which is removed from the oxidized sulfur-containing hydrocarbon material, can be dehydrated to isobutylene and further dimerized to form diisobutylene.

22 Claims, No Drawings

PROCESS FOR THE DESULFURIZATION OF HYDROCARBONS

The present invention relates to an improved process for catalytically reducing the sulfur content of hydrocarbon materials. More particularly, the invention relates to the reduction in sulfur content of hydrocarbon materials by the catalytic oxidation of the sulfur impurities contained therein, followed by removal of these oxidized impurities.

Petroleum crude oils and topped or reduced crude oils, as well as other heavy petroleum fractions and/or distillates including vacuum tower bottoms, atmospheric tower botttoms, black oils, heavy cycle stocks, visbreaker product effluent and the like, are normally contaminated by excessive concentrations of sulfur. This sulfur may be present in heteroatomic compound which have proven difficult to remove by conventional processing. The sulfur compounds are objectionable, for example, because combustion of fuels containing these impurities results in the release of sulfur oxides which are noxious, corrosive and, therefore, present a serious problem with respect to pollution of the atmosphere.

Many methods have been tried in attempts to remove the sulfur compounds from hydrocarbon material. For example, U.S. Pat. No. 3,565,793 relates to a method for desulfurization of hydrocarbon materials by oxidizing the sulfur-containing hydrocarbon with an oxidant in the presence of a catalyst, followed by a sulfur reducing step. However, many problems arise in trying to catalytically oxidize the sulfur compounds in these hydrocarbon materials. Thus, the sulfur-containing hydrocarbon material is a complex mixture of components and includes sulfur in the form of hetero-atomic sulfur compounds, e.g., thiophene sulfur compounds, which are known to be difficult to remove. The oxidation of sulfur, such as thiophene sulfur, contained in hydrocarbon material is difficult and time consuming even when this oxidation is promoted by a catalyst. The inability of many catalysts to provide a high rate of reaction of sulfur oxidation is one problem involved in the oxidative desulfurization of hydrocarbon material. Additional problems associated with many of the prior art catalysts, include, for example, toxicity, costs, preparation difficulties, handling difficulties and ample availability. It would be advantageous to provide an improved catalyst for the preferential oxidation of sulfur in a sulfur-containing hydrocarbon material.

A further problem associated with the processing of sulfur-containing heavy hydrocarbon materials, i.e., material the major amount of which boils above about 550°F., is the presence of components such as asphaltenes which are difficult to solubilize. This fact takes on added significance when the sulfur oxidation is promoted by a homogeneous, rather than heterogeneous, i.e., supported, catalyst system. Asphaltene solvents, such as benzene, have been used as oxidation solvents so as to provide more efficient contact between the sulfur-containing heavy hydrocarbon material, the oxidant and the homogeneous catalyst system. These extraneous solvents require additional processing to remove from the oxidation product and thus act to reduce process efficiency. Therefore, it would be advantageous to provide an oxidation system in which effective contact between reactants and catalyst is efficiently achieved.

A still further problem having to do with process efficiency is the problem of developing a plentiful and inexpensive source of oxidant effective to preferentially oxidize the sulfur in hydrocarbon materials. Closely linked with this problem is the additional concern of finding uses for the oxidant decomposition products which result from sulfur oxidation. Therefore, it would be advantageous to provide an efficient desulfurization process whereby a plentiful supply of effective oxidant is produced, the oxidant is utilized to preferentially oxidize the sulfur in hydrocarbon material and to provide useful oxidant decomposition product or products.

Therefore, it is an object of the present invention to provide an improved catalyst for the oxidation of sulfur compounds in sulfur-containing hydrocarbon materials.

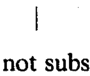
Another object of the present invention is to provide an improved process for the desulfurization of sulfur-containing hydrocarbon materials.

An additional object of the present invention is to provide an efficient process for producing hydrocarbon material having reduced sulfur content utilizing the catalytic oxidation of sulfur impurities contained in hydrocarbon material. Other objects and advantages of the present invention will become apparent hereinafter.

An improved process has now been discovered for reducing the sulfur content of sulfur-containing hydrocarbon material which comprises preferentially oxidizing at least a portion of the sulfur in the sulfur-containing hydrocarbon material with an oxidant in the present of a molybdenum-containing catalyst prepared by a method which comprises interacting molybdenum metal with at least one peroxy compound in the presence of at least one saturated aliphatic alcohol having from one to four carbon atoms per molecule to solubilize at least a portion of the molybdenum. The oxidized sulfur-containing hydrocarbon material is further processed by means of a sulfur reducing step, such as, for example, a base treatment step, a thermal treatment step, a solvent refining step, a hydro-desulfurization step and the like, to remove sulfur from the hydrocarbon material. A hydrocarbon material having reduced sulfur content is thereafter recovered.

In preparing the molybdenum-containing catalysts useful in the present invention, metallic molybdenum is interacted, i.e., co-mingled or contacted, with at least one peroxy compound, e.g., organic hydroperoxide, organic peroxide, organic peracid, hydrogen peroxide and mixtures thereof, in the presence of at least one low molecular weight saturated alcohol, either mono- or poly-hydroxy, containing from one to four carbon atoms per molecule to solubilize at least a portion of the molybdenum metal. It is believed that the molybdenum metal reacts with the peroxy compound to form a compound or complex which is soluble in the saturated alcohol and remaining peroxy compound.

Typical peroxides, hydroperoxides and peracids useful in the preparation of the molybdenum-containing catalyst are described hereinafter as oxidants. These peroxy compounds may also be substituted with groups such as halides, $-NH_2$, —SH,



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and the like, which do not substantially interfere with the catalyst forming process. The most preferred peroxy compound for use in preparing this molbdenum-containing catalyst is tertiary butyl hydroperoxide.

Hydrogen peroxide suitable for preparing the molybdenum-containing catalyst is preferably used in the form of an aqueous solution containing, for example, from about 10% to about 60%, preferably about 30 percent, by weight of hydrogen peroxide.

Typical examples of low molecular weight monohydroxy alcohols which are suitable for use in the preparation of the present molybdenum-containing catalyst include methyl alcohol, ethyl alcohol, isopropyl alcohol, n-butyl alcohol, tertiary butyl alcohol and the like. The low molecular weight polyhydroxy alcohols which are suitable include ethylene glycol, propylene glycol, 1,2-butylene glycol and glycerol. In general, either mono- or poly-hydroxy alcohols containing from one to four carbon atoms per molecule are suitable. Although the presence of the lower alcohols, e.g., methyl alcohol and ethyl alcohol, produces a faster solubilization of molybdenum, in order to maximize the benefit of the overall process of the present invention it is preferred that the molybdenum metal be interacted with tertiary butyl hydroperoxide in the presence of tertiary butyl alcohol. If tertiary butyl alcohol is used as the saturated alcohol, it is preferred, to enhance molybdenum solubility, that the interaction mixture comprise at least one mono- or poly-hydroxy alcohol having from one to about 16 carbon atoms per molecule, at least one primary hydroxy group, and be present in an amount of from about 1 to about 25 percent by weight of the total alcohol present. A particularly preferred alcohol mixture for use in combination with tertiary butyl alcohol is the stream of higher poly-hydroxy alcohols having a molecular weight in the range from about 200 to about 300 and containing from about 4 to about 6 hydroxy groups derived from propylene epoxidation and described in U.S. Pat. No. 3,573,226.

The relative proportions of peroxy compound and low molecular weight saturated alcohol employed in preparing the catalyst may vary over a broad range and is, therefore, not of critical importance to the invention. Typically, the peroxy compound comprises from about 5 to about 50 percent by weight of the total peroxy compound and saturated low molecular weight alcohol used in catalyst preparation.

The molybdenum concentration in the catalyst mixture, i.e., the mixture comprising the dissolved or soluble molybdenum plus any excess peroxy compound and alcohol, often is within the range from about 15 ppm. to about 5 percent, preferably in the range from about 1,000 ppm. to about 2 percent by weight of the total mixture. It may be desirable to prepare the catalyst in the presence of a solvent such as benzene, ethyl acetate and the like, in order to obtain the optimum molybdenum concentration in the final catalyst mixture. However, if this type of dilution is desired, it is preferred that an excess of tertiary butyl alcohol be maintained in the catalyst mixture for this purpose.

The molybdenum metal useful in the preparation of the present catalyst may be in the form of lumps, sheets, foil or powder. The powdered material, e.g., having a particle size such that it passes through a 50 mesh sieve, preferably through a 200 mesh sieve, on the Standard Screen Scale, is preferable since it offers increased surface area per unit volume and an increased rate of solubilization.

The molybdenum metal-peroxy compound interacting may be carried out at a wide range of temperatures, for example, temperatures within the range from about 25°C. to about 150°C. Interacting pressures should be set to avoid extensive vaporization of the peroxy compound and alcohol. Typical interacting pressures may range from about 1 psia. to about 100 psia. In many instances, atmospheric pressure may be used. After the interacting has been carried out for a desired length of time, e.g., from about 5 minutes to about 30 hours, preferably from about 15 minutes to about 6 hours, the product from the interacting may be filtered to separate the undissolved molybdenum from the catalyst mixture which is thereafter suitable for use as a catalyst for the oxidation of sulfur impurities in hydrocarbon materials.

The oxidants which may be used in the oxidation step of the present invention include organic peroxides, organic hydroperoxides, organic peracids, and mixtures thereof. These oxidants have been found to give excellent desulfurization when combined with the reducing and recovery steps described herein. In addition, the use of these oxidants have been found to be selective or preferential for oxidation of the sulfur, that is, substantial amounts of carbon oxidation products such as acids and ketones are not formed. In addition, high product yields in the oxidation step, both as to the high product yield of oxidized sulfur impurities and the high product yield of hydrocarbon materials which remains after the oxidation step and, in particular, after the sulfur reducing step, are obtained utilizing the above-noted oxidants. The organic oxidants suitable for use in the present invention, include, by way of example, hydrocarbon peroxides, hydrocarbon hydroperoxides and hydrocarbon peracids wherein the hydrocarbon radicals in general contain up to about 20 carbon atoms per active oxygen atom. With respect to the hydrocarbon peroxides and the hydrocarbon hydroperoxides, it is particularly preferred that such hydrocarbon radical contain from about four to about 18 carbon atoms per active oxygen atom and more particularly from four to 10 carbon atoms per active oxygen atom. With respect to the hydrocarbon peracids, the hydrocarbon radical is defined as that radical which is attached to the carbonyl carbon and it is preferred that such hydrocarbon radical contain from one to about 12 carbon atom, more preferably from one to about eight carbon atoms, per active oxygen atom. It is intended that the term organic peracid include, by way of definition, performic acid.

Typical examples of hydrocarbon radicals are alkyl such as methyl, ethyl, butyl, t-butyl, pentyl, n-octyl and those aliphatic radicals which represent the hydrocarbon portion of a middle distillate of kerosene, and the like; cycloalkyl radicals such as cyclopentyl and the like; alkylated cycloalkyl radicals such as mono- and polymethylcyclo-pentyl radicals and the like; aryl radicals such as phenyl, naphthyl and the like; cycloalkyl substituted alkyl radicals such as cyclohexyl methyl and ethyl radicals and the like; alkyl phenyl substituted alkyl radicals examples of which are benzyl, methylbenzyl, caprylbenzyl, phenylethyl, phenylpropyl, naphthylmethyl, naphthylethyl and the like; alkaryl radicals such as xylyl, methylphenyl and ethylphenyl and the like radicals.

Typical examples of oxidants are hydroxyheptyl peroxide, cyclohexanone peroxide, tertiary butyl peracetate, di-tertiary butyl diperphthalate, tertiary butyl perbenzoate methyl ethyl ketone peroxide, dicumyl peroxide, tertiary butyl hydroperoxide, di-tertiary butyl peroxide, p-methane hydroperoxide, pinane hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, cumene hydroperoxide and the like; as well as organic peracids such as performic acid, peracetic acid, trichloroperacetic acid, per-benzoic acid, perphthalic acid and the like.

In order to obtain the maximum benefits of the present invention, the most preferred oxidant for use in the present invention is tertiary butyl hydroperoxide.

The process of the present invention involves contacting a sulfur-containing hydrocarbon material with an oxidant, for example, of the type described above, in the presence of the above molybdenum-containing catalyst for a time sufficient to effect the oxidation of at least a portion of the sulfur present in the hydrocarbon material. In general, the time required for this oxidation to occur is from about 5 minutes to about 24 hours or more. It is preferred that the oxidation occur in a time from about 5 minutes to about 2 hours. Because of the improved oxidation efficiency of the present process, in a more preferred embodiment, the oxidation takes place in a period of time from about 5 minutes to about 25 minutes.

The catalyst is used in an amount sufficient to promote the preferential oxidation of sulfur in a sulfur-containing hydrocarbon material. It is preferred that the catalyst be soluble in the liquid portion of the oxidation reaction mass and be present in an amount based on the weight of molybdenum of at least about 5 ppm., more preferably from about 10 ppm. to about 500 ppm., by weight of the sulfur-containing hydrocarbon material.

The concentration of oxidant can be from about 0.1 to about 10 or more atoms of active, i.e., reducable, oxygen per atom of sulfur present in the hydrocarbon material. However, it is preferred that the oxidant be present in an amount from about 1 to about 4 atoms of active oxygen per atom of sulfur in the hydrocarbon material. A still more preferred oxidant concentration is from about 1.5 to about 3.0 atoms of active oxygen per atom of sulfur. Oxidants useful in the present invention include those having one, two or more atoms of active oxygen per molecule of oxidant.

The more preferred oxidant concentration range, i.e., from about 1.5 to about 3.0 active oxygen atoms per atom of sulfur, is of value if the oxidant decomposition product, for example, an alcohol in the case of hydroperoxide oxidant, is to be stripped from the hydrocarbon material after oxidation and used for different productive purposes. For example, if essentially pure, i.e., contaminated by no other peroxy compounds, tertiary butyl hydroperoxide is used as the oxidant, the decomposition product, i.e., tertiary butyl alcohol, can be separated from the hydrocarbon material and used to improve the quality of unleaded gasoline. However, in order to be useful as a gasoline improver, the tertiary butyl alcohol must be essentially free, i.e., less than about 100 ppm., of tertiary butyl hydroperoxide. It has been found that by providing an essentially pure tertiary butyl hydroperoxide oxidant in a concentration from about 1.5 moles to about 3.0 moles per mole of sulfur in the hydrocarbon fraction, a product stream of tertiary butyl alcohol, essentially free of excess oxidant can be obtained by stripping the alcohol from the hydrocarbon material after oxidation. Oxidant concentrations in excess of about 3.0 moles per mole of sulfur may result in oxidant carry over into the decomposition product stream thereby causing additional processing of this stream to eliminate the oxidant. This useful tertiary butyl alcohol product is obtained without sacrificing the substantial oxidation benefits of the invention.

Additional and distinct advantage flow from using oxidant concentration in the more preferred range regardless of oxidant purity. Included among these advantages are the efficient utilization of oxidant without sacrificing the substantial oxidation benefits of the present invention and a further minimizing of side reactions, e.g., carbon oxidation, during the oxidation step, thus improving the yield and quality of the final reduced sulfur hydrocarbon material.

The oxidation step of the present invention may be carried out over a wide range of temperatures, for example, from about 25°F. to about 450°F. and preferably from about 50°F. to about 300°F. The oxidation may be carried out at pressures ranging, for example, from about 1 atmosphere to about 100 atmospheres or more.

Many types of apparatus are suitable for carrying out the oxidation including rocking autoclave, mechanically stirred tanks, etc. The reactions can be carried out batch-wise, semi-continuously or continuously.

Before subjecting the hydrocarbon material to the sulfur reduction step, it is preferred to separate out the oxidant decomposition product or products, oxidation solvent, if any, and the alcohol or alcohols from the catalyst mixture. This separation can be obtained using conventional techniques, for example, simple distillation and/or stripping the hydrocarbon material during or after oxidation with a gas such as carbon dioxide or nitrogen.

In carrying out the process of this invention, a sulfur reduction step is utilized in combination with the oxidation step. A brief description of typical sulfur reduction steps is given below.

In the base treatment sulfur reducing 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 from 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 900°F., preferably from about 400°F. to about 750°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 carrying out the base treatment. In general, it is preferred to use an alkali metal hydroxide, preferably potassium or sodium hydroxide, although the alkaline earth metal hydroxides or oxides, calcined dolomitic materials and alkalized 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 at a concentration on a mole basis of generally 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 at temperatures above 300°F., preferably above 500°F. and particularly in the temperature range of from about 550°F. to about 900°F. for a period sufficient to ensure that substantially all the sulfur gaseous decomposition products are removed. This period of time in general is within the range from about 30 minutes to about 10 hours, preferably in the range from about 30 minutes to about 5 hours. Under these conditions, the oxidized sulfur compounds are decomposed and the sulfur is liberated mainly as SO_2 although at higher temperatures in the region of 550°F. and over, increasing quantities of H_2S 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, bausite, 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 step 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°F. to about 900°F., preferably from about 650°F. to about 800°F., and at a pressure within the range of from about 100 psig. to about 3,000 psig. or more.

A particularly preferred pressure range within which the hydrodesulfurization step provides extremely good sulfur removal while minimizing the amount of pressure and hydrogen required for the hydrodesulfurization step are pressures within the range of about 300 psig. to about 800 psig., more preferably from about 400 psig. to about 600 psig.

This invention involves the processing of various sulfur-containing hydrocarbon materials, such as those derived from petroleum sources. In general, the sulfur content of these materials may be greater than about 1 percent by weight. In many instances these hydrocarbon materials contain a significant amount of thiophene sulfur which is known to be difficult to remove. Examples of hydrocarbon materials which are particularly suited to the present process include heavy hydrocarbon materials such as petroleum fractions containing at least a major amount of material boiling above about 550°F., for example, crude oil and atmospheric and vacuum residues which contain about 1 percent by weight or more of sulfur. Additional examples of suitable hydrocarbon materials include cracked gas oils, residual fuel oils, topped or reduced crudes, crude petroleum from which the lighter fractions are absent, residues from cracking processes and sulfur-containing hydrocarbon materials from tar sands, oil shale and coal. The invention is especially suited to those sulfur-containing heavy hydrocarbon materials which cannot be deeply flashed without extensive carry over of sulfur-containing compounds. Typical examples of the 2,3,4, and 5-ring thiophene-containing materials found in heavy hydrocarbon materials which are difficult to remove include benzothiophene, dibenzothiophene, 5-thia-3,4-benzofluorene, tetraphenyl-thiophene, diacenaphtho (1,2-b,1′, 2′-d) thiophene and anthra (2,1,9-cde) thianaphthene. The hydrocarbon material may also contain non-thiophene sulfur, various sulfides, and elemental sulfur which can be removed by the process of the present invention.

As noted previously, the preferred oxidation catalyst for use in the present invention is prepared using a combination of molybdenum metal, tertiary butyl hydroperoxide and tertiary butyl alcohol. Also, the preferred oxidant for use is tertiary butyl hydroperoxide. In a particularly preferred embodiment of the present invention, it has been discovered that tertiary butyl hydroperoxide and tertiary butyl alcohol resulting from isobutane oxidation can be used in the process of this invention without requiring any other significant processing, e.g., purification step.

In this process, isobutane is oxidized to give a mixture of tertiary butyl hydroperoxide and tertiary butyl alcohol by various methods. For example, isobutane can be oxidized noncatalytically in the liquid phase with a free oxygen-containing gas, such as molecular oxygen and using reaction temperatures, for example, in the range from about 100°C. to about 150°C. and pressures above about 400 psig. It has been discovered that the complex isobutane oxidation product mixture comprising tertiary butyl hydroperoxide, tertiary butyl alcohol and small amounts, e.g., less than about 5 percent by weight each, of various other components such as acetone, water, carbon dioxide, formic acid, methanol, isobutanol, etc., can be used, without further significant processing, as the source of at least a major portion, preferably at least about 80 percent by weight and more preferably essentially all, of the tertiary butyl hydroperoxide used as oxidant and peroxy compound in the present invention without sacrificing oxidation efficiency. In addition, a portion of this isobutane oxidation product mixture may be used to prepare the molybdenum-containing catalyst in situ, e.g., in the presence of the sulfur-containing hydrocarbon material.

In this preferred process embodiment, the tertiary butyl alcohol in the complex product mixture from isobutane oxidation promotes the sulfur oxidation by reducing the viscosity of the oxidation reaction mass. When tertiary butyl alcohol is used as an oxidation solvent in the present process, from about 5 parts to about 2,000 parts, preferably from about 50 parts to about 2,000 parts, more preferably from about 50 parts to about 1,000 parts, by weight of alcohol is present per 100 parts of sulfur-containing hydrocarbon material. Quite unexpectedly, the use of this alcohol as a solvent in the oxidation step produces the same reaction efficiency and degree of desulfurization as when a more inclusive aromatic hydrocarbon solvent, such as benzene, is used. Using tertiary butyl alcohol rather than an extraneous oxidation solvent has a substantial processing benefits, e.g., the tertiary butyl hydroperoxide-alcohol-containing mixture from isobutane oxidation can be used without further processing to remove the alcohol. In addition, no solvent other than tertiary butyl alcohol need be removed from the hydrocarbon material after sulfur oxidation.

At least a portion of the tertiary butyl alcohol product from the sulfur oxidation step can be dehydrated to isobutylene which can be dimerized to form diisobutylene. The latter has many uses, for example, as an octane improver in gasoline.

The tertiary butyl alcohol dehydration may be carried out using conventional procedures. The dehydration may take place in the liquid, vapor or mixed liquid-vapor phase and is preferably catalyzed. Included among the catalysts which are known to promote the dehydration of alcohols such as tertiary butyl alcohol are acidic catalysts such as various Bronsted and Lewis Acids; silica, alumina and silica-alumina based solid acids; sulfuric acid; acidic ion exchange resins; acidic zeolites and the like. If the tertiary butyl alcohol dehydration is to be carried out in the vapor phase, reaction temperatures may range from about 200°F. to about 800°F., preferably from about 250°F. to about 600°F. while reaction pressures may range from about atmospheric pressure to about 500 psig. Liquid phase alcohol dehydration may be carried out at a temperature in the range from about 20°F. to about 300°F., preferably from about 100°F. to about 250°F., at a pressure sufficiently high to maintain the liquid phase in the reactor, e.g., typically in the range from about atmospheric pressure to about 1,000 psig. or higher. When a heterogeneous dehydration catalyst is employed, the weight hourly space velocity may vary over a broad range depending on the other reaction conditions and conversions desired. Typically, the dehydration reaction is carried out at a weight hourly space velocity in the range from about 1 to about 30, preferably from about 2 to about 10.

As stated above, the isobutylene can be dimerized to form diisobutylene, by any one of a number of procedures well known in the art. The isobutylene dimerization may be made to occur in the liquid vapor or mixed liquid-vapor phase and is preferably catalyzed. Among the catalysts which are useful in the dimerization reaction are Bronsted acids; sulfuric acid; phosphoric acid; silica, alumina and silica-alumina based solid acids; acidic ion exchange resins and the like, as well as Ziegler-Natta catalysts and transition metal complex catalysts. If the dimerization is to be carried out in the vapor phase, the reaction temperature may range from about 0°F. to about 450°F., preferably from about 40°F. to about 400°F., at a pressure in the range from about atmospheric pressure to about 300 psig. or more. If a liquid phase reaction is desired, typical dimerization temperatures range from about 0°F. to about 450°F. at a pressure sufficient to maintain the reactant in the liquid phase, e.g., from about atmospheric pressure to about 1,000 psig. or more. When a heterogeneous catalyst is employed in the dimerization reaction, the weight hourly space velocity is typically in the range from about 1 to about 50, preferably from about 20 to about 30.

Following the sulfur oxidation step the hydrocarbon material is sent to a sulfur removal step such as that described previously. Conventional procedures, e.g., flashing, stripping, distillation and the like may be employed to recover a hydrocarbon material having reduced sulfur content.

The following examples illustrate more clearly the process of the present invention. However, these illustrations are not to be interpreted as specific limitations on the invention.

EXAMPLE I

This example illustrates the desulfurization of a heavy hydrocarbon material.

The hydrocarbon material employed was a benzene soluble petroleum vacuum still residuum (Initial Boiling Point 610°F., 15 percent overhead - 962°F.) having the following composition.

	Weight %
Sulfur	3.13
Nitrogen	0.45
Carbon	85.38
Hydrogen	10.43
Oxygen	0.83

*The proportions listed here result from a series of independent chemical analyses and, therefore, the sum of the weight percents is slightly in excess of 100.

A soluble, i.e., homogeneous, oxidation catalyst was prepared by combining 0.74 weight percent molybdenum powder with tertiary butyl hydroperoxide in the presence of tertiary butyl alcohol and a mixture of C_{10} to C_{15} gylcols containing from 4 to 6 hydroxyl group per molecule wherein at least one of the hydroxyl groups was primary. The weight ratio of tertiary butyl hydroperoxide to tertiary butyl alcohol to glycols was about 2.1:4:1. This combination was heated to reflux temperature with constant stirring and maintained at this temperature until all the molybdenum had dissolved.

Tertiary butyl hydroperoxide was used as the oxidant to oxidize the sulfur impurities in the hydrocarbon material. This oxidant was used in the form of a commercially available mixture containing about 90 percent tertiary butyl hydroperoxide. Benzene was used as a solvent in the oxidation reaction and amounted to about 50 percent by weight of the oxidation reaction mixture.

The oxidation reaction mixture was formed by combining the hydrocarbon material, benzene catalyst and tertiary butyl hydroperoxide with constant stirring to insure uniformity. This mixture contained 3.6 moles of tertiary butyl hydroperoxide per mole of sulfur and 187 ppm. of molybdenum.

200 grams of this reaction mixture was placed in a glass reaction flask equipped with heating means, stirrer and a water-cooled condenser. The flask was heated to about 75° to 81°C. which caused the reaction mixture to reflux. This temperature was maintained for 16 hours to effect sulfur oxidation. After this period of time, the product in the flask was stripped free of essentially all benzene, tertiary butyl alcohol from tertiary butyl hydroperoxide decomposition and lighter components.

The remaining hydrocarbon product was cooled and placed in a glass vessel which itself was in a salt bath. This material was heated to a temperature within the range from 750°F. to 800°F. and maintained at this temperature for 4 hours. Throughout this period of time, hydrogen gas at atmospheric pressure was sent through the glass vessel. At the end of 4 hours, the liquid product was sampled and analyzed for sulfur content. It was determined that the above processing had removed about 50 percent of the sulfur which was originally contained in the vacuum residuum.

EXAMPLE II

This example illustrates the desulfurization of a heavy hydrocarbon material using tertiary butyl alcohol rather than benzene as solvent.

The hydrocarbon material used was the same as the benzene soluble petroleum vacuum still residuum employed in Example I. The oxidation catalyst used was prepared in the same manner and had the same composition as the catalyst used in Example I. Tertiary butyl hydroperoxide was used as oxidant and tertiary butyl alcohol, amounting to about 50 percent by weight of the oxidation reaction mixture, was used as oxidation solvent.

The tertiary butyl hydroperoxide employed as an oxidant in this example was the product of liquid phase, noncatalytic oxidation of isobutane. Thus, the tertiary butyl hydroperoxide used was present in a mixture of 42.1 percent by weight tertiary butyl hydroperoxide, about 52 percent by weight tertiary butyl alcohol and 5.9 percent by weight of other impurities such as, acetone, water, carbon dioxide, formic acid, methanol and isobutanol.

The oxidation reaction mixture was formed by combining the hydrocarbon material, tertiary butyl alcohol solvent, catalyst and tertiary butyl hydroperoxide with constant stirring. It was determined that not all of the hydrocarbon material was soluble in the tertiary butyl alcohol. This mixture contained 3.6 moles of tertiary butyl hydroperoxide per mole of sulfur and 80 ppm. of molybdenum.

This reaction mixture was placed in equipment similar to that described in Example I and heated to a temperature of about 82°C. which caused the reaction mixture to reflux. This temperature was maintained for 7.5 hours to effect sulfur oxidation. After this period of time, the product was stripped free of essentially all tertiary butyl alcohol and lighter components.

The remaining hydrocarbon product was cooled and placed in a glass vessel similar to that described in Example I. This product was heated to a temperature within the range from 734°F. to 750°F. and maintained at this temperature for 2 hours. Throughout this period of time, hydrogen gas at atmospheric pressure was sent through the glass vessel. At the end of two hours, the liquid product was sampled and analyzed for sulfur content. It was determined that the above processing had removed about 50 percent of the sulfur which was originally contained in the vacuum.

The above examples illustrate a number of the substantial benefits of the present invention. For instance, both Examples I and II show desulfurization using the improved oxidation catalyst disclosed herein. In addition, this catalyst provides for an improved rate of oxidation and thus can make possible reduced reaction times for the sulfur oxidation of the present invention.

Furthermore, Examples I and II illustrate the surprising discovery that tertiary butyl alcohol, admittedly a less inclusive solvent than benzene for certain components of heavy hydrocarbon materials, is as effective as benzene when used as solvent for oxidation of sulfur-containing heavy hydrocarbon material. The use of tertiary butyl alcohol as oxidation solvent has significant and substantial benefits, particularly when tertiary butyl hydroperoxide is used as oxidant. As tertiary butyl hydroperoxide is decomposed, tertiary butyl alcohol is formed. This decomposition product, i.e., tertiary butyl alcohol, must be removed from the final hydrocarbon product of reduced sulfur content. If benzene is used as oxidation solvent, additional processing equipment may be necessary to separate the benzene from the decomposition product tertiary butyl alcohol. However, if the oxidation solvent and oxidant decomposition product are one and the same compound, i.e., tertiary butyl alcohol, additional processing required to recover useable and/or saleable products is minimized. This processing benefit can be taken advantage of because of the discovery that tertiary butyl alcohol performs as well as benzene as an oxidation solvent in the present invention.

Examples I and II illustrate an added benefit of the present process. Example II, when compared to Example I, demonstrates that impure tertiary butyl hydroperoxide obtained from isobutane oxidation may be used as oxidant without adversely affecting the sulfur oxidation of the present invention. Thus, tertiary butyl hydroperoxide derived from isobutane oxidation may be used as oxidant rather than pure or near pure tertiary butyl hydroperoxide, such as used in Example I.

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.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a desulfurization process for producing a hydrocarbon material of reduced sulfur content wherein at least a portion of the sulfur in a sulfur-containing hydrocarbon material is preferentially oxidized and the oxidized sulfur-containing hydrocarbon material is further processed by means of a sulfur reducing step, the improvement which comprises preferentially oxidizing said sulfur with an oxidant selected from the group consisting of organic peroxides, organic hydroperoxides, organic peracids, and mixtures thereof in the presence of a molybdenum-containing catalyst prepared by a method which comprises interacting molybdenum metal with at least one peroxy compound in the presence of at least one saturated alcohol having from one to four carbon atoms per molecule to solubilize at least a portion of said molybdenum metal, said catalyst being present in an amount sufficient to promote the preferential oxidation of said sulfur.

2. The process of claim **1** wherein said interacting occurs at a temperature within the range from about 25°C. to about 150°C.

3. The process of claim **2** wherein said catalyst is soluble in the liquid portion of the oxidation reaction mass and is present in an amount based on the weight of molybdenum of at least about 5 ppm. by weight of the sulfur-containing hydrocarbon material.

4. The process of claim **1** wherein at least a major amount of said sulfur-containing hydrocarbon material boils above about 550°F.

5. The process of claim **3** wherein at least a major amount of said sulfur-containing hydrocarbon material boils above about 550°F.

6. The process of claim **5** wherein said oxidant is present in a concentration of from about 0.1 to about 10 atoms of active oxygen per atom of sulfur present in said sulfur-containing hydrocarbon material.

7. The process of claim **6** wherein said oxidant is present in a concentration of from about 1 to about 4 atoms of active oxygen per atom of sulfur present in said sulfur-containing hydrocarbon material.

8. The process of claim **6** wherein said catalyst is present in an amount based on the weight of molybdenum of from about 10 ppm. to about 500 ppm. by weight of said sulfur-containing hydrocarbon material.

9. The process of claim **8** wherein said oxidant and said peroxy compound are both tertiary butyl hydroperoxide, said saturated alcohol is tertiary butyl alcohol, and said interacting takes place in the presence of at least one primary alcohol containing from one to about 16 carbon atoms per molecule and having at least one primary hydroxy group present in an amount sufficient to enhance the solubility of molybdenum.

10. The process of claim **9** wherein said oxidant is present in a concentration of from about 1.5 to about 3.0 atoms of active oxygen per atom of sulfur present in said sulfur-containing hydrocarbon material.

11. The process of claim **10** wherein at least a portion of said tertiary butyl hydroperoxide is derived from oxidation of isobutane and said primary alcohol is a mixture of polyhydroxy alcohols which have a molecular weight in the range from about 200 to about 300 and contain from about four to about six hydroxy groups, said poly-hydroxy alcohols being derived from propylene epoxidation with tertiary butyl hydroperoxide.

12. A process for producing a hydrocarbon material of reduced sulfur-content which comprises:

1. preferentially oxidizing at least a portion of the sulfur in a hydrocarbon material with an oxidant selected from the group consisting of organic peroxides, organic hydroperoxides, organic peracids and mixtures thereof in the presence of a molybdenum-containing catalyst prepared by a method which comprises interacting molybdenum metal with at least one peroxy compound in the presence of at least one saturated alcohol having from one to four carbon atoms per molecule to solubilize at least a portion of said molybdenum metal, said catalyst being present in an amount sufficient to promote the preferential oxidation of said sulfur;
2. treating said oxidized sulfur-containing hydrocarbon material to remove at least a portion of said sulfur from said hydrocarbon material; and
3. recovering a hydrocarbon material having reduced sulfur content.

13. The process of claim **12** wherein said interacting occurs at a temperature within the range from about 25°C. to about 150°C.

14. The process of claim **13** wherein at least a major amount of said sulfur-containing hydrocarbon material boils above about 550°F. and said oxidation occurs in the presence of an added oxidation solvent in an amount sufficient to reduce the viscosity of the oxidation reaction mass.

15. The process of claim **14** wherein said oxidation solvent is present in an amount such that from about 5 parts to about 2,000 parts by weight of solvent is present for every 100 parts of sulfur-containing hydrocarbon material and said oxidant is present in a concentration of from about 0.1 to about 10 atoms of active oxygen per atom of sulfur present in said sulfur-containing hydrocarbon material.

16. The process of claim **15** wherein said oxidation solvent is tertiary butyl alcohol.

17. The process of claim **16** wherein said oxidant and said peroxy compound are both tertiary butyl hydroperoxide and said saturated alcohol is tertiary butyl alcohol, and said interacting takes place in the presence of at least one primary alcohol containing from one to about 16 carbon atoms per molecule and having at least one primary hydroxy group present in an amount sufficient to enhance the solubility of molybdenum.

18. The process of claim **17** wherein step (2) comprises:

A. separating at least a portion of said tertiary butyl alcohol contained in said oxidized sulfur-containing hydrocarbon material leaving an alcohol-poor hydrocarbon material; and

B. removing at least a portion of said sulfur from said alcohol-poor hydrocarbon material.

19. The process of claim **17** wherein at least a major portion of said tertiary butyl hydroperoxide is derived from oxidation of isobutane and said primary alcohol is a mixture of poly-hydroxy alcohol which have a molecular weight in the range from about 200 to about 300 and contain from about 4 to about 6 hydroxy groups, said poly-hydroxy alcohols derived from propylene epoxidation with tertiary butyl hydroperoxide.

20. The process of claim **18** comprising the additional step of dehydrating at least a portion of said separated tertiary butyl alcohol to form isobutylene.

21. The process of claim **20** wherein at least a portion of said isobutylene is dimerized to form diisobutylene.

22. The process of claim **21** wherein said sulfur removal step comprises subjecting said alcohol-poor hydrocarbon material to a thermal treatment step.

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