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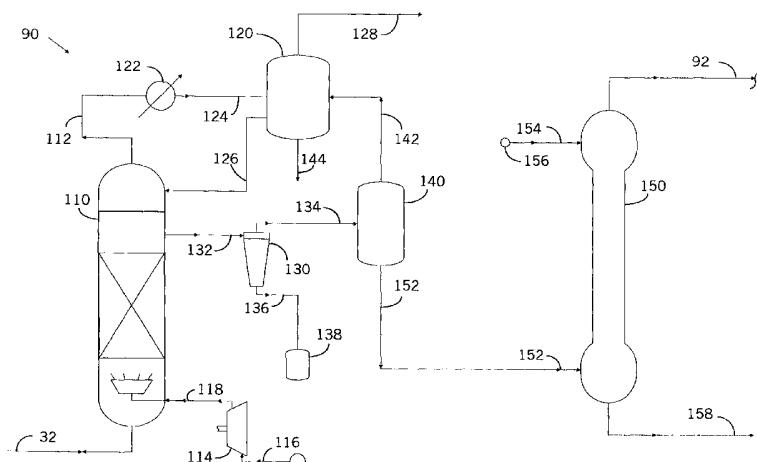
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(54) Title: PROCESS FOR OXYGENATION OF COMPONENTS FOR REFINERY BLENDING OF TRANSPORTATION FUELS



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(57) Abstract: Economical processes are disclosed for production of components for refinery blending of transportation fuels which are liquid at ambient conditions by selective oxygenation of refinery feedstocks comprising a mixture of organic compounds. The organic compounds are oxygenated in a liquid reaction medium with an oxidizing agent and heterogenous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a mixture of liquid organic compounds to form a mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products. The mixture is separated to recover at least a first organic liquid of low density and at least a portion of the catalyst metal, water of reaction and acidic co-products. Advantageously, the organic liquid is washed with an aqueous solution of sodium bicarbonate solution, or other soluble chemical base capable to neutralize and/or remove acidic co-products of oxidation, and recover oxygenated product.



*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

PROCESS FOR OXYGENATION OF COMPONENTS FOR REFINERY  
BLENDING OF TRANSPORTATION FUELS

TECHNICAL FIELD

5        The present invention relates to fuels for transportation which are derived from natural petroleum, particularly processes for the production of components for refinery blending of transportation fuels which are liquid at ambient conditions. More specifically, it relates to integrated processes which include  
10      selective oxygenation of organic compounds in suitable petroleum distillates. The organic compounds are oxygenated in a liquid reaction medium with an oxidizing agent and heterogeneous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a mixture of liquid organic  
15      compounds to form a mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products. The mixture is separated to recover at least a first organic liquid of low density and at least a portions of the catalyst metal, water of reaction and acidic co-products. Advantageously, the organic liquid  
20      is washed with an aqueous solution of sodium bicarbonate solution, or other soluble chemical base capable to neutralize and/or remove acidic co-products of oxidation, and recover oxygenated product. Product can be used directly as a blending component, or fractionated, as by further distillation, to provide, for example,  
25      more suitable components for blending into diesel fuel. Integrated processes of this invention can also provide their own source oxygenation feedstock as a low-boiling fraction of hydrotreated distillate. Beneficially, integrated processes include selective oxidation of the high-boiling fraction whereby the incorporation of  
30      oxygen into the hydrocarbon, sulfur-containing organic and/or nitrogen-containing organic compounds assists by oxidation removal of sulfur and/or nitrogen.

## BACKGROUND OF THE INVENTION

It is well known that internal combustion engines have revolutionized transportation following their invention during the last decades of the 19th century. While others, including Benz and 5 Gottlieb Wilhelm Daimler, invented and developed engines using electric ignition of fuel such as gasoline, Rudolf C. K. Diesel invented and built the engine named for him which employs compression for auto-ignition of the fuel in order to utilize low-cost organic fuels. Development of improved diesel engines for use in transportation 10 has proceeded hand-in-hand with improvements in diesel fuel compositions. Modern high performance diesel engines demand ever more advanced specification of fuel compositions, but cost remains an important consideration.

At the present time most fuels for transportation are derived 15 from natural petroleum. Indeed, petroleum as yet is the world's main source of hydrocarbons used as fuel and petrochemical feedstock. While compositions of natural petroleum or crude oils are significantly varied, all crudes contain sulfur compounds and most contain nitrogen compounds which may also contain oxygen, 20 but the oxygen content of most crudes is low. Generally, sulfur concentration in crude is less than about 8 percent, with most crudes having sulfur concentrations in the range from about 0.5 to about 1.5 percent. Nitrogen concentration is usually less than 0.2 percent, but it may be as high as 1.6 percent.

25 Crude oil seldom is used in the form produced at the well, but is converted in oil refineries into a wide range of fuels and petrochemical feedstocks. Typically fuels for transportation are produced by processing and blending of distilled fractions from the crude to meet the particular end use specifications. Because most 30 of the crudes available today in large quantity are high in sulfur, the distilled fractions must be desulfurized to yield products which meet performance specifications and/or environmental standards. Sulfur containing organic compounds in fuels continue to be a major source of environmental pollution. During combustion they are

converted to sulfur oxides which, in turn, give rise to sulfur oxyacids and, also, contribute to particulate emissions.

Even in newer, high performance diesel engines combustion of conventional fuel produces smoke in the exhaust. Oxygenated 5 compounds and compounds containing few or no carbon-to-carbon chemical bonds, such as methanol and dimethyl ether, are known to reduce smoke and engine exhaust emissions. However, most such compounds have high vapor pressure and/or are nearly insoluble in diesel fuel, and they have poor ignition quality, as indicated by 10 their cetane numbers. Furthermore, other methods of improving diesel fuels by chemical hydrogenation to reduce their sulfur and aromatics contents, also causes a reduction in fuel lubricity. Diesel fuels of low lubricity may cause excessive wear of fuel injectors and other moving parts which come in contact with the fuel under high 15 pressures.

Distilled fractions used for fuel or a blending component of fuel for use in compression ignition internal combustion engines (Diesel engines) are middle distillates that usually contain from about 1 to 3 percent by weight sulfur. In the past a typical 20 specifications for Diesel fuel was a maximum of 0.5 percent by weight. By 1993 legislation in Europe and United States limited sulfur in Diesel fuel to 0.3 weight percent. By 1996 in Europe and United States, and 1997 in Japan, maximum sulfur in Diesel fuel was reduced to no more than 0.05 weight percent. This world-wide 25 trend must be expected to continue to even lower levels for sulfur.

In one aspect, pending introduction of new emission regulations in California and Federal markets has prompted significant interest in catalytic exhaust treatment. Challenges of applying catalytic emission control for the diesel engine, 30 particularly the heavy-duty diesel engine, are significantly different from the spark ignition internal combustion engine (gasoline engine) due to two factors. First, the conventional TWC catalyst is ineffective in removing NO<sub>x</sub> emissions from diesel engines, and second, the need for particulate control is significantly 35 higher than with the gasoline engine.

Several exhaust treatment technologies are emerging for control of Diesel engine emissions, and in all sectors the level of sulfur in the fuel affects efficiency of the technology. Sulfur is a catalyst poison that reduces catalytic activity. Furthermore, in the 5 context of catalytic control of Diesel emissions, high fuel sulfur also creates a secondary problem of particulate emission, due to catalytic oxidation of sulfur and reaction with water to form a sulfuric acid mist. This mist is collected as a portion of particulate emissions.

10      Compression ignition engine emissions differ from those of spark ignition engines due to the different method employed to initiate combustion. Compression ignition requires combustion of fuel droplets in a very lean air/fuel mixture. The combustion process leaves tiny particles of carbon behind and leads to 15 significantly higher particulate emissions than are present in gasoline engines. Due to the lean operation the CO and gaseous hydrocarbon emissions are significantly lower than the gasoline engine. However, significant quantities of unburned hydrocarbon are adsorbed on the carbon particulate. These hydrocarbons are 20 referred to as SOF(soluble organic fraction). Thus, the root cause of health concerns over diesel emissions can be traced to the inhalation of these very small carbon particles containing toxic hydrocarbons deep into the lungs.

25      While an increase in combustion temperature can reduce particulate, this leads to an increase in NOx emission by the well-known Zeldovitch mechanism. Thus, it becomes necessary to trade off particulate and NOx emissions to meet emissions legislation.

30      Available evidence strongly suggests that ultra-low sulfur fuel is a significant technology enabler for catalytic treatment of diesel exhaust to control emissions. Fuel sulfur levels of below 15 ppm, likely, are required to achieve particulate levels below 0.01 g/bhp-hr. Such levels would be very compatible with catalyst combinations for exhaust treatment now emerging, which have shown capability to achieve NOx emissions around 0.5 g/bhp-hr. 35 Furthermore, NOx trap systems are extremely sensitive to fuel

sulfur and available evidence suggests that they need would sulfur levels below 10 ppm to remain active.

In the face of ever-tightening sulfur specifications in transportation fuels, sulfur removal from petroleum feedstocks and 5 products will become increasingly important in years to come. While legislation on sulfur in diesel fuel in Europe, Japan and the U.S. has recently lowered the specification to 0.05 percent by weight (max.), indications are that future specifications may go far below the current 0.05 percent by weight level.

10       Conventional hydrodesulfurization (HDS) catalysts can be used to remove a major portion of the sulfur from petroleum distillates for the blending of refinery transportation fuels, but they are not active for removing sulfur from compounds where the sulfur atom is sterically hindered as in multi-ring aromatic sulfur compounds. 15 This is especially true where the sulfur heteroatom is doubly hindered (e.g., 4,6-dimethyldibenzothiophene). Using conventional hydrodesulfurization catalysts at high temperatures would cause yield loss, faster catalyst coking, and product quality deterioration (e.g., color). Using high pressure requires a large capital outlay.

20       In order to meet stricter specifications in the future, such hindered sulfur compounds will also have to be removed from distillate feedstocks and products. There is a pressing need for economical removal of sulfur from distillates and other hydrocarbon products.

25       The art is replete with processes said to remove sulfur from distillate feedstocks and products. One known method involves the oxidation of petroleum fractions containing at least a major amount of material boiling above a very high-boiling hydrocarbon materials (petroleum fractrions containing at least a major amount of 30 material boiling above about 550° F.) followed by treating the effluent containing the oxidized compounds at elevated temperatures to form hydrogen sulfide (500° F. to 1350° F.) and/or hydroprocessing to reduce the sulfur content of the hydrocarbon material. See, for example, U.S. Patent Number 3,847,798 in the name 35 of Jin Sun Yoo and U.S. Patent Number 5,288,390 in the name

of Vincent A. Durante. Such methods have proven to be of only limited utility since only a rather low degree of desulfurization is achieved. In addition, substantial loss of valuable products may result due to cracking and/or coke formation during the practice of 5 these methods. Therefore, it would be advantageous to develop a process which gives an increased degree of desulfurization while decreasing cracking or coke formation.

Several different oxygenation methods for improving fuels have been described in the past. For example, U.S. Patent Number 10 2,521,698 describes a partial oxidation of hydrocarbon fuels as improving cetane number. This patent suggests that the fuel should have a relatively low aromatic ring content and a high paraffinic content. U.S. Patent Number 2,912,313 states that an increase in cetane number is obtained by adding both a peroxide 15 and a dihalo compound to middle distillate fuels. U.S. Patent Number 2,472,152 describes a method for improving the cetane number of middle distillate fractions by the oxidation of saturated cyclic hydrocarbon or naphthenic hydrocarbons in such fractions to form naphthenic peroxides. This patent suggests that the oxidation 20 may be accelerated in the presence of an oil-soluble metal salt as an initiator, but is preferably carried out in the presence of an inorganic base. However, the naphthenic peroxides formed are deleterious gum initiators. Consequently, gum inhibitors such as 25 phenols, cresols and cresylic acids must be added to the oxidized material to reduce or prevent gum formation. These latter compounds are toxic and carcinogenic.

U.S. Patent Number 4,494,961 in the name of Chaya Venkat and Dennis E. Walsh relates to improving the cetane number of raw, untreated, highly aromatic, middle distillate fractions having a 30 low hydrogen content by contacting the fraction at a temperature of from 50° C. to 350° C. and under mild oxidizing conditions in the presence of a catalyst which is either (i) an alkaline earth metal permanganate, (ii) an oxide of a metal of Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB or VIIIB of the periodic table, or a mixture of (i) and 35 (ii). European Patent Application 0 252 606 A2 also relates to improving cetane number of a middle distillate fuel fraction which

may be hydro-refined by contacting the fraction with oxygen or oxidant, in the presence of catalytic metals such as tin, antimony, lead, bismuth and transition metals of Groups IB, IIB, VB, VIB, VIIB and VIIIB of the periodic table, preferably as an oil-soluble metal salt. The application states that the catalyst selectively oxidizes 5 benzylic carbon atoms in the fuel to ketones.

Recently, U.S. Patent Number 4,723,963 in the name of William F. Taylor suggests that cetane number is improved by including at least 3 weight percent oxygenated aromatic compounds 10 in middle distillate hydrocarbon fuel boiling in the range of 160° C. to 400° C. This patent states that the oxygenated alkylaromatics and/or oxygenated hydroaromatics are preferably oxygenated at the benzylic carbon proton.

More recently, oxidative desulfurization of middle distillates 15 by reaction with aqueous hydrogen peroxide catalyzed by phosphotungstic acid and tri-*n*-octylmethylammonium chloride as phase transfer reagent followed by silica adsorption of oxidized sulfur compounds has been described by Collins et al. (Journal of Molecular Catalysis (A): Chemical 117 (1997) 397-403). Collins et 20 al. described the oxidative desulfurization of a winter grade diesel oil which had not undergone hydrotreating. While Collins et al. suggest that the sulfur species resistant to hydrodesulfurization should be susceptible to oxidative desulfurization, the concentrations of such resistant sulfur components in 25 hydrodesulfurized diesel may already be relatively low compared with the diesel oils treated by Collins et al.

U.S. Patent Number 5,814,109 in the name of Bruce R. Cook, Paul J. Berlowitz and Robert J. Wittenbrink relates to producing Diesel fuel additive, especially via a Fischer-Tropsch hydrocarbon 30 synthesis process, preferably a non-shifting process. In producing the additive, an essentially sulfur free product of these Fischer-Tropsch processes is separated into a high-boiling fraction and a low-boiling fraction, e.g., a fraction boiling below 700° F. The high-boiling of the Fischer-Tropsch reaction product is hydroisomerized 35 at conditions said to be sufficient to convert the high-boiling

fraction to a mixture of paraffins and isoparaffins boiling below 700° F. This mixture is blended with the low-boiling of the Fischer-Tropsch reaction product to recover the diesel additive said to be useful for improving the cetane number or lubricity, or both the 5 cetane number and lubricity, of a mid-distillate, Diesel fuel.

U.S. Patent Number 6,087,544 in the name of Robert J. Wittenbrink, Darryl P. Klein, Michele S Touvelle, Michel Daage and Paul J. Berlowitz relates to processing a distillate feedstream to produce distillate fuels having a level of sulfur below the distillate 10 feedstream. Such fuels are produced by fractionating a distillate feedstream into a light fraction, which contains only from about 50 to 100 ppm of sulfur, and a heavy fraction. The light fraction is hydrotreated to remove substantially all of the sulfur therein. The desulfurized light fraction, is then blended with one half of the 15 heavy fraction to produce a low sulfur distillate fuel, for example 85 percent by weight of desulfurized light fraction and 15 percent by weight of untreated heavy fraction reduced the level of sulfur from 663 ppm to 310 ppm. However, to obtain this low sulfur level only about 85 percent of the distillate feedstream is recovered as a low 20 sulfur distillate fuel product.

There is, therefore, a present need for catalytic processes to 25 prepare oxygenated aromatic compounds in middle distillate hydrocarbon fuel, particularly processes, which do not have the above disadvantages. An improved process should be carried out advantageously in the liquid phase using a suitable oxygenation-promoting catalyst system, preferably an oxygenation catalyst capable of enhancing the incorporation of oxygen into a mixture of 30 organic compounds and/or assisting by oxidation removal of sulfur or nitrogen from a mixture of organic compounds suitable as blending components for refinery transportation fuels liquid at ambient conditions.

This invention is directed to overcoming the problems set forth above in order to provide components for refinery blending of transportation fuels friendly to the environment.

## SUMMARY OF THE INVENTION

Economical processes are provided for production of components for refinery blending of transportation fuels by integrated processes which include selective oxygenation of organic compounds in suitable petroleum distillates, preferably a hydrotreated distillate. Integrated processes of this invention advantageously also provide their own source of oxygenation feedstock as a low-boiling fraction of hydrotreated distillate. Beneficially, integrated processes include selective oxidation of the high-boiling fraction whereby the incorporation of oxygen into hydrocarbon, sulfur-containing organic and/or nitrogen-containing organic compounds assists by oxidation removal of sulfur and/or nitrogen.

This invention contemplates the treatment of various type hydrocarbon materials, especially hydrocarbon oils of petroleum origin which contain sulfur. In general, the sulfur contents of the oils are in excess of 1 percent.

One aspect of this invention provides a process for production of refinery transportation fuel or blending components for refinery transportation fuel, which process comprises: providing organic feedstock comprising a mixture of organic compounds derived from natural petroleum, the mixture having a gravity ranging from about 10° API to about 75° API; contacting the organic feedstock with an oxidizing agent and heterogeneous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a mixture of liquid organic compounds, while maintaining the reaction medium substantially free of halogen and/or halogen-containing compounds, to form a liquid mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products; and separating from the reaction medium at least a first organic liquid of low density comprising hydrocarbons, oxygenated organic compounds and acidic co-products, and at least portions of the heterogeneous oxygenation catalyst system, water of reaction and acidic co-products.

In one aspect, this invention provides a process wherein the organic feedstock comprises sulfur-containing and/or nitrogen-containing organic compounds one or more of which are oxidized in the liquid reaction medium. Advantageously, at least a portion of 5 the oxidized sulfur-containing and/or nitrogen-containing organic compounds are sorbed onto the heterogeneous oxygenation catalyst. Typically, a second separated liquid is an aqueous solution containing at least a portion of the oxidized sulfur-containing and/or nitrogen-containing organic compounds.

10 Beneficially, processes according to the invention further comprise contacting the separated organic liquid with a neutralizing agent and recovering a product having a low content of acidic co-products.

15 Processes of the present invention advantageously include catalytic hydrotreating of the oxidation feedstock to form hydrogen sulfide which may be separated as a gas from the liquid feedstock, collected on a solid sorbent, and/or by washing with aqueous liquid. In a preferred aspect of the invention, the all or at least a portion of 20 the organic feedstock is a product of a hydrotreating process for petroleum distillates consisting essentially of material boiling between about 50° C. and about 425° C. which hydrotreating process includes reacting the petroleum distillate with a source of hydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur 25 and/or nitrogen from the hydrotreated petroleum distillate.

30 In another aspect, this invention provides a process for selective oxygenation of organic compounds wherein all or at least a portion of the organic feedstock is a product of a hydrotreating process for petroleum distillates consisting essentially of material boiling between about 50° C. and about 425° C. The hydrotreating process includes reacting the petroleum distillate with a source of hydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur and/or nitrogen from the hydrotreated petroleum distillate. 35 Generally, useful hydrogenation catalysts comprise at least one active metal, selected from the group consisting of the *d*-transition

elements in the Periodic Table, each incorporated onto an inert support in an amount of from about 0.1 percent to about 30 percent by weight of the total catalyst. Suitable active metals include the *d*-transition elements in the Periodic Table elements having atomic 5 number in from 21 to 30, 39 to 48, and 72 to 78.

Hydrogenation catalysts beneficially contain a combination of metals. Preferred are hydrogenation catalysts containing at least two metals selected from the group consisting of cobalt, nickel, molybdenum and tungsten. More preferably, co-metals are cobalt 10 and molybdenum or nickel and molybdenum. Advantageously, the hydrogenation catalyst comprises at least two active metals, each incorporated onto a metal oxide support, such as alumina in an amount of from about 0.1 percent to about 20 percent by weight of the total catalyst.

15 In one aspect, this invention provides for the production of refinery transportation fuel or blending components for refinery transportation fuel wherein the hydrotreating process further comprises partitioning of the hydrotreated petroleum distillate by distillation to provide at least one low-boiling liquid consisting of a 20 sulfur-lean, mono-aromatic-rich fraction, and a high-boiling liquid consisting of a sulfur-rich, mono-aromatic-lean fraction, and wherein the organic feedstock is predominantly the low-boiling liquid.

25 The heterogeneous oxygenation catalyst system for use according to the invention comprises an active metal selected from the group consisting of vanadium, chromium, molybdenum, tungsten manganese, iron, cobalt, nickel, palladium, platinum, copper, silver, or mixture thereof. The metal or metals may be employed in elemental, combined, or ionic form. Preferably the form of the 30 metal is as metal oxide, mixed metal oxide, and/or basic salts of the metal or mixed metal oxide. Advantageously the heterogeneous oxygenation catalyst system further comprises an alkali metal, alkaline earth metal and/or a member of group V of the periodic table. The alkali metal is any of the univalent mostly basic metals of 35 group I of the periodic table comprising lithium, sodium, potassium,

rubidium, cesium and francium, preferably potassium, and/or cesium. The alkali earth metal is any of the bivalent strongly basic metals comprising calcium, strontium and barium and magnesium, preferably magnesium. Useful group V metals are phosphorus, 5 arsenic, antimony, and bismuth, preferably phosphorus and/or bismuth. Beneficially, at least a portion of the catalyst system is recovered, and all or a portion of the recovered catalyst system is injected into the liquid reaction medium.

In one aspect of the invention, the heterogeneous oxygenation 10 catalyst system for selective oxygenation of organic compounds according to the invention comprises a particulate oxygenation catalyst containing from about 1 percent to about 30 percent chromium as oxide and from about 0.1 percent to about 5 percent platinum on a solid support. Preferably, the support comprises 15 gamma alumina ( $\gamma\text{-Al}_2\text{O}_3$ ).

Preferably, the heterogeneous oxygenation catalyst system for 20 selective oxygenation of organic compounds according to the invention comprises a source of a particulate form of chromium molybdate or bismuth molybdate and optionally magnesium. In another preferred aspect of the invention the heterogeneous 25 oxygenation catalyst system for selective oxygenation of organic compounds according to the invention comprises from about 0.1 percent to about 1.5 percent of a catalyst represented by formula  $\text{Na}_2\text{Cr}_2\text{O}_7$  on support comprising gamma alumina.

30 In another aspect of this invention there is provided a process for the production of refinery transportation fuel or blending components for refinery transportation fuel, which process comprises: partitioning by distillation an organic feedstock comprising a mixture of organic compounds derived from natural petroleum, the mixture having a gravity ranging from about 10° API to about 75° API, preferably having a gravity ranging from about 15° API to about 50° API, to provide at least one low-boiling organic part consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling organic part consisting of a sulfur-rich, 35 mono-aromatic-lean fraction; contacting a gaseous source of

dioxygen with at least a portion of the low-boiling organic part in a liquid reaction medium containing a heterogeneous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a mixture of liquid organic compounds 5 while maintaining the reaction medium substantially free of halogen and/or halogen-containing compounds, to form a liquid mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products; and, while maintaining the liquid reaction medium substantially free of halogen and/or 10 halogen-containing compounds, to form a mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products; separating from the mixture at least a first organic liquid of low density comprising hydrocarbons, oxygenated organic compounds and acidic co-products and at least portions of 15 the catalyst metal, water of reaction and acidic co-products; and contacting all or a portion of the separated organic liquid with a neutralizing agent thereby recovering a low-boiling oxygenated product having a low content of acidic co-products..

Beneficially, at least a portion of the separated organic liquid 20 is contacted with an aqueous solution of a chemical base, and the recovered oxygenated product exhibits a total acid number of less than about 20 mg KOH/g. The recovered oxygenated product advantageously exhibits a total acid number of less than about 10 mg KOH/g. More preferred are oxygenated products which exhibit 25 a total acid number of less than about 5, and most preferred less than about 1. Preferably, the chemical base is a compound selected from the group consisting of sodium, potassium, barium, calcium and magnesium in the form of hydroxide, carbonate or bicarbonate.

In one preferred aspect of the invention, all or at least a portion of the organic feedstock is a product of a process for 30 hydrogenation of a petroleum distillate consisting essentially of material boiling between about 50° C. and about 425° C. which hydrogenation process includes reacting the petroleum distillate with a source of hydrogen at hydrogenation conditions in the 35 presence of a hydrogenation catalyst to assist by hydrogenation

removal of sulfur and/or nitrogen from the hydrotreated petroleum distillate.

In another aspect this invention provides an integrate process for the production of refinery transportation fuel or blending components for refinery transportation fuel, which process comprises: partitioning by distillation an organic feedstock comprising a mixture of organic compounds derived from natural petroleum, the mixture consisting essentially of material boiling between about 75° C. and about 425° C. to provide at least one low-boiling organic part consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling organic part consisting of a sulfur-rich, mono-aromatic-lean fraction; contacting a gaseous source of dioxygen with at least a portion of the low-boiling organic part in a liquid reaction medium containing a heterogeneous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a mixture of liquid organic compounds while maintaining the reaction medium substantially free of halogen and/or halogen-containing compounds, to form a liquid mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products; and, while maintaining the liquid reaction medium substantially free of halogen and/or halogen-containing compounds, to form a mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products; separating from the mixture at least a first organic liquid of low density comprising hydrocarbons, oxygenated organic compounds and acidic co-products and at least portions of the catalyst metal, water of reaction and acidic co-products; and contacting all or a portion of the separated organic liquid with a neutralizing agent and recovering a low-boiling oxygenated product having a low content of acidic co-products. The integrated process further comprises contacting the high-boiling organic part with an immiscible phase comprising at least one organic peracid or precursors of organic peracid in a liquid reaction mixture maintained substantially free of catalytic active metals and/or active metal-containing compounds and under conditions suitable for oxidation of one or more of the sulfur-containing and/or nitrogen-containing organic compounds; separating at least a

portion of the immiscible peracid-containing phase from the oxidized phase of the reaction mixture; and contacting the oxidized phase of the reaction mixture with a solid sorbent, an ion exchange resin, and/or a suitable immiscible liquid containing a solvent or a 5 soluble basic chemical compound, to obtain a high-boiling product containing less sulfur and/or less nitrogen than the high-boiling fraction.

Generally for use in this invention, the immiscible phase is formed by admixing a source of hydrogen peroxide and/or 10 alkylhydroperoxide, an aliphatic monocarboxylic acid of 2 to about 6 carbon atoms, and water. Advantageously, the immiscible phase is formed by admixing hydrogen peroxide, acetic acid, and water. Advantageously, at least a portion of the separated peracid-containing phase is recycled to the reaction mixture. Preferably, 15 the conditions of oxidation include temperatures in a range upward from about 25° C. to about 250° C. and sufficient pressure to maintain the reaction mixture substantially in a liquid phase.

Sulfur-containing organic compounds in the oxidation feedstock include compounds in which a sulfur atom is sterically 20 hindered, as for example in multi-ring aromatic sulfur compounds. Typically, the sulfur-containing organic compounds include at least sulfides, heteroaromatic sulfides, and/or compounds selected from the group consisting of substituted benzothiophenes and dibenzothiophenes.

Beneficially, the instant oxidation process is very selective in 25 that selected organic peracids in a liquid phase reaction mixture maintained substantially free of catalytic active metals and/or active metal-containing compounds, preferentially oxidize compounds in which a sulfur atom is sterically hindered rather 30 than aromatic hydrocarbons.

According the present invention, suitable distillate fractions are preferably hydrodesulfureized before being selectively oxidized, and more preferably using a facility capable of providing effluents of at least one low-boiling fraction and one high-boiling 35 fraction.

This invention provides a process wherein all or at least a portion of the oxidation feedstock is a product of a process for hydrogenation of a petroleum distillate consisting essentially of material boiling between about 50° C. and about 425° C. Preferably 5 the petroleum distillate consisting essentially of material boiling between about 150° C. and about 400° C., and more preferably boiling between about 175° C. and about 375° C. According to a further aspect of this invention, the hydrogenation process includes reacting the petroleum distillate with a source of hydrogen at 10 hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur and/or nitrogen from the hydrotreated petroleum distillate.

Advantageously, the hydrogenation catalyst comprises at least one active metal, each incorporated onto an inert support in 15 an amount of from about 0.1 percent to about 2.0 percent by weight of the total catalyst. Preferably, the active metal is selected from the group consisting of palladium and platinum, and/or the support is mordenite.

According to a further aspect of this invention, the 20 hydrogenation process includes partitioning of the hydrotreated petroleum distillate by distillation to provide at least one low-boiling blending component consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling fraction consisting of a sulfur-rich, mono-aromatic-lean fraction. Advantageously, the 25 oxygenation feedstock consists essentially of the high-boiling fraction. Typically, an integrated process of this invention further comprises blending at least a portion of the low-boiling fraction with the acid-free product to obtain components for refinery blending of transportation fuel friendly to the environment.

30 Where the oxidation feedstock is a high-boiling distillate fraction derived from hydrogenation of a refinery stream, the refinery stream consists essentially of material boiling between about 200° C. and about 425° C. Preferably the refinery stream consisting essentially of material boiling between about 250° C. and

about 400° C., and more preferably boiling between about 275° C. and about 375° C.

In other aspects of this invention, continuous processes are provided wherein the step of contacting the oxidation feedstock and 5 immiscible phase is carried out continuously with counter-current, cross-current, or co-current flow of the two phases.

Where the oxidation feedstock is a high-boiling distillate fraction derived from hydrogenation of a refinery stream, the refinery stream consists essentially of material boiling between 10 about 200° C. and about 425° C. Preferably the refinery stream consisting essentially of material boiling between about 250° C. and about 400° C., and more preferably boiling between about 275° C. and about 375° C.

Preferably, the immiscible peracid-containing phase is an 15 aqueous liquid formed by admixing, water, a source of acetic acid, and a source of hydrogen peroxide in amounts which provide at least one mole acetic acid for each mole of and hydrogen peroxide. Beneficially, at least a portion of the separated peracid-containing phase is recycled to the reaction mixture.

20 In another aspect of this invention the treating of recovered organic phase includes use of at least one immiscible liquid comprising an aqueous solution of a soluble basic chemical compound selected from the group consisting of sodium, potassium, barium, calcium and magnesium in the form of hydroxide, 25 carbonate or bicarbonate. Particularly useful are aqueous solution of sodium hydroxide or bicarbonate.

In one aspect of this invention the treating of the recovered organic phase includes use of at least one solid sorbent comprising alumina.

30 In another aspect of this invention the treating of recovered organic phase includes use of at least one immiscible liquid comprising a solvent having a dielectric constant suitable to selectively extract oxidized sulfur-containing and/or nitrogen-

containing organic compounds. Advantageously, the solvent has a dielectric constant in a range from about 24 to about 80. Useful solvents include mono- and dihydric alcohols of 2 to about 6 carbon atoms, preferably methanol, ethanol, propanol, ethylene glycol, 5 propylene glycol, butylene glycol and aqueous solutions thereof. Particularly useful are immiscible liquids wherein the solvent comprises a compound that is selected from the group consisting of water, methanol, ethanol and mixtures thereof.

In yet another aspect of this invention the soluble basic 10 chemical compound is sodium bicarbonate, and the treating of the organic phase further comprises subsequent use of at least one other immiscible liquid comprising methanol.

In other aspects of this invention, continuous processes are provided wherein the step of contacting the oxidation feedstock and 15 immiscible phase is carried out continuously with counter-current, cross-current, or co-current flow of the two phases.

In one aspect of this invention, the recovered organic phase of the reaction mixture is contacted sequentially with (i) an ion 20 exchange resin and (ii) a heterogeneous sorbent to obtain a product having a suitable total acid number.

For a more complete understanding of the present invention, reference should now be made to the embodiments illustrated in greater detail in the accompanying drawing and described below by way of examples of the invention.

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#### BRIEF DESCRIPTION OF THE DRAWING

The drawings are schematic flow diagrams depicting preferred aspects of the present invention for continuous production of components for the blending of transportation fuels which are liquid at ambient conditions. Elements of the invention 30 in the schematic flow diagram of FIGURE 1 include oxygenating an organic feedstock with dioxygen in a liquid reaction medium containing a heterogeneous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a mixture of liquid organic compounds while maintaining the reaction

medium substantially free of halogen and/or halogen-containing compounds, to form a liquid mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products. The mixture is separated to recover at least a first 5 organic liquid of low density comprising hydrocarbons, oxygenated organic compounds and acidic co-products and at least portions of the catalyst metal, water of reaction and acidic co-products. The organic liquid is washed with an aqueous solution of sodium bicarbonate solution, or other soluble chemical base capable to 10 neutralize and/or remove acidic co-products of oxidation, and recover oxygenated product.

Elements of the invention in the schematic flow diagram of FIGURE 2 include hydrotreating a petroleum distillate with a source of dihydrogen (molecular hydrogen), and fractionating the 15 hydrotreated petroleum to provide a low-boiling blending component consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling oxidation feedstock consisting of a sulfur-rich, mono-aromatic-lean fraction. This high-boiling oxidation feedstock is contacted with an immiscible phase comprising at least one 20 organic peracid or precursors of organic peracid, in a liquid reaction mixture maintained substantially free of catalytic active metals and/or active metal-containing compounds and under conditions suitable for oxidation of one or more of the sulfur-containing and/or nitrogen-containing organic compounds. Thereafter, the 25 immiscible phases are separated by gravity to recover a portion of the acid-containing phase for recycle. The other portion of the reaction mixture is contacted with a solid sorbent and/or an ion exchange resin to recover a mixture of organic products containing less sulfur and/or less nitrogen than the oxidation feedstock.

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## GENERAL DESCRIPTION

For the purpose of the present invention, the term "heterogeneous oxygenation catalyst" means any composition solid at the conditions of oxygenation which enhances incorporation of oxygen into organic compounds and/or assists by oxidation removal 35 of sulfur or nitrogen from a mixture of organic compounds for

refinery blending of transportation fuels which are liquid at ambient conditions.

Useful heterogeneous oxygenation catalyst systems are based upon a variety of supported or unsupported transition metal compounds active for liquid phase oxidation of organic compounds comprising the low-boiling fraction. Generally, oxygenation catalyst systems comprise at least one active metal, selected from the group consisting of the *d*-transition elements in the Periodic Table, e.g., active metals are selected from the *d*-transition elements in the Periodic Table elements having atomic number in from 21 to 30, 39 to 48, and 72 to 78. Advantageously, one or more active metal is each incorporated onto an inert support in an amount of from about 0.01 percent to about 30 percent by weight of the total catalyst, preferably from about 0.1 percent to about 15 percent, and more preferably from about 0.1 percent to about 10 percent for best results.

Oxygenation catalysts beneficially contain a combination of active metals are selected from the *d*-transition elements in the Periodic Table elements and optionally a metal of Groups IV and V.

A preferred class of hydrogenation catalysts containing at least two metals selected from the group consisting of cobalt, nickel, molybdenum and tungsten. More preferably, co-metals are cobalt and molybdenum or nickel and molybdenum. Advantageously, the hydrogenation catalyst comprises at least two active metals, each incorporated onto a metal oxide support, such as alumina in an amount of from about 0.1 percent to about 20 percent by weight of the total catalyst. Other preferred heterogeneous oxygenation catalyst systems contain chromium molybdate and/or bismuth molybdate which optionally can be promoted with magnesium, CuO/SiO<sub>2</sub>, CrFeBiMoO, (chrome molybdate/iron promoted with magnesium) and MgFeBiMoO, (bismuth molybdate/iron promoted with magnesium).

A particularly preferred heterogeneous oxygenation catalyst system includes from about 0.1 percent to about 10 percent platinum and from about 5 percent to about 30 percent chromium

as oxide on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (CrOPt/Al<sub>2</sub>O<sub>3</sub>), and more preferably from about 1 percent to about 5 percent platinum and from about 15 percent to about 20 percent chromium as oxide on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.  
5 Another preferred heterogeneous oxygenation catalyst system contains from about 0.01 percent to about 5 percent Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), and more preferably from about 0.1 percent to about 3 percent Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Suitable feedstocks generally comprise most refinery streams consisting substantially of hydrocarbon compounds which are liquid 10 at ambient conditions. Suitable oxidation feedstock generally has an API gravity ranging from about 10° API to about 100° API, preferably from about 10° API to about 75° API, and more preferably from about 15° API to about 50° API for best results. These streams include, but are not limited to, fluid catalytic process 15 naphtha, fluid or delayed process naphtha, light virgin naphtha, hydrocracker naphtha, hydrotreating process naphthas, alkylate, isomerate, catalytic reformate, and aromatic derivatives of these streams such benzene, toluene, xylene, and combinations thereof. Catalytic reformate and catalytic cracking process naphthas can 20 often be split into narrower boiling range streams such as light and heavy catalytic naphthas and light and heavy catalytic reformate, which can be specifically customized for use as a feedstock in accordance with the present invention. The preferred streams are light virgin naphtha, catalytic cracking naphthas including light and 25 heavy catalytic cracking unit naphtha, catalytic reformate including light and heavy catalytic reformate and derivatives of such refinery hydrocarbon streams.

Suitable oxidation feedstocks generally include refinery 30 distillate streams boiling at a temperature range from about 50° C. to about 425° C., preferably 150° C. to about 400° C., and more preferably between about 175° C. and about 375° C. at atmospheric pressure for best results. These streams include, but are not limited to, virgin light middle distillate, virgin heavy middle distillate, fluid catalytic cracking process light catalytic cycle oil, 35 coker still distillate, hydrocracker distillate, and the collective and individually hydrotreated embodiments of these streams. The

preferred streams are the collective and individually hydrotreated embodiments of fluid catalytic cracking process light catalytic cycle oil, coker still distillate, and hydrocracker distillate.

It is also anticipated that one or more of the above distillate  
5 streams can be combined for use as oxidation feedstock. In many cases performance of the refinery transportation fuel or blending components for refinery transportation fuel obtained from the various alternative feedstocks may be comparable. In these cases, logistics such as the volume availability of a stream, location of the  
10 nearest connection and short term economics may be determinative as to what stream is utilized.

Typically, sulfur compounds in petroleum fractions are relatively non-polar, heteroaromatic sulfides such as substituted benzothiophenes and dibenzothiophenes. At first blush it might  
15 appear that heteroaromatic sulfur compounds could be selectively extracted based on some characteristic attributed only these heteroaromatics. Even though the sulfur atom in these compounds has two, non-bonding pairs of electrons which would classify them as a Lewis base, this characteristic is still not sufficient for them to  
20 be extracted by a Lewis acid. In other words, selectively extraction of heteroaromatic sulfur compounds to achieve lower levels of sulfur requires greater difference in polarity between the sulfides and the hydrocarbons.

By means of liquid phase oxidation according to this invention  
25 it is possible to selectively convert these sulfides into, more polar, Lewis basic, oxygenated sulfur compounds such as sulfoxides and sulfones. Compounds such as dimethylsulfide are very non-polar molecules. Accordingly, by selectively oxidizing heteroaromatic sulfides such as benzo- and dibenzothiophene found in a refinery  
30 streams, processes of the invention are able to selectively bring about a higher polarity characteristic to these heteroaromatic compounds. Where the polarity of these unwanted sulfur compounds is increased by means of liquid phase oxidation according to this invention, they can be selectively extracted by a

polar solvent and/or a Lewis acid sorbent while the bulk of the hydrocarbon stream is unaffected.

Other compounds which also have non-bonding pairs of electrons include amines. Heteroaromatic amines are also found in 5 the same stream that the above sulfides are found. Amines are more basic than sulfides. The lone pair of electrons functions as a Bronstad - Lowry base (proton acceptor) as well as a Lewis base (electron-donor). This pair of electrons on the atom makes it vulnerable to oxidation in manners similar to sulfides.

10 During contacting the oxidation feedstock with an immiscible phase comprising at least one organic peracid or precursors of organic peracid in the liquid phase, conditions suitable for oxidation include any pressure and temperature upward from about 10° C. at which the reaction proceeds. Preferred temperatures are between 15 about 25° C. and about 250° C., with between about 50° and about 150° C. being more preferred. The most preferred temperatures are between about 115° C. and about 125° C.

As disclosed herein oxidation feedstock is contacted with an immiscible phase comprising at least one organic peracid which 20 contains the -OOH substructure or precursors of organic peracid, and the liquid reaction mixture is maintained substantially free of catalytic active metals and/or active metal-containing compounds and under conditions suitable for oxidation of one or more of the sulfur-containing and/or nitrogen-containing organic compounds. 25 Organic peracids for use in this invention are preferably made from a combination of hydrogen peroxide and a carboxylic acid.

With respect to the organic peracids the carbonyl carbon is attached to hydrogen or a hydrocarbon radical. In general such hydrocarbon radical contains from 1 to about 12 carbon atoms, 30 preferably from about 1 to about 8 carbon atoms. More preferably, the organic peracid is selected from the group consisting of performic acid, peracetic acid, trichloroacetic acid, perbenzoic acid and perphthalic acid or precursors thereof. For best results processes of the present invention employ peracetic acid or 35 precursors of peracetic acid.

Broadly, the appropriate amount of organic peracid used herein is the stoichiometric amount necessary for oxidation of one or more of the sulfur-containing and/or nitrogen-containing organic compounds in the oxidation feedstock and is readily determined by 5 direct experimentation with a selected feedstock. With a higher concentration of organic peracid, the selectivity generally tends to favor the more highly oxidized sulfone which beneficially is even more polar than the sulfoxide.

Applicants believe the oxidation reaction involves rapid 10 reaction of organic peracid with the divalent sulfur atom by a concerted, non-radical mechanism whereby an oxygen atom is actually donated to the sulfur atom. As stated previously, in the presence of more peracid, the sulfoxide is further converted to the sulfone, presumably by the same mechanism. Similarly, it is 15 expected that the nitrogen atom of an amino is oxidized in the same manner by hydroperoxy compounds.

The statement that oxidation according to the invention in the liquid reaction mixture comprises a step whereby an oxygen atom is donated to the divalent sulfur atom is not to be taken to imply 20 that processes according to the invention actually proceeds via such a reaction mechanism.

By contacting oxidation feedstock with a peracid-containing immiscible phase in a liquid reaction mixture maintained substantially free of catalytic active metals and/or active metal-containing compounds, the tightly substituted sulfides are oxidized 25 into their corresponding sulfoxides and sulfones with negligible if any co-oxidation of mononuclear aromatics. These oxidation products due to their high polarity, can be readily removed by separation techniques such as adsorption and extraction. The high 30 selectivity of the oxidants, coupled with the small amount of tightly substituted sulfides in hydrotreated streams, makes the instant invention a particularly effective deep desulfurization means with minimum yield loss. The yield loss corresponds to the amount of tightly substituted sulfides oxidized. Since the amount of tightly

substituted sulfides present in a hydrotreated crude is rather small, the yield loss is correspondingly small.

Broadly, the liquid phase oxidation reactions are rather mild and can even be carried out at temperatures as low as room 5 temperature. More particularly, the liquid phase oxidation will be conducted under any conditions capable of converting the tightly substituted sulfides into their corresponding sulfoxides and sulfones at reasonable rates.

In accordance with this invention conditions of the liquid 10 mixture suitable for oxidation during the contacting the oxidation feedstock with the organic peracid-containing immiscible phase include any pressure at which the desired oxidation reactions proceed. Typically, temperatures upward from about 10° C. are suitable. Preferred temperatures are between about 25° C. and 15 about 250° C., with temperatures between about 50° and about 150° C. being more preferred. Most preferred temperatures are between about 115° C. and about 125° C.

Integrated processes of the invention can include one or more 20 selective separation steps using solid sorbents capable of removing sulfides and sulfones. Non-limiting examples of such sorbents, commonly known to the skilled artisan, include activated carbons, activated bauxite, activated clay, activated coke, alumina, and silica gel. The oxidized sulfur containing hydrocarbon material is contacted with solid sorbent for a time sufficient to reduce the 25 sulfur content of the hydrocarbon phase.

Integrated processes of the invention can include one or more 30 selective separation steps using an immiscible solvent having a dielectric constant suitable to selectively extract oxidized sulfur-containing and/or nitrogen-containing organic compounds. Preferably the present invention uses an solvent which exhibits a dielectric constant in a range from about 24 to about 80. For best results processes of the present invention employ solvent comprises a compound is selected from the group consisting of water, methanol, ethanol and mixtures thereof.

Integrated processes of the invention can include one or more selective separation steps using an immiscible liquid containing a soluble basic chemical compound. The oxidized sulfur containing hydrocarbon material is contacted with the solution of chemical 5 base for a time sufficient.

Generally, the suitable basic compounds include ammonia or any hydroxide, carbonate or bicarbonate of an element selected from Group I, II, and/or III of the periodic table, although calcined dolomitic materials and alkalized aluminas can be used. In addition 10 mixtures of different bases can be utilized. Preferably the basic compound is a hydroxide, carbonate or bicarbonate of an element selected from Group I and/or II element. More preferably, the basic compound is selected from the group consisting of sodium, potassium, barium, calcium and magnesium hydroxide, carbonate or 15 bicarbonate. For best results processes of the present invention employ an aqueous solvent containing an alkali metal hydroxide, preferably selected from the group consisting of sodium, potassium, barium, calcium and magnesium hydroxide. In general, an aqueous solution of the base hydroxide at a concentration on a mole basis of 20 from about 1 mole of base to 1 mole of sulfur up to about 4 moles, of base per mole of sulfur is suitable.

In carrying out a sulfur separation step according to this invention, pressures of near atmospheric and higher may be suitable. For example, pressures up to 100 atmosphere can be 25 used.

Processes of the present invention advantageously include catalytic hydrodesulfurization of the oxidation feedstock to form hydrogen sulfide which may be separated as a gas from the liquid feedstock, collected on a solid sorbent, and/or by washing with 30 aqueous liquid. Where the oxidation feedstock is a product of a process for hydrogenation of a petroleum distillate to facilitate removal of sulfur and/or nitrogen from the hydrotreated petroleum distillate, the amount of peracid necessary for the instant invention is the stoichiometric amount necessary to oxidize the tightly 35 substituted sulfides contained in the hydrotreated stream being

treated in accordance herewith. Preferably an amount which will oxidize all of the tightly substituted sulfides will be used.

- Useful distillate fractions for hydrogenation in the present invention consists essentially of any one, several, or all refinery streams boiling in a range from about 50° C. to about 425° C., preferably 150° C. to about 400° C., and more preferably between about 175° C. and about 375° C. at atmospheric pressure. For the purpose of the present invention, the term "consisting essentially of" is defined as at least 95 percent of the feedstock by volume.
- 5 The lighter hydrocarbon components in the distillate product are generally more profitably recovered to gasoline and the presence of these lower boiling materials in distillate fuels is often constrained by distillate fuel flash point specifications. Heavier hydrocarbon components boiling above 400° C. are generally more profitably
- 10 processed as FCCFeed and converted to gasoline. The presence of heavy hydrocarbon components in distillate fuels is further constrained by distillate fuel end point specifications.
- 15

The distillate fractions for hydrogenation in the present invention can comprise high and low sulfur virgin distillates derived from high- and low-sulfur crudes, coker distillates, catalytic cracker light and heavy catalytic cycle oils, and distillate boiling range products from hydrocracker and resid hydrotreater facilities. Generally, coker distillate and the light and heavy catalytic cycle oils are the most highly aromatic feedstock

20 components, ranging as high as 80 percent by weight. The majority of coker distillate and cycle oil aromatics are present as mono-aromatics and di-aromatics with a smaller portion present as tri-aromatics. Virgin stocks such as high and low sulfur virgin distillates are lower in aromatics content ranging as high as 20

25 percent by weight aromatics. Generally, the aromatics content of a combined hydrogenation facility feedstock will range from about 5 percent by weight to about 80 percent by weight, more typically from about 10 percent by weight to about 70 percent by weight, and most typically from about 20 percent by weight to about 60

30 percent by weight. In a distillate hydrogenation facility with limited operating capacity, it is generally profitable to process

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feedstocks in order of highest aromaticity, since catalytic processes often proceed to equilibrium product aromatics concentrations at sufficient space velocity. In this manner, maximum distillate pool dearomatization is generally achieved.

5       Sulfur concentration in distillate fractions for hydrogenation in the present invention is generally a function of the high and low sulfur crude mix, the hydrogenation capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrogenation feedstock components. The higher sulfur  
10      distillate feedstock components are generally virgin distillates derived from high sulfur crude, coker distillates, and catalytic cycle oils from fluid catalytic cracking units processing relatively higher sulfur feedstocks. These distillate feedstock components can range as high as 2 percent by weight elemental sulfur but generally range  
15      from about 0.1 percent by weight to about 0.9 percent by weight elemental sulfur. Where a hydrogenation facility is a two-stage process having a first-stage denitrogenation and desulfurization zone and a second-stage dearomatization zone, the dearomatization zone feedstock sulfur content can range from about 100 ppm to  
20      about 0.9 percent by weight or as low as from about 10 ppm to about 0.9 percent by weight elemental sulfur.

Nitrogen content of distillate fractions for hydrogenation in the present invention is also generally a function of the nitrogen content of the crude oil, the hydrogenation capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrogenation feedstock components. The higher nitrogen distillate feedstocks are generally coker distillate and the catalytic cycle oils. These distillate feedstock components can have total nitrogen concentrations ranging as high as 2000 ppm, but generally  
25      range from about 5 ppm to about 900 ppm.

The catalytic hydrogenation process may be carried out under relatively mild conditions in a fixed, moving fluidized or ebullient bed of catalyst. Preferably a fixed bed of catalyst is used under conditions such that relatively long periods elapse before  
30      regeneration becomes necessary, for example a an average reaction

zone temperature of from about 200° C. to about 450° C., preferably from about 250° C. to about 400° C., and most preferably from about 275° C to about 350° C. for best results, and at a pressure within the range of from about 6 to about 160 atmospheres.

- 5        A particularly preferred pressure range within which the hydrogenation provides extremely good sulfur removal while minimizing the amount of pressure and hydrogen required for the hydrodesulfurization step are pressures within the range of 20 to 60 atmospheres, more preferably from about 25 to 40 atmospheres.
- 10       According the present invention, suitable distillate fractions are preferably hydrodesulfureized before being selectively oxidized, and more preferably using a facility capable of providing effluents of at least one low-boiling fraction and one high-boiling fraction.
- 15       Where the particular hydrogenation facility is a two-stage process, the first stage is often designed to desulfurize and denitrogenate, and the second stage is designed to dearomatize. In these operations, the feedstocks entering the dearomatization stage are substantially lower in nitrogen and sulfur content and can be 20 lower in aromatics content than the feedstocks entering the hydrogenation facility.

Generally, the hydrogenation process useful in the present invention begins with a distillate fraction preheating step. The distillate fraction is preheated in feed/effluent heat exchangers 25 prior to entering a furnace for final preheating to a targeted reaction zone inlet temperature. The distillate fraction can be contacted with a hydrogen stream prior to, during, and/or after preheating. The hydrogen-containing stream can also be added in the hydrogenation reaction zone of a single-stage hydrogenation 30 process or in either the first or second stage of a two-stage hydrogenation process.

The hydrogen stream can be pure hydrogen or can be in admixture with diluents such as hydrocarbon, carbon monoxide, carbon dioxide, nitrogen, water, sulfur compounds, and the like.

The hydrogen stream purify should be at least about 50 percent by volume hydrogen, preferably at least about 65 percent by volume hydrogen, and more preferably at least about 75 percent by volume hydrogen for best results. Hydrogen can be supplied from 5 a hydrogen plant, a catalytic reforming facility or other hydrogen producing process.

The reaction zone can consist of one or more fixed bed reactors containing the same or different catalysts. Two-stage processes can be designed with at least one fixed bed reactor for 10 desulfurization and denitrogenation, and at least one fixed bed reactor for dearomatization. A fixed bed reactor can also comprise a plurality of catalyst beds. The plurality of catalyst beds in a single fixed bed reactor can also comprise the same or different catalysts. Where the catalysts are different in a multi-bed fixed 15 bed reactor, the initial bed is generally for desulfurization and denitrogenation, and subsequent beds are for dearomatization.

Since the hydrogenation reaction is generally exothermic, interstage cooling, consisting of heat transfer devices between fixed bed reactors or between catalyst beds in the same reactor shell, can 20 be employed. At least a portion of the heat generated from the hydrogenation process can often be profitably recovered for use in the hydrogenation process. Where this heat recovery option is not available, cooling may be performed through cooling utilities such as cooling water or air, or through use of a hydrogen quench stream 25 injected directly into the reactors. Two-stage processes can provide reduced temperature exotherm per reactor shell and provide better hydrogenation reactor temperature control.

The reaction zone effluent is generally cooled and the effluent stream is directed to a separator device to remove the hydrogen. 30 Some of the recovered hydrogen can be recycled back to the process while some of the hydrogen can be purged to external systems such as plant or refinery fuel. The hydrogen purge rate is often controlled to maintain a minimum hydrogen purity and remove hydrogen sulfide. Recycled hydrogen is generally

compressed, supplemented with "make-up" hydrogen, and injected into the process for further hydrogenation.

Liquid effluent of the separator device can be processed in a stripper device where light hydrocarbons can be removed and 5 directed to more appropriate hydrocarbon pools. Preferably the separator and/or stripper device includes means capable of providing effluents of at least one low-boiling liquid fraction and one high-boiling liquid fraction. Liquid effluent and/or one or more liquid fraction thereof is subsequently treated to incorporate 10 oxygen into the liquid organic compounds therein and/or assist by oxidation removal of sulfur or nitrogen from the liquid products. Liquid products are then generally conveyed to blending facilities for production of finished distillate products.

Operating conditions to be used in the hydrogenation process 15 include an average reaction zone temperature of from about 200° C. to about 450° C., preferably from about 250° C. to about 400° C., and most preferably from about 275° C. to about 350° C. for best results. Reaction temperatures below these ranges can result in less effective hydrogenation. Excessively high temperatures can cause 20 the process to reach a thermodynamic aromatic reduction limit, hydrocracking, catalyst deactivation, and increase energy costs. Desulfurization, in accordance with the process of the present invention, can be less effected by reaction zone temperature than prior art processes, especially at feed sulfur levels below 500 ppm, 25 such as in the second-stage dearomatization zone of a two-stage process.

The hydrogenation process typically operates at reaction zone pressures ranging from about 400 psig to about 2000 psig, more 30 preferably from about 500 psig to about 1500 psig, and most preferably from about 600 psig to about 1200 psig for best results. Hydrogen circulation rates generally range from about 500 SCF/Bbl to about 20,000 SCF/Bbl, preferably from about 2,000 SCF/Bbl to about 15,000 SCF/Bbl, and most preferably from about 3,000 to about 13,000 SCF/Bbl for best results. Reaction pressures and 35 hydrogen circulation rates below these ranges can result in higher

catalyst deactivation rates resulting in less effective desulfurization, denitrogenation, and dearomatization. Excessively high reaction pressures increase energy and equipment costs and provide diminishing marginal benefits.

5        The hydrogenation process typically operates at a liquid hourly space velocity of from about 0.2 hr<sup>-1</sup> to about 10.0 hr<sup>-1</sup>, preferably from about 0.5 hr<sup>-1</sup> to about 3.0 hr<sup>-1</sup>, and most preferably from about 1.0 hr<sup>-1</sup> to about 2.0 hr<sup>-1</sup> for best results. Excessively high space velocities will result in reduced overall 10 hydrogenation.

Useful catalyst for the hydrodesulfurization comprise a component capable to enhance the incorporation of hydrogen into a mixture of organic compounds to thereby form at least hydrogen sulfide, and a catalyst support component.

15       The catalyst support component typically comprises mordenite and a refractory inorganic oxide such as silica, alumina, or silica-alumina. The mordenite component is present in the support in an amount ranging from about 10 percent by weight to about 90 percent by weight, preferably from about 40 percent by weight to about 85 percent by weight, and most preferably from about 50 percent by weight to about 80 percent by weight for best results. The refractory inorganic oxide, suitable for use in the present invention, has a pore diameter ranging from about 50 to about 200 Angstroms and more preferably from about 80 to about 20 25 150 Angstroms for best results. Mordenite, as synthesized, is characterized by its silicon to aluminum ratio of about 5:1 and its crystal structure.

Further reduction of such heteroaromatic sulfides from a distillate petroleum fraction by hydrotreating would require that 30 the stream be subjected to very severe catalytic hydrogenation order to convert these compounds into hydrocarbons and hydrogen sulfide (H<sub>2</sub>S). Typically, the larger any hydrocarbon moiety is, the more difficult it is to hydrogenate the sulfide. Therefore, the residual organo-sulfur compounds remaining after a 35 hydrotreatment are the most tightly substituted sulfides.

Subsequent to desulfurization by catalytic hydrogenation, as disclosed herein further selective removal of sulfur or nitrogen from the desulfurized mixture of organic compounds can be accomplished by incorporation of oxygen into sulfur or nitrogen 5 containing organic compounds thereby assisting in selective removal of sulfur or nitrogen from oxidation feedstocks.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to better communicate the present invention, still another preferred aspect of the invention is depicted schematically 10 in FIGURE 1. Referring now to FIGURE 1, organic feedstock comprising a liquid mixture of organic compounds derived from natural petroleum, the mixture having a gravity ranging from about 10° API to about 80° API is supplied through conduit 32 and into oxygenation reactor 110 containing a fixed, ebullient, or fluidized 15 bed of heterogeneous oxygenation catalyst system for oxidation in the liquid phase with a gaseous source of dioxygen, such as air or nitrogen enriched air. In the embodiment illustrated in Figure 1, the oxygenation reactor 110 contains an ebullating bed of heterogeneous catalyst, for example a particulate form of chromium 20 molybdate or bismuth molybdate with or without magnesium.

Generally, oxygenation reactions are conducted at temperatures in a range of from about 25° C. to about 250° C., preferably at temperatures in a range of from about 65° C. to about 200° C., and more preferably at temperatures in a range of from 25 about 100° C. to about 180° C. Suitable pressure for oxygenation reactions is pressure sufficient to maintain the organic feedstock in substantially a liquid state, typically pressure are in a range of from about 50 psi to about 600 psi.

Air or nitrogen enriched air is supplied to compressor 114 30 through supply conduit 116, and the compressed gas is sparged into the bottom of oxygenation reactor 110 through conduit 118. Heat generated by the exothermic oxidation reaction may cause a portion of the volatile organic compounds in the reaction medium to vaporize. Gaseous reactor effluent containing any such vaporized 35 organic compounds, carbon oxides, nitrogen from the gas charged to

the oxidation reaction and unreacted dioxygen pass through conduit 112, effluent cooler 122, and thereafter into overhead knock-out drum 120 through conduit 124. Levels of dioxygen in the gaseous reactor effluent are low, preferably zero, but in some cases may be 5 as high as 8 percent by volume.

Separated organic liquid from drum 120 is returned to oxygenation reactor 110 through conduit 126. As needed aqueous liquid is discharged from drum 120 to blowdown disposal (not shown) through conduit 144. Gas is vented from drum 120, 10 through conduit 128, to a vent gas treatment unit (not shown) or flared. Beneficially, a portion of gases from drum 120 are supplied to compressor 114 for recycle to oxygenation reactor 110.

Reactor effluent containing entrained particles of the heterogeneous oxygenation catalyst system in a mixture of gases 15 and the liquid portion of the reaction mixture, is diverted from oxidation reactor 110 through conduit 132 and into centrifugal separator 130. While a portion of the separated solids may be returned directly to oxidation reactor 110, according to the embodiment illustrated in Figure 1, separated solids concentrated 20 in a liquid portion of the reaction mixture is supplied to catalyst recover/regeneration unit 138 from centrifugal separator 130 through conduit 136.

Gases and liquid portions of the reaction mixture are transferred from centrifugal separator 130 into separation drum 25 140. Gases separated by gravity from the other phase of the reaction mixture are transferred from separation drum 140 into the cooler overhead knock-out drum 120 through conduit 142.

The separated organic liquid phase of the reaction mixture is supplied from settling drum 140 to liquid-liquid extractor 150 30 through conduit 152. Preferably, the design of extractor 150 provides about 2 to about 5 theoretical stages of liquid-liquid extraction. Aqueous sodium bicarbonate solution, or other soluble chemical base capable to neutralize and/or remove acidic co-products of oxidation, is supplied to extractor 150 from source

**156** through conduit **154**. Oxygenated product is transferred from extractor **150** to fuel blending facility **100** through conduit **92**.

In order to better communicate the present invention, still another preferred aspect of the invention is depicted schematically 5 in FIGURE 2. Referring now to FIGURE 2, a substantially liquid stream of middle distillates from a refinery source **12** is charged through conduit **14** into catalytic reactor **20**. A gaseous mixture containing dihydrogen (molecular hydrogen) is supplied to catalytic reactor **20** from storage or a refinery source **16** through conduit 10 **18**. Catalytic reactor **20** contains one or more fixed bed of the same or different catalyst which have a hydrogenation-promoting action for desulfurization, denitrogenation, and dearomatization of middle distillates. The reactor maybe operated in upflow, downflow, or counter-current flow of the liquid and gases through 15 the bed.

One or more beds of catalyst and subsequent distillation operate together as an integrated hydrotreating and fractionation system. This fractionation system separates unreacted dihydrogen, 20 hydrogen sulfide and other non-condensable products of hydrogenation from the effluent stream and the resulting liquid mixture of condensable compounds is fractionated into a low-boiling fraction containing a minor amount of remaining sulfur and a high-boiling fraction containing a major amount of remaining sulfur.

25 Mixed effluents from catalytic reactor **20** are transferred into separation drum **24** through conduit **22**. Unreacted dihydrogen, hydrogen sulfide and other non-condensed compounds flow from separation drum **24** to hydrogen recovery (not shown) through conduit **28**. Advantageously, all or a portion of the unreacted 30 hydrogen may be recycled to catalytic reactor **20**, provided at least a portion of the hydrogen sulfide has been separated therefrom.

Hydrogenated liquids flow from separation drum **24** into distillation column **30** through conduit **26**. Gases and condensable vapors from the top of column **30** are transferred through 35 overhead cooler **40**, by means of conduits **34** and **42**, and into

overhead drum 46. Separated gases and non-condensed compounds flow from overhead drum 46 to disposal or further recovery (not shown) through conduit 49. A portion of the condensed organic compounds suitable for reflux is returned from 5 overhead drum 46 to column 30 through conduit 48. Other portions of the condensate are beneficially recycled from overhead drum 46 to separation drum 24 and/or transferred to other refinery uses (not shown).

10 The low-boiling fraction having the minor amount of sulfur-containing organic compounds is withdrawn from near the top of column 30. It should be apparent that this low-boiling fraction from the catalytic hydrogenation is a valuable product in itself. Beneficially, all or a portion of the low-boiling fraction in substantially liquid form is transferred through conduit 32 and into 15 an oxygenation process unit 90 for catalytic oxidation in the liquid phase with a gaseous source of dioxygen, such as air or oxygen enriched air, for example as shown in FIGURE 1. A stream containing oxygenated organic compounds is subsequently separated to recover, for example, a fuel or a blending component 20 of fuel and transferred to fuel blending facility 100 through conduit 92. The stream can alternatively be utilized as a source of feed stock for chemical manufacturing.

25 A portion of the high-boiling liquid at the bottom of column 30 is transferred to reboiler 36 through conduit 35, and a stream of vapor from reboiler 36 is returned to distillation column 30 through conduit 35.

30 From the bottom of column 30 another portion of the high-boiling liquid fraction having the major amount of the sulfur-containing organic compounds is supplied as oxidation feedstock to oxidation reactor 60 through conduit 38.

35 An immiscible phase including at least peracetic acid and/or other organic peracids, is supplied to oxidation reactor 60 through manifold 50. The liquid reaction mixture in oxidation reactor 60 is maintained substantially free of catalytic active metals and/or active metal-containing compounds and under conditions suitable

for oxidation of one or more of the sulfur-containing and/or nitrogen-containing organic compounds. Suitably the oxidation reactor **60** is maintained at temperatures in a range of from about 80° C to about 125° C, and at pressures in a range from about 15 psi to about 400 psi, preferably from about 15 psi to about 150 psi.

5 Liquid reaction mixture from reactor **60** is supplied to drum **64** through conduit **62**. At least a portion of the immiscible phase is separated by gravity from the other phase of the reaction mixture. While a portion of the immiscible phase may be returned 10 directly to reactor **60**, according to the embodiment illustrated in FIGURE 1 the phase is withdrawn from drum **64** through conduit **66** and transferred into separation unit **80**.

15 The immiscible phase contains water of reaction, carboxylic acids, and oxidized sulfur-containing and/or nitrogen-containing organic compounds which are now soluble in the immiscible phase. Acetic acid and excess water are separated from high-boiling sulfur-containing and/or nitrogen-containing organic compounds as by distillation. Recovered acetic acid is returned to oxidation reactor **60** through conduit **82** and manifold **50**. Hydrogen 20 peroxide is supplied to manifold **50** from storage **52** through conduit **54**. As needed, makeup acetic acid solution is supplied to manifold **50** from storage **56**, or another source of aqueous acetic acid, through conduit **58**. Excess water is withdrawn from separation unit **80** and transferred through conduit **86** to disposal 25 (not shown). At least a portion of the oxidized high-boiling sulfur-containing and/or nitrogen-containing organic compounds are transferred through conduit **84** and into catalytic reactor **20**.

30 The separated phase of the reaction mixture from drum **64** is supplied to vessel **70** through conduit **68**. Vessel **70** contains a bed of solid sorbent which exhibits the ability to retain acidic and/or other polar compounds, to obtain product containing less sulfur and/or less nitrogen than the feedstock to the oxidation. Product is transferred from vessel **70** to fuel blending facility **100** through conduit **72**. Preferably, in this embodiment a system of 35 two or more reactors a system of two or more reactors containing solid sorbent, configured for parallel flow, is used to allow

continuous operation while one bed of sorbent is regenerated or replaced.

Transportation fuels friendly to the environment are transferred from blending facility 100 through conduit 102 to 5 storage and/or shipping (not shown).

In view of the features and advantages of processes in accordance with this invention using selected organic peracids in a liquid phase reaction mixture maintained substantially free of catalytic active metals and/or active metal-containing compounds 10 to preferentially oxidize compounds in which a sulfur atom is sterically hindered rather than aromatic hydrocarbons, as compared to known desulfurization systems previously used, the following examples are given. The following examples are illustrative and are not meant to be limiting.

15

## GENERAL

Oxygenation of a hydrocarbon product was determined by the difference between the high precision carbon and hydrogen analysis of the feed and product.

20

$$\text{Oxygenation, percent,} = (\text{percent C} + \text{percent H}) \text{ analysis of feed} \\ - (\text{percent C} + \text{percent H}) \text{ analysis of oxygenated product}$$

## EXAMPLE 1

In this example a refinery distillate containing sulfur at a level of about 500 ppm was hydrotreated under conditions suitable to produce hydrodesulfurized distillate containing sulfur at a level 25 of about 130 ppm, which was identified as hydrotreated distillate 150. Hydrotreated distillate 150 was cut by distillation into four fractions which were collected at temperatures according to the following schedule.

	Fraction	Temperatures, °C
30	1	Below 260
	2	260 to 288
	3	288 to 316
	4	Above 316

Analysis of hydrotreated distillate 150 over this range of distillation cut points is shown in Table I. In accordance with this invention a fraction collected below a temperature in the range from about 260° C. to about 300° C. splits hydrotreated distillate 5 150 into a sulfur-lean, monoaromatic-rich fraction and a sulfur-rich, monoaromatic-lean fraction.

Table I

10 ANALYSIS OF DISTILLATION FRACTIONS OF HYDROTREATED DISTILLATE 150

Item	Fraction Number				Total
	1	2	3	4	
15 Weight, %	45	21	19	16	100
Sulfur, ppm	11.7	25	174	580	133
Mono-Ar, %	40.7	26.3	15.6	14.0	28.8
Di-Ar, %	0.4	5.0	5.4	5.6	3.1
Tri-Ar, %	0	0	0	0.8	0.1

20 Mono-Ar is mono-aromatics. Di-Ar is di-aromatics. Tri-Ar is tri-aromatics.

## EXAMPLE 2

In this example a refinery distillate containing sulfur at a 25 level of about 500 ppm was hydrotreated under conditions suitable to produce a hydrodesulfurized distillate containing sulfur at a level of about 15 ppm, which was identified as hydrotreated distillate 15.

Analysis of hydrotreated distillate 150 over the range of distillation cut points is shown in Table II. In accordance with this 30 invention a fraction collected below a temperature in the range from about 260° C. to about 300° C. splits hydrotreated distillate 15 into a sulfur-lean, monoaromatic-rich fraction and a sulfur-rich, monoaromatic-lean fraction.

Table II

ANALYSIS OF DISTILLATION FRACTIONS OF  
HYDROTREATED DISTILLATE 15

5	Fraction Number					
	Item	1	2	3	4	Total
	Weight, %	53	16	20	11	100
	Sulfur, ppm	1	2	13	80	12.3
10	Mono-Ar, %	35.8	20.9	14.8	12.0	5.6
	Di-Ar, %	1.3	8.0	7.4	5.6	4.0
	Tri-Ar, %	0	0	0	1.4	0.2

15 Mono-Ar is mono-aromatics. Di-Ar is di-aromatics. Tri-Ar is tri-aromatics.

## EXAMPLE 3

This example describes a heterogeneous catalytic oxygenation according to the invention of a refinery distillate with a gaseous source of dioxygen. The distillate had a gravity of 20° API. 20 Analysis of the distillate gave 233 ppm of sulfur, 4 ppm of nitrogen. A stirred autoclave, having a nominal volume of 1 liter, was charged with 299.5 g of distillate and 2.98 grams of a particulate oxygenation catalyst containing bismuth molybdate/iron promoted with magnesium. The oxygenation was carried out at a 25 temperature of 160° C. and a pressure of 200 psig using gaseous oxygen diluted to 7 percent with nitrogen at a flow rate of 1200 sccm for 180 minutes. Analyses of the product determined a sulfur content of 12 ppm, a nitrogen content of 6 ppm, and a total acid number of 12.9 mg KOH/g. Oxygenation of the hydrocarbon portion 30 of the product was 3.43 percent by weight.

## EXAMPLE 4

This example describes heterogeneous catalytic oxygenation with a gaseous source of dioxygen according to the invention of another portion of the refinery distillate oxygenated in Example 3.

5 The stirred autoclave was charged with 299.7 g of distillate and 3.01 grams of a particulate oxygenation catalyst containing 18 percent chromium as oxide and 1.5 percent platinum on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (CrOPt/Al<sub>2</sub>O<sub>3</sub>). This oxygenation was also carried out at a temperature of 160° C. and a pressure of 200 psig using gaseous

10 oxygen diluted to 7 percent with nitrogen at a flow rate of 1200 sccm, but for 300 minutes. Analyses of the product determined a sulfur content of 13 ppm, a nitrogen content of 2 ppm, and a total acid number of 0.7 mg KOH/g. Oxygenation of a hydrocarbon product was 1.01 percent by weight.

15

## EXAMPLE 5

This example describes a heterogeneous catalytic oxygenation according to the invention of a hydrotreated refinery distillate identified as S-25. This hydrotreated distillate had a gravity of 35° API. Analysis of the distillate gave 20 ppm of sulfur, 18 ppm of

20 nitrogen. The stirred autoclave was charged with 185.8 g of distillate and 1.84 grams of a particulate oxygenation catalyst containing bismuth molybdate/iron promoted with magnesium. The oxygenation was carried out at a temperature of 160° C. and a pressure of 200 psig using gaseous oxygen diluted to 7 percent with

25 nitrogen at a flow rate of 1200 sccm for 300 minutes. Analyses of the product determined a sulfur content of 12 ppm, a nitrogen content of 7 ppm, and a total acid number of 2.37 mg KOH/g. Oxygenation of the hydrocarbon portion of the product was 1.48 percent by weight.

30

## EXAMPLE 6

This example describes heterogeneous catalytic oxygenation with a gaseous source of dioxygen of another portion of the hydrotreated distillate oxygenated in Example 5. The stirred

autoclave was charged with 299.3 g of distillate and 3 grams of a particulate oxygenation catalyst containing 18 percent chromium as oxide and 1.5 percent platinum on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (CrOPt/Al<sub>2</sub>O<sub>3</sub>). The oxygenation was also carried out at a temperature of 160° C. and a 5 pressure of 200 psig using gaseous oxygen diluted to 7 percent with nitrogen at a flow rate of 1200 sccm, but for 245 minutes. Analyses of the product determined a sulfur content of 9 ppm, a nitrogen content of 8 ppm, and a total acid number of 2.89 mg KOH/g. Oxygenation of a hydrocarbon product was 1.01 percent by 10 weight.

#### EXAMPLE 7

This example describes heterogeneous catalytic oxygenation with a gaseous source of dioxygen of another portion of the hydrotreated distillate oxygenated in Example 5. The stirred 15 autoclave was charged with 299.4 g of distillate and 3 grams of a particulate oxygenation catalyst containing 0.5 percent Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The oxygenation was also carried out at a temperature of 160° C. and a pressure of 200 psig using gaseous oxygen diluted to 7 percent with nitrogen at a flow rate of 1200 sccm. Analyses of 20 the product determined a sulfur content of 6 ppm, a nitrogen content of 9 ppm, and a total acid number of 7.77 mg KOH/g. Oxygenation of a hydrocarbon product was 2.45 percent by weight.

#### EXAMPLES 8 - 11

Hydrotreated refinery distillate S-25 was partitioned by 25 distillation to provide feedstock for oxidation using hydrogen peroxide and acetic acid. The fraction collected below temperatures of about 300° C. was a sulfur-lean, monoaromatic-rich fraction identified as S-25-B300. Analyses of S-25-B300 determined a sulfur content of 3 ppm, a nitrogen content of 2 ppm, and 36.2 percent mono-aromatics, 1.8 percent di-aromatics, for a total 30 aromatics of 37.9 percent. The fraction collected above temperatures of about 300° C. was a sulfur-rich, monoaromatic-poor fraction identified as S-25-A300. Analyses of S-25-A300 determined a sulfur content of 35 ppm, a nitrogen content of 31 ppm, and aromatic content was 15.7 percent mono-aromatics, 5.8 35

percent di-aromatics, and 1.4 percent tri-aromatics, for a total aromatics of 22.9 percent.

5        Into a 250 mL, three-neck round bottom flask equipped with a reflux condenser, a mechanical agitator, a nitrogen inlet and outlet, were charged 100 g of S-25-A300. The reactor was also charged with varying amounts of glacial acetic acid, distilled and deionized water, and 30 percent aqueous hydrogen peroxide. The mixture is heated with stirring and under a slight flow of nitrogen at approximately 93° C. to 99° C. for approximately two hours. At 10 the end of the reaction period, the agitation ceased and the contents of the flask rapidly formed into two liquid layers. A sample of the top layer (organic) was withdrawn and dehydrated with anhydrous sodium sulfate. Contents of the flask was stirred and permitted to cool to ambient temperature before approximately 0.1 g of 15 manganese dioxide is added to decompose any residual hydrogen peroxide. At this point, the mixture was stirred for an additional 10 minutes before the entire reactor content was collected.

20        Table III gives variables and analytical data which demonstrate that increasing concentration of acetic acid increases concentration of total sulfur in the aqueous layer. Increasing level of acetic acid caused sulfur in the organic layer to decrease by 35 ppm. These data clearly indicate that an essential element of the present of invention is the use of organic peracids where the carbonyl carbon is attached to hydrogen or a hydrocarbon radical. 25        In general such hydrocarbon radical contains from 1 to about 12 carbon atoms, preferably from about 1 to about 8 carbon atoms. Acetic acid was shown to extract oxidized sulfur compounds from the organic phase and into the aqueous phase. Without acetic acid, no noticeable sulfur transfer into the aqueous phase was observed.

Table III

EXPERIMENTAL PARAMETERS AND ANALYTICAL RESULTS  
FOR OXIDATIONS OF LS-25-A300

EXAMPLE	8	9	10	11
H <sub>2</sub> O <sub>2</sub> , mL	34	34	34	34
HOAc ,mL	0	25	50	75
H <sub>2</sub> O , mL	100	75	50	25
Sulfur Aq, ppm	<2	<2	13	14
Sulfur Org, ppm	33	30	21	18

H<sub>2</sub>O<sub>2</sub> is 30 percent hydrogen peroxide. HOAc is glacial acetic acid.  
H<sub>2</sub>O is distilled water.

## EXAMPLE 12

Hydrotreated refinery distillate S-25 was partitioned by distillation to provide feedstock for oxidation using an immiscible aqueous solution phase containing hydrogen peroxide and acetic acid. The fraction of S-25 collected above temperatures of about 316° C. was a sulfur-rich, monoaromatic-poor fraction identified as S-25-A316. Analyses of S-25-A316 determined a sulfur content of 80 ppm, and a nitrogen content of 102 ppm.

A 250 mL, three-neck round bottom flask equipped with a reflux condenser, a magnetic stir bar or mechanical agitator, a nitrogen inlet and outlet, was charged with 100 g of the S-98-25-A316, 75 mL glacial acetic acid, 25 mL water, and 17 mL (30%) hydrogen peroxide. The mixture was heated to 100° C and stirred vigorously under a very slight flow of house nitrogen for two hours.

At the end of the reaction period, analysis of the top layer (organic) found total sulfur and nitrogen of 54 ppm sulfur and 5 ppm nitrogen. Contents of the flask was again stirred and cooled to room temperature. At room temperature, approximately 0.1 g of manganese dioxide (MnO<sub>2</sub>) was added to decompose any excess

hydrogen peroxide and stirring continued for 10 minutes. The entire contents of the flask were then poured into a bottle with a vented cap. Analysis of the bottom layer (aqueous) found 44 ppm of total sulfur.

5

#### EXAMPLE 12a

A second oxidation of hydrotreated refinery distillate S-25-A316 was conducted as described in Example 12 by charging 100 mL glacial acetic acid, but no water. The organic layer was found to contain 27 ppm sulfur and 3 ppm nitrogen. The aqueous layer 10 contained 81 ppm sulfur.

#### EXAMPLE 12b

The entire contents of the flask from both Example 12 and Example 12a were combined. A bottom layer was then removed, leaving behind a combined organic layer from both experiments. 15 The organic layer was dried over anhydrous sodium sulfate to remove any residual water from the process. After the spent sodium sulfate was removed via vacuum filtration, the filtrate was percolated through enough alumina so that the filtrate to alumina ratio ranged from 7:1 to 10:1. Analysis of organic layer emerging 20 from the alumina was 32 ppm of total sulfur and 5 ppm of total nitrogen.

#### EXAMPLE 13

A hydrotreated refinery distillate identified as S-150 was partitioned by distillation to provide feedstock for oxidations using 25 peracid formed with hydrogen peroxide and acetic acid. Analyses of S-150 determined a sulfur content of 113 ppm, and a nitrogen content of 36 ppm. The fraction of S-98 collected above temperatures of about 316° C. was a sulfur-rich, monoaromatic-poor fraction identified as S-150-A316. Analyses of S-150-A316 30 determined a sulfur content of 580 ppm and a nitrogen content of 147 ppm.

A 3 liter, three neck, round bottom flask equipped with a water-jacketed reflux condenser, a mechanical stirrer, a nitrogen

inlet and outlet, and a heating mantel controlled through a Variac auto-transformer, was charged with 1 kg of S-150-A316, 1 liter of glacial acetic acid and 170 mL of 30 percent hydrogen peroxide.

5 A slight flow of nitrogen was initiated and this gas then slowly swept over the surface of the reactor content. The agitator was started to provide efficient mixing and the contents were heated. Once the temperature reaches 93° C., the contents were held at this temperature for reaction time of 120 minutes.

10 After the reaction time had elapsed, the contents continued to be stirred while the heating mantel turned off and removed. At approximately 77° C., the agitator was stopped momentarily while approximately 1 g of manganese dioxide ( $MnO_2$ ) was added through one of the necks of the round bottom flask to the biphasic mixture to decompose any unreacted hydrogen peroxide. Mixing of the 15 contents with the agitator was then resumed until the temperature of the mixture was cooled to approximately 49° C. The agitation was ceased to allow both organic (top) and aqueous (bottom) layers to separate, which occurred immediately.

20 The bottom layer was removed and retained for further analysis in a lightly capped bottle to permit the possible evolution of oxygen from any undecomposed hydrogen peroxide. Analysis of the bottom layer was 252 ppm of sulfur.

25 The reactor was cautiously charged with 500 mL of saturated aqueous sodium bicarbonate to neutralize the organic layer. After the bicarbonate solution was added, the mixture was stirred rapidly for ten minutes to neutralize any remaining acetic acid. The organic material was dried over anhydrous 3A molecular sieve. Analysis of the dry organic layer, identified as PS-150-A316, was 143 ppm of sulfur, 4 ppm of nitrogen, and a total acid number of 0.1 mg KOH/g.

30

#### EXAMPLE 14

A 500 mL separatory funnel was charged with 150 mL of PS-150-A316 and 150 mL of methanol. The funnel was shaken and then the mixture was allowed to separate. The bottom methanol

layer was collected and saved for analytical testing. A 50 mL portion of the product was then collected for analytical testing and identified as sample ME14-1.

- 5 A 100 mL portion of fresh methanol was added to the funnel containing the remaining 100 mL of product. The funnel was again shaken and the mixture was allowed to separate. The bottom methanol layer was collected and saved for Analytical testing. A 50 mL portion of the methanol extracted product was collected for analytical testing and identified as sample ME14-2.
- 10 Into the remaining 50 mL of product in the funnel, 50 mL of fresh methanol was added. The funnel was again shaken and the two layers were allowed to separate. The bottom methanol layer was collected and saved for analytical testing. 50 mL of the product is collected for analytical testing and identified as sample 15 ME14-3.

The Analytical results obtained for this example are shown in Table IV.

Table IV

20 REDUCTION OF SULFUR & TOTAL ACID NUMBER  
BY METHANOL EXTRACTIONS

Sample	TAN, mg KOH/g	Sulfur, ppmw
PS-150-A316	0.11	143
ME14-1	0.02	35
ME14-2	0.02	14
ME14-3	0.02	7

- 25 These results clearly show that methanol was capable of selectively removing oxidized sulfur compounds. Additionally, acidic impurities were also removed by methanol extraction.

## EXAMPLE 15

A separatory funnel was charged with 50 mL of PS-150-A316 and 50 mL water. The funnel was shaken and the layers were allowed to separate. The bottom water layer was collected and saved for analytical testing. The hydrocarbon layer was collected for analytical testing and identified as E15-1W. Table V presents these results.

10

Table V

## REDUCTION OF SULFUR BY WATER EXTRACTION

Sample	TAN mg KOH/g	Nitrogen ppmw	Sulfur ppmw
PS-150-A316	0.11	4	143
E15-1W	---	5	100

15

The water extraction results show that water was useful in removing oxidized sulfur compounds from the distillate.

## EXAMPLE 16

20 Five hundred grams of PS-150-A316 were percolated through 50 grams of anhydrous acidic alumina. The collected product was identified as E16-1A and analyzed. The data are presented in Table VI.

25

Table VI

## REDUCTION OF SULFUR AND NITROGEN BY ALUMINA TREATMENT

Sample	Nitrogen ppmw	Sulfur ppmw
PS-150-A316	4	143
E16-1A	2	32

These data demonstrate that alumina treatment was also effective in the removal of oxidized sulfur and nitrogen compounds from the distillate.

Analysis was conducted on alumina treated material E16-1A 5 and compared with the PS-150-A316. The analysis showed an absence of any dibenzothiophene in the products, while the feed contained about 3,000 ppm of this impurity.

#### EXAMPLE 17

10 Hydrotreated refinery distillate S-25 was partitioned by distillation to provide a feedstock for oxidations using peracid formed with hydrogen peroxide and acetic acid. The fraction of S-25 collected below temperatures of about 288° C. was a sulfur-lean, monoaromatic-rich fraction identified as S-DF-B288. The fraction 15 of S-25 collected above temperatures of about 288° C. was a sulfur-rich, monoaromatic-poor fraction identified as S-DF-A288. Analyses of S-DF-A288 determined a sulfur content of 30 ppm.

20 A series of oxidation runs were conducted as described in Example 13 and the products combined to provide amounts of material needed for cetane rating and chemical analysis. A flask equipped as in Example 13 was charged with 1 kg of S-DF-A288, 1 liter of glacial acetic acid, 85 mL of deionized and distilled water and 85 mL of 30 percent hydrogen peroxide.

25 In one procedure a batch of dried oxidized distillate was percolated through a second column packed with 250 mL of dried, acidic alumina (150 mesh). The distillate to alumina ratio was about 4:1 (v/v). The alumina was used for approximately 4 batches of 1,000 mL, and replaced.

30 In another procedure approximately 100 grams of alumina was placed in a 600 mL Büchner funnel equipped with a fritted disc (fine). Dried distillate was poured over the alumina and more quickly treated as the vacuum draws the distillate through the alumina in a shorter time.

Every batch of post-alumina treated material was submitted for total sulfur analysis to quantify the sulfur removal efficiency from the feed. All alumina treated materials had a sulfur concentration of less than 3 ppmw, and in general about 1 ppmw 5 sulfur. A blend of 32 batches of alumina treated material was identified as BA-DF-A288.

For the purposes of the present invention, "predominantly" is defined as more than about fifty percent. "Substantially" is defined as occurring with sufficient frequency or being present in such 10 proportions as to measurably affect macroscopic properties of an associated compound or system. Where the frequency or proportion for such impact is not clear, substantially is to be regarded as about twenty per cent or more. The term "essentially" is defined as absolutely except that small variations which have no 15 more than a negligible effect on macroscopic qualities and final outcome are permitted, typically up to about one percent.

That which is claimed is:

1. A process for the production of refinery transportation fuel or blending components for refinery transportation fuel, which process comprises:
  - 5 providing organic feedstock comprising a mixture of organic compounds derived from natural petroleum, the mixture having a gravity ranging from about 10° API to about 75° API;
  - 10 contacting the organic feedstock with an oxidizing agent and heterogeneous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a mixture of liquid organic compounds, while maintaining the reaction medium substantially free of halogen and/or halogen-containing compounds, to form a liquid mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products; and
  - 15 separating from the reaction medium at least a first organic liquid of low density comprising hydrocarbons, oxygenated organic compounds and acidic co-products, and at least portions of the heterogeneous oxygenation catalyst system, water of reaction and acidic co-products.
- 20 2. The process according to claim 1 wherein the organic feedstock comprises sulfur-containing and/or nitrogen-containing organic compounds one or more of which are oxidized in the liquid reaction medium, and wherein a second separated liquid is an aqueous solution containing at least a portion of the oxidized sulfur-containing and/or nitrogen-containing organic compounds.
- 25 3. The process according to claim 2 which further comprises contacting the separated organic liquid with a neutralizing agent and recovering a product having a low content of acidic co-products.
- 30 4. The process according to claim 1 wherein the oxidizing agent comprises a gaseous source of dioxygen, the heterogeneous oxygenation catalyst system comprises an active metal selected from the group consisting of vanadium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, palladium, platinum, copper, silver,

or mixture thereof, employed as metal oxide, mixed metal oxide, and/or basic salts of the metal or mixed metal oxide, and which process further comprises recovering at least a portion of the catalyst system and injecting all or a portion of the recovered catalyst system into the liquid reaction medium.

5. The process according to claim 1 wherein all or at least a portion of the organic feedstock is a product of a hydrotreating process for petroleum distillates consisting essentially of material boiling between about 50° C. and about 425° C. which hydrotreating process includes reacting the petroleum distillate with a source of hydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur and/or nitrogen from the hydrotreated petroleum distillate.

10 6. The process according to claim 5 wherein the hydrogenation catalyst comprises at least one active metal, selected from the group consisting of the *d*-transition elements in the Periodic Table, each incorporated onto an inert support in an amount of from about 0.1 percent to about 20 percent by weight of the total catalyst.

20 7. The process according to claim 5 wherein the hydrotreating process further comprises partitioning of the hydrotreated petroleum distillate by distillation to provide at least one low-boiling liquid consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling liquid consisting of a sulfur-rich, 25 mono-aromatic-lean fraction, and wherein the organic feedstock is predominantly the low-boiling liquid.

30 8. The process according to claim 1 wherein the heterogeneous oxygenation catalyst system comprises an oxygenation catalyst containing from about 1 percent to about 30 percent chromium as oxide and from about 0.1 percent to about 5 percent platinum on a support comprising gamma alumina.

9. The process according to claim 1 wherein the heterogeneous oxygenation catalyst system comprises chromium molybdate or bismuth molybdate and optionally magnesium.

10. The process according to claim 1 wherein the heterogeneous oxygenation catalyst system comprises gamma alumina and a catalyst represented by the formula  $Na_2Cr_2O_7$  in an amount of from about 0.1 percent to about 1.5 percent of the total catalyst system.

11. A process for the production of refinery transportation fuel or blending components for refinery transportation fuel, which process comprises:

partitioning by distillation an organic feedstock comprising a mixture of organic compounds derived from natural petroleum, the mixture having a gravity ranging from about 10° API to about 75° API to provide at least one low-boiling organic part consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling organic part consisting of a sulfur-rich, mono-aromatic-lean fraction;

15 contacting a gaseous source of dioxygen with at least a portion of the low-boiling organic part in a liquid reaction medium containing a heterogeneous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a mixture of liquid organic compounds, while maintaining the reaction 20 medium substantially free of halogen and/or halogen-containing compounds, to form a liquid mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products; and, while maintaining the liquid reaction medium substantially free of halogen and/or halogen-containing compounds, 25 to form a mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products;

separating from the mixture at least a first organic liquid of low density comprising hydrocarbons, oxygenated organic compounds and acidic co-products and at least portions of the 30 catalyst metal, water of reaction and acidic co-products; and

contacting all or a portion of the separated organic liquid with a neutralizing agent thereby recovering a low-boiling oxygenated product having a low content of acidic co-products.

12. The process according to claim 11 wherein at least a 35 portion of the separated organic liquid is contacted with an aqueous

solution of a chemical base, and the recovered oxygenated product exhibits a total acid number of less than about 20 mg KOH/g.

13. The process according to claim 12 wherein the chemical base is a compound selected from the group consisting of sodium, 5 potassium, barium, calcium and magnesium in the form of hydroxide, carbonate or bicarbonate.

14. The process according to claim 11 wherein all or at least a portion of the organic feedstock is a product of a process for hydrogenation of a petroleum distillate consisting essentially of 10 material boiling between about 50° C. and about 425° C. which hydrogenation process includes reacting the petroleum distillate with a source of hydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur and/or nitrogen from the hydrotreated petroleum 15 distillate.

15. A process for the production of refinery transportation fuel or blending components for refinery transportation fuel, which process comprises:

partitioning by distillation an organic feedstock comprising a 20 mixture of organic compounds derived from natural petroleum, the mixture consisting essentially of material boiling between about 75° C. and about 425° C. to provide at least one low-boiling organic part consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling organic part consisting of a sulfur-rich, mono-aromatic-lean 25 fraction;

contacting a gaseous source of dioxygen with at least a portion of the low-boiling organic part in a liquid reaction medium containing a heterogeneous oxygenation catalyst system which exhibits a capability to enhance the incorporation of oxygen into a 30 mixture of liquid organic compounds, while maintaining the reaction medium substantially free of halogen and/or halogen-containing compounds, to form a liquid mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products; and, while maintaining the liquid reaction medium 35 substantially free of halogen and/or halogen-containing compounds,

- to form a mixture comprising hydrocarbons, oxygenated organic compounds, water of reaction, and acidic co-products;
- 5 separating from the mixture at least a first organic liquid of low density comprising hydrocarbons, oxygenated organic compounds and acidic co-products and at least portions of the catalyst metal, water of reaction and acidic co-products; and
- 10 contacting all or a portion of the separated organic liquid with a neutralizing agent and recovering a low-boiling oxygenated product having a low content of acidic co-products; and
- 15 10 contacting the high-boiling organic part with an immiscible phase comprising at least one organic peracid or precursors of organic peracid in a liquid reaction mixture maintained substantially free of catalytic active metals and/or active metal-containing compounds and under conditions suitable for oxidation of one or more of the sulfur-containing and/or nitrogen-containing organic compounds;
- separating at least a portion of the immiscible peracid-containing phase from the oxidized phase of the reaction mixture; and
- 20 15 contacting the oxidized phase of the reaction mixture with a solid sorbent, an ion exchange resin, and/or a suitable immiscible liquid containing a solvent or a soluble basic chemical compound, to obtain a high-boiling product containing less sulfur and/or less nitrogen than the high-boiling fraction.
- 25 16. The process according to claim 15 wherein the immiscible phase is formed by admixing a source of hydrogen peroxide and/or alkylhydroperoxide, an aliphatic monocarboxylic acid of 2 to about 6 carbon atoms, and water.
- 30 17. The process according to claim 15 wherein the immiscible phase is formed by admixing hydrogen peroxide, acetic acid, and water.
18. The process according to claim 15 wherein at least a portion of the separated peracid-containing phase is recycled to the reaction mixture.

19. The process according to claim 15 further comprising blending at least a portion of the low-boiling oxygenated product with at least a portion of the high-boiling product to obtain components for refinery blending of transportation fuel.
- 5 20. The process according to claim 15 wherein the oxidation feedstock is a high-boiling distillate fraction consists essentially of material boiling between about 200° C and about 425° C derived from hydrotreating of a refinery stream.

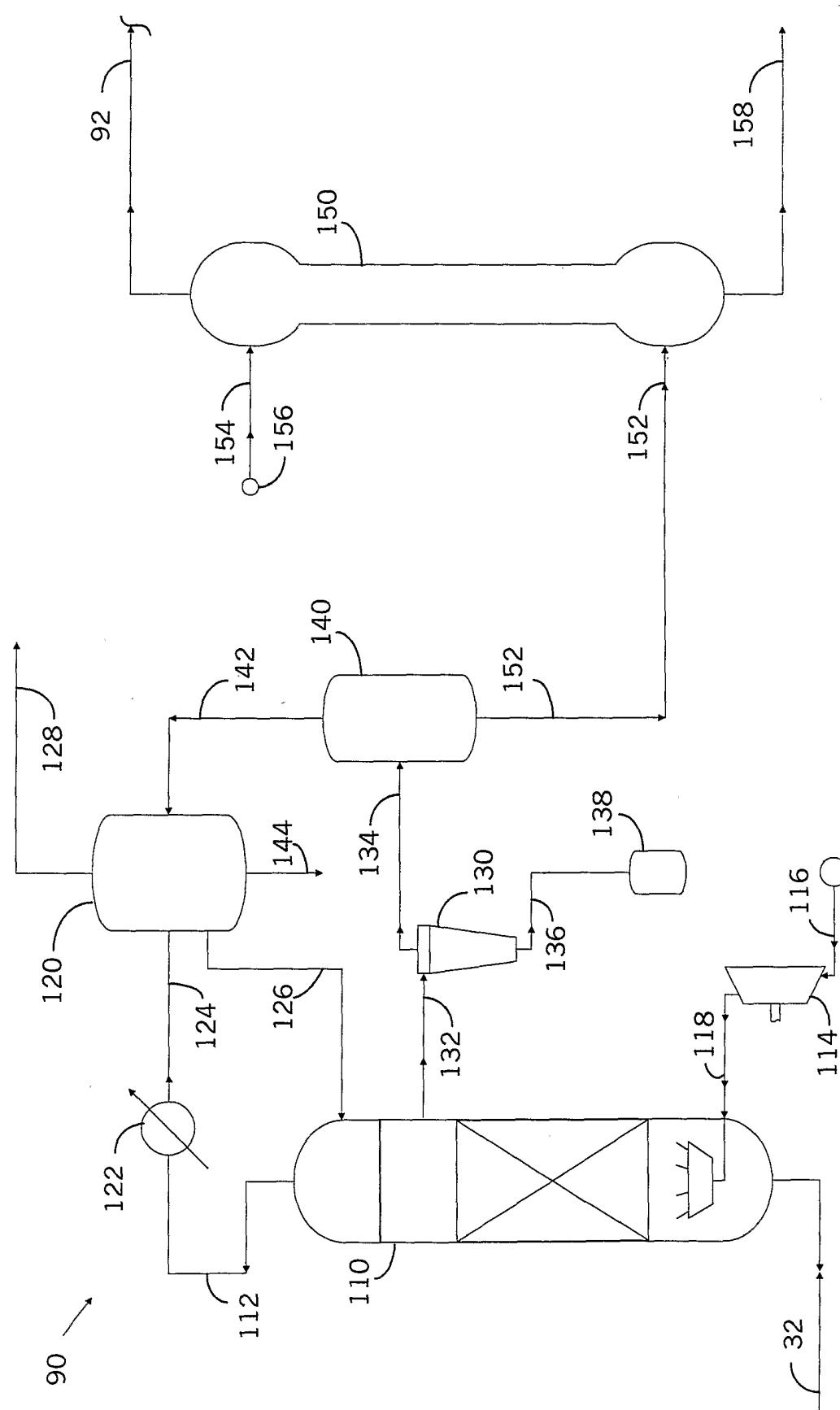


FIG. 1

FIG. 2

