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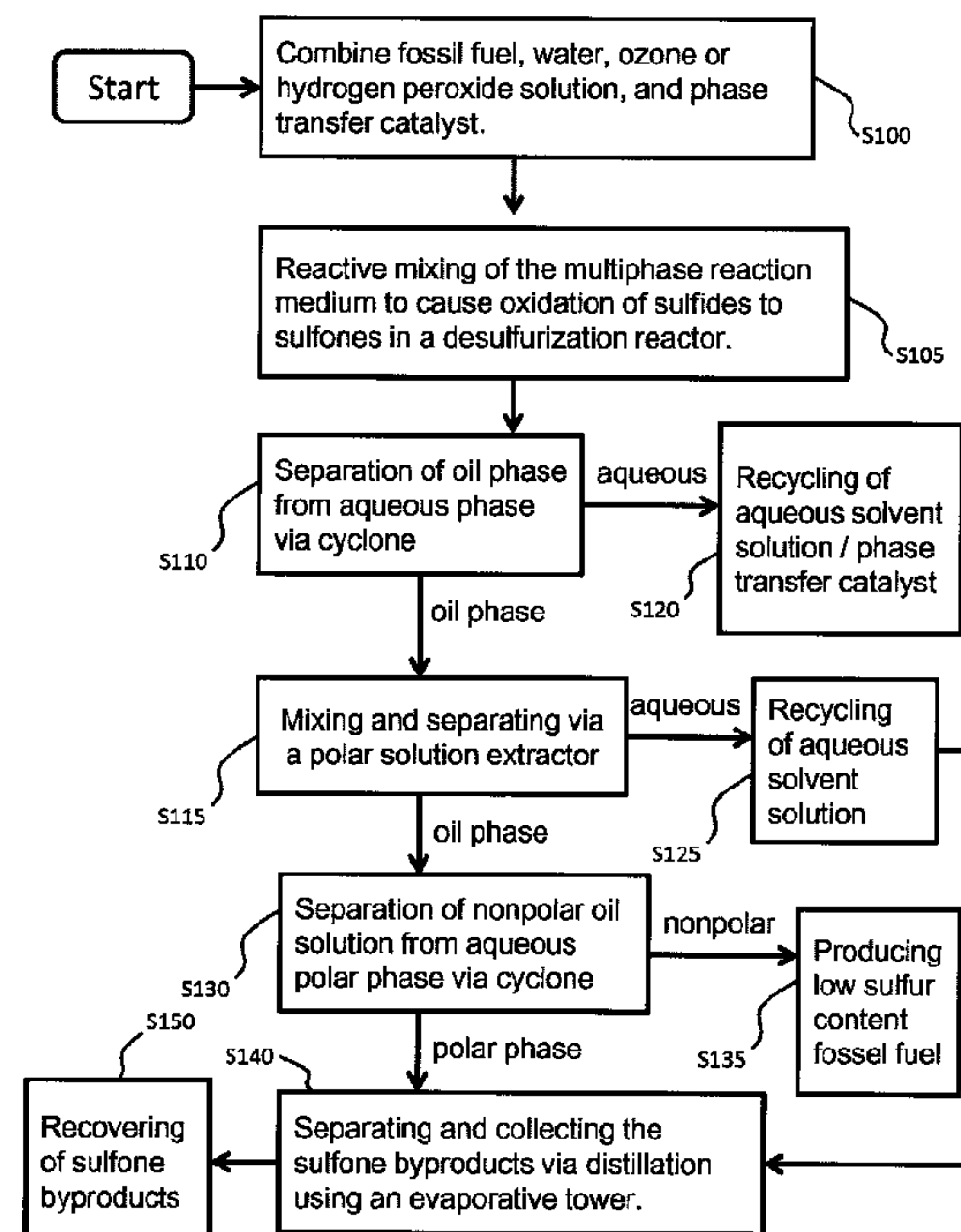
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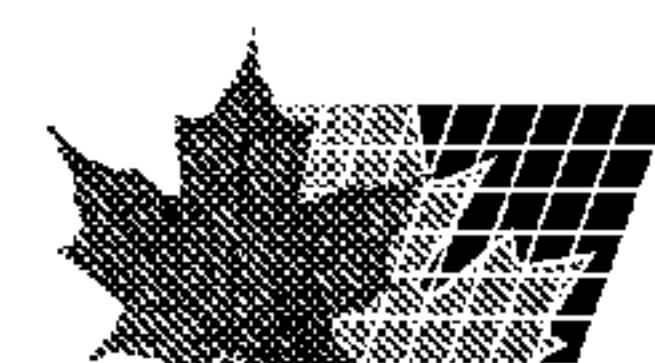
(54) Titre : METHODE DE DESULFURATION OXYDATIVE AVEC MELANGE POUR DU CARBURANT DIESEL ET
DISPOSITIF A CET EFFET

(54) Title: MIXING-ASSISTED OXIDATIVE DESULFURIZATION METHOD OF DIESEL FUEL AND DEVICE THEREOF



(57) Abrégé/Abstract:

Mixing-assisted oxidative desulfurization method of diesel fuel and the continuous desulfurization device thereof is disclosed herein. Because of the dangers of sulfur content in gasoline and other petroleum products, many governments have required the sulfur content of these petroleum products to be reduced so as to safeguard public safety and health. Desulfurization of fossil fuels is provided by the combination of fossil fuels with an aqueous mixture of ozone or hydrogen peroxide and a Tetraoctylphosphonium salt phase transfer catalyst, and the mixture is then reactive mixed to form oxidize sulfur compounds in the fuel. The polar oxidized sulfones species are removed via another mixing step. The desulfurization device (10) can be in the form of a portable device which provides for continuous mixing- assisted desulfurization for the selective removal of sulfur containing compounds from fossil fuels such as diesel fuel or other hydrocarbons.



ABSTRACT

Mixing-assisted oxidative desulfurization method of diesel fuel and the continuous desulfurization device thereof is disclosed herein. Because of the dangers of sulfur content in gasoline and other petroleum products, many governments have required the sulfur content of these petroleum products to be reduced so as to safeguard public safety and health. Desulfurization of fossil fuels is provided by the combination of fossil fuels with an aqueous mixture of ozone or hydrogen peroxide and a Tetraoctylphosphonium salt phase transfer catalyst, and the mixture is then reactive mixed to form oxidize sulfur compounds in the fuel. The polar oxidized sulfones species are removed via another mixing step. The desulfurization device (10) can be in the form of a portable device which provides for continuous mixing-assisted desulfurization for the selective removal of sulfur containing compounds from fossil fuels such as diesel fuel or other hydrocarbons.

MIXING-ASSISTED OXIDATIVE DESULFURIZATION METHOD OF DIESEL FUEL AND DEVICE THEREOF

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BACKGROUND

1. Field of the Invention

[0001] This disclosure resides in the field of the desulfurization of petroleum, fossil fuel, and/or petroleum-based fuels.

10 2. Description of the Related Art

[0002] Diesel fuel is one of the more commonly-used fossil fuels today in transportation. Because it is widely known that diesel engines are inherently more thermally and energy efficient than gasoline engines, it is expected that the demand for diesel fuel will likely increase more and more in the future due to higher global
15 environmental consciousness as well as the green movement as was seen happening in recent years. Diesel fuels are generally relatively complex mixtures of alkanes, cycloalkanes, and aromatic hydrocarbons with carbon numbers in the range of C9-C28 and with a boiling-range of 150-390 degrees C. Their relative distribution depends on the specific fuel feedstock, refining process, and actual blending schemes
20 based on day-to-day commercial demands of the end user. Two commonly found sulfur compounds in diesel fuel are, for example, alkylbenzothiophenes (BTs) and alkyldibenzothiophenes (DBTs).

[0003] The presence of sulfur in diesel fuel is an environmental concern. Upon combustion, the sulfur leads directly to the emission of SO₂ and sulfate particulate
25 matter, which are serious health hazards and can easily endanger public health. Moreover, the sulfur can also lead to other problems such as poisoning of the catalytic converters, corrosion of parts of internal combustion engines, and increased air

pollution. Indeed, because of the dangers of the sulfur content in gasoline and other petroleum products, the United States EPA has issued regulations that require the reduction of sulfur content of gasoline from 300 ppm to 30 ppm, and that of diesel fuel from 500 ppm to 15 ppm so as to safeguard public safety and health.

5 [0004] The hydrodesulfurization (HDS) is one of the largest scale conventional chemical processes to remove sulfur from diesel. Traditional HDS is a hydro-treatment process that requires hydrogen and a catalyst to break up the sulfur-containing compounds in diesel to form hydrogen sulfide.

[0005] However, even small amounts of unreacted hydrogen sulfide from the
10 desulfurization process can be harmful. Hydrogen sulfide has an extremely high acute toxicity, which has caused many deaths in the workplace, and is thus hazardous to workers. One of the difficulties with the newer United States EPA regulations on reducing sulfur contents is that when the hydrodesulfurization is performed under these more stringent conditions, there would be an increased risk of hydrogen leakage
15 through the walls of the reactor.

[0006] One conventional method for desulfurization of diesel fuels is by means of oxidative desulfurization. This method is based on the operating principle that sulfur compounds are known to be slightly more polar than hydrocarbons. In addition, oxidized sulfur compounds such as sulfones are substantially more polar than sulfides.
20 More importantly, the oxidation of sulfides to sulfones is usually much easier and faster than the oxidation of most hydrocarbons. As such, the conversion of the slightly polar sulfides to the more polar sulfones or sulfoxides allows for the sulfur compounds to be more easily extracted from the fossil fuels into an aqueous phase.

[0007] U.S. Pat. No. 6,402,939 describes a technique in which organic sulfur
25 compounds are removed from a fossil fuel by a process that combines oxidative desulfurization with ultrasound technology. The oxidative desulfurization is achieved

by combining the fossil fuel with a hydroperoxide oxidizing agent in an aqueous fluid, and the ultrasound is applied to the resulting mixture to increase the reactivity of the various species in the mixture. Ultrasound-assisted oxidative desulfurization (UAOD) process, which is operated at ambient temperature and atmospheric pressure conditions, permits the selective removal of sulfur compounds from hydrocarbons; however, it was found that some bromo by-products were formed by using the quaternary ammonium bromides as phase transfer agents or catalysts. Moreover, the sonoreactor utilized in the desulfurization process also possesses many disadvantages such as, for example, requiring very expensive equipments which also requires technical sophisticated parts such as an RF amplifier and a function generator, requiring higher electrical power consumption due to the generation of ultrasonic fields, requiring to operate at higher operating temperatures, typical at between 70 to 80°C, and the ultrasound potentially present long term detriment to possible chain cracking of long chain hydrocarbons. Moreover, the conventional sonoreactor or ultrasonic desulfurization equipment possess practical limitations with respect to scale up to mass production because of also the need to scale up of the corresponding function generator and RF amplifier.

[0008] Furthermore, although ultrasound applied to oxidative desulfurization has accomplished higher sulfur removal capability using a probe type reactor in a batch scale, nevertheless, during a batch process, all the reaction components are combined and held under controlled conditions until for a prolonged period of time in which the desired process endpoint has been reached. Therefore, such reactions are typically slow, taking hours, and the product has to be isolated at the end of the process cycle.

25 SUMMARY OF INVENTION

[0009] In order to overcome the above mentioned problems, one aspect of this

disclosure is directed to a method of mixing-assisted oxidative desulfurization (MAOD) of fossil fuels in which the fossil fuel is combined with an aqueous oxidizer solution including hydrogen peroxide or ozone solution containing a quaternary ammonium salt having at least one carbon chain of 8 or more carbon atoms as a phase transfer catalyst to achieve improved conversion of sulfides to sulfoxides with higher yield and without the unwanted formation of brominated side products.

[0010] In another aspect of this disclosure is directed to a method of mixing-assisted oxidative desulfurization of fossil fuels in which the fossil fuel is combined with an aqueous hydrogen peroxide solution or ozone solution containing a quaternary ammonium salt as a phase transfer catalyst to achieve improved conversion of sulfides to sulfoxides as contained in the organic phase fuel using a plurality of mixing tanks and a plurality of cyclones, without having to require the use of any sonoreactor or ultrasonic device, which can be complex, unreliable, and expensive. In addition, by not using any sonoreactor, there would be no need for cooling the multiphase reaction medium by thermal contact with a coolant medium during the oxidative desulfurization of fossil fuels process using the mixing tank/cyclone system, as well as requiring much less energy consumption during desulfurization. The mixing-assisted oxidative desulfurization process of this disclosure is also advantageous over the conventional sonoreactor or ultrasonic desulfurization process, for example, with respect to having much fewer problems relating to scale up to mass production because of the lack of the accompanying corresponding function generator and RF amplifier that are found in sonoreactors, and not presenting long term detriment to possible chain cracking of long chain hydrocarbons.

[0011] In another aspect of this disclosure, a continuous flow system for the oxidative desulfurization of fossil fuels is disclosed. This oxidative desulfurization system utilizes a plurality of mixing tanks of module design along with a portable and

continuous flow unit, which includes at least two mixing tanks, a mixer connected to each mixing tank for agitation and mixing to effect emulsion bubble formations, at least two cyclones coupled to the mixing tanks in series, respectively, in tandem, and an evaporative tower. The evaporative tower is coupled to one cyclone and to one
5 mixing tank so as to produce sulfones. One of the cyclone yields an organic phase that is substantially sulfone-free. In addition, to achieve higher processing of fuel and/or increased oxidation, multiple sets of mixing tank and cyclone combinations, in conjunction with multiple units of evaporator towers can be scaled up to connect in series or in parallel, respectively.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a schematic diagram of a continuous desulfurization device in accordance with an embodiment of the present disclosure.

[0013] FIG. 2 is a flow diagram of the continuous desulfurization process in
15 accordance with the embodiment shown in FIG. 1.

DETAILED DESCRIPTION OF EMBODIMENTS

[0014] Quaternary ammonium salts are compounds comprised of a positively charged nitrogen atom having four substituents, paired with a negatively charged
20 counterion.

[0015] The term "hydroperoxide" is used herein to denote a compound of the molecular structure in which R represents either a hydrogen atom or an organic or inorganic group. Examples of hydroperoxides in which R is an organic group are water-soluble hydroperoxides such as methyl hydroperoxide, ethyl hydroperoxide,
25 isopropyl hydroperoxide, n-butyl hydroperoxide, sec-butyl hydroperoxide, tert-butyl hydroperoxide, 2-methoxy-2-propyl hydroperoxide, tert-amyl hydroperoxide, and

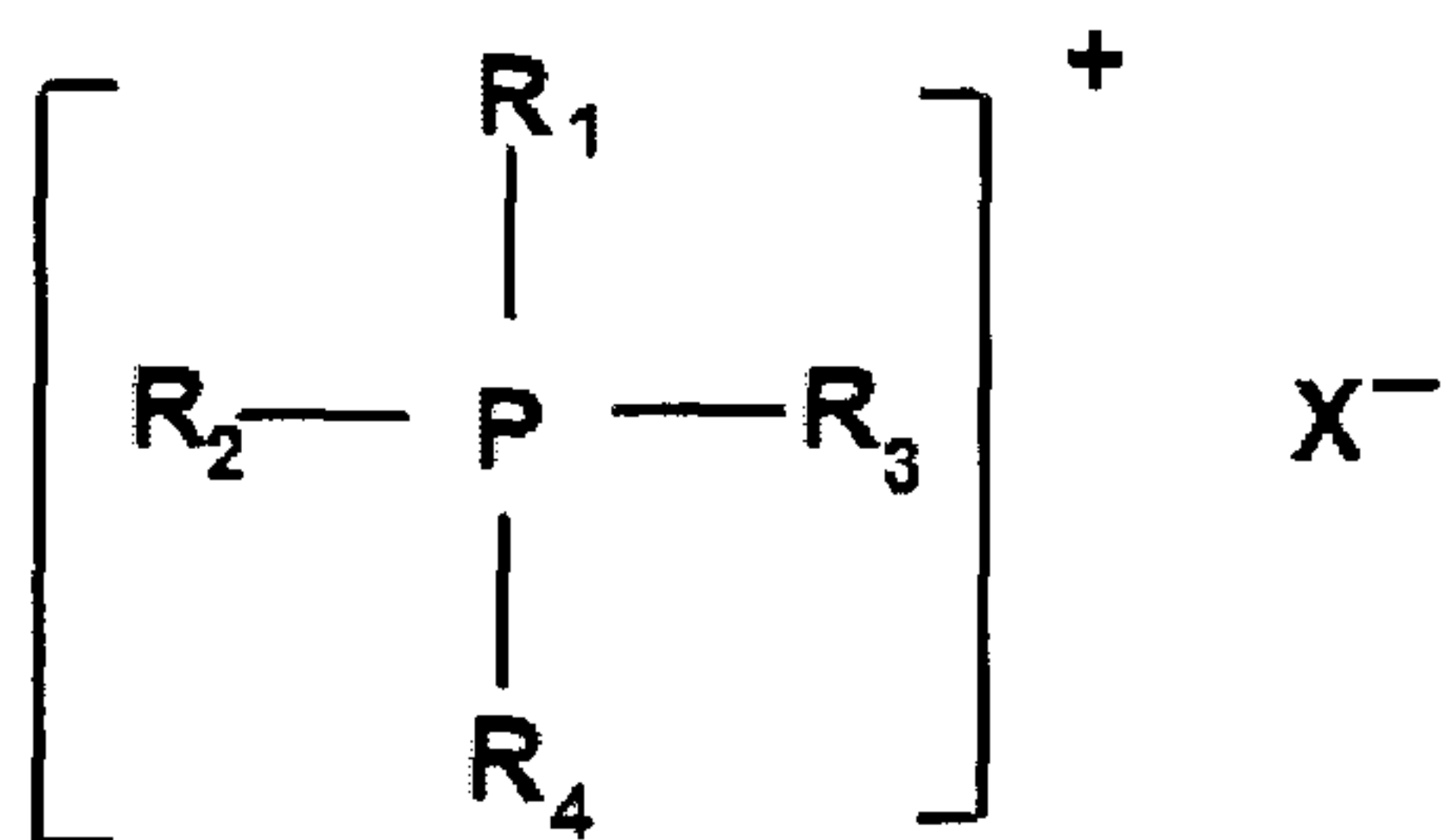
cyclohexyl hydroperoxide. Examples of hydroperoxides in which R is an inorganic group are peroxonitrous acid, peroxophosphoric acid, and peroxosulfuric acid. Preferred hydroperoxides are hydrogen peroxide (in which R is a hydrogen atom) and tertiary-alkyl peroxides, notably tert-butyl peroxide.

- 5 [0016] The aqueous fluid that is combined with the fossil fuel and the oxidizer aqueous solution including hydrogen peroxide, hydroperoxide or ozone. The relative amounts of the liquid fossil fuel and oxidizer aqueous solution may vary from about 1:1 to about 1: 3, and preferably about 1:1.25. The concentration of hydrogen peroxide in the oxidizer aqueous solution is substantially in the range of 1% to 30%.
- 10 And although they may affect the efficiency of the process or the ease of handling the fluids, the relative amounts are not critical to this invention. In most cases, however, improved results will be achieved when adding some ozone into the oxidizer aqueous solution by introducing ozone bubble in to the aqueous fluid by ozone generator (Pacific Ozone L22) or directly introducing ozone gas into the solution. The flow rate
- 15 of ozone is substantially in the range of 0.01g/hr to 1g/hr. Moreover, the mixture concentration of ozone in the oxidizer aqueous solution can also be dictated by the amount of ozone substantially in the range of 0.01g/l to 1g/l, and preferably about saturated in the oxidizer aqueous solution at the operating conditions.

- [0017] The amount of hydroperoxide relative to the fossil fuel and the aqueous fluid
- 20 can also be varied, and although the conversion rate may vary somewhat with the proportion of hydroperoxide. When the hydroperoxide is H_2O_2 , improved results are generally achieved in most systems with an H_2O_2 concentration within the range of from about 1% to about 30% by volume (as H_2O_2) of the combined aqueous and organic phases, and preferably from about 3%. For hydroperoxides other than H_2O_2 ,
- 25 the preferred relative volumes will be those of equivalent molar amounts.

[0018] In the present embodiment, a metal catalyst is included in the reaction

system to regulate the activity of the hydroxyl radical produced by the hydroperoxide. Examples of such catalysts are transition metal catalysts and Fenton catalysts (ferrous salts) and metal ion catalysts in general such as iron (II), iron (III), copper (I), copper (II), chromium (III), chromium (VI), molybdenum, tungsten, and vanadium ions. Of these, iron (II), iron (III), copper (II), and tungsten catalysts are preferred. For some systems, such as crude oil, Fenton-type catalysts are preferred, while for others, such as diesel and other systems where dibenzylthiophene is a prominent component, tungstates are preferred. Tungstates include tungstic acid, substituted tungstic acids such as phosphotungstic acid, and metal tungstates. The metal catalyst when present will be used in a catalytically effective amount, which means any amount that will enhance the progress of the reaction toward the desired goal, which is the oxidation of the sulfides to sulfones. In most cases, the catalytically effective amount will range from about 0.01g to about 0.5g, and preferably will be about 0.2g, when mixed to 25g of hydrogen peroxide solution (3~30 vol. % solution). In this embodiment, the phase transfer catalyst can be Tetraoctylphosphonium salt, and the Tetraoctylphosphonium salt can be, for example, tetraoctylphosphonium bromide, tetraoctylphosphonium chloride, tetraoctylphosphonium iodide, tetraoctylphosphonium acetate and tetraoctylphosphonium chromate. The Tetraoctylphosphonium salt can have the following formula, where



R_1 , R_2 , R_3 , and R_4 are alkyl radicals having 8 carbon atoms in a branched or linear alkyl chain and X^- is an anionic species. In most cases, the catalytically effective

amount of the Tetraoctylphosphonium salt phase transfer catalyst will range from about 0.01g to about 0.5g, and preferably will be about 0.2g, when mixed to 25g of hydrogen peroxide solution (3~30 vol. % solution). The oxidizer aqueous solution, the phase transfer catalyst, the metal catalyst, and the diesel fuel containing relatively high concentration of sulfur are mixed together and transported to a first mixing tank through a plurality of pipes. Each of the feed streams can be independent flow-regulated by means of conventional flow valves and flow control system. The reaction mixture is thoroughly mixed in the first mixing tank using a mixer. The extensive amount of bubble contact surface facilitation formations found in the oil/aqueous emulsion inside the first mixing tank during the reactive mixing process help to improve upon the oxidation reaction rate of sulfides to form sulfoxides or sulfone.

[0019] Once the reactive mixing is terminated, the product mixture will contain both aqueous and organic phases, and the organic phase will contain the bulk of the sulfones produced by the oxidation reaction. The product mixture can be phase-separated prior to sulfone removal. Phase separation can be accomplished by breaking the emulsion caused by the reactive mixing. The breaking of the emulsion is also performed by conventional means. The various possibilities for methods of performing these procedures will be readily apparent to anyone skilled in the art of handling emulsions and continuous stirred tank reactors, and particularly oil-in-water emulsions.

[0020] With their increased polarity relative to the sulfides originally present in the fossil fuels, the sulfones produced are readily removable from either the aqueous phase, the organic phase, or both, by further extracting of the polar species through mixing and separating via a polar solution extractor. The polar solution extractor can be realized in the form of a "mixing tank", which is fitted with a mixer, in the present

embodiment. One mechanism to improve the extraction efficiency is to creating a lot of tiny bubbles in the well-agitated and thoroughly mixed emulsion mixture, to increase the contact area of the polar solution and the fossil fuel. The tiny bubbles may be in the form of liquid bubbles such as oil bubbles or aqueous bubbles, or in the form of gas bubbles. In another embodiment, the polar solution extractor can be realized in the form of a liquid-solid adsorption unit. Alumina oxide can be filled inside the columns of the solid adsorption unit, and gravity or vacuum can be used to assist in the adsorption process. A solvent such as Acetonitrile can be used as the polar solvent in the polar solution extractor. Acetonitrile can be easily separated by distillation from the sulfones with boiling point ranging from 550 to 950 K. Each time, the solvent-to-oil (S/O) ratio can be kept at 1:1 by weight (for example, 1 g diesel per 1 g Acetonitrile).

[0021] The term "liquid fossil fuels" is used herein to denote any carbonaceous liquid that is derived from petroleum, coal, or any other naturally occurring material. Included among these fuels are automotive fuels such as gasoline, diesel fuel, jet fuel, and rocket fuel, as well as petroleum residual-based fuel oils including bunker fuels and residual fuels.

[0022] One method for conducting MAOD utilizes a continuous flow system which can be operated at steady state with reactants continuously coming into the reaction vessel and the product continuously being removed.

[0023] In one embodiment of the present disclosure, a continuous desulfurization device 10 is described, and the continuous desulfurization device 10 can be a portable unit. This continuous desulfurization device 10 has demonstrated that large amounts of diesel fuels can be treated in a short time to reach high desulfurization efficiency with low capital investment and maintenance cost. Moreover, this desulfurization device 10 may be operated in the temperature lower than that of sonoreactor.

Normally, the operating temperature was raised to around 50-60°C by the chemical reaction of the aqueous fluid. This technology can potentially provide sulfur reduction of 95%. For higher throughput rate and performance, two of these desulfurization devices 10 can be connected in parallel to reach even higher sulfur reduction.

5 [0024] A diagram of the continuous desulfurization device 10 is shown in FIG. 1. An oxidizing agent supply tank 30 for supplying the oxidizer aqueous solution, and a diesel supply tank 20 for supplying a diesel fuel containing relatively high concentration of sulfur are coupled to a first mixing tank 100 through a plurality of pipes. A phase transfer catalyst vessel 40 and a metal catalyst vessel 50 are further
10 coupled to the first mixing tank 100. Each of the oxidizing agent supply tank 30, the diesel supply tank 20, the phase transfer catalyst vessel 40, and the metal catalyst vessel 50 can be independent flow-regulated by means of conventional flow valves and flow control system, respectively.

[0025] By adding the surfactant, also known as a phase transfer catalyst, and the
15 metal catalyst, the reaction mixture was mixed in the first mixing tank 100 by a mixer 110. The first mixing tank 100 is also referred to as a desulfurization reactor herein. The reactive mixing which takes place in the oil/aqueous emulsion inside the first mixing tank 100 involves the oxidation of sulfides to sulfoxides or sulfone. The reaction mixture then is fed to the first cyclone 140. The first cyclone 140 can be
20 seen as a diesel/aqueous separation chamber in which the aqueous phase (containing oxidizer and catalysts) is separated from the organic phase (containing diesel fuel and sulfones), which results in the production of the low sulfur diesel fuel by further processing. The aqueous phase was then re-circulated to the first mixing tank 100 through a recirculation loop via to a catalyst activation vessel 55 for a period of time.

25 [0026] Between the two cyclones 140, 240, there is a second mixing tank 200, the polar solution extractor, in where the solvent mixture containing the sulfone

byproduct and the low sulfur diesel (oil phase) are partitioned out after mixing and extraction using the mixer 110, and the oil phase mixture is delivered to the second cyclone 240, The low sulfur diesel thus was obtained and stored in vessel 11. The polar solvent phase mixture containing the sulfone byproduct is further sent to an
5 evaporative tower 300 for recycling the polar solvent—by storing it in a solvent recovery tank 65. From this evaporative tower 300, the sulfone byproducts are obtained.

[0027] For various fuels containing different levels of sulfur concentration, the optimized MAOD process can reach or exceed 95% sulfur reduction, or final sulfur
10 concentration less than 15 ppm in high efficiency. The use of the Tetraoctylphosphonium salt also prevents the formation of unwanted brominated side products. Moreover, improving phase transfer capabilities also permits the improved recovery and highly efficient reuse of the transition metal catalyst, thus executing the same desulfurization efficiency with diluted hydrogen peroxide or ozone solutions.

15 [0028] Referring to Fig. 2, a flow diagram of the continuous desulfurization process for removing sulfides from a liquid fossil fuel in accordance with the embodiment shown in FIG. 1 is presented, as including the following steps:

[0029] A liquid fossil fuel from the diesel supply tank 20 is combined with an oxidizer solution comprising water ozone or hydroperoxide solution which are stored
20 in the oxidizing agent supply tank 30, a phase transfer catalyst stored in the phase transfer catalyst vessel 40, and a metal catalyst stored in the metal catalyst vessel 50 are combined together to form a multiphase reaction medium. The phase transfer catalyst such as Tetraoctylphosphonium salt, having four substituents, and the substituents are from the group consisting of an alkyl group having a chain length of
25 from 1 to 20 carbon atoms, an aryl group, or an aralkyl group, and at least one of the substituents is an alkyl group of 8 or more carbon atoms in length. The metal catalyst

stored in the metal catalyst vessel 50 above is a transition metal catalyst such as phosphotungstic acid. The amount of the phase transfer catalyst used is 0.1 g and the amount of metal catalyst used is 0.2 g per 25 g of a liquid fossil fuel in the form of a sulfur containing diesel fuel, and equal volume of 3~30 vol. % solution of H_2O_2 or
5 ozone solution being used, for example. (S100).

[0030] Reactive mixing of the multiphase reaction medium is performed for a time sufficient to cause oxidation of sulfides in the fossil fuel to sulfones and to permit emulsion bubble formations which include either bubble sizes all less than 1 mm or a substantial number of bubbles having bubble sizes of less than 1 mm, and a
10 substantial number of bubbles preferably at about substantially 10 microns, and also where many bubbles can also be less than substantially 0.1mm, in diameter through a substantial amount of agitation and mixing of the multiphase reaction medium inside the first mixing tank 100. (S105)

[0031] The oil phase is separated from the aqueous phase via the first cyclone 140
15 (S110), and later the polar solvent phase solution is separated from the nonpolar phase solution via the second cyclone 240 (S130).

[0032] The oil phase from the polar solvent phase are mixed and separated by using the second mixing tank 200, which is also called the polar solution extractor.

Solvent such as Acetonitrile can be used as the polar solvent phase in the second
20 mixing tank 200. Acetonitrile can be easily separated by distillation from the sulfones with boiling point ranging from 550 to 950 K. Each time, the solvent-to-oil (S/O) ratio can be kept at 1:1 by weight (for example, 1 g diesel per 1 g Acetonitrile). A plurality of emulsion bubbles are formed comprising of bubble sizes less than 1 mm or a substantial number of bubbles having bubble sizes of less than 1 mm, and a
25 substantial number of bubbles preferably at about substantially 10 microns in diameter, where many of the bubbles can also be less than substantially 0.1 mm. (S115). The

bubbles formation produced during steps S105 and S115 can be comprised of gas bubbles and/or immiscible liquid bubbles.

[0033] The phase transfer catalyst and the metal catalyst are collected using the first cyclone 140 and then recycled in the catalyst activation vessel 55 (S120). Meanwhile,
5 the solvent solution such as Acetonitrile used in the second mixing tank 200 are collected and recycled by a distillation process using the evaporative tower 300 (S125).

[0034] The sulfones byproducts are separated from the polar phase and the nonpolar phase at both the second mixing tank 200 and the second cyclone 240 by using the
10 evaporative tower 300 (S140). Then the sulfones are sent from the evaporative tower 300 to a sulfones holding vessel 70 to be collected (S150). Later, an organic phase that is nonpolar and substantially sulfone-free is collected in a clean diesel fuel holding tank 11 (S135).

[0035] The foregoing is offered primarily for illustrative purposes. The present
15 disclosure is not limited to the above described embodiments, and various variations and modifications may be possible without departing from the scope of the present invention.

CLAIMS

1. A method for removing sulfides from a liquid fossil fuel, comprising:
combining a liquid fossil fuel with an oxidizer solution, a metal catalyst, and a
phase transfer catalyst to form a multiphase reaction medium;
5 reactive mixing the multiphase reaction medium for a time sufficient to cause
oxidation of sulfides in the fossil fuel to sulfones and to produce a plurality of bubble
formations comprising a substantial number of bubbles of less than 1 mm in diameter
in a desulfurization reactor; and
separating the oil phase from the aqueous phase using a first cyclone.
- 10 2. The method for removing sulfides in accordance with claim 1, further
comprising of mixing and separating of the oil phase from a polar solvent phase via a
polar solution extractor and producing a plurality of bubble formations comprising a
substantial number of bubbles of less than 0.1 mm in diameter in the polar solution
extractor.
- 15 3. The method for removing sulfides in accordance with claim 1, further
comprising of recycling the aqueous solvent solution including the phase transfer
catalyst, the oxidizer solution, and the metal catalyst.
- 20 4. The method for removing sulfides in accordance with claim 3, further
comprising of separating the oil phase from the polar solvent phase using a second
cyclone, and separating and collecting the sulfones to yield an organic phase that is
substantially sulfone-free.
- 25 5. The method for removing sulfides in accordance with any one of the preceding
claims, wherein the phase transfer catalyst is a quaternary ammonium salt, the
quaternary ammonium salt having four substituents, the substituents are from the
group consisting of an alkyl group having a chain length of from 1 to 20 carbon atoms,
an aryl group, or an aralkyl group, and at least one of the substituents is an alkyl group

of 8 or more carbon atoms in length.

6. The method for removing sulfides in accordance with any one of the preceding claims, wherein the oxidizer solution comprising of hydrogen peroxide, hydroperoxide, or ozone.

5 7. The method for removing sulfides in accordance with any one of the preceding claims, wherein the mixing ratio of liquid fossil fuel and the oxidizer solution is about 1:1 to about 1:3.

8. The method for removing sulfides in accordance with any one of the preceding claims, wherein the metal catalyst is selected from the group consisting of iron (II),
10 iron (III), copper (I), copper (II), chromium (III), and chromium (VI) compounds, and molybdates, tungstates, and vanadates with the liquid fossil fuel and the oxidizer solution to form the multiphase reaction medium.

9. A continuous desulfurization device, comprising:

a plurality of mixing tanks;

15 a mixer connected to each mixing tank for agitation and mixing to produce a plurality of bubble formations;

a plurality of cyclones coupled to the mixing tanks in series, respectively; and

an evaporative tower, wherein the evaporative tower is coupled to one cyclone, and the continuous desulfurization device is characterized by the mixing tank being
20 agitated and mixed to produce a plurality of bubble formations comprising of bubble sizes less than substantially 1 mm in diameter, and the second cyclone yielding an organic phase that is substantially sulfone-free.

10. The continuous desulfurization device in accordance with claim 9, wherein the mixer is connected to the first mixing tank with a recirculation loop, the
25 recirculation loop providing recycling of the aqueous solvent solution, and the aqueous solvent solution including the phase transfer catalyst, the oxidizer solution,

and the metal catalyst.

11. The continuous desulfurization device in accordance with claim 9 or 10, wherein the mixing tank containing a liquid fossil fuel, an oxidizer solution, a metal catalyst, and a phase transfer catalyst to form a multiphase reaction medium, and the
5 multiphase reaction medium is reactive mixed for a time sufficient to cause oxidation of sulfides in the fossil fuel to sulfones in the mixing tank, and the first cyclone is used for separating the oil phase from the aqueous phase.

12. The continuous desulfurization device in accordance with any one of claims 9 ~ 11, wherein the polar solution extractor is provided for mixing and separating of
10 the oil phase from a polar solvent phase and producing a plurality of bubble formations comprising a substantial number of bubbles of less than 0.1 mm in diameter.

13. The continuous desulfurization device in accordance with any one of claims 9 ~ 12, wherein a second cyclone is provided for separating the oil phase from the
15 polar solvent phase, and an evaporative tower via a distillation process provides separating and collecting of the sulfones to yield an organic phase that is substantially sulfone-free.

14. The continuous desulfurization device in accordance with any one of claims 9 ~ 13, wherein the mixing ratio of liquid fossil fuel and the oxidizer solution is about
20 1:1 to about 1:3, and the continuous desulfurization device is a portable unit.

15. The continuous desulfurization device in accordance with any one of claims 9 ~ 14, wherein the metal catalyst is a phosphotungstic acid, the oxidizer solution is ozone and the phase transfer catalyst is Tetraoctylphosphonium salt.

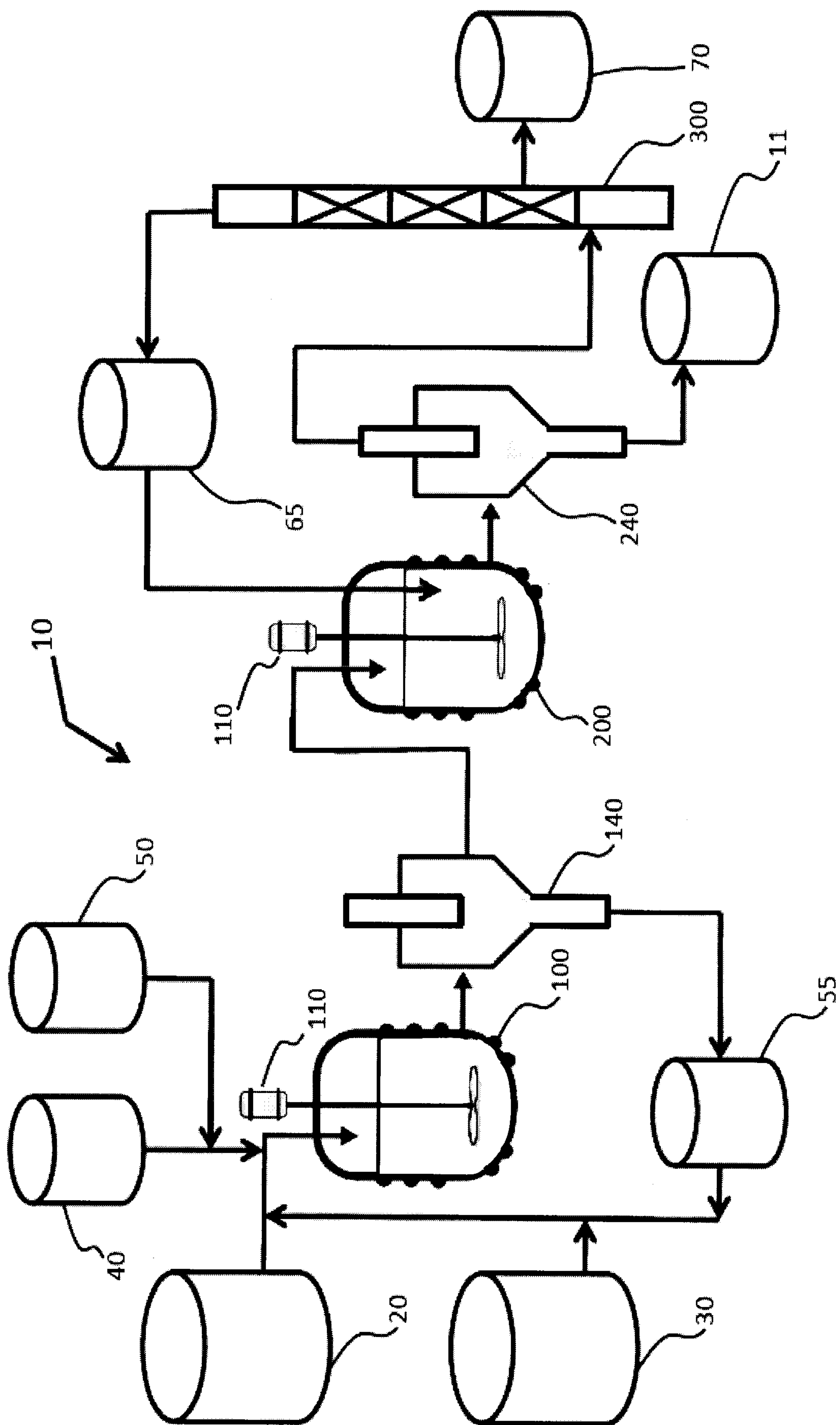


FIG. 1

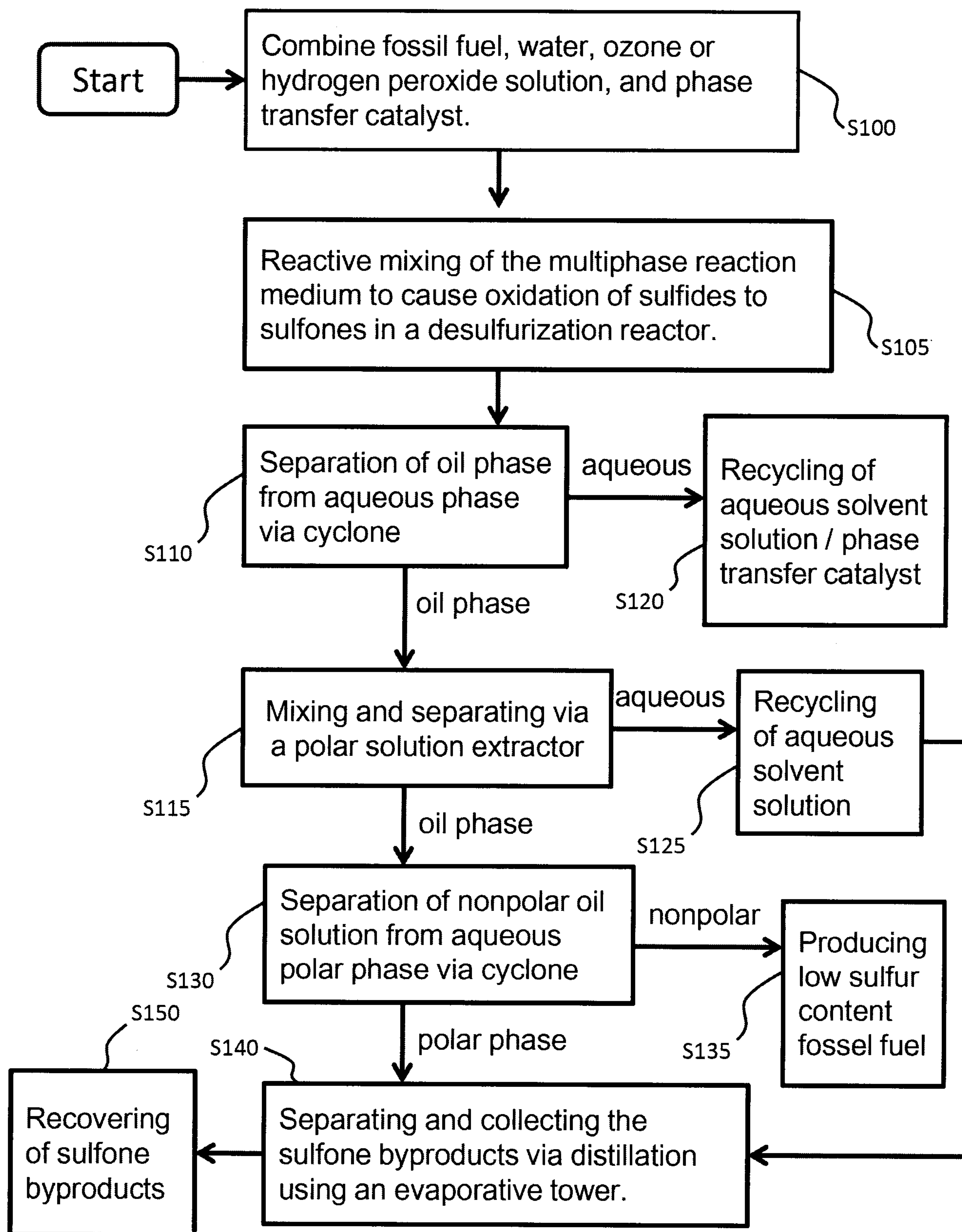


FIG. 2

