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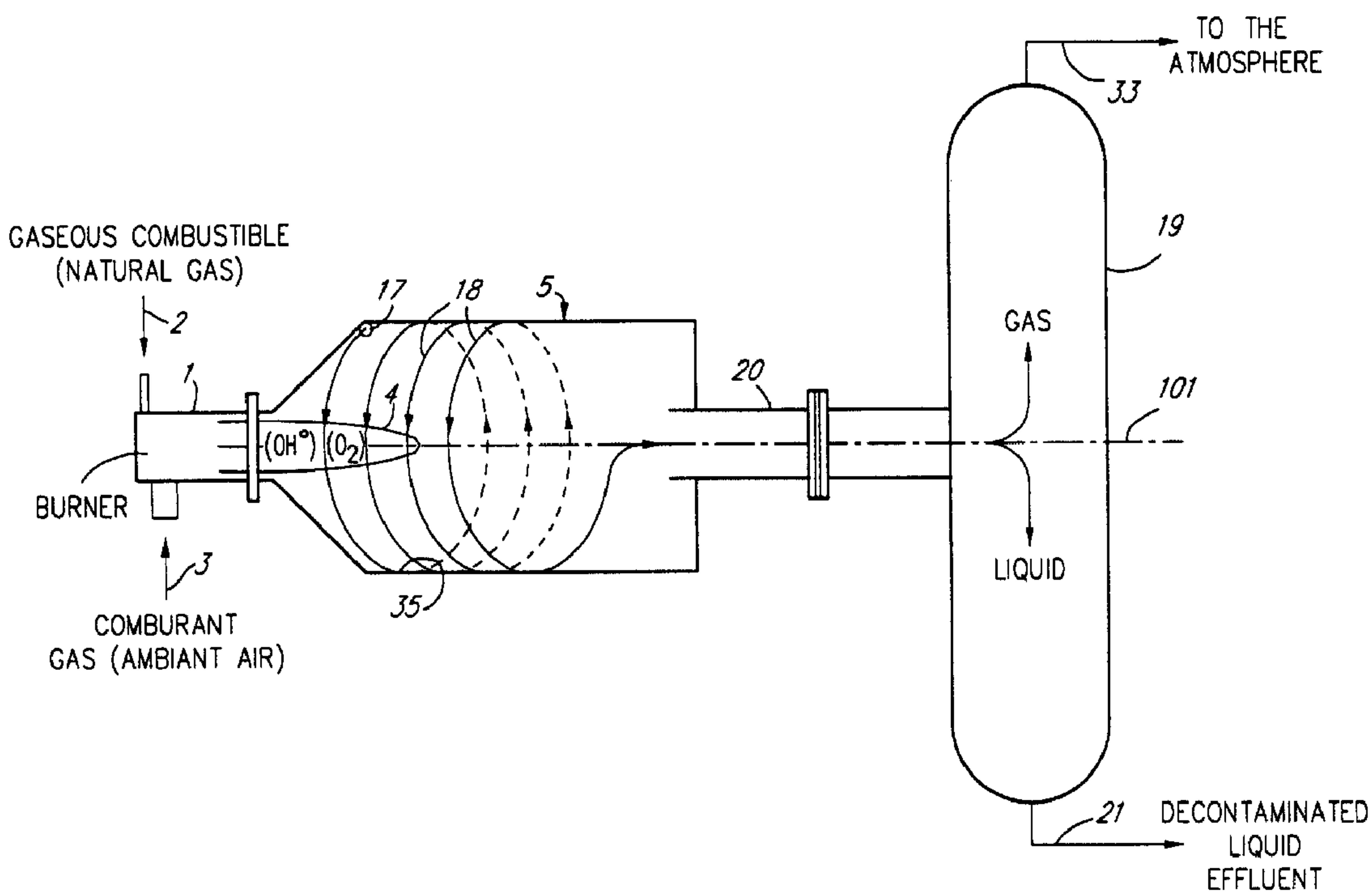
(54) Titre : PROCEDE D'OXYDATION RADICALAIRE ET INSTALLATION POUR LE TRAITEMENT D'EFFLUENTS LIQUIDES CONTAMINES PAR DES MATIERES ORGANIQUES

(54) Title: FREE RADICAL OXIDATION PROCESS AND INSTALLATION FOR TREATING LIQUID EFFLUENTS CONTAMINATED BY ORGANIC SUBSTANCES



(57) Abrégé/Abstract:
In the process and installation for decontaminating a liquid effluent contaminated by at least one organic substance, a gaseous combustible is burned in a reactor to produce a flame containing hydroxyl free radicals OH° and oxygen O_2 and that flame is centered on the geometrical axis of the reactor. A helical flow of liquid effluent is produced on the inner cylindrical wall of the reactor to cause a direct contact between the hydroxyl free radicals and the organic substance contaminating the liquid effluent.

(57) **Abrégé(suite)/Abstract(continued):**
By means of the hydroxyl free radicals, the organic substance is oxidized in liquid phase. The high temperature of the flame enables completion of the oxidation of the organic substance, in liquid phase, by means of the oxygen O_2 present in the flame. At the outlet of the reactor, the liquid and gaseous products are separated; the liquid product is collected while the gaseous product is evacuated.

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ABSTRACT OF THE DISCLOSURE

In the process and installation for decontaminating a liquid effluent contaminated by at least one organic substance, a gaseous combustible is burned in a reactor to produce a flame containing hydroxyl free radicals OH° and oxygen O_2 and that flame is centered on the geometrical axis of the reactor. A helical flow of liquid effluent is produced on the inner cylindrical wall of the reactor to cause a direct contact between the hydroxyl free radicals and the organic substance contaminating the liquid effluent. By means of the hydroxyl free radicals, the organic substance is oxidized in liquid phase. The high temperature of the flame enables completion of the oxidation of the organic substance, in liquid phase, by means of the oxygen O_2 present in the flame. At the outlet of the reactor, the liquid and gaseous products are separated; the liquid product is collected while the gaseous product is evacuated.

FREE RADICAL OXIDATION PROCESS AND INSTALLATION FOR TREATING LIQUID EFFLUENTS CONTAMINATED BY ORGANIC SUBSTANCES

BACKGROUND OF THE INVENTION

1. Field of the invention:

The present invention relates to a process and installation using a free radical oxidation reaction to treat liquid effluents contaminated by at least one organic substance.

2. Brief description of the prior art:

The industrial liquid effluents are often contaminated by organic substances such as phenol, benzene, toluene, chloro- or nitro-benzene, methanol, xylene, styrene, and other volatile or halogenated organic compounds. The main sources of such effluents are: treatment/disposal processes for industrial waste waters and liquid wastes, oil refineries and petrochemical plants, pulp and paper mills, foundries and metal refineries, metal/plastic product manufacturing, organic chemicals plants, tanneries, food industry and mineral industry. The numerous, available processes for treating such liquid effluents can be divided into three categories: biological processes, physical processes and chemical processes. A combination of biological, physical and/or chemical processes may also be used.

The efficiency of the biological processes in destroying organic substances can be as high as 97%. However, certain factors such as a concentration of organic matter higher than 500 mg/l or lower than 5 mg/l, and/or a temperature lower than 10 °C may adversely affect the efficiency of such biological processes.

The basic concept of the prior art physical processes is to transfer one organic substance toward another one. These physical processes present two drawbacks: they are selective in the treatment of the liquid effluent, and they require storage and/or disposal of the eliminated contaminants.

The chemical processes use conventional oxidation agents such as chlorine, chlorine dioxide, potassium permanganate, hydrogen peroxide, ozone, ultraviolet radiations, sulphite ions, etc. They are often limited in regard of the volume of liquid effluent to be treated. A prior art process is characterized by a wet oxidation with air, without flame, and is restricted by severe operation conditions: pressures of the order of 3 000 kPa to 300 000 kPa.

OBJECTS OF THE INVENTION

An object of the present invention is therefore to provide a decontamination process and installation capable of substantially eliminating the above discussed drawbacks of the prior art processes.

Another object of the present invention is to provide a process and an installation for conducting free radical oxidation of liquid effluents contaminated by organic substances, having an increased efficiency for destroying organic substances and that at a minimal cost.

SUMMARY OF THE INVENTION

More particularly, in accordance with the present invention, there is provided a process for decontaminating a liquid effluent contaminated by at least one organic substance, comprising the steps of:

in a reactor having an outlet and an inner wall defining a geometrical axis, burning a gaseous combustible to produce a flame with free radicals and oxygen;

centering the flame on the geometrical axis;

producing a flow of liquid effluent on the inner wall of the reactor to cause a direct contact between the flame containing free radicals and oxygen, and the organic substance contaminating the liquid effluent of the flow;

by means of the flame containing free radicals and oxygen, oxidizing in liquid phase the organic substance contaminating the liquid effluent of the flow;

at the outlet of the reactor, separating a liquid product leaving the reactor from a gaseous product also leaving the reactor; and

after the separating step, collecting the liquid product and evacuating the gaseous product.

In the above process, the direct exposition of the liquid effluent to the flame containing free radicals and oxygen produce an oxidation, in liquid phase, of the organic substance contaminating the liquid effluent.

In accordance with preferred embodiments of the process of the invention:

- the oxygen comprises oxygen O_2, and the oxidizing step comprises completing the oxidation, in liquid phase, of the organic substance contaminating the liquid effluent of the flow by means of the oxygen O_2 present in the flame;

- the inner wall of the reactor is generally cylindrical, and the flow producing step comprises injecting the liquid effluent to be decontaminated generally tangentially in the reactor to establish a substantially helical flow of liquid effluent on the inner, generally cylindrical wall of the reactor;

- the inner, generally cylindrical wall of the reactor is substantially horizontal or vertical;

- the gaseous combustible comprises natural gas, and the free radicals comprise hydroxyl free radicals OH° and/or other free radicals such as CH_3°, CH_2°, CHO°;

- the burning step comprises supplying a burner with natural gas constituting the gaseous combustible and a comburant gas selected from the group consisting of ambient air, oxygen-enriched air and pure oxygen; and

- the process further comprises the step of injecting a liquid oxidizing agent generally tangentially in the reactor, and/or the step of injecting a gaseous oxidizing agent generally axially in the reactor.

The present invention further relates to an installation for decontaminating a liquid effluent contaminated by at least one organic substance, comprising:

a reactor having an outlet and an inner, generally cylindrical wall defining a geometrical axis;

a burner supplied with a gaseous combustible and a comburant gas to produce in the reactor a flame centered on the geometrical axis and including free radicals and oxygen O_2;

liquid effluent supply means for injecting the liquid effluent tangentially in the reactor and producing a helical flow of liquid effluent on the inner, generally cylindrical wall of the reactor; and

a liquid/air separator for separating liquid and gaseous products leaving the outlet of the reactor.

Advantageously, (a) the gaseous combustible comprises natural gas and the comburant gas is selected from the group consisting of ambient air, oxygen-enriched air, and pure oxygen, (b) the burner comprises means for adjusting the length of the flame, and (c) the reactor, inner wall and geometrical axis are generally horizontal or vertical.

In accordance with a preferred embodiment of the installation, the reactor comprises mechanical means, for example physical barrier means selected from the group consisting of grooves and baffles, for increasing the time of residence in the reactor of the liquid effluent. The reactor may further comprise non mechanical aerodynamic means for increasing the time of residence of the liquid effluent.

The objects, advantages and other features of the present invention will become more apparent upon reading of the following non restrictive description of a preferred embodiment thereof, given by way of example only with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In the appended drawings:

Figure 1 is a schematic diagram of a basic installation comprising a generally horizontal reactor, for conducting the process in accordance with the present invention, i.e. conducting free radical oxidation of liquid effluents contaminated by organic substances;

Figure 2 is a schematic diagram of a basic installation comprising a generally vertical reactor, for conducting the process in accordance with the present invention, i.e. conducting free radical oxidation of liquid effluents contaminated by organic substances;

Figure 3 is a schematic diagram of an installation in accordance with the present invention, for treating liquid effluents contaminated by organic substances; and

Figure 4 is a flow chart showing the mechanism ruling the oxidation of phenol C_6H_5OH.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Figures 1 and 2 are schematic diagrams of a basic installation for conducting the process in accordance with the present invention. Figure 3 is a schematic diagram of a more complete version of the installations of Figures 1 and 2.

The first step of the process according to the present invention consists of generating free radicals such as OH°, CH_3°, CH_2°, CHO°, etc. These free radicals are generated from the combustion of a gaseous combustible. As illustrated in Figures 1 and 2, the installation comprises, for that purpose, a burner 1 supplied with a gaseous combustible 2 and a comburant gas 3 to produce a flame 4 (Figures 1 and 2).

The installation of Figures 1 and 2 also comprises a reactor 5 having an inner, generally cylindrical wall defining a longitudinal, geometrical axis 101 (Figures 1 and 2). The reactor 5 is also provided with an inlet 6 (Figure 3) and presents the general geometry a hydrocyclone. As illustrated in Figures 1 and 2, the flame 4 is produced in the reactor 5 and is generally coaxial, i.e. centered on the axis 101. As illustrated in Figure 1, the reactor 5 and its geometrical axis 101 may be generally horizontal. Figure 2 illustrates that the reactor 5 as well as the geometrical axis 101 thereof may be generally vertical.

The liquid effluent 7 (Figure 3) contaminated by organic substances is stocked in a reservoir 8 and supplied from the reservoir 8 to the inlet 6 of the reactor 5 through a pump 9, a valve 10 and a line 11.

Another pump 12 is provided to mix the different constituents of the liquid effluent 7 and thereby form an uniform mixture. To that effect, pump 12 pumps liquid effluent 7 from the bottom portion of the reservoir 8 through the valve 10 and another valve 13, and returns the pumped liquid effluent 7 to the top portion of the reservoir 8 (valve 15 being then closed).

A valve 14 can be opened to drain the line 11 and the reservoir 8 through the valve 10. A further valve 15 and line 15' provides for access to the contaminated liquid effluent 7, for example to add an oxidizing agent to that effluent 7. Finally, the reservoir 8 comprises an overflow 16.

The contaminated liquid effluent 7 supplied to the inlet 6 is injected tangentially in the reactor 5 through a tangentially oriented nozzle 17 (Figures 1 and 2) so as to produce on the generally cylindrical inner wall 35 of the reactor 5 a helical flow 18 of contaminated liquid effluent 7.

With the geometry of the arrangement of Figures 1 and 2, the helical flow 18 produces a direct and intimate contact of the liquid effluent 7 with the free radicals of the flame 4 to cause oxidation, in liquid phase, of the organic substances contaminating the liquid effluent 7. The helical flow 18 also increases the surface of contact between the free radicals OH° present in the flame 4 and the liquid effluent 7. The high temperature of the flame 4 contributes to the performance of this free radical oxidation reaction. Simultaneously, the high temperature of the flame 4 enables completion of the process of oxidation, in liquid phase, of the organic substances by means of the excess oxygen present in the flame 4.

It is within the scope of the present invention to provide the reactor 5 with mechanical and/or non mechanical tools (not shown) to increase the residence time of the helically flowing liquid effluent 17 in this reactor 5. The mechanical tools may comprise physical barrier means such as grooves and/or baffles, and/or any other geometric shapes. The non mechanical tool may be of the aerodynamic type.

A liquid oxidizing agent such as potassium permanganate can be added to the effluent 7, for example through the valve 15 and the line 15'; this oxidizing agent is then injected generally tangentially in the reactor 5 along with the effluent 7.

Also, a gaseous oxidizing agent such as ozone can be injected axially in the reactor 5 to further improve the performance of the above mentioned free radical oxidation reaction.

A vertical, generally cylindrical liquid/gas separator 19 is connected to the outlet 20 of the reactor 5 to separate the liquid and gaseous phases of the products leaving the reactor 5. The structure of such liquid/gas separators are well known to those of ordinary skill in the art and, accordingly, will not be further described in the present specification. However, it should be mentioned that the upper portion of the separator 19 has an inner lining (not shown) with a large contact area to favour the separation of the treated liquid effluent from the hot gaseous products leaving the reactor 5.

Also, a device (not shown) can be installed to recuperate the energy contained in the hot gaseous products leaving the reactor 5. Moreover, the upper portion of the liquid/gas separator 19 may be connected to a device for scrubbing the hot gaseous products, the latter device forming a post-treatment chamber.

The liquid extracted by the liquid/gas separator 19 is the decontaminated liquid effluent 21. The decontaminated liquid effluent 21 from the separator 19 is supplied through a line 23 (Figure 3) to a decontaminated effluent reservoir 22 in which the decontaminated liquid effluent 21 accumulates. Draining of the line 23 is provided for through a valve 24 while draining of the effluent-collecting reservoir 22 is provided for through a valve 25. The effluent-collecting reservoir 22 finally includes a liquid level indicator 26.

Decontaminated effluent 21 from the reservoir 22 can be transferred to a treated effluent collector (not shown) through a pump 27, a valve 28, a valve 29, and a line 30 (valve 31 being then closed). It should be pointed out here that the pump 27 can be automatically activated when the decontaminated liquid effluent accumulating in the reservoir 22 reaches a predetermined level detected by the liquid-level indicator 26. Decontaminated effluent 21 from the reservoir 22 can also be returned to the contaminated effluent reservoir 8 for further decontamination thereof through the pump 27, the valve 28, a valve 31 and lines 30 and 32 (valve 29 being then closed).

The gaseous products 33 (Figures 1 and 2) leaving the liquid/gas separator 19 comprises gaseous substances produced by the above mentioned oxidation reaction and eventually combustion residue from the flame 4. As illustrated in Figure 3, the gaseous products 33 can be evacuated for example through a line 34 to a chimney (not shown).

Example #1

The following example relates to the free radical oxidation of waste water contaminated with phenol C_6H_5OH. However, it should be kept in mind that the process in accordance with the present invention can also be applied to the decontamination of liquid effluents contaminated by organic substances other than phenol.

Referring to Figures 1, 2 and 3, natural gas 2 and ambient air 3 are supplied to the burner 1 to produce the flame 4 containing hydroxyl free radicals OH° and oxygen O_2. The comburant gas can be oxygen-enriched air and/or pure oxygen as well. Preferably, the burner 1 will produce a rich mixture of gaseous combustible 2 and comburant gas 3, and will provide for adjustment of the length of the flame 4.

The major constituent of natural gas is methane CH_4. Methane reacts very rapidly with the oxygen O_2 of the ambient air. The general reaction of combustion of methane with oxygen is the following:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

In reality, decomposition of methane in the presence of oxygen involves a very complex mechanism. This mechanism comprises more than 200 steps including the formation of intermediary compounds such as the free radicals O°, H° and OH°. A flame of methane such as 4 in Figures 1 and 2 can be divided into three distinct zones:

- a first, pre-heating zone extending from the cold wall 35 of the reactor 5 to the flame 4;

- a second, reaction zone represented by the visible flame 4; and

- within the flame 4, a third recombination zone in which the excess free radicals O°, H° and OH°, created in the second zone (visible flame 4) are destroyed by recombination reactions.

In the second reaction zone, the temperature may reach 1000°K to 1500°K. At that temperature, the radicals O°, H° and OH° are responsible, in the third zone, for the chain of reactions, and the recombination reactions, including the phenol oxidation reactions, are dominated by the free radical reactions. Again, as indicated in the foregoing description, the high temperature of the flame 4 enables completion of the process of oxidation, in liquid phase, of the organic substances by means of the excess oxygen present in the flame 4.

In general, the products resulting from the oxidation of phenol are organic salts, simplified forms of biodegradable compounds or, in the presence of complete oxidation, carbon dioxide and water. The tendency of phenol C_6H_5OH to react is directly related to the polarization of the two bonds C-O and O-H and the presence of two pairs of free electrons on the oxygen atom. The two following types of behaviour can therefore be anticipated:

a) rupture of the bond O-H:

$$C_6H_5O\text{-}H \rightarrow C_6H_5O^- \ H^+$$

b) rupture of the bond C-O:

$$C_6H_5O\text{-}H \rightarrow C_6H_5^+ \ OH^-$$

Oxidation of phenol in aqueous phase follows a free radical mechanism. Consequently, the speed of reaction is slow during the initial induction period. However, this initial induction period is followed by a fast period during which the speed of reaction is high and the major part of the process of degradation of the phenol occurs. Figure 4 shows the main steps involved in the mechanism ruling the oxidation of phenol C_6H_5OH. At high temperature, the side chain of phenol is decayed; this decay is characterized by the rupture of the bond O-H, and leads to the formation of a phenyl radical (step 301) in passing by a sequence of formation of unstable aromatic intermediates (step 302). The oxidation reaction propagates and leads to the rupture of the ring. Accordingly, as phenol disappears, carbon monoxide is produced (step 304). Carbon dioxide is formed (step 304) after a substantial increase of the concentration of carbon monoxide accompanied by a rapid increase of temperature. The formation of these carbon oxides is preceded, in particular, by the formation of aliphatic intermediates (step 305) including aldehydes and carboxylic acids.

In conclusion, in the presence of oxygen O_2, phenol $_6$ Ç H OH is involved in the following oxidation reaction:

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_20$$

Example #2

In this example, the said at least one organic substance contains at least two species, one that can be easily oxidized and the other more refractory. Then, the oxidizing step may comprise aqueous-phase oxidation reactions proceeding according to a free-radical mechanism and being characterized by an induction period followed by a rapid reaction phase.

Although the present invention has been described hereinabove with reference to a preferred embodiment thereof, this embodiment can be modified at will, within the scope of the appended claims, without departing from the spirit and nature of the subject invention.

WHAT IS CLAIMED IS:

1. A process for decontaminating a liquid effluent contaminated by at least one organic substance, comprising the steps of:

in a reactor having an outlet and an inner wall defining a geometrical axis, burning a gaseous combustible to produce a flame with free radicals and oxygen;

centering the flame on said geometrical axis;

producing a flow of said liquid effluent on the inner wall of the reactor to cause a direct contact between the flame containing free radicals and oxygen, and the organic substance contaminating the liquid effluent of said flow;

by means of the flame containing free radicals and oxygen, oxidizing in liquid phase the organic substance contaminating the liquid effluent of said flow;

at the outlet of the reactor, separating a liquid product leaving the reactor from a gaseous product also leaving the reactor; and

after said separating step, collecting the liquid product and evacuating the gaseous product.

2. A process for decontaminating a liquid effluent as recited in claim 1, wherein:

said oxygen comprises oxygen O_2; and

said oxidizing step comprises completing the oxidation, in liquid phase, of the organic substance contaminating the liquid effluent of said flow by means of the oxygen O_2 present in the flame.

3. A process for decontaminating a liquid effluent as recited in claim 1, wherein (a) said inner wall of the reactor is generally cylindrical, and (b) said flow producing step comprises injecting the liquid effluent to be decontaminated generally tangentially in said reactor to establish a substantially helical flow of said liquid effluent on the inner, generally cylindrical wall of the reactor.

4. A process for decontaminating a liquid effluent as recited in claim 3, wherein said inner, generally cylindrical wall of the reactor is substantially horizontal.

5. A process for decontaminating a liquid effluent as recited in claim 3, wherein said inner, generally cylindrical wall of the reactor is substantially vertical.

6. A process for decontaminating a liquid effluent as recited in claim 1, wherein said gaseous combustible comprises natural gas, and wherein said free radicals comprise hydroxyl free radicals OH°.

7. A process for decontaminating a liquid effluent as recited in claim 6, in which said burning step comprises supplying a burner with (a) said natural gas constituting the gaseous combustible and (b) a comburant gas selected from the group consisting of ambient air, oxygen-enriched air and pure oxygen.

8. A process for decontaminating a liquid effluent as recited in claim 1, in which said at least one organic substance comprises phenol C_6H_5OH, and in which said oxidizing step comprises subjecting the phenol C_6H_5OH to the following oxidation reaction:

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_20.$$

9. A process for decontaminating a liquid effluent as recited in claim 1, in which said at least one organic substance contains a first easily oxidized species and a second refractory species, and in which said oxidizing step comprises aqueous-phase oxidation reactions proceeding according to a free-radical mechanism and being characterized by an induction period followed by a rapid reaction phase.

10. A process for decontaminating a liquid effluent as recited in claim 3, further comprising the step of injecting an oxidizing agent generally tangentially in the reactor, said oxidizing agent being in liquid phase.

11. A process for decontaminating a liquid effluent as recited in claim 1, further comprising the step of injecting an oxidizing agent generally axially in the reactor, said oxidizing agent being in gaseous phase.

12. An installation for decontaminating a liquid effluent contaminated by at least one organic substance, comprising:

a reactor having an outlet and an inner, generally cylindrical wall defining a geometrical axis;

a burner supplied with a gaseous combustible and a comburant gas to produce in said reactor a flame centered on said geometrical axis and including free radicals and oxygen O_2;

liquid effluent supply means for injecting the liquid effluent tangentially in said reactor and producing a helical flow of liquid effluent on the inner, generally cylindrical wall of the reactor; and

a liquid/air separator for separating liquid and gaseous products leaving the outlet of the reactor.

13. An installation for decontaminating a liquid effluent as recited in claim 12, wherein said gaseous combustible comprises natural gas, and wherein said comburant gas is selected from the group consisting of ambient air, oxygen-enriched air, and pure oxygen.

14. An installation for decontaminating a liquid effluent as recited in claim 12, wherein said burner comprises means for adjusting the length of the flame.

15. An installation for decontaminating a liquid effluent as recited in claim 12, wherein said reactor, inner wall and geometrical axis are generally horizontal.

16. An installation for decontaminating a liquid effluent as recited in claim 12, wherein said reactor, inner wall and geometrical axis are generally vertical.

17. An installation for decontaminating a liquid effluent as recited in claim 12, in which the reactor comprises mechanical means for increasing the time of residence in said reactor of the liquid effluent contaminated by at least one organic substance and flowing on the inner, generally cylindrical wall according to said helical flow.

18. An installation for decontaminating a liquid effluent as recited in claim 17, in which said mechanical means comprises physical barrier means selected from the group consisting of grooves and baffles.

19. An installation for decontaminating a liquid effluent as recited in claim 12, in which said reactor comprises non mechanical aerodynamic means for increasing the time of residence in said reactor of the liquid effluent contaminated with at least one organic substance and flowing on the inner, generally cylindrical wall according to said helical flow.

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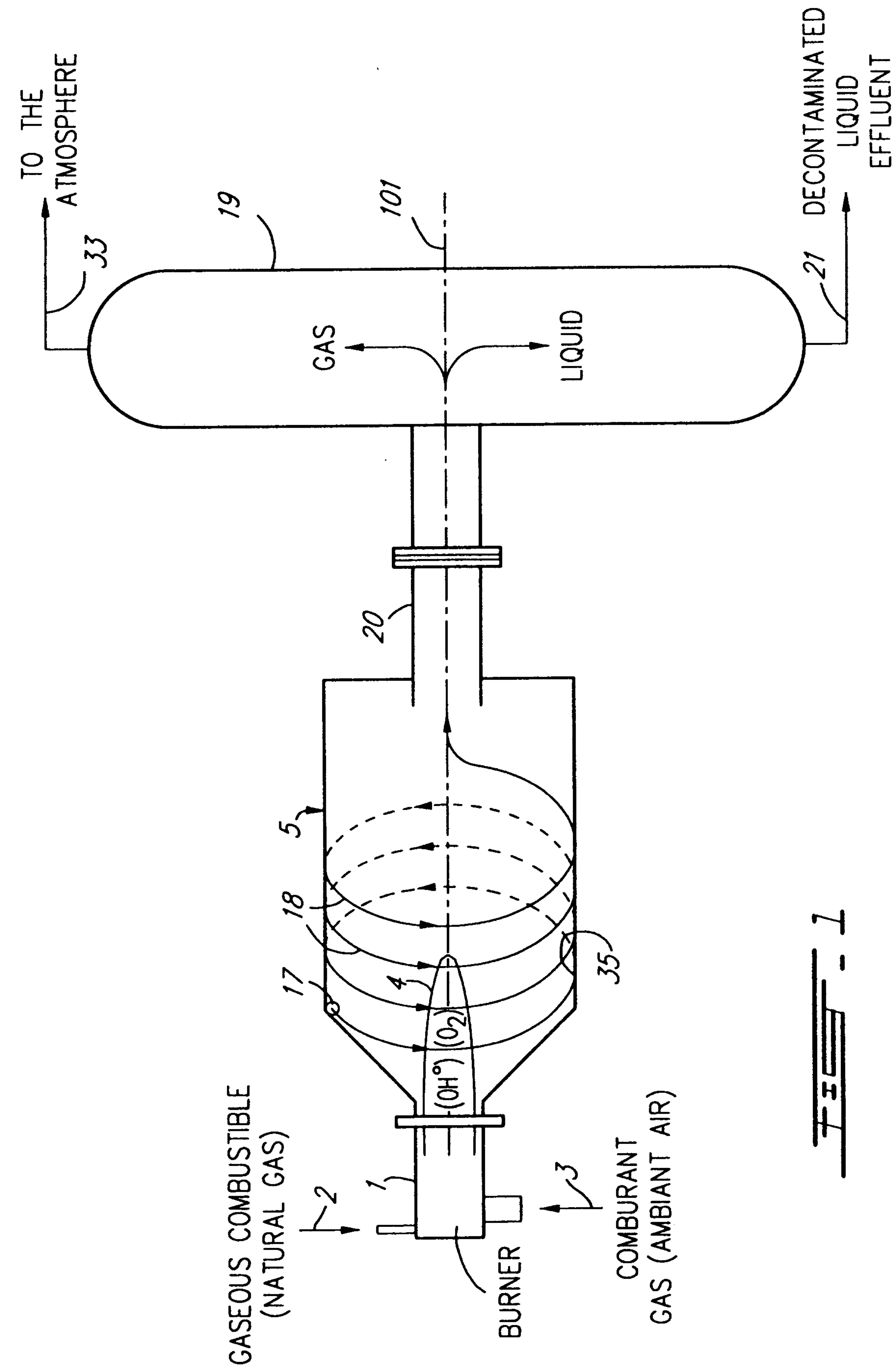

FIG. 1

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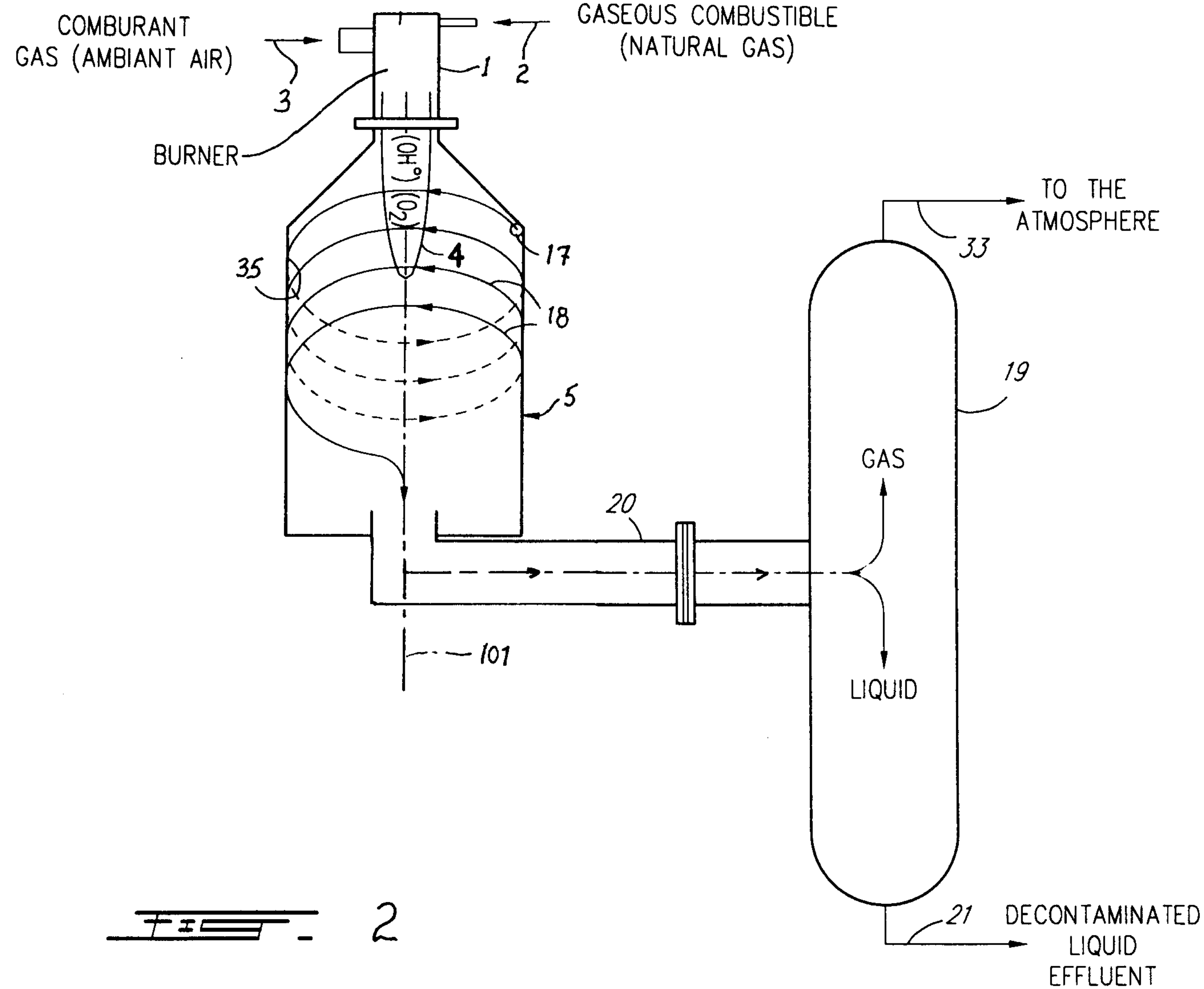

FIG. 2

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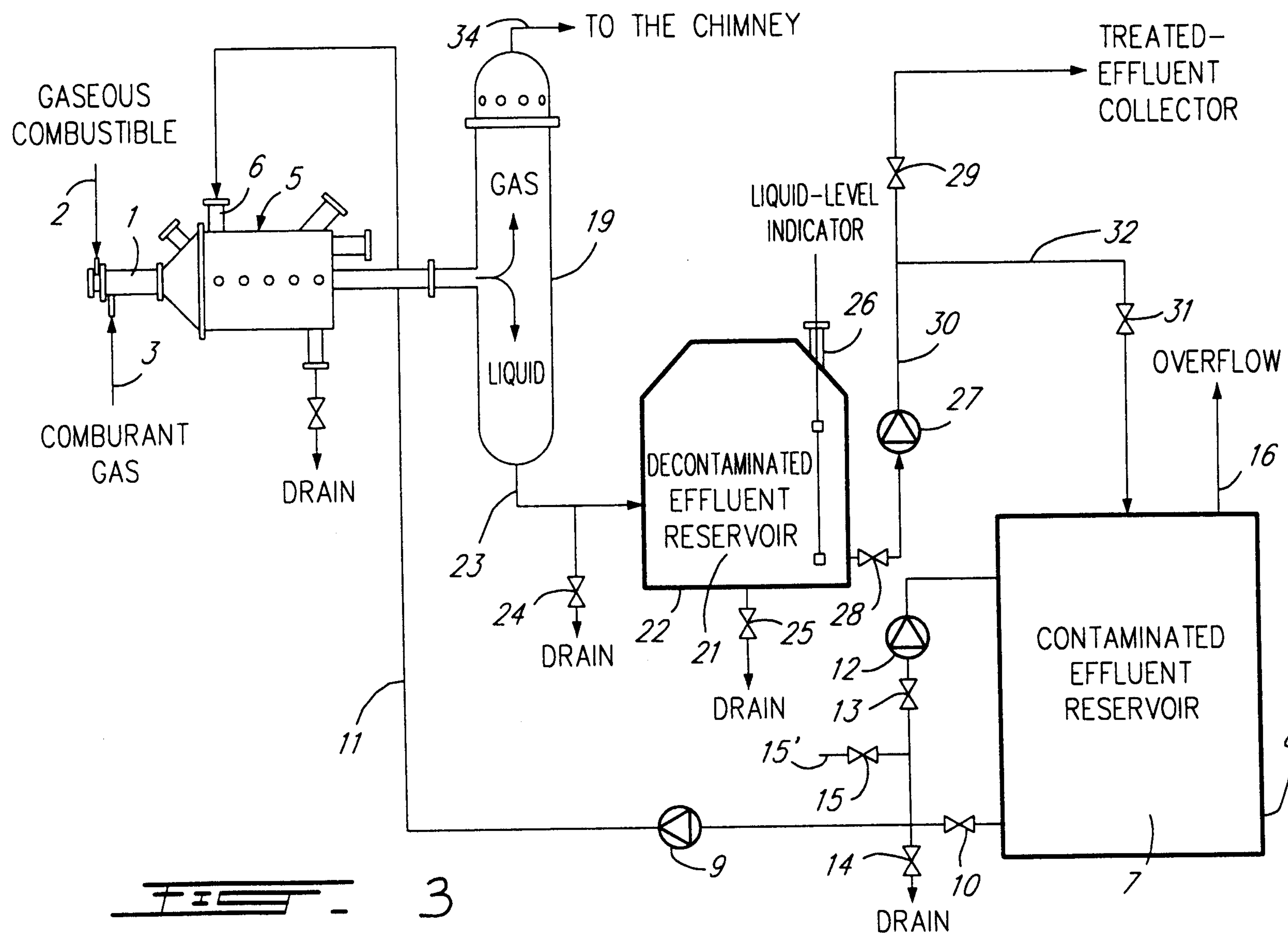

FIG. 3

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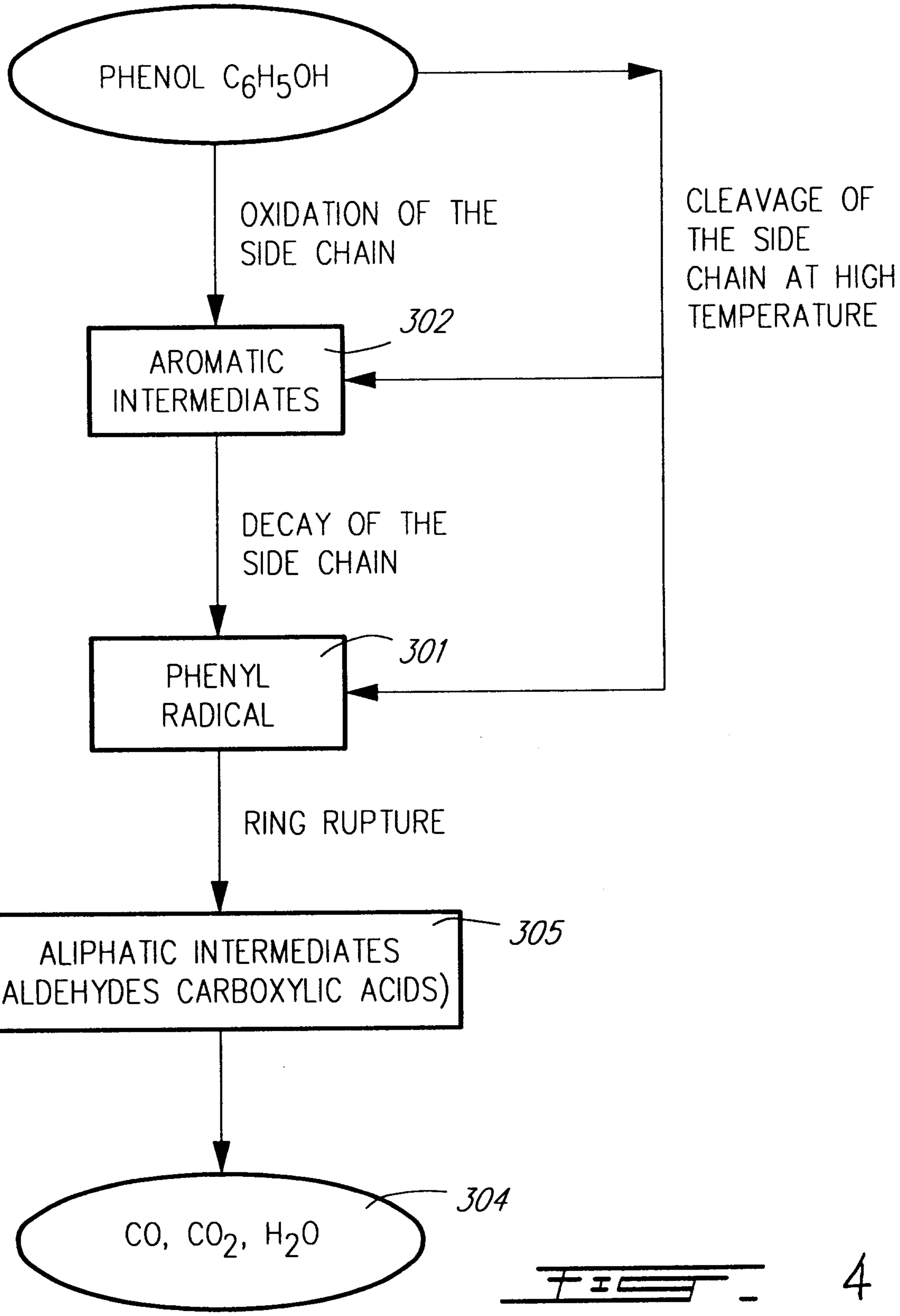
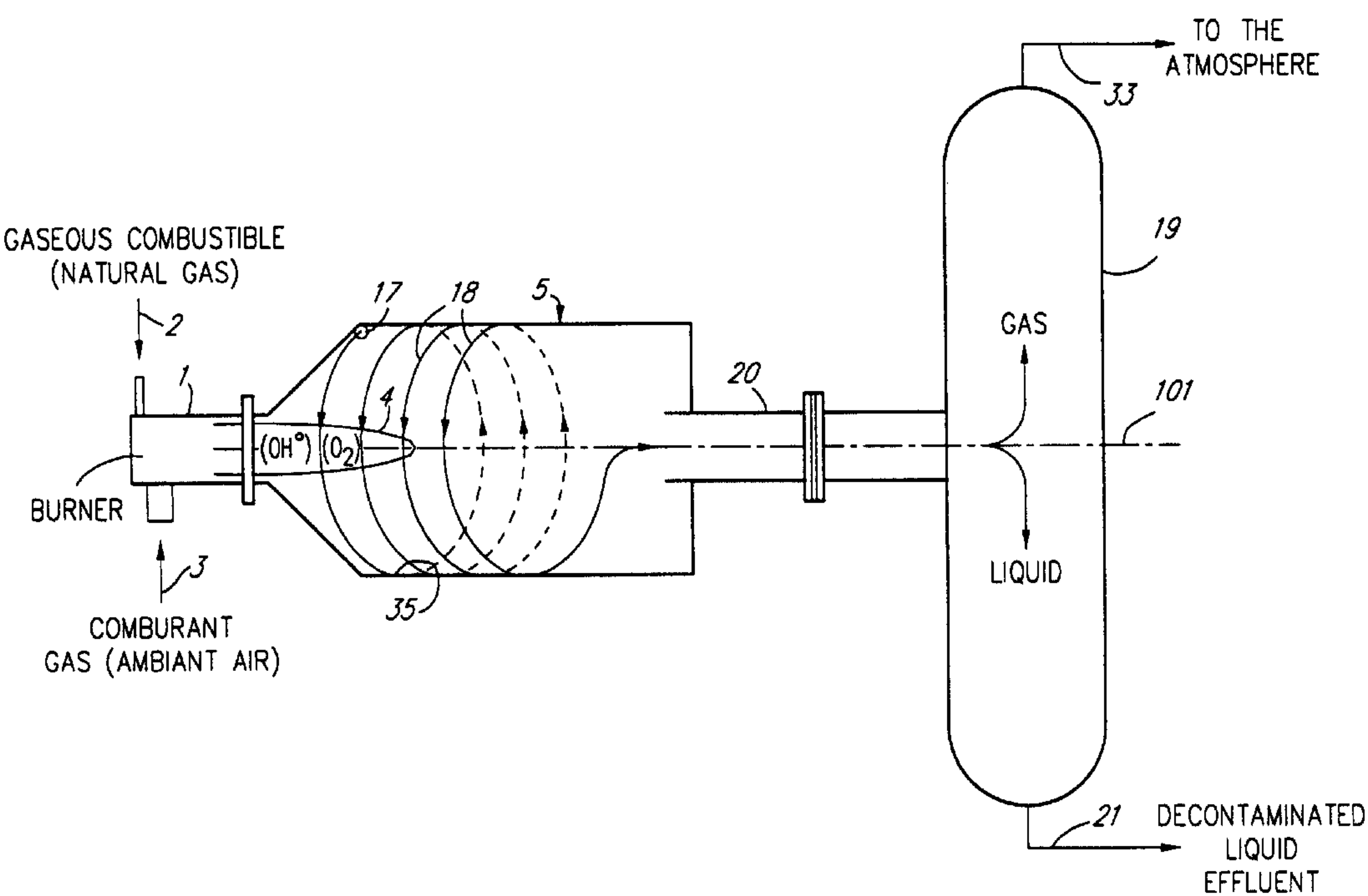


FIG. 4



TO THE ATMOSPHERE
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20
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BURNER
LIQUID
3
35
COMBURANT GAS (AMBIANT AIR)
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DECONTAMINATED LIQUID EFFLUENT