

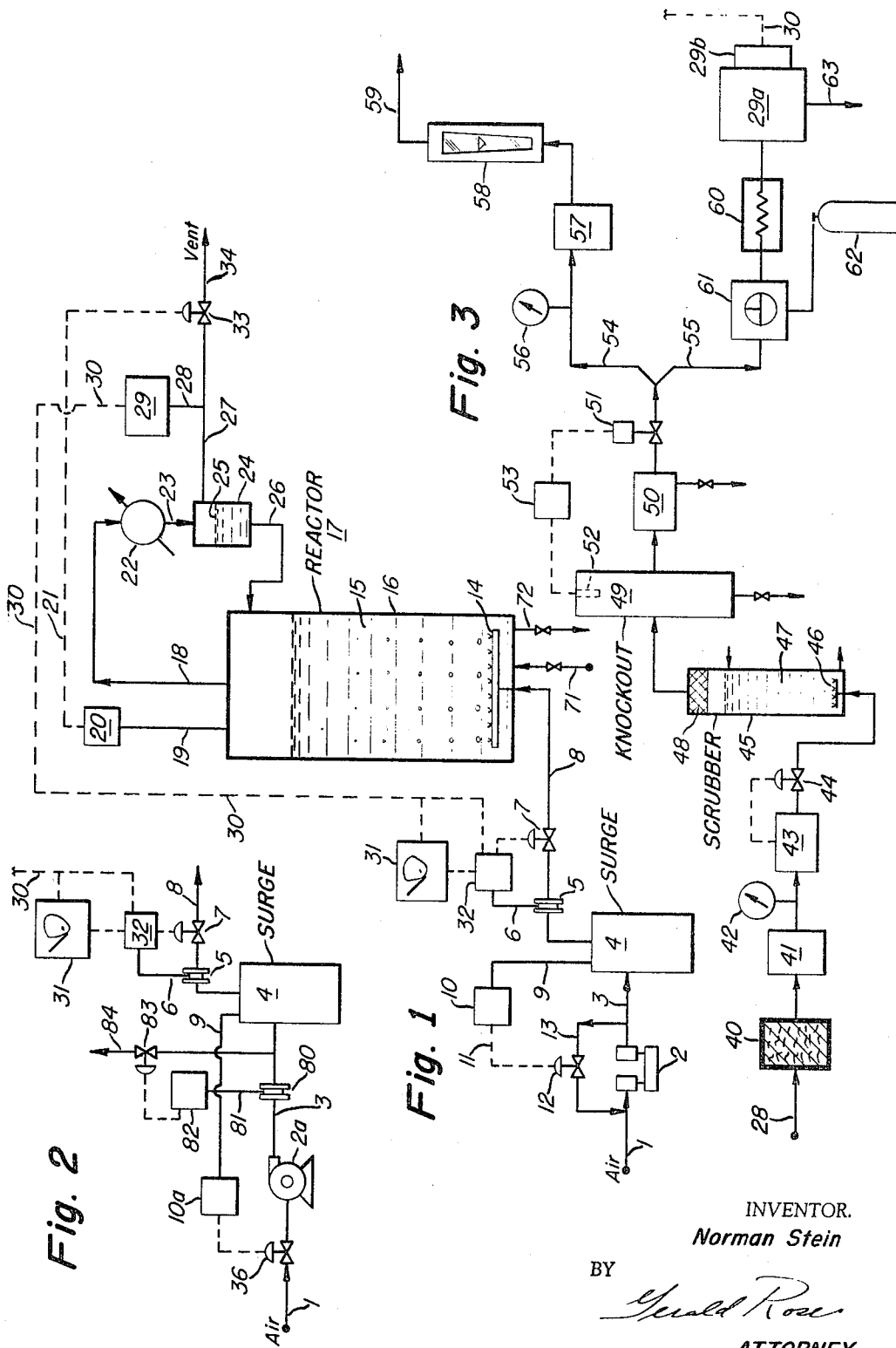
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APPARATUS FOR OXIDATION OF ORGANIC COMPOUNDS

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APPARATUS FOR OXIDATION OF ORGANIC COMPOUNDS

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3 Claims. (Cl. 23—285)

This application is a division of my copending application Serial No. 779,969, filed December 12, 1958, now abandoned, and entitled, "Chemical Process."

This invention relates to the liquid phase oxidation of organic compounds with an oxygen containing gas, and more particularly is concerned with providing an automatic control system for safely conducting a liquid phase oxidation process.

The catalytic liquid phase oxidation of organic compounds with molecular oxygen has, within past several years, become exceedingly important from a commercial standpoint. In processes of this type, an oxidizing gas such as air is passed through a reaction mixture containing the organic compound, thereby converting the feedstock to desirable products such as carboxylic acids, ketones, etc. These processes are generally conducted in a batchwise manner; that is, the reaction zone is charged with the feedstock and catalyst, and an oxidizing gas is passed through the zone continuously until oxidation is complete, when gas flow is interrupted, the reactor dumped, and the cycle repeated. When employing an active catalyst, oxygen utilization is high throughout much of the run, and hence the low concentration of free oxygen in the spent gas leaving the reaction zone is an effective bar to the formation of an explosive gas composition. However, at the initial portion of an oxidation process and for a considerable period toward the end, oxygen utilization may be relatively poor. Consequently, the presence of oxidizable (flammable) organic vapors and free-oxygen in the off-gas can and often does form a mixture which is capable of exploding or detonating. In the laboratory where oxidizing gas rates are held low for ease of control, little risk of explosion is experienced. But from a practical standpoint, in oxidations conducted on a commercial scale it is essential to maximize both the rate of oxidation and the extent of feedstock conversion to achieve high product output. At high gas rates, this has heretofore required the installation of elaborate and expensive means for preventing the formation or detonation of explosive mixtures, or else has not infrequently resulted in oxidation processes being conducted in an exceedingly hazardous manner, with potentially disastrous results.

It is therefore, a primary object of the instant invention to provide a control system for conducting a process for the liquid phase oxidation of organic compounds with an oxygen containing gas. An additional object is to provide a control system permitting the employment of maximum oxidizing gas flow-rate during all periods of an oxidation reaction despite changes in the extent of oxygen utilization during the reaction. A further object is to avoid the formation of combustible gas or vapor mixtures in a liquid phase oxidation process employing an oxygen containing gas. Yet another object is to minimize the time necessary for an oxidizing cycle. A particular object is to provide a control system for a liquid phase oxidation process employing an oxidizing gas wherein the control system is less vulnerable to human error or equipment failure than control systems heretofore avail-

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able. Other and more particular objects will become apparent as the description of the invention proceeds in detail.

In an oxidation process adaptable for employing the practice of the instant invention, an organic compound which has a changing extent of oxygen utilization during the reaction, is oxidized in the liquid phase at superatmospheric pressure while in a reaction zone having means for supplying thereto an oxidizing gas comprising oxygen and an inert component, and means for automatically venting the spent or off gas from the reaction zone in response to the reaction zone pressure. Then, in accordance with the invention, oxidizing gas is fed into the reaction zone at a rate which varies with respect to time in response to a predetermined oxidizing gas flow program. Meanwhile, the oxygen content of the spent gas is being continuously monitored, and whenever the oxygen exceeds a limiting value—below the explosive composition limit—oxidizing gas input flow is interrupted independent of the flow program. Thus by tailoring the oxidizing gas input program to correspond with a predetermined instantaneous oxygen utilization rate during an oxidation process, the oxidation is conducted at near maximum rate throughout all portions of a run. In addition, by providing automatic means for terminating the flow of oxidizing gas independent of the flow program (in response to a limiting value of the spent gas oxygen content), inadvertent formation of an explosive gas or vapor mixture is prevented. In addition, the cycle is automatically terminated when the reaction is complete.

The invention will be more fully understood by reference to the accompanying drawings, in which

FIGURE 1 is the preferred embodiment of the invention wherein a reciprocating compressor is employed to supply the oxidizing gas.

FIGURE 2 shows the preferred embodiment when a centrifugal compressor is substituted for the reciprocating compressor of FIGURE 1.

FIGURE 3 is the sampling system utilized to collect a sample of the vent gas and remove condensible components therefrom prior to monitoring the oxygen content.

Referring to FIGURE 1, oxidation is effected in reactor 16 by passing a stream of an oxidizing gas, for example air, comprising molecular oxygen and an inert component supplied from line 8 into the body of liquid reaction mixture 15 in reactor 16. The spent gas comprising inert components of the oxidizing gas and containing vaporized portions of liquid reaction mixture 15 disengages from the liquid of mixture 15 in disengaging space 17 at the top of reactor 16 and leaves reactor 16 via line 18.

Air is originally supplied to reactor 16 by reciprocating compressor 2 which obtains atmospheric air from suction 1 and compresses it to a suitable pressure in excess of that obtaining in reactor 16, thereafter discharging through line 3 into surge tank 4. From surge tank 4, discharge line 8 conducts the compressed air to reactor 16. The pressure in surge tank 4 is maintained constant by means of spill back line 13 and pneumatic control valve 12 connected around compressor 2. Valve 12 receives an air signal via control line 11 from pressure receiver transmitter 10 which is tapped into surge drum 4 at connection 9; this signal is proportional to the air pressure in drum 4. Pressure receiver controller 10 thus controls the pressure in surge drum 4 by spilling back excess air into compressor 2 through spill back line 13 and valve 12.

Flow meter 5, which may be an orifice plate, in line 8 connects via line 6 to automatic flow controller 32 (a conventional instrument having a pneumatic set point) which positions air-to-open control valve 7 in line 8 to regulate

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the air input to reactor 16. The desired air input rate which flow controller 32 maintains is governed throughout the cycle by time cycle programming controller 31, such as a Foxboro Model 40 instrument. Programming controller 31 is equipped with a rotary cam shaped to correspond with the desired air input for a normal oxidizing cycle. The air output signal of programming controller 31 is fed into air flow rate controller 32 where it establishes the instantaneous set point of the instrument.

Reactor 16 is provided with a pressure indicating controller 20 connected to reactor 16 by tap 19. This controller delivers a pneumatic signal (related to the pressure in reactor 16) through control line 21 to control valve 33 in vent line 34 and, by releasing vent gas maintains a desired pressure in the reaction zone. This pressure may be set so that the system pressure in reactor 16 is maintained essentially constant during an oxidizing cycle despite the variations in oxidizing gas input rate established by programming controller 31. It may, however, be varied by a program controller, not shown.

Gases leaving reactor 16 through line 18 comprise the spent oxidizing gas, essentially nitrogen, together with vaporous and entrained normally-liquid components such as water of oxidation, organic feedstock, organic products, inert reaction solvents, etc. This stream is conducted to condenser 22 where at least a portion of the normally liquid components are condensed, passing thereafter through line 23 to condensate receiver 24. The spent uncondensed gas containing only a small portion of normally liquid components is withdrawn from condensate receiver 24 via line 27, while the liquid condensate is returned to reactor 16 through dip leg 26. Spent gas exiting through line 27 passes through pressure control valve 33 and is vented through line 34, optionally with scrubbing for secondary recovery of normally liquid components. Sample tap 28 in line 27 collects a portion of the spent gas leaving the reaction zone and conducts it to oxygen monitoring system 29, shown schematically in this figure and in considerable detail in FIG. 3. In monitoring system 29 the oxygen content is determined, as for example by an instrument operating on paramagnetic principles. The output signal of monitoring system 29 is in the form of an air pressure which has one value when the off-gas oxygen content is below the predetermined limit and another value when the concentration exceeds this limit, and is transmitted through control line 30 to time cycle programming controller 31 and flow controller 32. This signal, in a manner to be described hereinafter, overrides the action of programming controller 31 such that the presence of the preselected limiting oxygen concentration in the off-gas causes the closing of valve 7 and terminates oxidizing gas input into the reaction zone.

Now turning to FIGURE 2, the control system is modified somewhat when a centrifugal compressor 2a is employed in lieu of the reciprocating compressor 2 in FIGURE 1. Air is collected at inlet 1 and is passed through pneumatically controlled butterfly valve 36 in the suction line of compressor 2a. Compressor 2a may be a multistage unit discharging through line 3 into surge drum 4. In order to maintain a constant load on centrifugal compressor 2a, the discharge pressure thereof is controlled by varying the suction pressure by means of butterfly valve 36 (in response to the discharge pressure measured by controller 10a which is tapped into surge drum 4). The system comprising orifice plate 80, line 81, flow controller 82, and control valve 83 in vent line 84 insures that compressor 2a never operates below its surge point; this is accomplished by venting air through line 84 when valve 7 is closed off. Programmed air flow in FIGURE 2 is accomplished in the same manner as in FIGURE 1. Time cycle program controller 31 controls directly the air flow through line 8 by resetting flow controller 32 and thus activating control valve 7.

The preferred vent gas sampling and oxygen monitor-

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ing installation is shown in FIGURE 3. Sample tap 28 is located in line 27 of FIGURE 1 to obtain a sample of the spent gas after condensation of the major portion of normally liquid components in condenser 22. Alternatively, tap 28 may connect into receiver 24, line 18 or 23, or directly into reactor 16. The sample is filtered through filter 40 and then conducted to pressure reducing valve 41 where its pressure is reduced to about 10 p.s.i.g., as read on pressure gage 42. The gas is then passed into differential pressure controller 43 which drives control valve 44 to maintain a constant pressure differential across controller 43 and thereby assure a constant gas flow rate. From control valve 44, the gas is passed into water scrubber 45 where, after distribution by stainless steel diffusion disc 46, the gas is bubbled through a body of water 47 for the purpose of removing organic components such as reaction solvent, etc. Water scrubber 45 is provided with a glass wool entrainment separator 48 at the top portion thereof, and with a dip leg (not shown) to prevent over-pressuring. The gas leaving water scrubber 45 passes into a knockout trap 49 where additional entrained water is separated and returned to water scrubber 45 by a suitable trap leg.

The gas is then passed through an entrainment trap 50 of the Selas Liqui-Jector type, for example, and thence into an automatic system comprising solenoid valve 51, electrode 52 (in trap 49) and analyzer relay 53 for the purpose of positively terminating the vent gas sampling in the event any water should pass through entrainment separator 48 and knockout trap 49. This is quite important since most paramagnetic oxygen detectors are exceedingly sensitive to the presence of liquids and can be permanently harmed if steps are not taken to exclude this. The gas stream leaving solenoid valve 51 is divided into two portions, the major portion passing through line 54, back pressure regulator 57, and flow-indicating rotometer 58 and thence to exhaust. Back pressure controller 57 controls a back pressure from several inches of water to about 4 p.s.i.g., as indicated by pressure gage 56.

A minor portion of the gas, approximately 50-100 cc.'s per minute, is conducted through line 55 and three-way valve 61 to a high resistance capillary or orifice 60 which withdraws the sample of gas to be passed into oxygen analyzer 29a. Oxygen analyzer 29a may be a Pauling paramagnetic instrument, described by Pauling et al. in the Journal of American Chemical Society, vol. 68, pp. 795-798, 1946. This meter is standardized by passing a sample of nitrogen or similar standardizing gas stored in container 62 into sample system through 3-way valve 61. The output of oxygen analyzer 29a is in the form of an electrical voltage which is proportional to the oxygen concentration, and this voltage is converted by transducer 29b into a visual signal on a dial and to a pneumatic signal. The signal has one value, for example 0 p.s.i.g., at all oxygen concentrations below a preselected limiting amount (below the explosive limit), say three volume percent, and another value, for example 20 p.s.i.g., for all oxygen contents above 3%. This pneumatic signal supplies air through line 30 to time cycle programming controller 31 and flow controller 32 in FIGURE 1. Thus when an oxygen content above 3% is read by analyzer 29a, controller 29b terminates the air pressure to programming controller 31 and to flow controller 32, thereby overriding the action of the latter and causing flow controller 32 to close control valve 7 and discontinue the flow of air into reactor 16.

The control system of the present invention is particularly suitable for conducting liquid phase oxidations according to the process disclosed in Belgium Patents 546,191 and 550,529. Briefly, this oxidation process is for the oxidation of organic compounds such as polyalkyl benzenes by means of an oxygen-containing gas to produce aromatic carboxylic acids, typified by the air oxidation of paraxylene to produce terephthalic acid. The

oxidation is conducted in the presence of a heavy metal, supplied either as an elemental metal or as an organic or inorganic compound, and in the presence of a substance capable of affording bromine, which functions as a catalyst promoter. The reaction is desirably conducted in the presence of a lower fatty acid such as acetic acid as an inert liquid medium. Oxidations conducted according to the foregoing process result in nearly quantitative consumption of oxygen during the early portions of the reaction, in some cases from about one-third to about two-thirds of cycle, so that the spent gas in this period normally contains less than a percent or so of oxygen. If oxygen input is properly diminished thereafter an essentially oxygen-free off gas can be obtained during virtually the entire run until conversion of the feedstock to the desired product is nearly complete.

As a specific example of the use of the control process of the invention, an apparatus is assembled according to the drawing of FIGURE 1 and instrumented as shown. Paraxylene 12 liters, glacial acetic acid 8 liters, and about 1% based on paraxylene of a mixture of cobalt and manganese bromides are fed into reactor 16 via valved line 17. Pressure controller 20 is adjusted to control a back pressure in reactor 16 of 325 p.s.i.g.; reaction mixture 15, before oxidation is commenced, is initially at a temperature of 325° F. This inlet air program for this oxidation may be determined from a preceding run with the same equipment and feedstock or from a previous pilot plant run. In either event, the instantaneous maximum rate may be measured by periodically adjusting the air rate during the experimental run to determine the maximum rate which can be used at each portion of the run without experiencing a substantial increase in oxygen content of the vent gas. A record is kept of the instantaneous rates; from this record a curve of a suitable flow program is plotted. The air rate to be used in subsequent runs thereafter is at or just below the maximum rate curve as above obtained.

Pressure controller 10 is set for 400 p.s.i.g., and compressor 2 is started. Compressor 2 can deliver 1750-1800 standard cubic feet per hour at this pressure. Time cycle programming controller 31 causes flow controller 32 to open control valve 7 and admit compressed air from surge tank 4 into sparger 14 of reactor 16. If the pressure in surge tank 4 should exceed 400 p.s.i.g., pressure controller 10 opens spill back valve 12 to release excess pressure back to the suction of compressor 2.

Time cycle programming controller 31 is, in this oxidation-adjusted to provide, in sequence, an initial low flow rate period (say 20-70% of full rate for not more than about five minutes), a period of not more than about five minutes of rapidly increasing flow rate, then a period of 10-20 minutes of relatively constant flow at 1750-1800 s.c.f./hr. followed by a 20-30-minute period of gradually decreasing flow rate and then a period of constant flow at a low, e.g., 1/3 of full, rate. The initial low flow rate period is for the purpose of limiting oxygen input at the start of an oxidation until the heat of oxidation can increase the temperature of reaction mixture 15 to about 380-400° F., which temperature is more conducive to rapid oxidation rates. As the temperature of reaction mixture 15 gradually rises, programming controller 31 rapidly increases the air flow rate into reactor 16 until substantially the entire output of compressor 2 is being utilized to supply air to the oxidation zone.

The spent gas leaving reaction mixture 15, essentially nitrogen with large amounts of vaporized acetic acid, paraxylene, and water, passes through line 18 to condenser 22, where the water and organic material are condensed and collected in condensate receiver 24. This condensate flows back to reactor 16 through dip leg 26 where it serves to control the temperature of reaction mixture 15. The balance of the vent gas leaves receiver 24 and passes through line 28, back pressure control valve 33, and line 34 to the vent.

After the period of oxidation at substantially maximum air flow rate, the air rate, as controlled by programming controller 31, is gradually tapered off. This is for the purpose of lowering the oxygen input toward the end of the reaction when the concentration of oxidizable feedstock decreases and hence the extent of oxygen utilization falls off. This tapering-off period, it will be observed, maintains the oxygen input at a rate which—based on the experimental run—corresponds with the capacity of the reaction mixture to consume oxygen, and keeps the oxygen content of the spent gas below the present limit. This limit, of course, is below the explosive limit of approximately 8% for mixtures of oxygen, acetic acid and nitrogen.

All throughout the cycle the spent gas is being sampled through tap 28 and analyzed by analyzer-controller 29, which may be a Beckman Model F-3 fast-response oxygen analyzer. Thus, should oxygen in the spent gas increase for any reason, as may occur for oxidizing gas flow-control equipment failure or unforeseeable catalyst poisoning, this increase would be detected by analyzer-controller 29, and air flow would be terminated. It is convenient to set the control limit of analyzer-controller 29 at a point below the explosive concentration limit, e.g., 3%, so as to provide an extra margin of safety in the event of a sharp oxygen breakthrough. When the three percent limit is reacted—either during the course of a run or at the end thereof when conversion is essentially complete—analyzer-controller 29 deprives time cycle programming controller 31 (and flow controller 32) of its supply air, causing the set point of flow controller 32 to demand zero flow, which in turn closes control valve 7 in oxidizing gas line 8. In an analyzer-controller 29 of the Beckman type, supply air to controllers 31 and 32 cannot be resumed until the instrument is reset manually.

It is apparent that many variations of the foregoing system may be made within the spirit and scope of the present invention. For example, the valve in line 71 may be connected to time cycle programming controller 31 to introduce feedstock, solvent, and catalyst automatically and thus conduct the entire process, including liquid flow, without manual control. Reaction product effluent line 18 may be controlled similarly. Also, while the control system has been described with particular reference to a pneumatic control system, it is manifest that hydraulic and/or electrical controllers may be substituted in whole or in part for the particular apparatus described above.

From the foregoing, it is seen that the system of the invention is particularly suitable for controlling a cyclic oxidation process used in the liquid phase oxidation of an organic compound with an oxidizing gas comprising oxygen and an inert component. By maintaining a back pressure in the reaction zone and automatically programming the oxidizing gas input rate in response to a predetermined optimum flow program, an oxidation process employing an oxidizing gas can be conducted entirely safely and in a rapid and highly economical manner. Moreover, by automatically monitoring the oxygen content of the spent gas and terminating oxidizing gas input independent of the programming system, the reaction is terminated when complete, and any unpredictable rise in oxygen content of the spent gas at any portion of the reaction cycle can be effectively prevented.

I claim:

1. Apparatus for oxidizing an organic compound which comprises in combination:

- a time cycle programming controller set to a predetermined flow program,
- a control valve for controlling a flow of an oxidizing gas, said control valve operating in response to said time cycle programming controller,
- a reaction chamber receiving said flow of oxidizing gas,
- a connection for venting spent gas, fitted to said reaction chamber,

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- (e) a back pressure controller upon said connection for controlling spent gas venting in response to pressure in said reaction chamber,
- (f) a continuous oxygen analyzer for monitoring the oxygen content of at least a part of said spent gas, 5
- (g) means connected to said analyzer and operating in response to a signal from said analyzer for terminating oxidizing gas input to said reactor independently of said time cycle programming controller.
2. Apparatus of claim 1 including means for removing normally liquid components from at least a portion of the spent inert gas prior to oxygen content monitoring. 10
3. Apparatus of claim 1 in which the means for monitoring the oxygen content of the spent gas includes a paramagnetic oxygen detector. 15

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