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(12) **Patent:**

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(54) PRODUCTION OF HOT REDUCING GAS CONSISTING SUBSTANTIALLY OF CARBON MONOXIDE AND HYDROGEN

(54)

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The present invention relates to a process for the production of hot reducing gas consisting substantially of carbon monoxide and hydrogen, which gas is suitable for the reduction of iron ore either for the ultimate production of metallic iron, or for the production of substantially pure hydrogen by the steam-iron process.

It is known that for the iron ore reduction reaction to be effective and to proceed at an adequate speed, the reaction must take place at a temperature generally exceeding 950°C, and the reducing gas must contain a low concentration of carbon dioxide plus water vapour, generally not exceeding 12 per cent by volume.

It is also known that at reaction temperatures exceeding 1050°C for iron ore reduction, rapid disintegration of the iron ore may take place, which is to be avoided when producing hydrogen by the steam-iron process, and at reaction temperatures in the vicinity of 1200°C, sintering of the iron ore may occur, partly due to the presence of fluxing impurities and partly due to the occurrence of a eutectic composition within the Wustite range of iron oxides.

Consequently for the purpose of reducing iron ore it is desirable to produce a hot reducing gas at a temperature between 950° and 1150°C, consisting substantially of carbon monoxide and hydrogen and containing not more than 12 per cent by volume of carbon dioxide plus water vapour.

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It is known that paraffin hydrocarbons such as methane, ethane, propane, butane, etc. and a light distillate corresponding approximately to heptane, can be reformed into a gas consisting substantially of carbon monoxide and hydrogen by reacting the hydrocarbons with steam at an elevated temperature in contact with a catalyst such as nickel supported on alumina, magnesia or silica. The gas also contains some methane, carbon dioxide and water vapour, the concentrations of which will depend, for a given catalyst, on the steam/hydrocarbon ratio, the reaction temperature and the space velocity of the reactants.

In practice the catalytic reforming of hydrocarbons with steam has been carried out continuously by passing the reactants through catalyst beds contained in heat resisting metal tubes indirectly heated by hot products of combustion in a furnace. The product gas leaves the tubes at a temperature usually within the range 700° to 900°C. and consists substantially of carbon monoxide and hydrogen and with low concentrations of methane and carbon dioxide, but containing a substantial proportion of steam. Such a gas would require cooling, for condensing out steam, followed by reheating in order to obtain a hot reducing gas as hereinbefore described.

If it were practicable to catalytically reform a hydrocarbon or hydrocarbons with steam, at a suitable steam/hydrocarbon ratio and space velocity, at a sufficiently high temperature, a hot reducing gas as hereinbefore described could be produced directly. However, it is known from experience that a nickel catalyst supported on materials such as alumina or magnesia rapidly becomes inactive and a silica support may disintegrate at temperatures above 900°C, and that to maintain the activity of the catalyst over a period it is preferable that the catalyst is not heated above 850°C. It is also known that in a continuous process for catalytically reforming a hydrocarbon or hydrocarbons with steam, carbon is deposited on the catalyst material at low steam/hydrocarbon ratios, resulting in an increased carbon dioxide content in the product gas and in the deterioration of the catalyst.

According to the present invention there is provided a cyclic process for the production of a hot reducing gas at a temperature of at least 950°C, consisting substantially of carbon monoxide and hydrogen and containing not more than 12 per cent by volume of carbon dioxide plus water vapour, by a catalytic reforming of fluid hydrocarbons, in which each cycle of the process comprises a plant heating period, during which hot products of combustion of a gaseous or liquid fuel with air are passed through a first regenerator containing refractory heat storing material so that the catalyst material is heated to a temperature not exceeding 900°C., and hot products of combustion are passed through a second regenerator containing refractory heat storing material so that the refractory heat storing material is heated to a temperature above 950°C., and a gas making period, during which steam is passed through said first regenerator, becoming superheated therein, at least one hydrocarbon is added to said steam either before or after the steam has passed through the first regenerator, the resulting heated mixture of steam and hydrocarbon or hydrocarbons is passed through said catalyst bed to provide a hot reducing gas consisting substantially of carbon monoxide and hydrogen and containing not more than 12 per cent by volume of carbon dioxide plus water vapour, and said hot reducing gas is passed through said second regenerator so that it becomes heated to a temperature of at least 950°C.

Examples of catalyst materials which may be used in the process of the invention are materials containing nickel supported on alumina, magnesia or silica.

The hot products of combustion which are passed through the first regenerator may be generated in a combustion chamber or space preceding the first regenerator, and additional products of combustion may be generated and/or air added in a combustion chamber or space between the first regenerator and bed of catalyst material, so as to control the temperature to which the bed of catalyst material is heated.

The hot products of combustion which are passed through the second regenerator may consist of the products of combustion leaving the bed of catalyst material mixed with hot products of combustion generated in a combustion chamber or space between the bed of catalyst material and the second regenerator. In this case during the plant heating period of a cycle the bed of catalyst material and the second regenerator in the same direction as the reactants and make gas pass during the gas making period of the cycle.

Alternatively, the hot products of combustion which are passed through the second regenerator may be generated in a combustion chamber or space at the opposite end to the gas outlet of the bed of catalyst material, and are separate from the products of combustion leaving the bed of catalyst material. In this case during the plant heating period of a cycle the products of combustion pass through the second regenerator in the opposite direction to that in which the make gas passes during the gas making period of the cycle.

The hot products of combustion leaving the second regenerator, or the combined hot products of combustion leaving the first and second regenerators, may be passed through a waste heat boiler for raising steam and then to a stack. The steam raised in the waste heat boiler may be used for providing the steam required during the gas making and purge periods. Usually surplus steam over that required for the process is available from the waste heat boiler and this surplus steam may be passed for external use, such as generating electric power.

The gaseous or liquid fuel and/or the air from which the hot products of combustion are derived may be preheated by indirect heat exchange with the hot products of combustion leaving the waste heat boiler before they pass to the stack.

The hydrocarbon or hydrocarbons which are catalytically reformed with steam may be used as the fuel for generating the hot products of combustion.

In the case where the hot reducing gas leaving the second regenerator is passed to a process stage for the reduction of iron ore, an effluent gas is produced which may be of a substantial calorific value and leaves the process stage hot.

For the continuous supply of the hot reducing gas to said process stage two or more units generating hot reducing gas cyclically will be required and the sequence of operation can be staggered so that while hot reducing gas is passed to the process stage from one unit, hot effluent gas from the process stage is passed to another unit for generating hot products of combustion.

When the hydrocarbon which is catalytically reformed with steam is methane, or natural gas consisting largely of methane, during the gas making period the methane or natural gas is preferably added to the steam before entry into the first regenerator, so that the mixture of steam and methane or natural gas becomes heated in the regenerator. When the hydrocarbon is a liquified petroleum gas or a light distillate, the hydrocarbon is preferably added to the superheated steam resulting from passing steam alone through the first regenerator.

Each cycle of the process also includes a short purge period between the plant heating period and the gas making period and between the gas making period and the plant heating period of the next cycle, during which the vessels of the plant are purged with steam and then make gas, or with steam alone.

During the post-heating purge period steam is passed through the first regenerator, bed of catalyst material and the second regenerator, sweeping out the products of combustion containing in these vessels through a stack. The hydrocarbon is then added to the steam and reforming of the hydrocarbon takes place in the bed of catalyst material, and the resultant make gas passes through said bed and the second regenerator, sweeping out the steam contained therein through the stack. When the make gas at the exit end of the second regenerator is such that it contains an acceptable proportion of water vapour the stack is closed and the gas making period of the cycle commenced.

Towards the end of the post-heating purge period make gas passes through the stack to waste which may contain an acceptable proportion of carbon dioxide but more water vapour than is acceptable. By closing the stack before the commencement of the gas making period and passing this make gas to a sealed wash-box and then to a gasholder, this gas may be cooled, causing water vapour to condense out, and a cold but otherwise acceptable make gas collected in the gasholder. The collected cold make gas may be used for purging during the post-heating purge period, between purging with steam and purging with make gas generated by reforming of the hydrocarbon. Alternatively the collected cold make gas may be passed into the first regenerator during the succeeding gas making period. In either case a booster is used for boosting the gas withdrawn from the gas holder to the required pressure.

During the post-make purge period the supply of hydrocarbon is cut off and steam is passed through the first regenerator, bed of catalyst material and the second regenerator, sweeping out the make gas therein. When the steam is approaching the exit end of the second regenerator the stack is opened and the remaining make gas and steam allowed to pass through the stack.

The operation of the cycle is achieved by means of control valves, the movement of which may be effected either mechanically, hydraulically or pneumatically, in accordance with established practice, and the sequence of valve movements may be automatically effected by a mechanical, electrical or electronic device.

The present invention will now be further described by way of example with reference to the accompanying drawings in which:-

Fig. 1 is a flow diagram of one embodiment of the invention, and

Fig. 2 is a flow diagram of a second embodiment of the invention.

In the Figs. 1 and 2 like numbers denote like parts.

Referring to Fig. 1, a vessel 1 contains a zone 2 filled with chequered refractory material, constituting a first regenerator, and a branch 3 in the bottom region of the vessel constitutes a combustion chamber. The top of the vessel 1 is connected by a conduit 4 to a top part 7 of a vessel 5, which contains a bed 6 of catalyst material and which is connected by a restricted throat 7a to the top part 7. The bottom of the vessel 5 is connected by a conduit 8 to the bottom region of a vessel 9, which contains a zone 10 filled with chequered refractory material, constituting a second regenerator. The top of the vessel 9 is connected by a conduit 12 to the tube side of a waste heat boiler 13 and the outlet of the tube side of the boiler is connected by a conduit 14 to a stack 15. A conduit 11 is connected to the top region of the vessel 9. The stack 15 is provided with a stack valve 16 at the top, and the conduit 11 is provided with a make gas control valve 17. A blower 18 is provided for boosting air entering through a line 19 into a conduit 20. A gaseous or liquid fuel is supplied through a conduit 25. Steam is supplied through a conduit 31, which is connected through a valve 50 to a conduit 30 connected to the shell side of the waste heat boiler

13. Methane, or natural gas consisting largely of methane, is supplied through a conduit 32.

The cycle of operation consists of a plant heating period, followed by a post - heating purge period, followed by a gas make period, followed be a post-make purge period.

At the commencement of the plant heating period, the stack valve 16 will already be open and all the other control valves will be closed. Control valves 37, 39 and 34 are opened, passing primary air through a conduit 23 and regulating valve 36 and fuel through a conduit 28 and regulating valve 33 to a burner 35 provided in the combustion chamber 3, and passing secondary air through a conduit 22 and regulating valve 38 to the combustion chamber 3. After a delay of a few seconds control valves 44 and 41 are opened, passing air through a conduit 24 and regulating valve 43 and fuel through a conduit 26 and regulating valve 40 to a burner 42 provided in the top part 7 of the vessel 5, and after a further delay of a few seconds control valves 49 and 46 are opened, passing air through a conduit 21 and regulating valve 48 and fuel through a conduit 29 and regulating valve 45 to a burner 47 provided in a combustion space in the conduit 8.

The various regulating valves are adjusted so that during the plant heating period the greater part of the combustion of the fuel takes place in the combustion chamber 3 and minor proportions of the fuel are burned in the burners 42 and 47. The chequered refractory material in the first regenerator zone 2 and second regenerator zone 10 and the catalyst material in the bed 6 become heated by the hot products of combustion, and hot products of combustion pass out from the top of the vessel 9 through the conduit 12 and waste heat boiler 13 to the open stack 15. Water is fed to the boiler through a conduit 57 and steam is raised in the boiler. The combustion of the fuel at the various points is controlled so that the catalyst material in the bed 6 is heated to a temperature not exceeding 900°C, and the chequered refractory material in the second regenerator zone 10 is heated to a temperature above 950°C.

At the end of the plant heating period, the control valves 37, 39, 44, 49, 34, 41 and 46 are closed simultaneously and the post-heating purge period is commenced by opening control valve 53, passing steam through the conduit 31 and regulating valve 52 to an inlet 54 in the bottom region of the vessel 1. The valve 52 is regulated so that steam flows through the vessels of the plant at a comparatively high rate, for example at two to three times the rate of flow of steam during the succeeding gas make period. The steam sweeps out the products of combustion contained in the vessels, which products of combustion pass to atmosphere through the open stack 15. After a few seconds the valve 52 is regulated to give a rate of steam flow required for the gas make period and control valve 56 is opened, passing methane or natural gas through the conduit 32 and regulating valve 55 to the inlet 54, mixing with the steam. Reforming of the methane or natural gas takes place in the bed 6 and the resultant gas passes out of the vessel 5 and through the vessel 9, sweeping out the steam contained therein through the open stack 15. When the make gas at the top end of the vessel 9 is such that it contains an acceptable proportion of water vapour, the stack valve 16 is closed and the control valve 17 is opened, and the gas make period is commenced.

The regulating valves 52 and 55 are adjusted to give a suitable steam/hydrocarbon ratio and space velocity through the bed 6 during the gas make period so as to obtain a reducing gas leaving the vessel 5 containing not more than 12 per cen by volume of carbon dioxide plus water vapour.

The reducing gas leaving the vessel 5 passes through the second regenerator zone 10 and becomes heated by the hot chequered refractory material contained therein to a temperature of at least 950°C. The hot reducing gas passes through the control valve 17 and conduit 11 for process use.

At the end of the gas make period the control valve 56 is closed and the regulating valve 52 is adjusted to give a high rate of steam flow, as during the first part of the post-heating purge period. The post-make purge period is then commenced. Steam passes through the vessels of the plant and sweeps out the make gas contained in the vessels 5 and 9, this gas passing through the control valve 17 into the conduit 11. When most of the make gas has so been swept out of the vessels and when steam is approaching the top region of the vessel 9, the control valve 17 is closed and the stack valve 16 opened. The control valve 53 is then closed and the plant is set ready for commencement of the next plant heating period.

During the gas make and purge periods the required steam is supplied from the waste heat boiler 13 through the conduit 30, valve 50 and conduit 31. Surplus steam passes through a valve 51 and a conduit 30a for external use.

Referring to Fig. 2, the vessel 9, which contains a zone 10 filled with chequered refractory material, is provided with a branch 61 constituting a combustion chamber in the region above the zone 10 and with a stack 58 at the top, provided with a stack valve 59. The bottom of the vessel 9 is connected by a conduit 60 to the tube side of a waste heat boiler 13 and the outlet of the tube side of the boiler is connected by a conduit 14 to a stack 15 provided with a stack valve 16. Liquified petroleum gas or light distillate is supplied through a conduit 32.

At the commencement of the plant heating period of a cycle the stack valve 59 will be closed and the stack valve 16 open. All the other control valves will be closed. Control valves 37, 39, 34, 44 and 41 are opened in the manner hereinbefore described with reference to Fig. 1. After a delay of a few seconds control valves 69, 73 and 65 are opened, passing primary air through a conduit 70 and regulating valve 68 and fuel through a conduit 63 and regulating valve 64 to a burner 66 provided in the combustion chamber 61, and passing secondary air through a conduit 71 and regulating valve 72 to the combustion chamber 61. The hot products of combustion generated in the combustion chamber 61 pass downwardly through the second regenerator zone 10, the chequered refractory material in this zone being heated to a temperature above 950°C, and in the bottom region of the vessel 9 they mix with hot products of combustion leaving the vessel 5 through conduit 8. The combined hot products of combustion pass out from the bottom of the vessel 9 through the conduit 60 and waste heat boiler 13 to the open stack 15.

At the end of the plant heating period, the control valves 37, 39, 44, 69, 73, 34, 41 and 65 are closed simultaneously and the post-heating purge period is commenced by opening control valve 53 and in the manner hereinbefore described with reference to Fig. 1.

On opening the control valve 56 liquefied petroleum gas or light distillate passes through the conduit 32 and regulating valve 55 to an inlet 74 in a region of the vessel 1 above the first regenerator zone 2 and becomes vaporised by and mixes with the superheated steam passing upwards from the zone 2. Reforming of hydrocarbons takes place in the bed 6 and the resultant gas passes out of the vessel 5 and through the bottom region of the vessel 9 sweeping out the steam contained therein through the waste heat boiler 13 and open stack 15. A few seconds after opening the control valve 56 the stack valve 16 is closed and stack valve 59 opened. The make gas then pass upwardly through the vessel 9, sweeping out the products of combustion and steam contained therein through the open stack 58. When the make gas at the top end of the vessel 9 is such that it contains an acceptable proportion of water vapor, the stack valve 59 is closed and the control valve 17 is opened, and the gas make period is commenced.

The gas make period is carried out in the manner hereinbefore described with reference to Fig. 1.

The post-make purge period is commenced by closing the control valve 56 and adjusting the regulating valve 52 to give a high rate of steam flow, in the manner hereinbefore described with reference to Fig. 1. Steam passes through the vessels of the plant and sweeps out the make gas contained in the vessels 5 and 9, this gas passing through the control valve 17 into the conduit 11. When most of the make gas has been so swept out of the vessels and when steam is approaching the top region of the vessel 9, the control valve 17 is closed and the stack valve 59 opened for a few seconds. The stack valve 59 is then closed and the stack valve 16 opened, the steam then passing through the conduit 60 and waste heat boiler 13 to the open stack 15, sweeping out gases contained therein. The control valve 53 is then closed and the plant is set ready for the commencement of the next plant heating period.

Example 1

An arrangement of flow according to Fig. 1 is employed.

During the heating period of a cycle a gaseous fuel is burned at the various points so that products of combustion leave the bed 6 at 900°C., become heated in the combustion space of the conduit 8 to 1200°C., and leave the top of the vessel 9 at 1150°C., the chequered refractory material in the second regenerator zone 10 being heated to a temperature between 1150°C., at the bottom of the zone and 1100°C. at the top. The catalyst material (a material containing nickel supported on alumina) in the bed 6 is heated to a temperature between 800° and 850°C.

During the gas making period substantially pure methane is fed, together with steam, at a steam/methane ratio of 1.3 vol/vol and a space velocity through the bed 6 of 400 $hrs.^{-1}$.

The gas which leaves the bed 6 has the composition:

CH_4 = 1.7, CO = 19.4, H_2 = 65.4, CO_2 = 2.3, H_2O = 7.6, O_2 = 0.1, N_2 = 3.5 per cent by volume (CO_2+H_2O = 9.9%)

The make gas leaving the top of the vessel 9 is heated to 1000°C and passes through the control valve 17 into the conduit 11.

Example 2

An arrangement of flow according to Fig. 2 is employed.

During the heating period of a cycle a liquid petroleum fuel is burned at the various points so that one lot of products of combustion leaves the bed 6 at 900°C and another lot of products of combustion leaves the combustion chamber 61 of the vessel 9 at 1450°C., being cooled to 1150°C in passing through the second regenerator zone 10 before mixing with said one lot of products of combustion in the bottom region of the vessel 9. The chequered refractory material in the zone 10 is heated to a temperature between 1300°C at the top of the zone and 1100°C at the bottom. The catalyst materials (a material containing nickel supported on alumina) in the bed 6 is heated to a temperature between 800°C and 850°C.

During the gas making period a light petroleum naphtha of specific gravity = 0.71 and final boiling point = 125°C. (equivalent to C_7H_{15}) is fed, together with steam, at a steam/hydrocarbon ratio of 1.3 wgt/wgt. and a space velocity through the bed 6 of 80 to 100 hrs. $^{-1}$.

The gas which leaves the bed 6 has the composition:

CH_4 = 3.0, CO=21.5, H_2=57.8, CO_2=3.4, H_2O=7.4,

O_2=0.1

N_2=5.3, per cent by volume (CO_2 + H_2O = 10.6%)

The make gas leaving the top of the vessel 9 is heated to 1100°C. and passes through the control valve 17 into the conduit 11.

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

1. A cyclic process for the production of a hot reducing gas at a temperature of at least 950°C, consisting substantially of carbon monoxide and hydrogen and containing not more than 12 per cent by volume of carbon dioxide plus water vapour, by a catalytic reforming of fluid hydrocarbons, in which each cycle of the process comprises a plant heating period, during which hot products of combustion of a gaseous or liquid fuel with air are passed through a first regenerator containing refractory heat storing material and then through a bed of catalyst material so that the catalyst material is heated to a temperature not exceeding 900°C., and hot products of combustion are passed through a second regenerator containing refractory heat storing material so that the refractory heat storing material is heated to a temperature above 950°C., and a gas making period, during which steam is passed through said first regenerator, becoming superheated therein, at least one hydrocarbon is added to said steam either before or after the steam has passed through the first regenerator, the resulting heated mixture of steam and hydrocarbon or hydrocarbons is passed through said catalyst bed to provide a hot reducing gas consisting substantially of carbon monoxide and hydrogen and containing not more than 12 per cent by volume of carbon dioxide plus water vapour, and said hot reducing gas is passed through said second regenerator so that it becomes heated to a temperature of at least 950°C.

2. A process as claimed in claim 1, in which the catalyst material comprises a material containing nickel supported on alumina, magnesia or silica.

3. A process as claimed in claim 1 in which the hot product of combustion which are passed through the first regenerator

are generated in a combustion which are passed through the first regenerator are generated in a combustion chamber or space preceding the first regenerator.

4. A process as claimed in claim 1, in which additional products of combustion and/or air are added in a combustion chamber or space between the first regenerator and bed of catalyst material, so as to control the temperature to which the bed of catalyst material is heated.

5. A process as claimed in claim 1, 2 or 3 in which the hot products of combustion which are passed through the second regenerator comprise the products of combustion leaving the bed of catalyst material mixed with hot products of combustion generated in a combustion chamber or space between the bed of catalyst material and the second regenerator.

6. A process as claimed in claim 1, 2 or 3, in which the hot products of combustion which are passed through the second regenerator are generated in a combustion chamber or space at the opposite end to the gas outlet of the bed of catalyst material, and are separate from the products of combustion leaving the bed of catalyst material.

7. A process as claimed in claim 1, in which the hot products of combustion leaving the second regenerator, or the combined hot products of combustion leaving the first and second regenerators, are passed through a waste heat boiler for raising steam and then to a stack.

8. A process as claimed in claim 7, in which the gaseous or liquid fuel and/or the air from which the hot products of combustion are derived and preheated by indirect heat exchange with the hot products of combustion leaving the waste heat boiler before they pass to the stack.

9. A process as claimed in claim 1, 2 or 3, in which two or more units generating hot reducing gas cyclically are utilised, the sequence of operation being staggered so that while hot reducing gas is passed from one unit to a process stage for the reduction of iron ore, hot effluent gas from the process stage is passed to another unit for use as the fuel for generating hot products of combustion.

10. A process as claimed in claim 1, 2 or 3 in which each cycle includes a short purge period between the plant heating period and the gas making period and between the gas making period and the plant heating period of the next cycle, during which the vessels of the plant are purged with steam and then make gas, or with steam alone.

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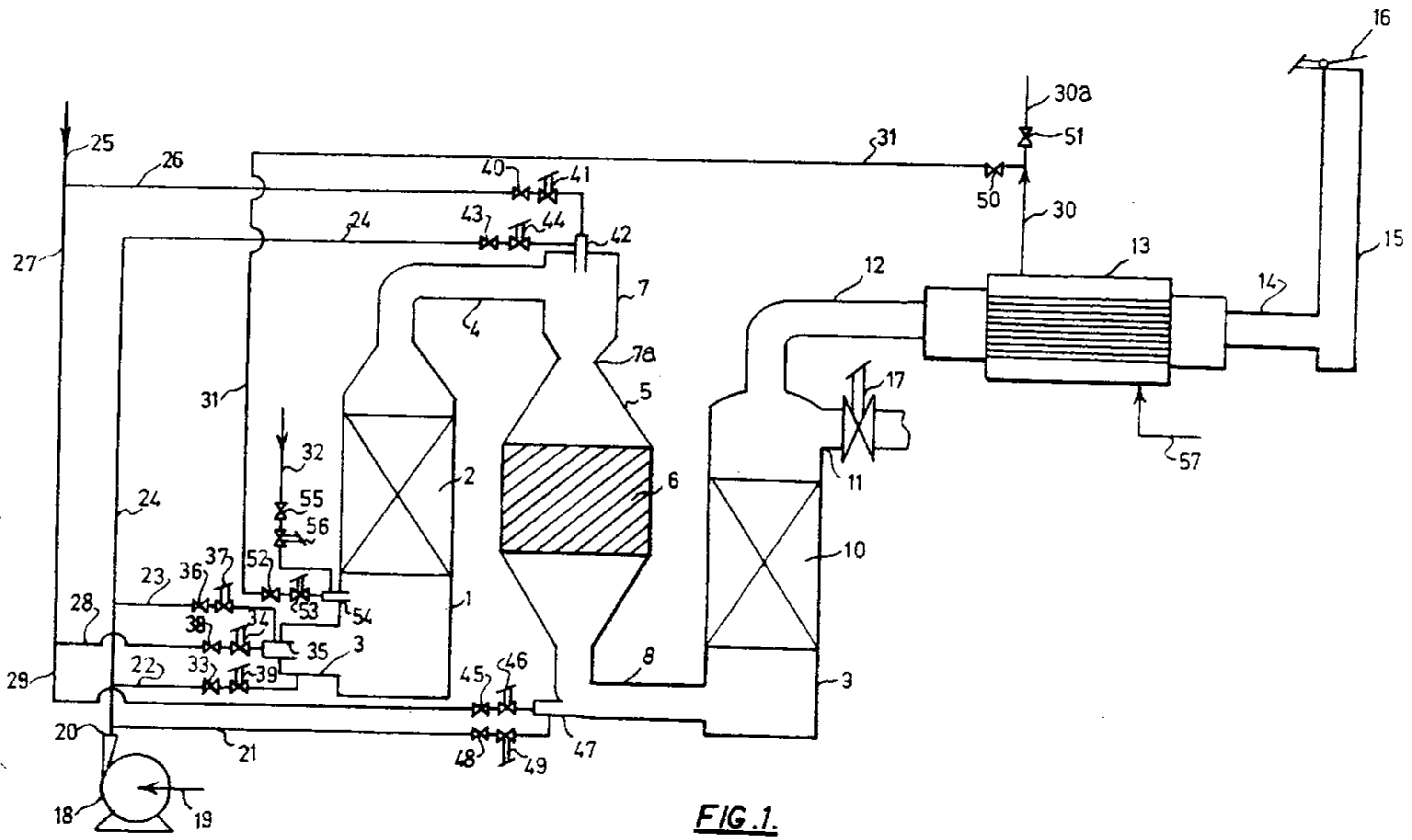

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FIG.1.

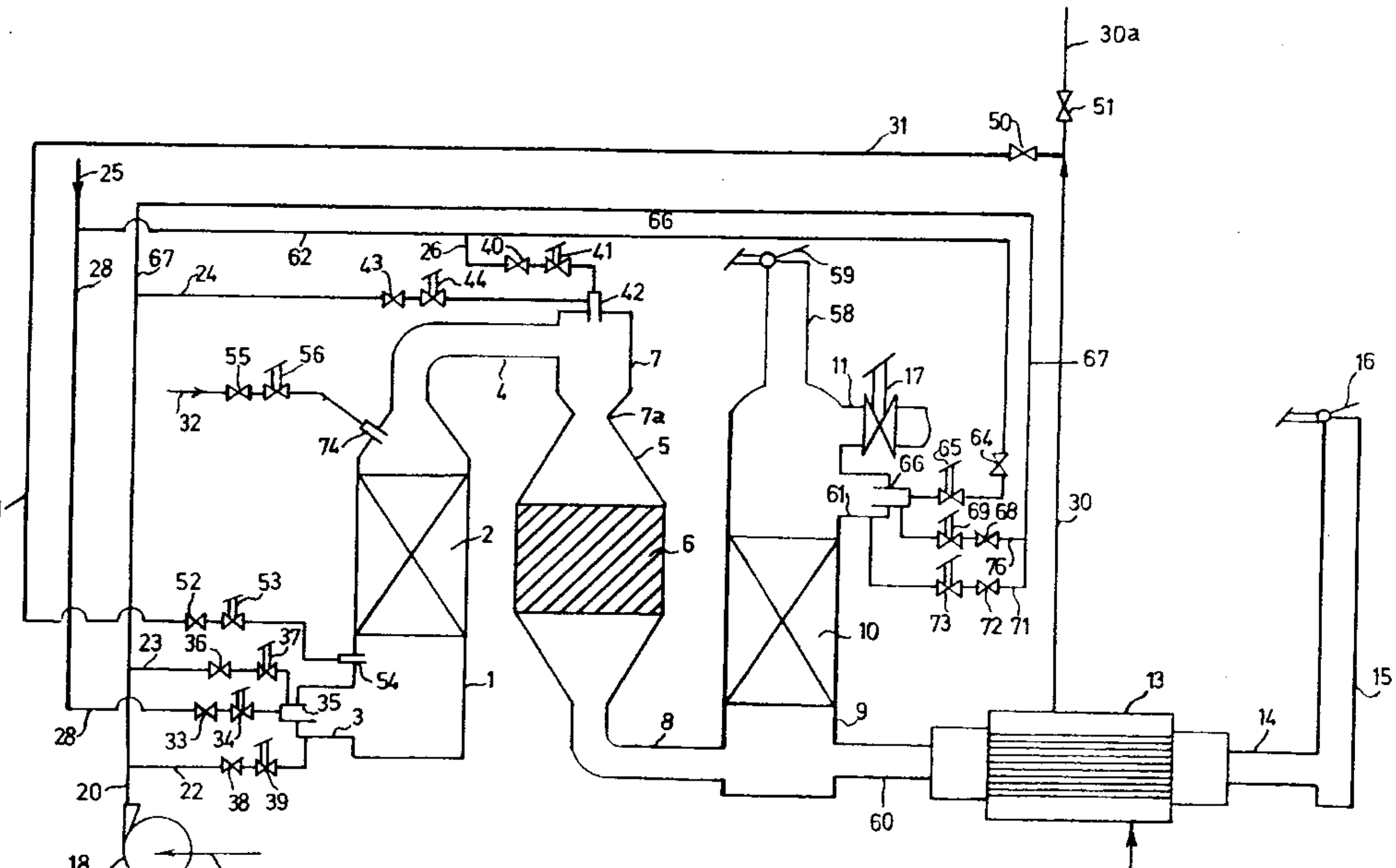

FIG. 2.

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