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(71) Demandeur/Applicant:
HYDROGENICS CORPORATION, CA

(72) Inventeur/Inventor:
KLUG, KARL H., DE

(74) Agent: BERESKIN & PARR

(54) Titre : REFORMEUR ELECTROCATALYTIQUE POUR LA PRODUCTION DE GAZ DE SYNTHÈSE

(54) Title: ELECTROCATALYTIC REFORMER FOR SYNTHESIS GAS PRODUCTION

(57) **Abrégé/Abstract:**

The invention relates to a method and devices for the chemical reaction of liquid, vapor or gaseous hydrocarbons with either water or water vapor and either air or oxygen, to produce a hydrogen-rich synthesized gas for use in fuel cells. In the process, the chemical reaction of the reactants takes place on the catalytically coated surface of a material that is electrically conductive, and as a consequence of the feeding an electrical voltage, directly heatable and consequently temperature-controllable.



ABSTRACT OF THE DISCLOSURE

The invention relates to a method and devices for the chemical reaction of liquid, vapor or gaseous hydrocarbons with either water or water vapor and either air or oxygen, to produce a hydrogen-rich synthesized gas for use in fuel cells. In the process, the chemical reaction of the reactants takes place on the catalytically coated surface of a material that is electrically conductive, and as a consequence of the feeding an electrical voltage, directly heatable and consequently temperature-controllable.

Title: ELECTROCATALYTIC REFORMER FOR SYNTHESIS GAS PRODUCTION

FIELD OF THE INVENTION

[0001] This invention relates to a method of and an apparatus for the chemical conversion of liquid, vapor or gaseous hydrocarbons.

BACKGROUND OF THE INVENTION

[0002] This invention relates to a method of and an application for the chemical reaction of liquid, vapor, or gaseous hydrocarbons with either water or water vapor and/or either air or oxygen, into hydrogen-rich reaction gases for use in fuel cells, among other devices.

[0003] Fuel cells, particularly PEM fuel cells, are an interesting option for the provision of a decentralized energy supply and for use in vehicles. In fuel cells, hydrogen is converted in an electrochemical process with a high degree of efficiency directly into electric current. For various reasons, hydrogen is often not used directly when operating fuel cells, but is produced from gaseous (e.g., natural gas) or liquid (e.g., methanol, benzine, diesel, propane/butane mixtures) hydrocarbons in a chemical reaction taking place prior to the electrochemical process. In the process, the hydrocarbons, with one of: water or water vapor (steam reforming); air or oxygen (partial oxidation); or a combination of these two processes (auto thermal reforming), are turned into hydrogen-rich gases.

[0004] In terms of the hydrogen yield, which is important for the overall efficiency of a fuel cell, steam reforming is superior to the other, above-mentioned methods. For instance, methanol is, in the steam reforming process, ideally completely turned into carbon dioxide and hydrogen in the presence of a catalytic converter (nickel or platinum), in accordance with the following overall reaction.



[0005] Steam reforming is endothermic, and for methanol, takes place at approx. 300°C [1]. If natural gas is used, the temperatures are around 700 to 800°C.

[0006] A considerable disadvantage of steam reforming is its inherent bad cold start performance and its sluggish transitional properties when there are load variations, since the energy required for the reaction, e.g., using a burner, must be supplied from the exterior. In the process, the catalytic converter and the housing must first be brought to the required operating temperature. The required time, during which the reformer delivers a product gas with a composition unacceptable for the electrochemical process, depends on the thermal capacity of the materials to be heated up. So-called cold spots are a further disadvantage, in which, because of the low temperatures present, there could be less conversion, and as a result, formation of increased quantities of carbon monoxide as well as soot formation.

SUMMARY OF THE INVENTION

[0007] It is therefore desirable to eliminate, to the greatest possible extent, the previously described disadvantages that may incidentally also appear in more or lesser form in the other mentioned methods of hydrogen generation.

[0008] In the present invention, gas proof or porous silicon carbide SiC is used as a catalyst carrier. Its advantageous thermo mechanical and electrical properties are, among other things, described in [2], [3], and [4]. Its high temperature resistance (in reducing atmosphere, up to 2000°C), paired with a good thermal and electrical conductivity, stands out, in particular. By applying an appropriate electrical voltage, the latter is used to always ensure optimal thermal conditions either in the reformed or on the catalytically coated surface, preferably in a honeycomb shape. Depending on the operating state, the heat necessary for the chemical reaction can be partially or completely covered by providing Joule heat, that is, from the conversion of electrical energy into heat within the SiC matrix. In the following, this device will be called an electrocatalytic reformer (ECR) for short.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] For a better understanding of the present invention and show more clearly how it may be carried into effect, reference will now be made, by way of example, to the accompanying drawings which show preferred embodiments of the present invention and in which:

[0010] Figure 1 shows schematically an electrocatalytic reformer (ECR) in accordance with the first embodiment of the present invention, in partial section;

[0011] Figure 2 shows a second embodiment of the present invention including a plurality of electrocatalytic reformer elements arranged in a reaction vessel;

[0012] Figure 3 shows a variant of the embodiment of Figure 2, showing an alternative flow configuration;

[0013] Figure 4 shows, schematically, a circuit, including an electrocatalytic reformer in accordance with the present invention and a fuel cell stack; and

[0014] Figure 5 shows a further embodiment of a circuit including an electrocatalytic reformer in accordance with the present invention and a fuel cell stack.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Figure 1 shows one possible embodiment of an electrocatalytic reformer (ECR) element, in accordance with the present invention. Here, the ECR element is made of either silicon or silicon carbide and is preferably shaped like a pipe and has inner and outer pipes.

[0016] The silicon carbide SiC is porous and has a surface catalytically coated with at least one Group VIII metals of the periodic table (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt), as well as Cu and Zn and their combinations to promote the endothermic reforming reactions. In the present case, the porous pipe is an inner pipe indicated at 10 and is enclosed by a non-porous outer pipe 12, that is a gastight pipe made of metal or ceramic, which can be

catalytically coated on its outer surface with the Group VIII metals of the periodic table (Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt), as well as Cu and Zn and their combinations, to promote any exothermal reactions of the anode exhaust gas with air or oxygen, which take place on the outer surface thereof, as detailed in Figure 2.

[0017] The inner and outer pipes 10,12 together define an annular chamber 14. One end of the inner pipe 10 is closed with a contact plug 16, secured to the inner part 10 and forming an electrical contact therewith. The annular chamber 14 has an inlet provided adjacent and around the contact plug 16. At the other end, the annular chamber 14 is closed, and the inner pipe 10 forms an outlet 18.

[0018] Consequently, in use, reactants, e.g. hydrocarbon and water, preferably in vapor state, flow into the inlet of the annular chamber 14 around the plug 16. The gas and vapor then flow along the annular chamber 14, and progressively pass through the porous inner pipe 10, to the inside of the pipe 10. The catalyst on the pipe 10 promotes reaction to generate hydrogen and carbon dioxide as a synthesized gas, as detailed above. This synthesized gas then leaves through the outlet 18.

[0019] The coating on the inner pipe 10 is advantageously provided on the surface, which will give optimum performance. For this purpose, it can be provided uniformly over the matrix of the porous inner pipe 10, so that the incoming hydrocarbon and water vapor contact the catalyst as they pass through the porous inner pipe 10, and are consequently heated.

[0020] The heat necessary for the endothermal reaction of hydrocarbon with water can be supplied in a number of ways. It can be supplied either through simple heat emission from a gaseous or liquid heat transfer medium flowing around the outside of the outer pipe 12, together, optionally, with exothermal reactions taking place on the outer surface of the outer pipe 12. Additionally, the contacts provided by the contact plug 16 and the outlet 18 can be used to pass an electric current through the inner pipe 12, to generate Joule heat, released in the SiC matrix of the pipe 12.

[0021] Reference will now be made to Figure 2, which shows a second embodiment of the present invention, which provides a tube assembly including a number of the ECR elements of Figure 1, the ECR elements being designated at 20 in Figure 2.

[0022] The ECR elements 20 are contained within a vessel 22. At one end, the vessel 22 includes a plate 24 defining a first manifold 26. A first port 28 is provided for reactants or reaction components, opening into the first manifold 26.

[0023] Correspondingly, at the other end, a second plate 30 defines a second manifold 32, having a second port 34 for synthesized gas. Here, the port 28 and manifold 26 form an inlet port and an inlet manifold, while the second manifold 32 and the second port 34 form an outlet manifold and an outlet port.

[0024] The ECR elements 20 are mounted in the plates 24,30 and hence a chamber 36 is defined around the ECR elements 20. An exhaust gas inlet 38 and an exhaust gas outlet 40 are provided, for forcing a mixture of exhaust gas and air through the chamber 36.

[0025] In use, the individual ECR elements 20 function as described for Figure 1. Thus, a mixture of hydrocarbon and water is delivered through the first or inlet port 28 and through the first or inlet manifold 26 into the annular chambers 14 of the various ECR elements 20 as shown by the arrows 42. The reactants then flow through the porous inner tubes of the elements 20 and out of the elements 20 into the second or outlet manifold 32 (arrows 44), as synthesized gas, so the synthesized gas then exhausts from the vessel 22 through the second or outlet port 34.

[0026] At the same time, to provide additional heat to the ECR elements 20, either a stream of gas comprising hydrogen containing anode exhaust gas and air, or a hot exhaust gas from a catalytic burner, is delivered to the exhaust gas inlet 38. This gas flows around the exterior of the ECR elements 20 and out through the exhaust gas outlet 40. In the case of the gas flow comprising a combination of hydrogen containing anode exhaust gas and air, the outside of the ECR elements 20 can be provided with the catalytic

coating mentioned above, to promote reaction of remaining hydrogen with oxygen from the air, both to consume the hydrogen and to generate additional heat to heat the ECR elements 20. Where the gas delivered to the inlet 30 is from a catalytic burner, then any excess hydrogen will already have been consumed and heat generated, so that the gas should be at a higher temperature, suitable for heating the ECR elements 20. Where the gas mixture of air/oxygen and reactive substances is provided, the reactive substances can include hydrogen, carbon monoxide and hydrocarbons. By causing reaction of remaining reactive substances to occur on the outside of the ECR elements 20, this optimizes heat transfer of the generated heat into the ECR elements 20.

[0027] It will also be understood that the necessary electrical contacts would be made to the contact plug 16 and outlets 18 of the ECR elements 20.

[0028] Reference will now be made to Figure 3 which shows an apparatus similar to that of Figure 2, and for simplicity and brevity, like components are given the same reference numeral and the description of these components is not repeated.

[0029] In Figure 3, the flow of the reaction substances or components is reversed. Thus, here the second inlet 34 and second manifold 32 receive the incoming reactive substances, as indicated by the arrows 48. The incoming reaction components then flow along the inside of the tubes 10 of the ECR elements 20, through the porous SiC matrix to the outer annular chambers of the ECR elements 20. The components react as before on a catalyst coated on the surface of the inner pipes 10, to form the synthesized gas. The synthesized gas then exits from the annular chambers to the first manifold 26 and out through the first port 28, as indicated by the arrows 50. Thus, the first manifold 26 and the first port 28 forms an outlet manifold and an outlet port in this embodiment.

[0030] In this embodiment, the catalytic coating on the pipes 10 can again be located to optimize performance. For this purpose, as described above the coating is provided uniformly over the matrix of the inner pipes 10, so that the reaction components are heated, by passage through the SiC

matrix, during which they contact the catalyst . Additionally, exhaust gases, as detailed above for Figure 2, can be passed around the outside of the ECR elements 20, to heat the outside of the elements 20. This provides radiant heat that serves to heat the outside of the pipes 10, further promoting the endothermic reaction of the reaction components.

[0031] It is also noted that the invention is applicable not just to the tubular bodies described as examples but basically to any shaped bodies, for examples, plates or blocks that the reactants pass over and/or flow thorough. In porous bodies, the catalytic coating may cover the entire porous surface.

[0032] For reasons of efficiency, when using an ECR, it should be ensured that the heat needed for the chemical reaction is made available only as a small, additional portion by supplying Joule heat, i.e. from the conversion of electrical energy within the heat derived from the SiC matrix. This can be ensured through an optimized heat integration of the reformer into the entire process and the implementation of dynamic energy management.

[0033] Reference is now being made to Figure 4, which shows, schematically, a circuit incorporating a fuel cell stack and an electrocatalytic reformer in accordance with the present invention. The circuit or arrangement is indicated generally by the reference 60, and includes an electrocatalytic reformer 62 and a fuel cell stack 64. A process control computer 66 is connected, directly or indirectly, to various components of the circuit, for control thereof, and the function of the computer 66 is detailed below.

[0034] A water supply 68 and a methanol supply 70 are connected to a pump 72 . In known manner, appropriate valves, pumps and the like would be provided to ensure delivery of required water and methanol, or other hydrocarbon, at suitable pressures and flow rates. The pump 72 is controlled by a load signal indicated at 74. The water and methanol mixture then pass through a flow meter 76, to a heat exchanger 78, in which the water and methanol are heated.

[0035] From the heat exchanger 78, the water and methanol flow to the electrocatalytic reformer 62, which is indicated schematically includes a plurality of ECR elements 20. As detailed above, within the electrocatalytic

reformer 62, the water and methanol are reacted to form a synthesized gas comprising mainly hydrogen and carbon dioxide. The synthesized gas then passes to the anode of the fuel cell stack 64. In known manner, an oxidant would be supplied to the cathode of the fuel cell stack 64.

[0036] Exhausted anode gas flows along a line 80 to a catalytic burner 82. The burner 82 also has inlets 84 and 86 for air and methanol. Within the catalytic burner 82 any residual hydrogen, hydrocarbons and other combustible materials are consumed. Air is provided for this purpose, and additional methanol can be supplied, to ensure full consumption of all residual reactive components and generation of sufficient heat. The heated gas is then passed to the heat exchanger 78, for heating the incoming methanol and water, and finally, the anode gas is exhausted as indicated at 88.

[0037] To monitor and control the system, a variety of sensors can be provided. Exemplary sensors are shown. Thus, temperature sensors are indicated at 90, for monitoring the temperature of the incoming methanol and water mixture both upstream and downstream from the electrocatalytic reformer 62, and also the temperature within the electrocatalytic reformer 62. A pressure sensor is indicated at 92, and a flow sensor 76/94.

[0038] A power source 96 is connected to the electrocatalytic reformer, for supplying power to the individual elements thereof, to generate heat, as described above.

[0039] The various sensors 90, 92 and 94, and also the power supply 96 are connected to the process control computer 66. It will also be understood that the computer 66 could be connected to other sensors, and other control elements, for example, the load signal 74.

[0040] Accordingly, the process control computer 66 can constantly control the temperature in the electrocatalytic reformer 62. In addition to the sensors shown, the specific electrical resistance of the reformer 62 can be measured as an indication of its temperature. In this way, the electrical energy supplied to the electrocatalytic reformer 62 can be adjusted such that the reaction temperature in the reformer 62 is maintained in the optimal range. More specifically, it is preferred to use "forward-looking" power regulation, i.e.

anticipating future demand and adjusting the catalytic reformer 62 accordingly. This provides a dynamic operating characteristic, without having to accept the disadvantages with respect to the degree of conversion and the composition of the synthesized gas. In effect, this requires that, when the power demand from the fuel cell stack 64 increases, simultaneously, the heating power supplied to the electrocatalytic reformer 62 and the flow of methanol and water from the supplies 68,70 are all increased.

[0041] It will also be understood that all the heating strategies for the electrocatalytic reformer 62, as detailed at Figures 1, 2 and 3 can be employed simultaneously or in various combinations.

[0042] Reference will now be made to Figure 5, which shows a variant of the system or circuit of Figure 4. Again, for simplicity and brevity, like components are given the same reference numeral and the description of these components is not repeated. The system of Figure 5 is indicated generally by the reference 100.

[0043] In Figure 5, the heat exchanger 78 has been replaced by a thermocatalytic reformer 102. This provides for reformation of the methanol and water mixture, to generate hydrogen and carbon dioxide by use of catalysts and heat supplied from a catalytic burner 104. As for the catalytic burner of Figure 4, the anode exhaust line 80 is connected to the catalytic burner 104, together with inlets 106 for air and 108 for methanol. Thus, again, residual hydrocarbons and the like, together with added methanol are consumed in the catalytic burner 104, to generate carbon dioxide, water and heat. Resultant waste gas is exhausted at 110 and heat is transferred as indicated schematically, to the thermocatalytic reformer 102.

[0044] In this embodiment, the electrocatalytic reformer 62 then acts merely as a booster reformer, to carry out any residual reformation required. Its size and dimensions can be adjusted accordingly. Thus, the electrocatalytic reformer 62 provides two main functions here. Firstly, it provides a security function, to assure an optimal composition of the synthesized gas flowing to the fuel cell stack, on account of the ability to adjust its reaction conditions to an optimal state. Secondly, the "booster"

function of the electrocatalytic reformer 62 is in a sense that, on account of its high internal dynamics, it can respond much faster to change in demand by the fuel stack 64 as compared to the thermocatalytic reformer 102.

[0045] The individual ECR elements 20 are preferably made of a ceramic, more preferably silicon or silicon carbide, which preferably is in the shape of a monolithic honeycomb structure. The elements 20 can also be formed from wire meshes of a suitable metal, for example, an aluminum-chrome-iron alloy, these meshes can be provided in the form of a rolled up sheet.

[0046] Where the elements 20 are formed from silicon or silicon carbide, it is preferred for the material to have porosity in the range of 20 to 80%, more preferably in the range of 40 to 70%, with an electrical resistance in the range 0.001 Ωcm to 10M Ωcm .

[0047] Advantageously, the ceramic, either silicon or silicon carbide, is formed as a porous, lateral, flowable pipe. In accordance with the present invention, one or both surfaces of the pipe are coated with a catalyst selected from the Group VIII metals of the periodic table (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt), Cu and Zn. It will be understood that the catalyst can comprise combinations of two or more of these metals, for promoting endothermal reforming reactions.

[0048] Similarly, the outer pipe 12 can also be coated with a catalyst selected from the same group of metals in the same manner. It is preferably coated on the outside, to provide a catalyst for conversion of anode exhaust gases; it is also possible to consider coating the outer pipe 12 on the inside thereof, to enhance a catalytic reformation of the incoming reactive components.

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CLAIMS:

1. An apparatus for the chemical conversion of a hydrocarbon with at least water, to produce a hydrogen-rich synthesized gas for use in fuel cells, the apparatus including a component formed of an electrically conductive material and having a catalytically coated surface, whereby, in use, the component can be electrically heated, to promote endothermic reactions catalyzed by the catalytically coated surface.
2. An apparatus as claimed in claim 1, wherein the component is formed from one of silicon and silicon carbide.
3. An apparatus as claimed in claim 2, wherein the material of the component has a monolithic honeycomb structure.
4. An apparatus as claimed in claim 1, wherein the material of the component comprises an aluminum-chrome-iron alloy.
5. An apparatus as claimed in claim 4 wherein the aluminum-chrome-iron alloy is formed as a wire mesh formed into a roll.
6. An apparatus as claimed in claim 3, wherein the material of the component has porosity in the range 20-80%.
7. An apparatus as claimed in claim 6, wherein the material of the component has porosity in the range 40-70%.
8. An apparatus as claimed in claim 6, wherein the material of the component has an electrical resistance in the range 0.001Ωcm to 10MΩcm.
9. An apparatus as claimed in claim 2, wherein the material of the component is provided in the form of a porous, lateral, flowable pipe.
10. An apparatus as claimed in any one of claims 1-9, wherein the catalytically coated surface of the component includes a catalyst

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comprising at least one metal selected from Group VIII metals of the periodic table (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt), Cu and Zn.

11. An apparatus as claimed in claim 10, wherein the catalyst comprises a combination of two or more of said metals.
12. An apparatus as claimed in claim 1, wherein the component comprises an elongate, inner pipe, and wherein the apparatus includes an outer pipe enclosing the inner pipe and defining an annular chamber, thereby to form an electrocatalytic reformer element.
13. An apparatus as claimed in claim 12, wherein the outer pipe is provided with a catalytic coating for promoting exothermal reactions of anode exhaust gas with at least one of air and oxygen.
14. An apparatus as claimed in claim 13 which includes a plurality of electrocatalytic reformer elements, a vessel enclosing the elements, a first port and a first manifold providing communication to the annular chambers of the electrocatalytic reformer elements, a second port and a second manifold providing communication to the interior of the inner pipes of the electrocatalytic reformer elements, a chamber around the electrocatalytic reformer elements, and third and fourth ports providing an inlet and an outlet for anodized exhaust gases around the electrocatalytic reformer elements.
15. A method of chemically converting a hydrocarbon to generate a hydrogen-rich synthesized gas, the method comprising:
 - (a) Providing the hydrocarbon as one of a liquid, vapor and gas;
 - (b) Supplying water to at least one of the liquid and vapor state;
 - (c) Supplying the hydrocarbon and the water to an apparatus including at least one electrocatalytic reformer element having a component with a catalytically coated surface, whereby the

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hydrocarbon and the water are exposed to the catalytically coated surface;

- (d) Passing electric current through the component, to heat the component and to provide heat for endothermic reaction of the hydrocarbon and the water.
16. A method as claimed in claim 15, which includes supplying a mixture of water with one of air and oxygen.
17. A method as claimed in claim 15, that includes measuring the resistance of at least one electrocatalytic reformer element, and determining the temperature from the measured resistance.
18. A method as claimed in claim 17, which includes adjusting the electric current to maintain said at least one reformer element at a desired temperature, and adjusting the temperature in dependence upon anticipated changes in demand for converted hydrocarbon.
19. A method as claimed in claim 15, which includes providing the component of the electrocatalytic reformer element as a porous component, and passing the hydrocarbon and the water through the porous component.
20. A method as claimed in claim 19, which includes providing the component as a porous pipe, and forming the catalytically coated surface on exposed surfaces of the pipe.
21. A method as claimed in claim 20, which includes passing the hydrocarbon and the water radially inwards from the outside to the inside of the pipe.
22. A method as claimed in claim 20, which includes passing the hydrocarbon and the water radially outwards from the inside to the outside of the pipe.

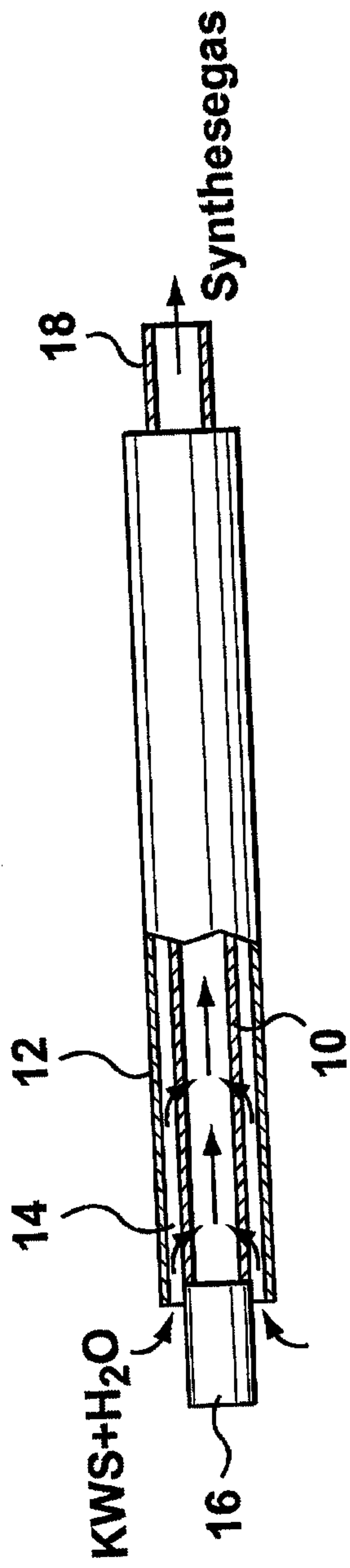


FIG. 1

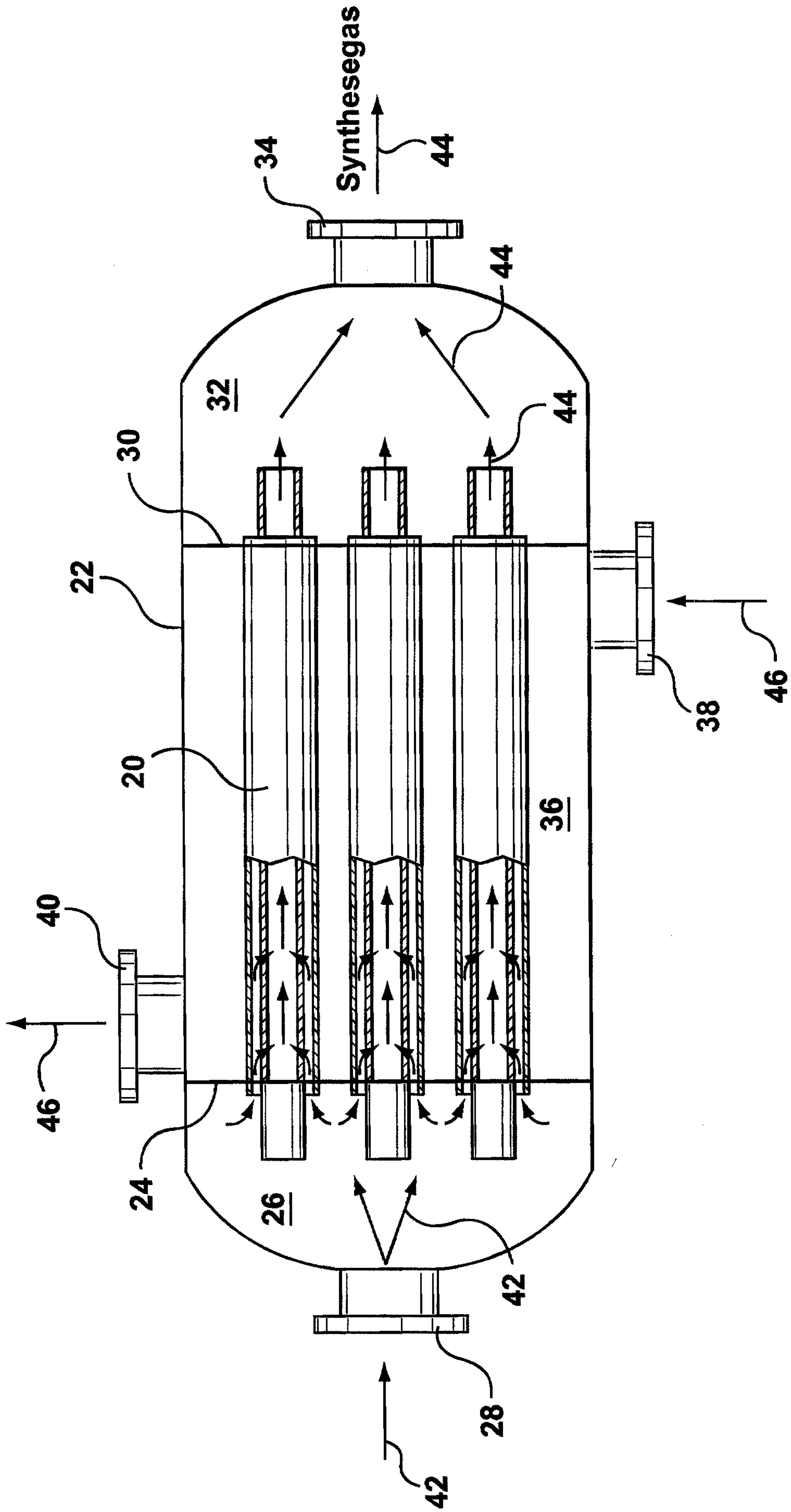


FIG. 2

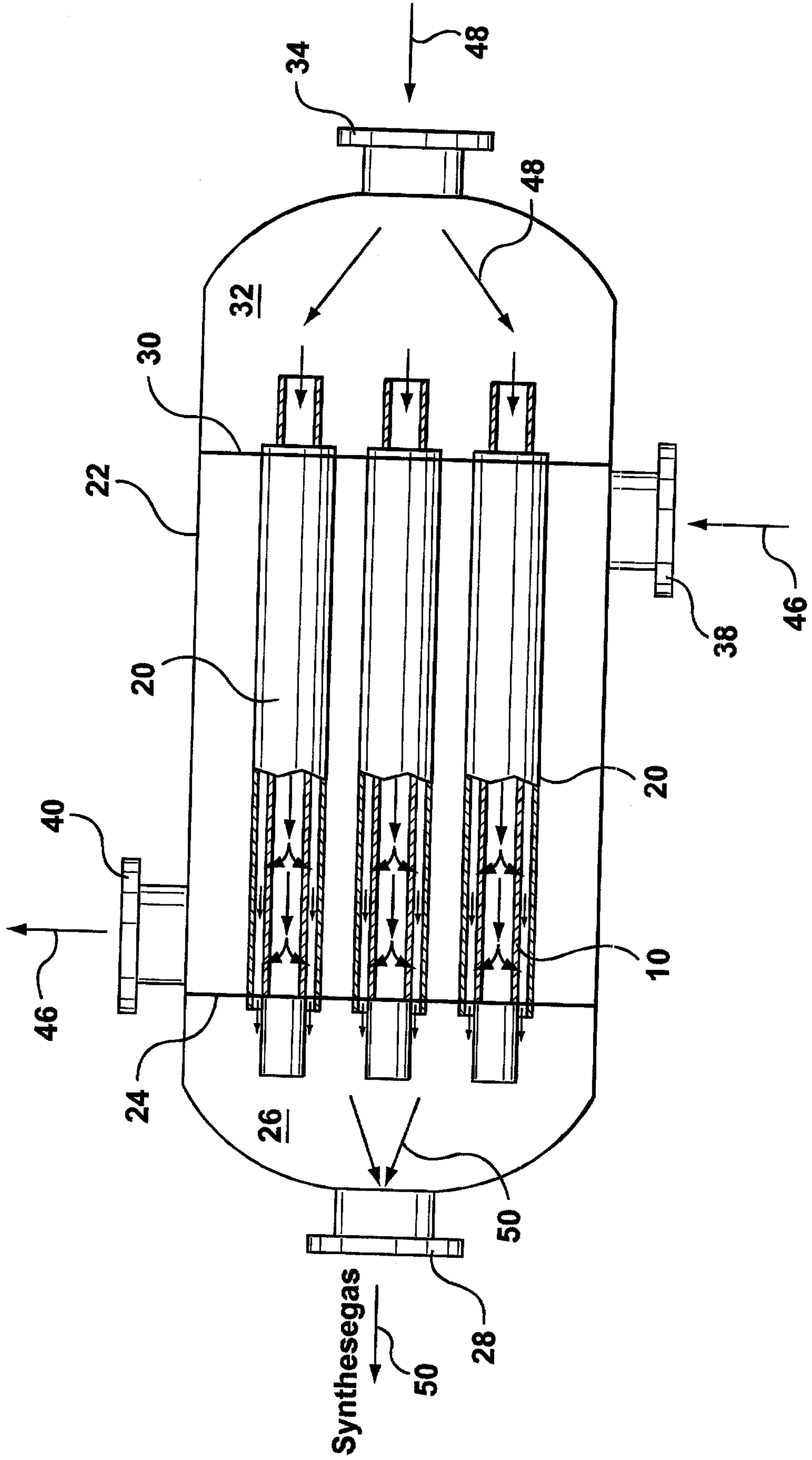


FIG. 3

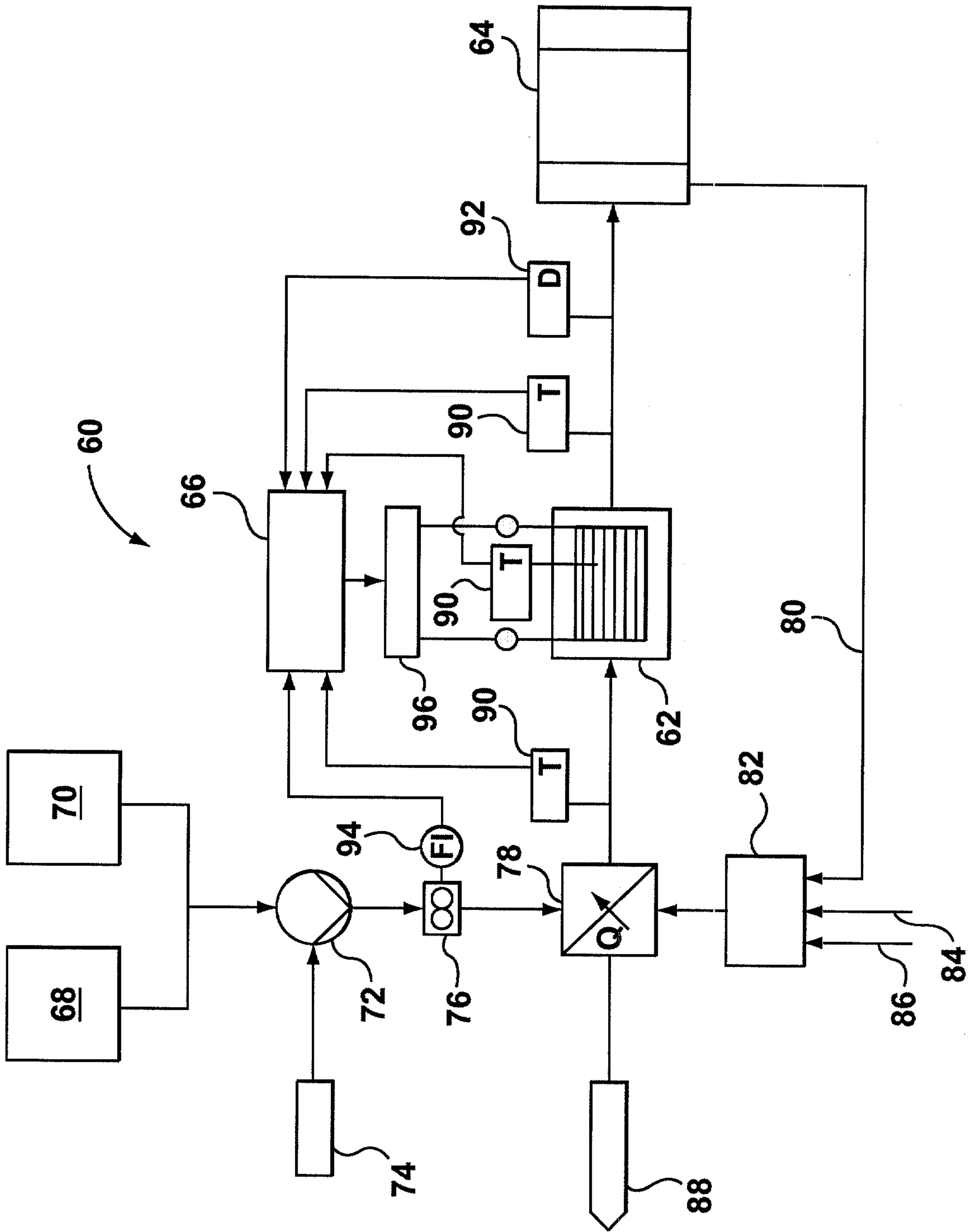


FIG. 4

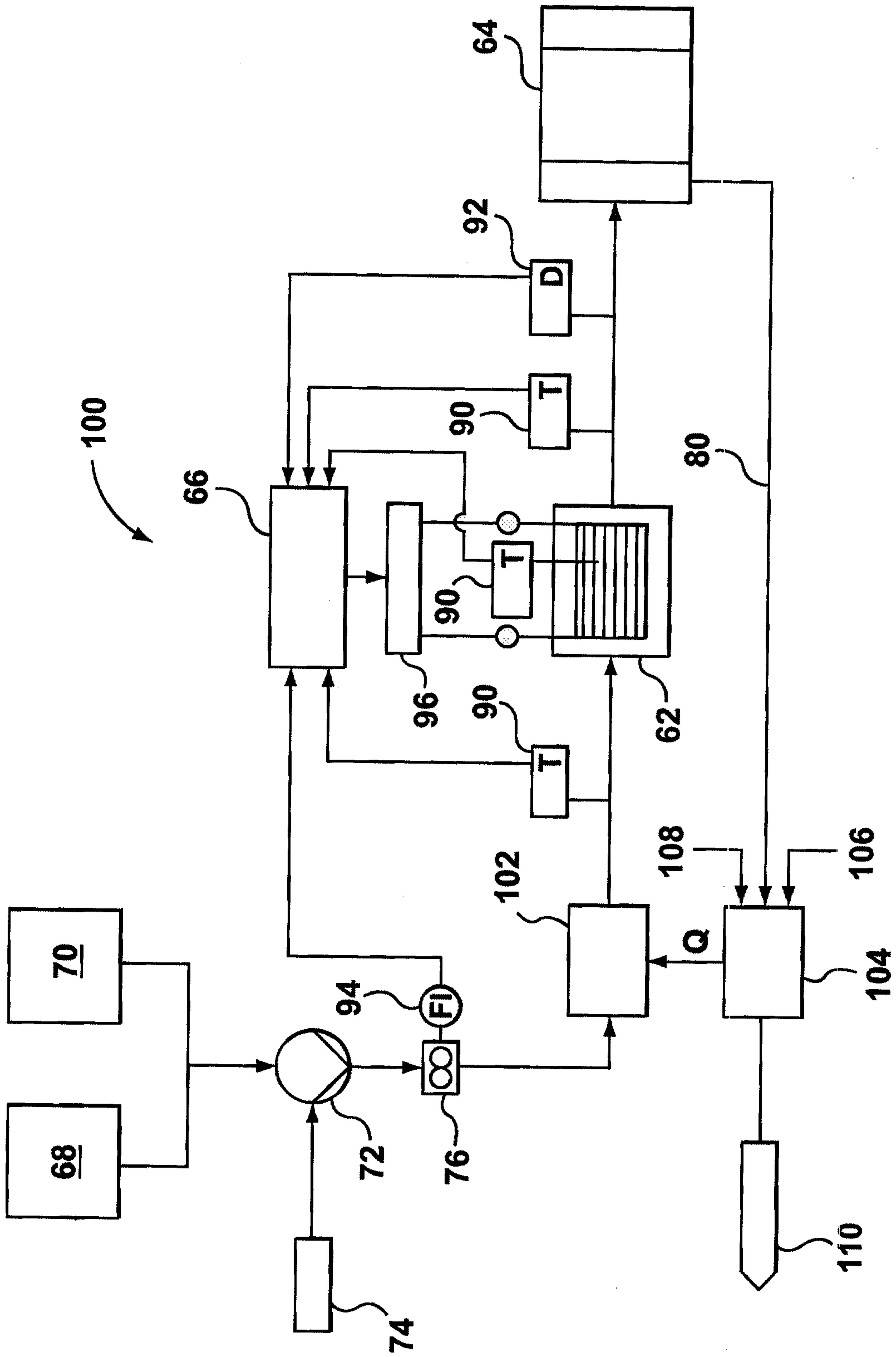


FIG. 5