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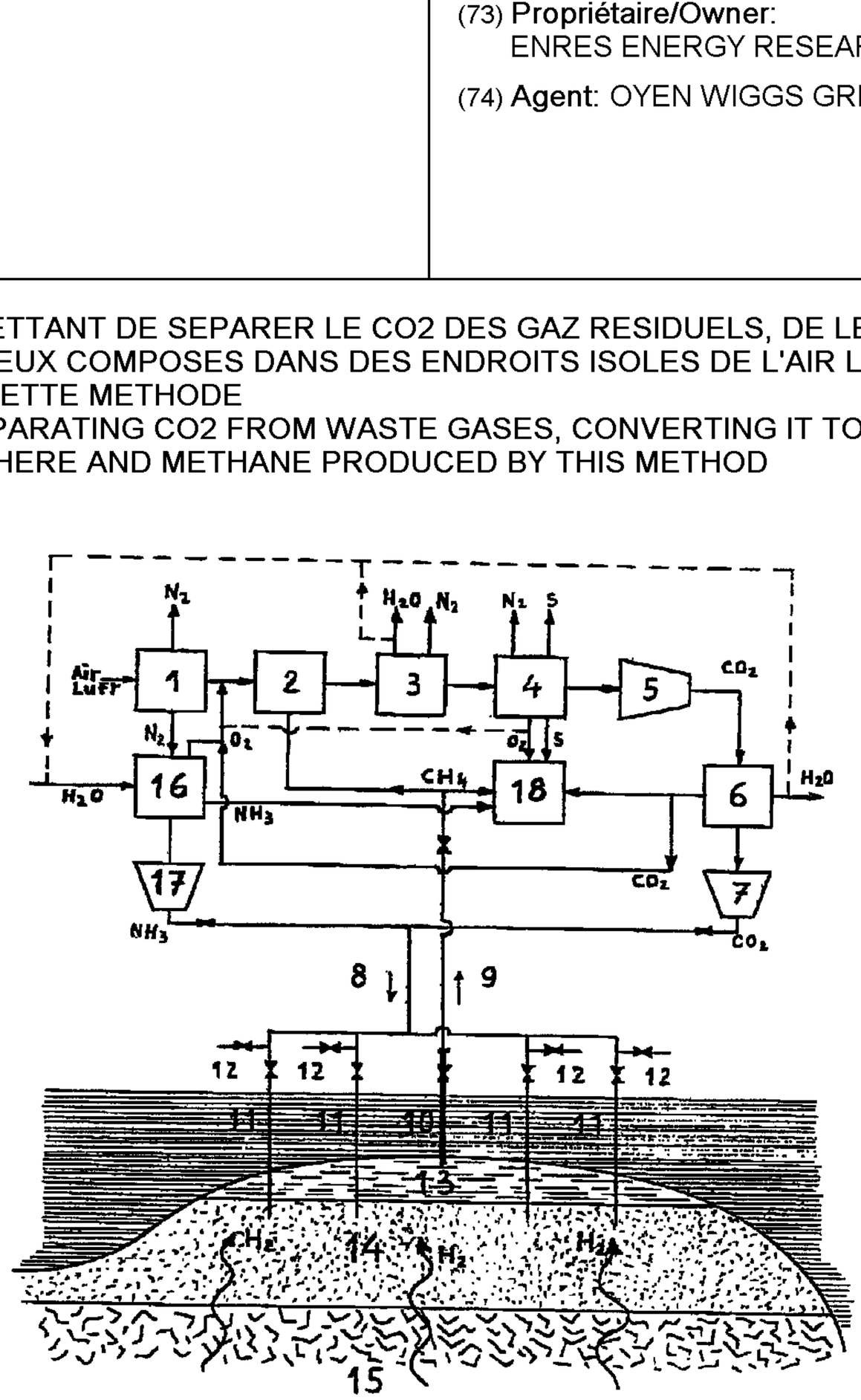
(54) Titre : METHODE PERMETTANT DE SEPARER LE CO2 DES GAZ RESIDUELS, DE LE TRANSFORMER EN CH4 ET DE STOCKER LES DEUX COMPOSES DANS DES ENDROITS ISOLES DE L'AIR LIBRE, ET METHANE PRODUIT A L'AIDE DE CETTE METHODE

(54) Title: METHOD FOR SEPARATING CO2 FROM WASTE GASES, CONVERTING IT TO CH4 AND STORING BOTH OUTSIDE THE ATMOSPHERE AND METHANE PRODUCED BY THIS METHOD



(57) Abrégé/Abstract:
The CO_2 is separated from waste gases by known technical means and stored in the underground (see drawing). By additions to the CO_2, according to the invention, of H_2 or NH_3, methano-genic bacteria, bacteria substrate, catalysators and/or inhibitors the CO_2 is reduced during the underground sto-rage to CH_4. The storage is possible in aquifers, natural gas reservoirs or oil and/or gas generating rock formations. Due to the equal volumes of CO_2 and CH_4 the process is a closed cycle and of constant pressure. Natural gas becomes a renewable energy.

Abstract

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Method for separating CO_2 from waste gases, converting it to CH_4 and storing both outside the atmosphere and methane produced by this method

Beside the methane emanating from technical installations and by a natural way from the soil, carbon dioxide is the most important greenhouse gas. It destructs the ozone belt which is protecting life on earth from to intensive ultraviolet radiation.

Since more than a decade technicians and scientists are seeking for methods and means in order to eliminate the noxious CO_2 from waste gases and to store it in the form of an insoluble chemical compound or outside of the atmosphere of the earth. There are technically feasible proposals (partly tested in pilot plants) in order to separate the CO_2 from combustion or other waste gases, to concentrate it (by liquefiing), to use it industrially or to store it underground (in aquifers, deep sea or to stimulate poorly producing oil reservoirs). One of the practical ways to concentrate the CO_2 consists of reintroducing the combustion CO_2 by a secondary cycle in the combustion process after having made the combustion-air nitrogen-free by catalytic and/or cryogenic separation. Instead of the use in neighbouring chemical plants, the binding of CO_2 on sea weed as well as the bacterial fermentation of the CO_2 in special reactors have been technically examined in pilot plants. These latter processes need either large storing volumes for the CO_2 resp. CH_4 produced or an absolutely constant operation of the CO_2 producing installations, because these binding resp. fermentation processes are not flexible. Specially thermal power plants demand such flexibility in order to cover daily, weekly and seasonal peaks.

The present invention permits such flexible operation. The invention comprises the pumping of the separated, purified, liquefied and dryed CO_2 in a pipeline to a nearby aquifer, a natural gas reservoir or an oil bearing structure and in-

jecting the CO_2 into it and treating the structures in the first two cases previously with bacteria cultures (and ev. suitable substrate). In the third case the methanogenic bacteria and the substrate will be already naturally present so that the conversion of the CO_2 to CH_4 may immediately begin. For that purpose the following conditions have to be naturally present or artificially created (see bibliography in the annex):

1. There has to be enough H_2 for reduction of the CO_2 (or as electron donor) in the structure, either
   - in free form produced by metamorphic rock in the depth, or
   - by bacterial direct transmission from organic H_2 containing substrate, or
   - by bacterial splitting off of the pore water, or
   - by artificial feeding of H_2 in pure form or in form of ammonia (NH_3) which forms in the structure, in contact with the pore water, partly ammoniumhydroxide NH_4OH and with the CO_2 urea $(H_2N)_2CO$ which, by bacteria-aided hydrolizing, splits off free H_2, or
   - e.g. by artificial feeding of formiates $NaHCO_2$ or $Ca(HCO_2)_2$.

2. The sulfate content of the sediment in the structure has to be either
   - enough poor that the sulfate no more can selectively bind the H_2 necessary for the CO_2 reduction, and/or
   - no H_2S or other sulfide may act as methanogenic poison, or
   - the sulfate competing with the CO_2 reduction may be artificially blocked by an inhibitor (e.g. Na-molybdate or fluorlactate), or
   - by feeding H_2 into the structure enough long before the CO_2 injection, so that the sulfate will be sufficiently reduced.

3. There must be present in the sediment a methanogenic bacterial population large enough (e.g. methanococcus, methanobacterium formicicum, methanobacterium thermoautotrophicum, methanosarcina barkerii, or other photosynthetic bacteria) which is able,

   - to split off free H_2 from the pore water or from H_2S, and
   - to reduce the CO_2 to CH_4 sufficiently,
   - eventually by addition of catalysators like e.g. palladium,
   - adding, if necessary, the needed bacterial population and/or the substrate artificially.

The main condition to realize the CO_2 conversion is a drilling (in a aquifer, a natural gas reservoir or an oil bearing formation) across the gas or oil containing structure till in the aquatic phase thereunder, with cores from the interesting stratums and analyzing these cores in the laboratory. The main aim is finding (or not) the necessary bacteria, the substrate whereon they live, the chemical composition of all sediment parts, the presence of H_2, sulfate as well as the absence of Na-AL-silicates. With these results it will be further established under which conditions the found (or added) bacteria and the substrate are able to produce CH_4 from CO_2 and how much.

By adding other substrates (e.g. acetate, methanol, methylamine, dihydronicotinamide, dihydro-5-diazaflavine, 2-mercaptoethane-sulfonic acid and like) it will be established if the CO_2 reduction to CH_4 is intensified resp. accelerated. With a given substrate the addition of CO_2, in the presence of H_2, increases the CH_4 production normally by more than one magnitude. The same is the result when H_2 is added in presence of CO_2. Consequently, both gases have to be present together for ensuring an optimal CH_4 production. In this connection it may be noted that the 4 H atoms needed for the CH_4 do not originate from the added H_2 gas (or NH_3), but from the pore

water. The H_2 gas serves only as electron donor. All research work hitherto existing shows that bacteria and substrate are only a transition station for the H_2 necessary for CO_2 reduction. Consequently, during the laboratory experiments the consumption of bacteria and substrate, as well naturally present as also artificially added matter, has to be established. Concerning the practical use of the invention, a consumption of bacteria and/or substrate to high could dictate an economic limit.

As soon as the different questions are resolved by the laboratory experiments, the same tests are following under in situ conditions of pressure and temperature (still in the laboratory). This clarifying by steps conducts to the optimum method which is than tryed out in a pilot test 1 : 1 after a second drilling (observation drilling) in relative vicinity to the first drilling. If there is a flow direction of the pore water, the testing has to be made on the low side and the CO_2 addition on the high side of the flow. An increasing CH_4 content signifies a positive conversion, which is confirmed by an also increasing H_2 content.

This is specially the case with the addition of ammonia gas instead of pure H_2. The basic chemical transformation according to the formula $CO_2 + 4\ H_2 = CH_4 + 2\ H_2O$ becomes with ammonia in molecular writing $2\ CO_2 + 6\ NH_3 = 2\ CH_4 + 3\ N_2 + 4\ H_2O + H_2$, what means that the transformation yields a H_2 excess which passes over in the next step, so that, in constant operation, will be an equilibrium $CO_2 : NH_3$ of approx. 1 : 2,7. But this will only be the case if the H_2 procurement is not aided by bacterial assistance. Such bacterial assistance liberates practically always supplemental H_2 from organic substrates or from pore water, eventually supported by H_2 from metamorphic rock, what reduces the CO_2/NH_3 proportion from 2,7 to 1 and less.

The CO_2 reduction produces in every case additional pore water. The use of NH_3 as H_2 donor has the special disadvantage of producing the double quantity of pore water compared to the use of pure H_2 and that 40 % of the NH_3 gas remain as N_2 (ballast) in the structure and appear occasionally as pollution in the produced CH_4 and demand a separation (purification). Economically it could be better to inject pure H_2 under high pressure as emulsion in the liquid CO_2 (with or without emulgators). At the maximum possible proportion of volume CO_2 : H_2 of 1 : 4 the emulsion becomes foamy and at smaller H_2 requirements and higher pressure the H_2 is broken up in small gas bubbles in the liquid CO_2.

The liquid medium CO_2 covers than the inner surface of the steel tube and not the H_2 gas and forms a protection layer having itself a soluted proportion H_2 : CO_2 (volume) of approx. 1 : 100 (at the normally present conditions of pressure and temperature) and protects in such manner the steel from brittleness by direct Hydrogen attack. For this protection it is essential that there is a turbulent flow in order to maintain the CO_2/H_2 emulsion during injection in the structure. Moreover the structure temperature (approx. 80°C) is not high enough to really cause hydrogen brittleness (over 300°C). Because of the difficulty to control long pipelines, the H_2 should be produced in the field at the injection point. But there is no danger for an autoreduction of the CO_2 to CH_4 within the CO_2/H_2 mix in the injection tube at the existing temperatures.

If the CO_2 conversion takes place in a aquifer, the addition of H_2, bacteria and/or substrate is unavoidable, .. but may be avoidable in a natural gas reservoir created by gas migration and is most probably not necessary in oil and gas bearing (generating) formations. The eventual additions beside the CO_2 (NH_3, H_2, bacteria, substrates, catalysators,

inhibitors) shall not pollute the groundwater of aquifers being situated above the deep lying brack waters. For these latter the pollution aspect is of minor significance.

The enclosed drawing shows schematically and as an example a modern installation according to the invention, applied on a anticlinal structure. The drawing considers only process phases. In the whole process N_2 is considered as ballast. It is separated from the combustion air catalytically or cryogenically in phase 1, being afterwards vented directly to the atmosphere or e.g. in a NH_3 production plant 16. The remaining O_2, CO_2 from air, noble gases and some polluants are burnt in the following combustion plant 2 (gas turbine, gas motor, boiler and like). In the separation plant 3 the combustion products H_2 and CO_2 as well as N_2 (remaining N_2 or total N_2 in the case of absence of phase 1) are separated from each other. The catalysator plant 4 reduces resp. oxidizes the oxides NOx, SO_2, CO to N_2, elemental sulfur, oxygen and CO_2, feeding practically pure CO_2 in the compressor 5. Here the CO_2 is liquefied, cooled down (not shown in the drawing) and is stored in the reservoir 6. Eventually here accumulating water may be drained off in order to be reconducted in the process phase 16 or to the environment. Such reconduction is also possible for CO_2 from the reservoir 6 to the burning installation 2 (if there is air separation in phase 1) in order to create a combustion in a O_2/CO_2 atmosphere.

If there is no or not enough H_2 present in the storage and conversion structure 13, 14 to ensure complete reduction of the CO_2, the process is equipped with an ammonia plant 16. The nitrogen N_2 for the production of NH_3 comes from the phase 1, the necessary H_2 from fresh water and the stripped off O_2 will be sent in the combustion process in phase 2.

CO_2 and NH_3 are pumped on identical high pressure in the compressors 7 resp. 17 and flow as a mix along the pipeline 8 to the storage field 13. If during this transport urea $(H_2N)_2CO$ should be formed from the CO_2/NH_3 mix, it is only of interest in view to the also forming H_2O as byproduct, because this water would form together with the CO_2 the acid H_2CO_3 which could attack the pipeline by internal corrosion. At the same moment the NH_3 would form in the presence of H_2O the basic NH_4OH able to neutralize - at least partly - the dangerous H_2CO_3. It is indicated to check for internal corrosion and to add eventually a corrosion inhibitor. Another possibility is the batchwise separated transport of the liquid CO_2 and NH_3 as usual in oil and product pipelines.

According to the idea of the present invention, the storage field (aquifer, natural gas reservoir, oil generating rock structure) serves as conversion reactor for the CO_2:
The injection drillings 11 for the CO_2, the H_2 (or NH_3) are arranged around the extraction drilling 10 for the CH_4 in such a manner that there will be a central flowing.
In the drawing the 4 injection drillings 11 are unrolled to one plane, but in reality they are arranged in a square around the extraction drilling 10. The injection drillings 11 reach in the pore water containing part 14 of the anticlinale, because the reduction of the CO_2 to CH_4 takes place in this part. In order to take the cores for the laboratory experiments mentioned further above, the drilling 10 reaches initially the pore water part 14, is later cemented and than perforated. The CH_4 produced from the CO_2 is first stored in the water part 14 and - with increasing volume - comes in contact with the gaseous part 13 and forms so a compact gas phase. During the in situ tests in scale 1 : 1 mentioned above the drilling 10 reaches in the water part 14. From the injection drillings 11 the produced CH_4 is driven by a small overpressure to the extraction drilling 10. This tech-

nique is also used in the case of CO_2 pressuring (stimulation) of poorly producing oil fields. This known technique also provides for a rich experience concerning the compatibility of the rock and CO_2.

Each injection drilling 11 has a nozzle 12 for the injection of separate additions of bacteria, substrates, inhibitors and/or catalysators. The extraction drilling 10 is joined at his head to the gas pipeline 9 which in her turn is joined to the combustion plant 2. Under the aquifer 14 with the gas reservoir 13 there is the rock basis 15, furnishing eventually enough H_2 diffusing from metamorphic rock in the depth to the top.

The operation of the field installations is very similar to that of a natural gas storing field with injection and extraction drillings. The volumes of the consumed CO_2 and CH_4 formed from it being theoretically equal (appart from small losses), the pressure in the storage structure 13 (or conversion reactor 13) remains stable for a long time because there is a practically closed circuit CO_2-CH_4. The only supplemental feeding quantities are the H_2 donor (e.g. NH_3), catalysators, inhibitors and eventually bacteria and substrates. Natural gas becomes in this way a renewable energy.

In order to preserve clearness, the following installations are omitted from the drawing: pumps and compressors only for feeding and circulation purposes between the process phases, coolers, separators, compensation tanks and regulator parts.

In view to completeness the drawing shows also industries 18 in vicinity to the power plant 2, which can use as well CH_4 as CO_2 and other byproducts of the whole process. This guarantees an optimal utilization combined with high flexibility.

Claims

1. Method for separating CO_2 from waste gases of combustion plants, storing said CO_2 and bacterially converting said CO_2 to CH_4, comprising the steps of:

obtaining CO_2 separated from waste gases of combustion plants;

injecting said separated CO_2 in an underground natural reservoir in geological porous or finely cleaved sediment of an underground gas or oil field or aquifer which forms said natural reservoir, said reservoir being surrounded and covered by non-porous material; and

converting said CO_2 to CH_4 through bacterial conversion and storing said CO_2 and CH_4 gases within said reservoir.

2. Method according to claim 1, wherein the underground natural reservoir serves simultaneously as a bacterial-chemical reactor for the conversion of the CO_2 to CH_4 as well as storage space for CO_2 and CH_4.

3. Method according to claim 1, wherein the CO_2 is injected in the underground natural reservoir by means of drillings.

4. Method according to claim 3, wherein the injection of the CO_2 is accompanied by hydrogen spending substances, in gaseous or liquid form, continuously or batchwise.

5. Method according to claim 4, wherein H_2 gas is injected together with CO_2 in the form of a H_2 /CO_2 foam or in the form of small H_2 bubbles emulgated in liquid CO_2.

6. Method according to claim 5, wherein said drillings are provided above ground with a connecting pipe and nozzle in order to pump methanogenic bacteria, substrate as well as eventual catalysators or inhibitors, or both catalysators and inhibitors.

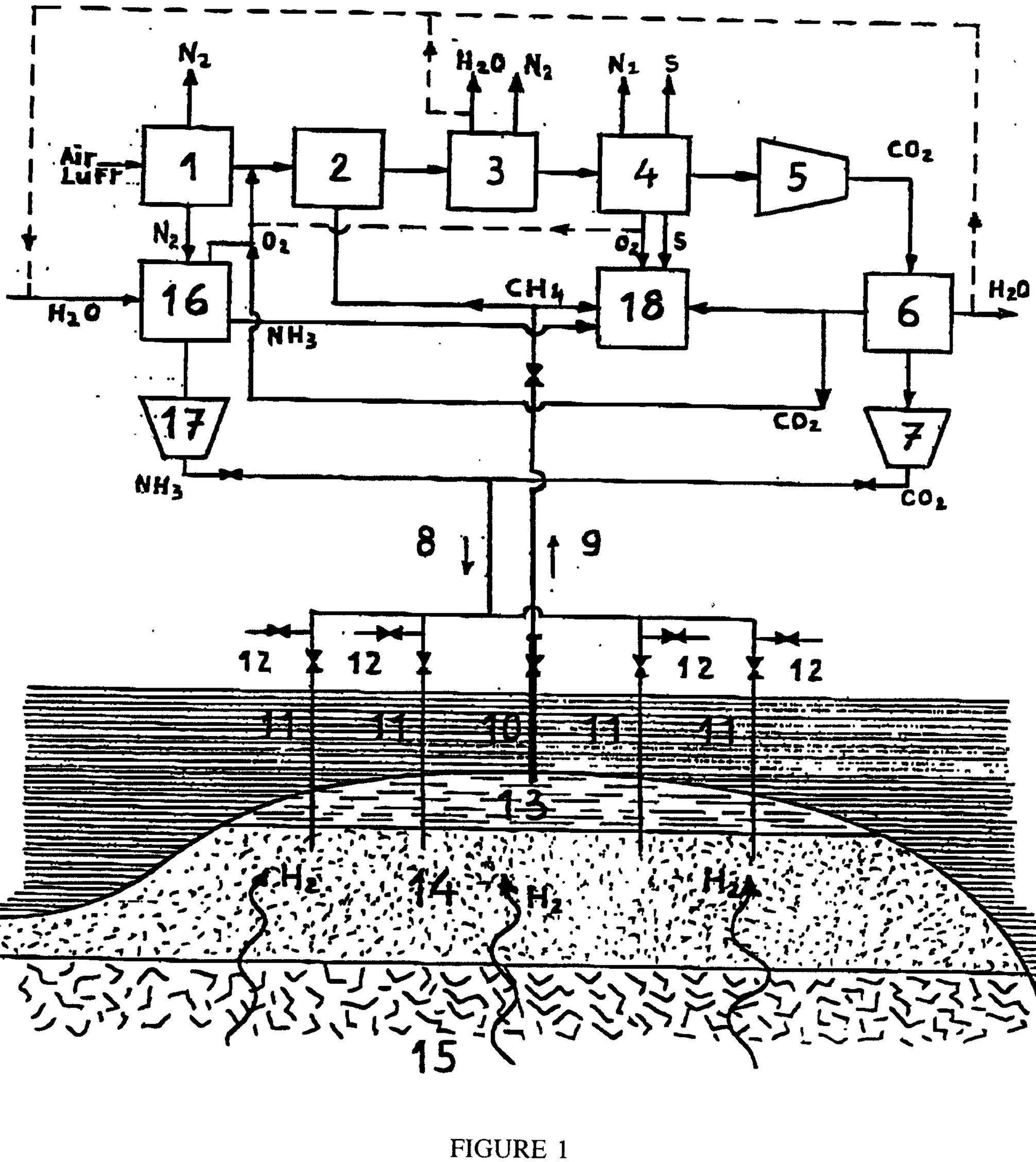
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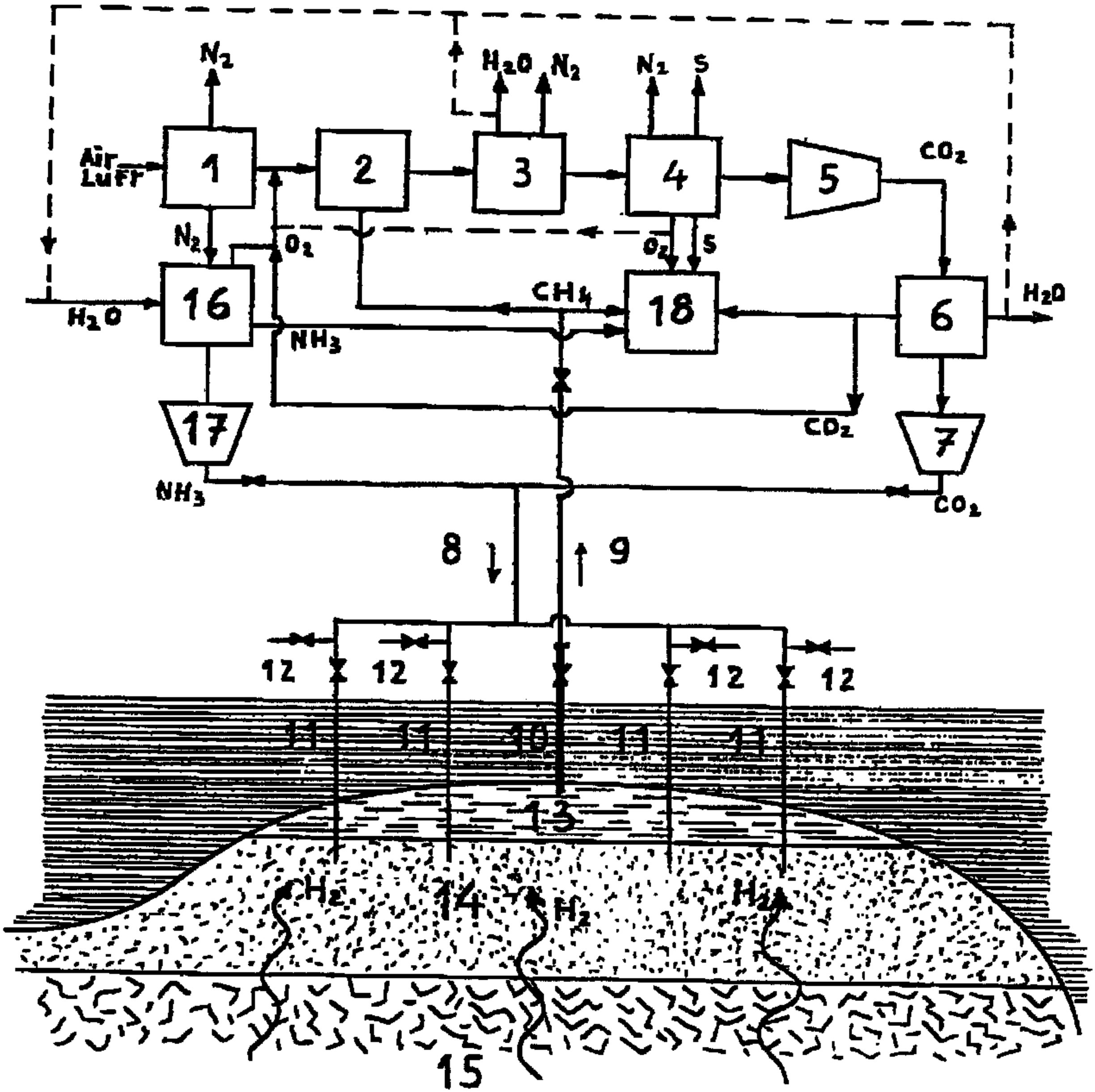
FIGURE 1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