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(54) METHOD FOR PRODUCING FUEL FROM CAPTURED CARBON DIOXIDE

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(57) **ABSTRACT**

The invention provides a method for producing combustible fuels from a gaseous mixture containing carbon dioxide, which comprises: (i) capturing CO2 from said gaseous mixture by means of K2CO3, thus forming KHCO3; (ii) releasing the CO2 from said KHCO3; and (iii) subsequently producing fuel from the released CO2 by reaction with hydrogen.

METHOD FOR PRODUCING FUEL FROM CAPTURED CARBON DIOXIDE

FIELD OF THE INVENTION

[0001] The present invention relates to a method for capturing carbon dioxide from a gaseous mixture containing carbon dioxide, e.g., from the atmosphere, and subsequently using this carbon dioxide for the production of fuel.

BACKGROUND OF THE INVENTION

[0002] Greenhouse gases include carbon dioxide, methane, nitrous oxide and water vapor. While greenhouse gases occur naturally in the atmosphere, human activities also produce greenhouse gas emissions and are responsible for creating new ones. Carbon dioxide (CO_2) is the most common greenhouse gas released by human activities, resulting from the extensive use of fossil fuel (coal, petroleum, natural gas). One of the main challenges modern civilization is facing is the increase of carbon dioxide in the atmosphere, affecting the greenhouse effect and global warming. Another problem arises from the extensive use of fossil fuel thus diminishing the global fuel reserves.

[0003] Renewable energy sources, that capture their energy from existing flows of energy, from on-going natural processes, such as sunshine, wind, flowing water, biological processes and geothermal heat flows, can be used for generating electricity, and there is a growing demand for methods of producing fuel using electricity.

[0004] Numerous attempts for extracting CO_2 directly from car exhausts or power plants have been made, most of them involving reactions of exhausted gases with organic amine compounds or strong bases like calcium hydroxide or sodium hydroxide. In processes using organic amines, a solution of amine and water is contacted with the gas, whereby the amine and the CO_2 undergo a chemical reaction forming a rich amine that is soluble in the water. The rich amine solution is pumped to a desorber where it is heated, reversing the reaction and releasing pure CO_2 gas. The disadvantage of this method is the fact that organic amine bases are expensive and unstable.

[0005] Carbon dioxide and mixtures containing it have been proposed for production of combustible fuels. For example, U.S. Pat. No. 4,140,602 discloses a chemical method for combustible fuel production by converting carbon dioxide in the atmosphere to a carbonate such as an alkali carbonate, following which the recovered carbonate is combined with hydrogen gas to produce combustible fuels e.g. methane and methanol. The method includes the additional step of reacting the alkali carbonate with calcium hydroxide to form calcium carbonate. The disadvantages of this method resides in the use of the strong base compound $Ca(OH)_2$, forming $CaCO_3$, that requires considerable amount of energy for the thermal release of CO_2.

SUMMARY OF THE INVENTION

[0006] The present invention relates to a method for producing combustible fuels from a gaseous mixture containing carbon dioxide, which comprises:

[0007] (i) capturing CO_2 from said gaseous mixture by means of K_2CO_3, thus forming $KHCO_3$;

[0008] (ii) releasing the CO_2 from said $KHCO_3$; and

[0009] (iii) subsequently producing fuel from the released CO_2 by reaction with hydrogen.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The method of the present invention enables the production of combustible fuels, using as preferred starting material the highly available atmospheric carbon dioxide, and returning the CO_2 produced by fuel combustion to the atmosphere, thus maintaining the equilibrium of the CO_2 in the atmosphere. The method is based on well known in the art reactions such as thermal catalytic and electrochemical reactions, utilizing the reversibility of these reactions and carrying out the reverse reaction by modifying the operating pressure and/or the electrical voltage supplied to the process.

[0011] The reaction between the CO_2 and K_2CO_3 in step (i) may be performed by bubbling air in water through an aqueous solution of K_2CO_3 or by spraying droplets of K_2CO_3 in aqueous solution into a stream of air. In both methods, the atmospheric CO_2 reacts with the K_2CO_3 to form $KHCO_3$ according to the following reaction:

$$K_2CO_3+H_2O+CO_2 \rightarrow 2KHCO_3$$

[0012] In the next step, CO_2 is released from the $KHCO_3$.

[0013] In one embodiment of the invention, the CO_2 is released by heating the $KHCO_3$ to a temperature sufficient to liberate the CO_2, according to the following reaction, thus recycling the K_2CO_3:

$$2KHCO_3+\text{Heat} \rightarrow K_2CO_3+H_2O+CO_2$$

[0014] In another embodiment, the CO_2 is released from the $KHCO_3$ obtained by an electrochemical process, according to the following reaction:

$$HCO_3^- - e \rightarrow .OH+CO_2$$

$$4(.OH) \rightarrow 2H_2O+O_2$$

[0015] The CO_2 obtained in step (ii) is then reacted with hydrogen to produce combustible fuels, such as methane and methanol.

[0016] In one embodiment, in which heat source producing very high temperatures is available, the reaction of CO_2 and hydrogen is conducted as a thermal catalytic reaction. One possible thermal catalytic reaction is a reverse operation of methane reforming. In steam methane reforming, methane is brought into contact with (excess) steam at high temperature and pressure, typically 800-1000° C. and 30-40 bar, over a catalyst, to produce a mixture of H_2, CO and CO_2. In the industry, the process is usually carried out in fixed bed or fluidized bed membrane reactors, using a Ni as the preferred catalyst, because of its low cost, or a noble metal catalyst such as Ru, Rh, Pd, Ir or Pt. The reverse methane reforming according to the invention is carried in the same type of reactors and using the same catalysts as in steam methane reforming, but using pressures varying according to the characteristics of the specific process, said pressure being always higher than the pressure used for the methane reforming.

[0017] In another embodiment, the reaction of CO_2 and hydrogen according to the invention is an electrochemical process, such as a reverse operation of a fuel cell.

[0018] A fuel cell is an electrochemical energy conversion device that converts the chemical energy of a fuel, e.g. hydrogen, and an oxidant, e.g. oxygen, to electrical energy and heat, without combustion. The device is similar to a battery but, unlike a battery, the fuel cell is designed for continuous replenishment of the reactants consumed, i.e., the fuel and the oxidant are typically stored outside of the fuel cell and transferred into the fuel cell as the reactants are consumed. In a typical fuel cell, the fuel is consumed at the anode and the oxidizer is consumed at the cathode. There are several types of fuel cells, each using a different chemistry. Fuel cells are usually classified by the type of electrolyte they use, and include phosphoric acid-based, proton exchange membrane, solid polymer, molten carbonate, solid oxide, alkaline, direct methanol, regenerative, zinc-air and protonic ceramic fuel cells.

[0019] In a fuel cell, if a hydrocarbon, such as methane, is the fuel, said hydrocarbon is reacted with oxygen obtained by electrolysis of water within the cell, thus forming CO_2 and hydrogen and generating electricity.

[0020] According to the present invention, a reverse operation of a fuel cell is carried out whereby electricity is supplied to a fuel cell containing CO_2, that reacts with hydrogen formed in situ by electrolysis of water, thus producing the desired hydrocarbon, e.g. methane fuel. The electrical voltage supplied to the process is determined based on the characteristics of the specific process performed but it is always higher than the electrical voltage generated in the opposite process, namely, the regular operation of the fuel cell.

[0021] In one preferred embodiment, the electrochemical process corresponds to an inverted direct methanol fuel cell (DMFC) and the fuel obtained is methanol.

[0022] DMFCs are low-temperature fuel cells operating at temperatures of 30-130° C. and using liquid methanol as the electrolyte, according to the reaction:

$$CH_3OH+\tfrac{3}{2}O_2 \rightarrow CO_2+2H_2O$$

[0023] The central component of DMFCs is the membrane electrode assembly, composed of membrane, catalyst and diffusion layers. The membrane may be a polymer with acid groups that are capable of splitting off protons and has them migrate through the membrane. The diffusion layer passes the fuels to the catalyst layer and removes the combustion products. In the catalyst layers, the electrochemical reaction takes place, in which chemical energy is converted into electric energy. The catalyst is provided with additives to apply it as a paste on a substrate, and it is usually based on a noble metal, such as platinum and platinum/ruthenium.

[0024] According to the present invention, the catalysts used for the reverse operation of the DMFC are the same used in the regular operation mode of the methanol fuel cell, and other parameters such as temperature and electrical voltage supplied to the process are determined based on the characteristics of the specific process performed.

[0025] In another preferred embodiment, the electrochemical process corresponds to an inverted molten carbonate fuel cell (MCFC) and the fuel obtained is a hydrocarbon, such as methane.

[0026] MCFCs are high-temperature fuel cell operating at temperatures of 600-650° C., and thus can achieve higher fuel-to-electricity and overall energy use efficiencies than low temperature fuel cells. The electrolyte used in MCFCs is an alkali carbonate such as Na_2CO_3, K_2CO_3, Li_2CO_3 or combinations thereof, that may be retained in a ceramic matrix, e.g. of $LiAlO_2$. In the fuel cell, the alkali carbonates melt into a highly conductive molten salt with carbonate ions providing ionic conduction through the electrolyte matrix. Nickel and nickel oxide are adequate to promote reaction on the anode and cathode, respectively, and expensive catalysts (noble metals) are not required.

[0027] The fuel consumed in MCFCs is usually a natural gas, mainly methane, and in this case methane and steam are converted into a hydrogen-rich gas inside the fuel cell stack (a process called "internal reforming"). The overall reaction performed within the cell is:

$$CH_4+O_2 \rightarrow CO_2+2H_2$$

[0028] According to the present invention, the operating conditions for the reverse operation of the MCFC (temperature and pressure) are similar to these in the regular operation mode of this cell. The exact conditions, as well as the voltage supplied to the process, are determined based on the characteristics of the specific process performed.

[0029] The methane or methanol obtained by the method of the invention may later be converted into longer hydrocarbons, using known chemical reactions.

1. A method for producing combustible fuels from a gaseous mixture containing carbon dioxide, which comprises:

(i) capturing CO_2 from said gaseous mixture by means of K_2CO_3, thus forming $KHCO_3$;

(ii) releasing the CO_2 from said $KHCO_3$; and

(iii) subsequently producing fuel from the released CO_2 by reaction with hydrogen.

2. The method of claim 1, wherein said gaseous mixture is air.

3. The method of claim 2, wherein the capture of CO_2 is performed by bubbling air in water through an aqueous solution of K_2CO_3.

4. The method of claim 2, wherein the capture of CO_2 is performed by spraying droplets of K_2CO_3 aqueous solution into a stream of air.

5. The method of claim 1, wherein the CO_2 in step (ii) is released from the $KHCO_3$ by heating the $KHCO_3$ to a temperature sufficient to liberate the CO_2, thus recycling the K_2CO_3.

6. The method of claim 1, wherein the CO_2 in step (ii) is released from the $KHCO_3$ by an electrochemical process.

7. The method of claim 1, wherein the reaction of CO_2 with hydrogen in step (iii) is a catalytic thermal reaction.

8. The method of claim 1, wherein the reaction of CO_2 with hydrogen in step (iii) is an electrochemical reaction.

9. The method of claim 8, wherein said electrochemical reaction corresponds to a reverse operation of a fuel cell and the hydrogen is produced in situ.

10. The method of claim 9, wherein said electrochemical reaction corresponds to a reverse operation of a direct methanol fuel cell (DMFC) and the fuel produced is methanol.

11. The method of claim 6, wherein said electrochemical reaction corresponds to a reverse operation of a molten carbonate fuel cell (MCFC) and the fuel produced is a hydrocarbon such as methane.

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