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(54) Title: CONVERSION OF METHANE AND CARBON DIOXIDE USING MICROWAVE RADIATION

(57) Abstract

A mixture of methane and carbon dioxide can be effectively converted to carbon monoxide and hydrogen by subjecting the mixture to microwave radiation in the presence of at least one plasma initiator that is capable of initiating an electric discharge in an electromagnetic field.

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CONVERSION OF METHANE AND CARBON DIOXIDE USING MICROWAVE RADIATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for converting methane and carbon dioxide to carbon monoxide and hydrogen using microwave radiation.

2. Description of Related Art

Microwave energy has been used to convert methane to other hydrocarbons. For example, U.S. Patent 4,574,038 discloses that methane can be converted to ethylene and hydrogen in a batch process at pressures of from 0.3 to 1 atmosphere by subjecting the methane to microwave radiation in the presence of a metal powder catalyst. Another example of methane conversion using microwave energy is disclosed in U.S. Patent 3,663,394.

In addition, the conversion of methane and carbon dioxide into carbon monoxide and hydrogen using a microwave discharge at ~5 torr pressure has been disclosed by Tanaka et al, J. Chem. Soc., Chem. Comm., pp. 921-922, (1982).

However, neither publication suggests the particular conversion process described below, which requires the presence of a plasma initiator.

SUMMARY OF THE INVENTION

This invention concerns the manufacture of synthesis gas (carbon monoxide and hydrogen) from methane and carbon dioxide. More specifically, methane

and carbon dioxide can be converted into synthesis gas (i.e. CO + nH_2, where n is a function of feed composition) by irradiating the methane/carbon dioxide mixture with microwave radiation in the presence of at least one elongated plasma initiator that is capable of initiating an electric discharge in an electromagnetic field. In a preferred embodiment, the plasma initiator will comprise a plurality of elongated metal wire segments arranged in close proximity to one another.

DETAILED DESCRIPTION OF THE INVENTION

This invention requires the presence of methane, carbon dioxide, at least one elongated plasma initiator capable of initiating an electric discharge in an electromagnetic field, and a source of microwave energy.

The methane and carbon dioxide may be pure or mixed with other hydrocarbons (e.g., methane may be a component of natural gas), or both may be components of gas streams from a gas producing well. Non-hydrocarbons (e.g. H_2O, H_2S, N_2, H_2, etc.) may be present in either or both as well. Both can be added to the reaction zone separately or as a mixture.

The plasma initiator may be essentially any material capable of accumulating an electric charge when placed in an electromagnetic field and then dissipating the charge (or initiating an electric discharge), for example, by ionizing a gas environment. This includes metal initiators, non-metal initiators (including semi-conductors), and composites of metal and non-metal initiators. As used herein, "composite" is meant to include mixtures (or combinations) of metals and non-metals. Examples of suitable metal initiators are tungsten, iron, nickel, copper, their

alloys, or mixtures thereof. Preferred metal initiators are tungsten, iron, or mixtures thereof, with iron being particularly preferred. Examples of suitable non-metal initiators include carbon, alumina, manganese dioxide, magnetite, nickel oxide (e.g. NiO), iron oxide (e.g. Fe_3O_4), calcium aluminate, cobalt oxide, chromium nitride, iron sulfide (e.g. FeS_2, $Fe_{1-x}S$), copper sulfide (e.g. CuS_2), or mixtures thereof. Calcium aluminate, carbon, iron oxide, or their mixtures are preferred non-metal initiators, with carbon being particularly preferred. Silica is not a suitable non-metal initiator. However, silica composited with a metal initiator or another non-metal initiator would be a suitable plasma initiator.

Although methane/carbon dioxide conversion can be effected using only one plasma initiator, conversion is enhanced if more than one (e.g., 6 or more) plasma initiators are used. Preferably, a plurality of plasma initiators are used. Most preferably, the plasma initiator will comprise a plurality of metal wire segments. Each plasma initiator should be of at least a minimum length that is sufficient to initiate an electric discharge when placed in an electromagnetic field. However, the precise minimum length of each initiator may vary with the frequency of the microwave source as well as the geometry of the reaction zone and of the initiator.

If more than one plasma initiator is used, a minimum distance should be maintained between each initiator to facilitate dissipation of the electric charge. However, the minimum distance will vary depending upon the frequency of the microwave source. As an example, the minimum distance should be at least about 0.25 cm, preferably at least about 0.5 cm, for a frequency of 2.45 GHz.

The plasma initiators should be elongated, but may be formed, combined, or bent in any convenient shape (e.g., straight, helix, spiral, and the like). Preferably, the initiators should be formed such that there are points or sharp edges at the ends or on the surface of the initiators. Particulate powders are not suitable plasma initiators.

The plasma initiators may be stationary within the reaction zone or they may be in motion. The motion can result from the initiators being fluidized by a gas (e.g. the methane feedstock) or by other means (e.g. an external magnetic field gradient).

The frequency of the microwave source can vary broadly. Typically, the microwave energy will have a frequency of at least 0.3 GHz, with frequencies centered around 0.915, 2.45, 5.80, or 22.0 GHz being presently preferred in North America; particularly frequencies centered around 0.915, 2.45, or 5.80 GHz; especially frequencies centered around 0.915 or 2.45 GHz.

The microwave energy used in this invention may be continuous or pulsed. If pulsed, the duration of on-time pulses can vary broadly, but typically will range from about 1 nanosecond to about 20 seconds, preferably from about 1 millisecond to about 10 seconds, and most preferably from about 0.01 to about 0.2 seconds. The duration of off-time rests can vary broadly as well, but typically will range from about 1 nanosecond to about 100 seconds, preferably from about 0.003 to about 60 seconds, and most preferably from about 0.3 to about 5 seconds.

This invention can be practiced at any convenient temperature and pressure, including ambient conditions.

This invention will be further understood by reference to the following Examples which are not intended to restrict the scope of the claims appended hereto.

Example 1 - Conversion of Methane and Carbon Dioxide Using Plasma Initiators

A methane/carbon dioxide mixture (1:1 mole ratio) flowing at 20 ml/minute (milliliters/minute) at atmospheric pressure was contacted with 1.5 gm of tungsten wire (about 0.03 inches in diameter and cut into 45 mm lengths) in a reactor fabricated from WR430 waveguide bounded by quartz plate glass windows and positioned approximately one-quarter waveguide wavelength from a short circuit plate. The reactor was irradiated with microwave radiation centered at a 2.45 GHz frequency and pulsed in an on/off cycle (0.14 seconds on in a total of 3.5 seconds) with a power ranging from 3.2 to 6.2 watts. Methane conversion was calculated to be 40% using to the following equation:

$$\% \text{ Methane Conversion} = \left[1 - \frac{\text{wt.\% methane in the products}}{\text{wt.\% methane in the feed}} \right] \times 100$$

Similarly, carbon dioxide conversion was calculated to be 43% using the following equation:

$$\% \text{ Carbon Dioxide Conversion} = \left[1 - \frac{\text{wt.\% carbon dioxide in the products}}{\text{wt.\% carbon dioxide in the feed}} \right] \times 100$$

The primary products produced were 35.7% carbon monoxide, 2.9 wt% hydrogen, and 2-3 wt% water.

Example 2 - Conversion of Methane and Carbon Dioxide Using Plasma Initiators

Using the apparatus and procedure of Example 1 (except that the average power was 6.4 watts), a methane/carbon dioxide mixture (1:2 mole ratio) flowing at 15 ml/min was converted to 47.5 wt% carbon monoxide, 1.7 wt% hydrogen, and 2-3 wt% water. Methane and carbon dioxide conversions were 53.6% and 52.6%, respectively.

Example 3 - Conversion of Methane and Carbon Dioxide Using Plasma Initiators

Using the apparatus and procedure of Example 1 (except that the average power was 7.4 watts), a methane/carbon dioxide mixture (1:~18 mole ratio) flowing at 10 ml/min was converted to 43.4 wt% carbon monoxide, 0.7 wt% hydrogen, and 2-3 wt% water. Methane and carbon dioxide conversions were 60% and 46.4%, respectively.

Example 4 - Conversion of Methane and Carbon Dioxide Using Particulate Metal Powder

A methane/carbon dioxide mixture (1:1.09 mole ratio) was passed through an empty quartz glass tube at a total flow rate of 20 ml/min at atmospheric pressure. The tube was irradiated with up to 1170 watts of microwave radiation centered at a frequency of 2.45 GHz, but no plasma was formed and no conversion products obtained. Attempts to initiate a plasma using the discharge from a Tesla coil also failed.

Particulate nickel powder (0.1 g) was then evenly distributed over an approximately 1 cm diameter sintered glass disc contained in a quartz reactor and contacted with the methane/carbon dioxide mixture

described above flowing at 20 ml/min through the sintered disc. The reactor was located in a WR430 waveguide positioned approximately one quarter wave-guide wave-length from a short circuit plate. The reactor was irradiated with pulsed microwave radiation centered at a frequency of 2.45 GHz and having an on/off cycle of 0.14 seconds on in a total of 3.5 seconds. After 18 minutes onstream at an average power of 1.4 watts, methane and carbon dioxide conversions were calculated to be 1.4% and 1.0%, respectively, with the primary products being 0.7 wt.% carbon monoxide, 0.09 wt.% hydrogen, and 0.15 wt.% water. After an additional 18 minutes onstream, methane and carbon dioxide conversions were calculated to be 1.2% and 0.45%, respectively, with the primary products being 0.56 wt.% carbon monoxide and 0.07 wt.% hydrogen (no water was detected). At higher average power (e.g. 2.6 watts), the powders glowed but no conversion was obtained.

The data in Example 4 show that particulate metal powders are not effective in converting methane and carbon dioxide.

CLAIMS:

1. A method for converting methane and carbon dioxide to carbon monoxide and hydrogen which comprises:

(a) introducing methane and carbon dioxide into a reaction zone that contains at least one plasma initiator capable of initiating an electric discharge in an electromagnetic field, and

(b) subjecting the methane, carbon dioxide, and plasma initiator to microwave radiation for a period of time sufficient to convert at least a portion of the methane and carbon dioxide to carbon monoxide and hydrogen.

2. The method of claim 1 wherein the plasma initiator is a metal.

3. The method of claim 2 wherein the metal is tungsten, iron, nickel, copper, their alloys, or mixtures thereof.

4. The method of claim 3 wherein the metal is tungsten, iron, or mixtures thereof.

5. The method of claim 1 wherein the plasma initiator is a non-metal other than silica.

6. The method of claim 5 wherein the non-metal is calcium aluminate, carbon, iron oxide, or mixtures thereof.

7. The method of claim 1 wherein the plasma initiator is a composite of a metal initiator and a non-metal initiator.

8. The method of claim 1 wherein a plurality of plasma initiators are present in the reaction zone.

9. The method of claim 8 wherein the plasma initiators are elongated.

10. The method of claim 1 wherein the frequency of the microwave radiation is at least 0.3 GHz.

11. A method for converting methane and carbon dioxide to carbon monoxide and hydrogen which comprises:

(a) introducing methane and carbon dioxide into a reaction zone that contains at least one elongated plasma initiator capable of initiating an electric discharge in an electromagnetic field, and

(b) subjecting the methane, carbon dioxide, and plasma initiator to microwave radiation having a frequency of at least 0.3 GHz for a period of time sufficient to convert at least a portion of the methane and carbon dioxide to carbon monoxide and hydrogen.

12. The method of claim 11 wherein a plurality of plasma initiators are present in the reaction zone.

13. The method of claim 12 wherein the plasma initiators are a metal and the metal is tungsten, iron, nickel, copper, their alloys, or mixtures thereof.

14. The method of claim 13 wherein the metal is tungsten, iron, or mixtures thereof.

15. The method of claim 14 wherein the frequency of microwave radiation is centered around 0.915, 2.45, or 5.8 GHz.

16. The method of claim 11 wherein at least one plasma initiator is a metal.

17. The method of claim 16 wherein the metal is tungsten, iron, nickel, copper, their alloys, or mixtures thereof.

18. The method of claim 17 wherein the metal comprises tungsten, iron, or mixtures thereof.

19. The method of claim 16 wherein the plasma initiator is a plurality of metal wires.

20. The method of claim 11 wherein at least one plasma initiator is a non-metal other than silica.

21. The method of claim 20 wherein the non-metal is calcium aluminate, carbon, iron oxide, or mixtures thereof.

22. The method of claim 11 wherein at least one plasma initiator is a composite of a metal initiator and a non-metal initiator.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/04622

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): C01B 13/00

US CL : 204/157.43,157.47,157.5,157.52,168,170

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	204/157.43,157.47,157.5,157.52,168,170

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	TANAKA, "A STOICHEIOMETRIC CONVERSION OF CO_2+CH_4 into 2CO + $2H_2$ by MICROWAVE DISCHARGE", J. CHEM. SOC., 1982 (SEE ENTIRE DOCUMENT).	1-22
Y	HARAGUCHI, CHEMICAL ABSTRACTS 93:70223u, 1980	1-22
Y	GASNER, CHEMICAL ABSTRACTS 106:7281h, 1987.	1-22

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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IV. CERTIFICATION

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