



US 20190382871A1

(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2019/0382871 A1**
Han et al. (43) **Pub. Date: Dec. 19, 2019**(54) **METHOD FOR HIGH-PURITY TIN
RECOVERY AND HYDROGEN
PRODUCTION USING METHANE
REDUCTION****Publication Classification**(51) **Int. Cl.**
C22B 25/02 (2006.01)
C22B 5/12 (2006.01)
(52) **U.S. Cl.**
CPC **C22B 25/02** (2013.01); **C22B 5/12**
(2013.01)(71) Applicant: **AIENGINEERING**(72) Inventors: **Jun Hyun Han**, Daejeon (KR); **Hyun
You Kim**, Daejeon (KR); **Sang Ro Lee**,
Suncheon-si (KR); **Hyung Chul Wie**,
Suncheon-si (KR); **Sang Yeol Kim**,
Gwangyang-si (KR)(57) **ABSTRACT**(73) Assignees: **AIENGINEERING**, Suncheon-si (KR);
**THE INDUSTRIAL & ACADEMIC
COOPERATION IN CHUNGNAM
NATIONAL UNIVERSITY**, Daejeon
(KR)

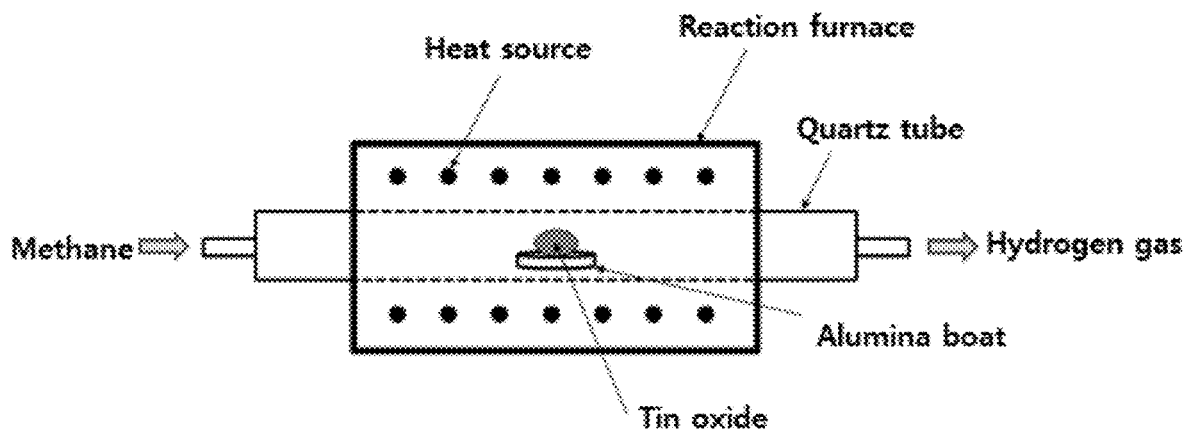
The present invention relates to a method of using a methane gas to recover tin with high purity and to produce hydrogen at once, and the method uses the methane reduction technique that combines the two different processes of tin recovery and hydrogen production, thereby recovering tin with high purity from a methane gas and a tin oxide according to the methane reduction technique stably without emission of environmental pollutants, such as carbon dioxide, sulfur dioxide, nitrogen oxide, etc., and also producing hydrogen available as a new energy resource. Further, the present invention enables the recycling of waste materials containing tin oxides generated in all kinds of industries to prevent environmental contaminations and to offer solutions to the stable recovery of expensive tin with high purity and the dramatic reduction of hydrogen production costs at once, increasing economical efficiency and thus contributing to the efficient use of resources.

(21) Appl. No.: **15/566,719**(22) PCT Filed: **Jul. 21, 2017**(86) PCT No.: **PCT/KR2017/007918**

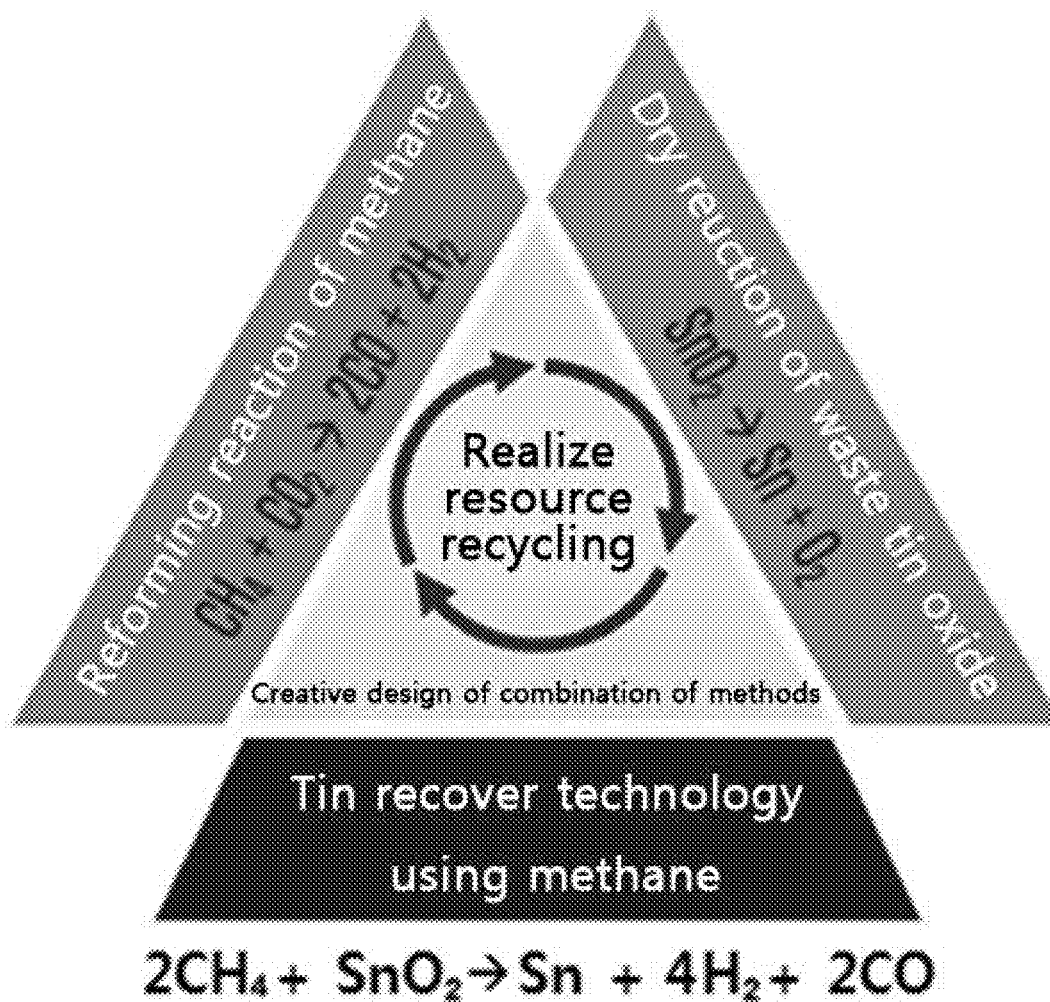
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(2) Date: **Oct. 15, 2017**(30) **Foreign Application Priority Data**

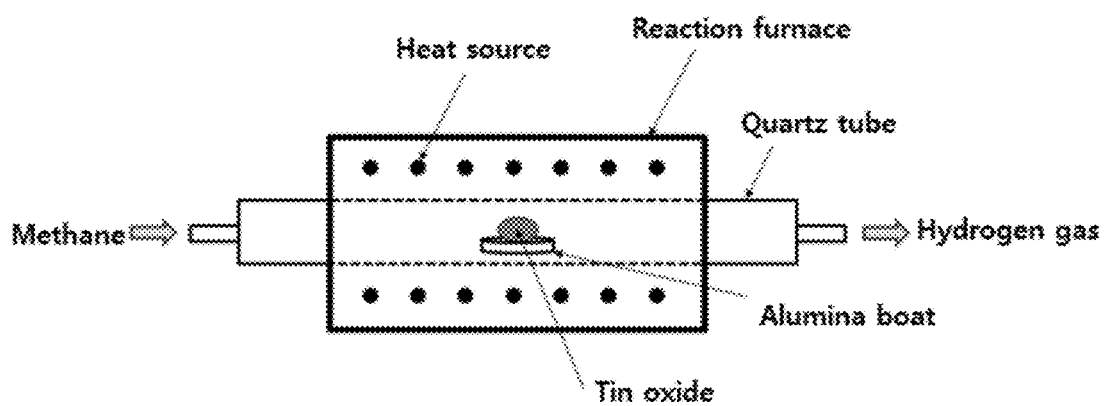
May 8, 2017 (KR) 10-2017-0057272



【FIG. 1】



【FIG. 2】



METHOD FOR HIGH-PURITY TIN RECOVERY AND HYDROGEN PRODUCTION USING METHANE REDUCTION

TECHNICAL FIELD

[0001] The present invention relates to a method for high-purity tin recovery and hydrogen production using methane reduction, and more particularly to a method of conducting a dry reduction of tin oxide using methane gas as a reducing agent not only to recover high-purity tin but also to produce hydrogen as a byproduct from the methane gas used as a reducing agent without production of environmental pollutants.

BACKGROUND ART

[0002] Tin is a carbon-group chemical element with symbol Sn in group 14 and period 5 of the periodic table. It is a post-transition metal that is highly malleable, ductile and corrosion-resistant and ready to melt and hence extensively used with its high castability. Particularly, it plays an important role as a Pb-free solder in the electronic components and materials industry and is extensively used as a core material in the manufacture of LED TVs, alloy materials, plating materials, electric contact materials for electric and electronic products, transparent electrodes, flat-panel glass, and glass materials for LCD panel. And the tin usage today is on the increase.

[0003] Most tin resources are found in some of the South-east Asian countries exclusively and tin smelting is a tactic for those countries. This results in an imbalance between supply and demand, a high rise of price and high price fluctuations in the international tin markets. The current price of tin in the international transactions is \$21,000 per ton, about three times the price of copper and ten times the price of aluminum. In recent years, the importance of the technologies for recovering tin from tin-containing waste resources is thus emphasized and the related techniques are receiving a lot of attention. For the recovery of tin, many studies have been made on the techniques of fusion, dry reduction, solvent extraction, wet reduction, or the like.

[0004] The methods of recovering tin from tin oxides using dry reduction or wet reduction are deployed on a commercial scale, but mostly involving the recovery of tin from waste solders or scraps or sludge having a relatively high tin content, and results in the emission of slags, chemical waste water, and carbon dioxide in large quantity. Accordingly, there is a need for a novel tin recovery method based on a more eco-friendly cleaning technique.

[0005] In reference to the dry reduction method, KR Patent No. 10-1619340 discloses a method of recovering tin from a tin-containing dross using a carbon-based substance and a dry reduction process. Unavoidably, this method also involves the emission of slags and carbon dioxide in large quantity to cause environmental contaminations.

[0006] In regards to the wet reduction method, KR Patent No. 10-1431532 is directed to a method for separation and recovery of valuable metals in waste Pb-free solders, where the method involves the recovery of tin by adding waste Pb-free solders in a leaching solvent to extract tin. But, the method is so problematic as it has high cost of process,

spending long time for purification and using a large amount of reagents, as well as generating chemical wastewater in large quantity.

[0007] In addition to the methods for increasing the recovery rate of tin, techniques for recovering tin with high purity have been studied in Korea and other countries. Yet, the conventional methods have more serious problems, such as low thermal efficiency, poor economical efficiency and low expandability, than the above-mentioned ones with the dry reduction or wet reduction method regarding emission of pollutants and formation of waste residues. There is thus a demand for developing a novel technique to improve those problems.

[0008] With the current environmental contaminations and depletion of petroleum resources, new energy technologies have been brought to the fore. One of the new energy technologies is the fuel cell that uses the electrical reaction of hydrogen and oxygen to convert chemical energy into electrical energy. The fuel cell has excellent energy efficiency, so studies have been actively made on the utilization of the fuel cell for personal, industrial or automobile uses.

[0009] The hydrogen sources for fuel cells are methanol, liquefied natural gas containing methanol as a principal ingredient, city gas, synthetic liquid fuel, and petroleum hydrocarbons such as petroleum naphtha or paraffin. The methods of producing hydrogen from petroleum hydrocarbons are accomplished through various technologies, such as catalytic reforming using steam as a catalyst or autothermal reforming, partial oxidation, and plasma reforming.

[0010] The reforming method of using steam as a catalyst involves a considerably complicated process and results in emission of a byproduct, carbon dioxide, in addition to the desired product, hydrogen. In the case of using a catalyst, the reaction of the reforming method is endothermic due to its characteristic as it takes place only at high temperatures of about 700 to 1,200° C., so the method requires the use of a specialized reforming furnace and incurs additional expenses in association with the reduced life span and durability of the catalyst at high temperatures. The method using the partial oxidation of hydrocarbons also requires the use of a specialized furnace for partial oxidation and creates a lot of shoot, which necessarily adds a separate process of disposal and leads to deterioration of the catalyst. The high-temperature pyrolysis using plasma is a process not causing the emission of carbon dioxide, but energy intensive in the pyrolysis of methane, increasing the hydrogen production cost.

[0011] Accordingly, there is a demand for an innovative method to offset the demerits of the conventional hydrogen production methods in order to make the better use of hydrogen as an energy resource.

[0012] In an attempt to making studies on the recovery of tin with high purity from tin oxide and the approaches to the higher production yield of hydrogen used as a new clean energy resource, the inventors of the present invention have invented a method of reducing methane using a combination of the tin recovery process and the hydrogen production process and contrived a process of using methane reduction not only to recover tin with high purity from tin oxide stably without emissions of environmental pollutants, such as carbon dioxide, sulfur dioxide, nitrogen oxide, etc., but also to produce hydrogen as a new clean energy resource with efficiency, thereby completing the present invention.

DISCLOSURE OF INVENTION

[0013] It is an object of the present invention to provide a method of using methane not only to recover tin with high purity from tin oxides but also to produce hydrogen.

[0014] To achieve the object of the present invention, there is provided a method of adding a methane gas into a reaction furnace containing a tin oxide and activating a reduction reaction to recover tin with high purity and to produce hydrogen as a byproduct.

[0015] More specifically, the present invention provides a method for recovering tin with high purity and producing hydrogen using methane that includes: adding a methane gas into a reaction furnace containing a tin oxide and activating a reduction reaction at 600 to 1,500° C.; and collecting tin and hydrogen gas produced through the reduction reaction.

[0016] The reaction used in the recovery of high-purity tin and the production of hydrogen can be represented in terms of the following chemical formula 1:



[0017] The process (reaction process) of adding a methane gas into a reaction furnace containing a tin oxide and causing a reduction reaction between the methane gas and the tin oxide employs the liquid-state methane gas rather than a solid-state reducing agent to enhance the efficiency of the reduction reaction and uses the characteristic of the methane composed of carbons and hydrogen to effectively reduce the tin oxide through a multi-step reduction reaction of carbons and hydrogen, thereby recovering tin with efficiency and producing hydrogen as a byproduct through the decomposition of the methane gas.

[0018] In the present invention, the examples of the tin oxide may include wastes containing tin oxides or salts of tin oxide that are created in the production or disposal process of, if not specifically limited to, LED TVs, alloy materials, plating materials, electric contact materials of electric and electronic products, transparent electrodes, flat-panel glass, and glass materials for LCD panel. In other words, the tin oxide as used herein may be any material containing an oxidized form of tin (i.e., tin oxides) or the salts of tin oxide.

[0019] In one specific embodiment of the present invention, when the waste material contains tin oxides or the salts of tin oxide, a pretreatment process, such as pulverization or crushing of the waste material, calcination of organic substances, filtration and separation of impurities, etc., may be performed in order to enhance the efficiency of the hydrogen production process.

[0020] In one specific embodiment of the present invention, when the waste material is process sludge, wastewater sludge or wastewater, the pretreatment process may be performed by removing impurities, such as sand, soil, plastic, waste residue, etc., using, if not specifically limited to, filter films, separations films, or screens.

[0021] The methane gas of the present invention contains 80 to 99% methane, preferably 85 to 98.5% methane, more preferably 90 to 98% methane. When the content of methane is less than 80%, the efficiency of the reduction reaction with the tin oxide in the reaction furnace is reduced only to noticeably lower the tin recovery rate and the hydrogen production rate. When the content of methane is greater than 90%, it incurs excess costs and processes for hydrogen production and thus reduces the efficiency of the process.

[0022] The mixing molar ratio of the tin oxide to the methane gas is 1:1 to 6. When the proportion of the methane

gas in the mixing ratio is less than 1 mole, it may be possible to recover pure tin and produce hydrogen, but with high carbon dioxide (CO₂) emission. When the proportion of the methane gas in the mixing ratio is greater than 6 moles, it incurs very low carbon dioxide emission but reduces the efficiency of the process with a great quantity of unreacted methane gas.

[0023] The reaction process of the present invention is carried out at 600 to 1,500° C., preferably 700 to 1,400° C., more preferably 800 to 1,000° C. When the temperature is lower than 60° C., the reduction reaction between the mixed reactants, that is, the tin oxide and the methane gas hardly occurs, reducing the tin recovery rate and the hydrogen production rate. When the temperature is higher than 1,500° C., it leads to a nearly zero increase in the tin recovery rate accompanied by an increase in the temperature, reducing the efficiency in the aspect of the processing time and costs, and incurs carbon deposition due to a direct decomposition of methane only to reduce the purity of the recovered tin.

[0024] After the completion of the reaction process, high-purity tin and hydrogen gas may be separately isolated from the reaction furnace.

Effects of the Invention

[0025] The method of using a methane gas to recover tin with high purity and to produce hydrogen at once according to the present invention is an invention based on a combination of the two different processes of tin recovery and hydrogen production, thereby recovering tin with high purity from a methane gas and a tin oxide according to the methane reduction technique stably without emission of environmental pollutants, such as carbon dioxide, sulfur dioxide, nitrogen oxide, etc., and also producing hydrogen available as a new energy resource. Further, the present invention enables the recycling of waste materials containing tin oxides generated in all kinds of industries to prevent environmental contaminations and to offer solutions to the stable recovery of expensive tin with high purity and the dramatic reduction of hydrogen production costs at once, increasing economical efficiency and thus contributing to the efficient use of resources.

BRIEF DESCRIPTIONS OF DRAWINGS

[0026] FIG. 1 is an illustration showing the chemical reaction in the tin recovery and hydrogen production technique of the present invention combining the reforming reaction of a methane gas and the reduction reaction of a tin oxide together.

[0027] FIG. 2 is a schematic illustration of the method for recovering tin with high purity and producing hydrogen using the methane reduction technique according to one embodiment of the present invention.

BEST MODES FOR CARRYING OUT THE INVENTION

[0028] Hereinafter, the present invention will be described in detail with reference to the following examples, which are given for the illustrations of the present invention only and not construed to limit the scope of the present invention. The examples of the present invention are subjected to various changes and modification and provided for those skilled in the art to understand the present invention more completely.

Example 1: High-Purity Tin Recovery and
Hydrogen Production Using Methane Reduction

[0029] A lump of tin oxide was pulverized into powder. 25 g of the tin oxide powder was put in an alumina boat and placed in a quartz tube of a reduction furnace, as illustrated in FIG. 2. Both ends of the quartz tube were sealed with fixtures, the one capable of gas injection and the other gas collection. After the sealing, the temperature of the reduction furnace was raised up to 1,000° C. and a methane gas was injected from the one end of the quartz tube. In this process, the methane gas was controlled with a mass flow controller (MFC). In the Example 1, the methane gas was injected into the reduction furnace at a rate of 250 sccm (standard cubic centimeter per minute). Under the injection conditions of the methane gas at 250 sccm, the mixing ratio (molar ratio) of tin oxide (SnO_2) and methane (CH_4) amounts to 1:37. A gas-capturing was attached to the opposite side to the methane-injecting portion in the quartz tube in order to capture the potential emissions of carbon monoxide and carbon dioxide and the unreacted methane gas as well as the hydrogen gas produced from the reaction. The tin reduction reaction using the methane gas took place for one hour. After the completion of the reaction, the remaining methane gas in the reduction furnace was discharged out of the reduction furnace and combusted.

Test Example 1: Qualitative Analysis on Reduced
Tin

[0030] The reduced tin of Example 1 was subjected to a qualitative analysis according to the KS D 1720. The results are presented in Table 1.

TABLE 1

Element	Composition (%)	Test method
Sn	99.34	KS D 1720: 1994
Pb	Not detected	KS D 1720: 1994
Sb	0.13	KS D 1720: 1994
As	0.001	KS D 1720: 1994
Cu	0.49	KS D 1720: 1994
Fe	0.04	KS D 1720: 1994

[0031] As can be seen from Table 1, the elements to detect were Sn, Pb, Sb, As, Cu, and Fe. The reduced tin contained 99.34% Sn and, as impurities, 0.13% Sb, 0.001% As, 0.49% Cu, and 0.04% Fe. Namely, it was possible to recover tin with high purity of 99.34% through the reduction of the tin oxide using the methane gas.

Test Example 2: Qualitative and Concentration
Analysis on Emission Gas

[0032] The emission gas captured by the gas-sampling bag in Example 1 was analyzed in regards to composition and concentration by way of the gas chromatograph (GC-TCD) and the mass spectrometer (QMS). The results are presented in Table 2.

TABLE 2

Component	Concentration (%)
H_2	83.5
CO	14.0

TABLE 2-continued

Component	Concentration (%)
CH_4	1.7
CO_2	0.4

[0033] As can be seen from Table 2, the emission gas was composed of 83.9% hydrogen, 14.0% carbon monoxide, 1.7% methane, and 0.4% carbon dioxide. Namely, it was possible to obtain a hydrogen-mixed gas containing hydrogen at concentration of 83.9% from the reduction reaction of a tin oxide using methane.

Comparative Example 1: High-Purity Tin Recovery
and Hydrogen Production Using Excess Methane

[0034] The procedures were performed in the same manner as described in Example 1 to reduce the tin oxide powder, excepting that the methane gas was injected at 416 sccm so that the mixing ratio (molar ratio) of tin oxide (SnO_2) to methane (CH_4) was 1:6.1.

Test Example 3: Qualitative Analysis on Reduced
Tin

[0035] The reduced tin of Comparative Example 1 was subjected to a qualitative analysis according to the KS D 1720. The results are presented in Table 3.

TABLE 3

Element	Composition (%)	Test method
Sn	99.88	KS D 1720: 1994
Pb	0.013	KS D 1720: 1994
Sb	Not detected	KS D 1720: 1994
As	Not detected	KS D 1720: 1994
Cu	0.11	KS D 1720: 1994
Fe	Not detected	KS D 1720: 1994

[0036] As can be seen from Table 3, the elements to detect were Sn, Pb, Sb, As, Cu, and Fe. The reduced tin contained 99.88% Sn and, as impurities, 0.013% Pb and 0.011% Cu. Namely, it was possible to recover tin with high purity of 99.88% through the reduction of the tin oxide using the methane gas.

Test Example 4: Qualitative and Concentration
Analysis on Emission Gas

[0037] The emission gas captured by the gas-sampling bag in Comparative Example 1 was analyzed in regards to composition and concentration by way of the gas chromatograph (GC-TCD) and the mass spectrometer (QMS). The results are presented in Table 4.

TABLE 4

Component	Concentration (%)
H_2	43.8
CO	6.7
CH_4	0.2
CO_2	46.4

[0038] As can be seen from Table 4, the emission gas was composed of 43.8% hydrogen, 6.7% carbon monoxide, 0.2% methane, and 46.4% carbon dioxide. When the

injected amount of the methane gas was increased to 416 sccm so that the mixing ratio (molar ratio) of tin oxide (SnO_2) to methane (CH_4) was 1:6.1, it reduced the hydrogen concentration and increased the methane concentration in the emission gas. This result comes down to the supply of excess methane, which contributes to an increase in the amount of methane gas discharged while remaining unreacted rather than participating in the reduction of the tin oxide.

1. A method for recovering tin with high purity and producing hydrogen using methane gas, the method comprising:

- (S1) adding a methane gas (CH_4) into a reaction furnace containing a tin oxide;
- (S2) activating a reduction reaction of a mixture of the tin oxide and the methane gas of step (S1); and
- (S3) collecting tin and hydrogen gas produced after the reduction reaction of the step (S2).

2. The method as claimed in claim 1, wherein the tin oxide includes an oxidized tin, a salt of tin oxide, or a waste containing the oxidized tin and the salt of tin oxide.

3. The method as claimed in claim 1, wherein a mixing molar ratio of the tin oxide and the methane gas is 1:1 to 6.

4. The method as claimed in claim 1, wherein the reduction reaction of the step (S2) is performed at 600 to 1,500° C.

5. The method as claimed in claim 1, wherein the methane gas contains 80 to 99% methane.

6. The method as claimed in claim 2, wherein the methane gas contains 80 to 99% methane.

7. The method as claimed in claim 3, wherein the methane gas contains 80 to 99% methane.

8. The method as claimed in claim 4, wherein the methane gas contains 80 to 99% methane.

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