Study on efficiency of DCP for nuclear hydrogen production

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Abstract With many advantages, hydrogen is considered as the fuel of the future. But there is no natural resource of hydrogen and it must be produced by other kinds of energy. As for the primary energy, nuclear energy is a promising alternative. Using heat from nuclear reactor to produce hydrogen is receiving more and more concerns in recent years. This paper mainly emphasizes the study of the direct contact pyrolysis (DCP) of methane using heat from nuclear reactor. A facility was designed to investigate the efficiency of DCP process in certain conditions. The experimental results show that this process produces only hydrogen and carbon. The conversion efficiency increases with temperature and residence time, but decreases as flow rate increases. The highest efficiency of DCP obtained in this experiment is about 22%.

Key words Hydrogen production, Nuclear reactor, Methane pyrolysis

CLC numbers TL99, TK91

1 Introduction

As a kind of clean energy and with high combustion heat, hydrogen is believed to be a promising energy form in the future. And also because of the recent progress of the promising hydrogen utilization technology, more hydrogen will be needed.[1] Although hydrogen is the most common element in the universe, there is no natural resource of hydrogen. Hydrogen is not a primary energy and it must be produced from other abundant resources by other kinds of energy.

Nuclear energy has been considered to be one of the primary energy to produce hydrogen, which can produce hydrogen in very large quantities consistently over long periods of time without emitting greenhouse gases or other harmful gases. NHT (Nuclear Hydrogen Transition) is anticipated to play an important role in this century. In the transition, hydrogen is produced by direct thermochemical processes of water or methane at high temperature, and the heat is provided by nuclear reactor. Since the electricity output of nuclear power plant is marginal in off-peak periods, using heat from nuclear reactor to produce hydrogen is also one of the good approaches to utilize nuclear energy comprehensively.

2 Principle

2.1 Methods for producing hydrogen

Presently the most widely used source of hydrogen is produced by means of steam reforming of natural gas. This method is used for supplying hydrogen for the production of such basic chemicals as methanol and ammonia. It also provides hydrogen as a rocket fuel for the space program. The main problem is that this process produces large quantities of CO_2, which is a greenhouse gas that causes global warming leading to adverse global climate change effects, and more primary energy is consumed in this process.

Hydrogen could also be produced from water by several ways.[2] The promising methods include the sulfur-iodine [S-I] cycle, bromide-calcium [Br-Ca] cycle, and copper-chloride [Cu-Cl] cycle. But high temperature is needed for all these methods. Some others are doing research on these methods by using heat from current and near-future reactors which could supply high temperature of coolant.

Apart from the methods mentioned above, another way to produce hydrogen is believed to be promising. That is the DCP (direct contact pyrolysis) of methane using heat from nuclear power plant. The

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reaction of pyrolysis is expressed by Eq.(1).[3]

$$CH_4 \rightarrow C + 2H_2,\ \Delta H^0_{298K} = 75.6\ \text{kJ/mol} \quad (1)$$

The DCP process to produce hydrogen has many advantages over other approaches. This method may be environment-friendly, energy-efficient, and process- simple. In this way hydrogen is generated as a major product. There is no CO or CO_2 gas produced, because oxygen is isolated from the process. Besides, the process also produces a very valuable by-product: clean carbon, which is a very important material in rubber industry and can be used as a commodity product or sequestered (or stored) for future use. The DCP process is a one-step reaction, simply to design the equipment. Thermodynamic analysis[4,5] shows that DCP of methane is a feasible approach to produce hydrogen and less primary energy is consumed in this process.

2.2 Nuclear hydrogen transition system

Various nuclear reactors have been evaluated for their ability to provide the high temperature heat needed by the hydrogen production process, and to be interfaced safe and economical. Thus three potentially-suitable reactor concepts have been identified:[6] high-temperature gas-cooled reactor (HTGR), advanced high-temperature reactor (AHTR), and liquid metal fast breeder reactor (LMFBR).

Extensive work has been done in the field of Nuclear Hydrogen Transition.[6] The Japan Atomic Energy Research Institute is preparing to demonstrate the production of hydrogen by using the heat from its high-temperature engineering test reactor (HTTR) initially in steam re-forming of natural gas, and later with this iodine-sulfur thermo-chemical process. University of Tokyo (Japan) is studying UT-3 cycle. Argonne National Lab (USA) is designing the secure transportable autonomous reactor for hydrogen production, STAR-H2, which is a Pb-cooled, fast neutron spectrum, 400 MWh modular-sized reactor, using revision of UT-3 cycle belonged to Br-Ca cycle. Also the Oak Ridge National Laboratory in the USA and the French CEA are developing the sulfur-iodine process with a view to using high-temperature reactors for it. Some research has been done by Tsinghua University of China on the S-I cycle to produce hydrogen using their high-temperature gas-cooled reactor (HTGR).[7]

One of the scheme of nuclear hydrogen transition is that methane be pyrolyzed using the heat from the liquid metal coolant in nuclear reactors. As shown in Fig.1, the left part is one typical liquid metal fast breeder reactor (LMFBR), while the right part is hydrogen production vessel. The liquid metal is pumped to hydrogen production vessel, and the methane is bubbled in the liquid metal and decomposed into hydrogen and carbon. Carbon is collected on the liquid surface and methane is recycled after being separated from the mixed gases.

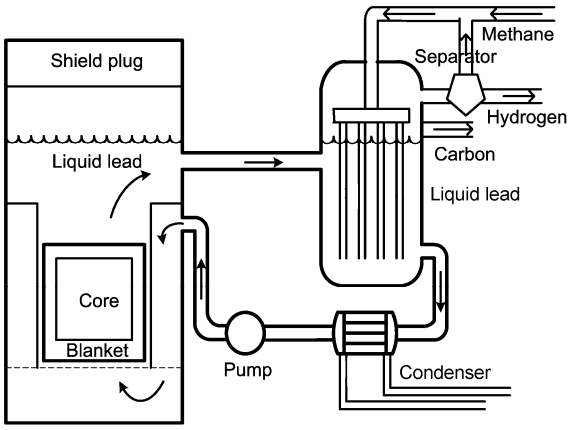

Fig.1 Schematic of a nuclear hydrogen transition system.

3 Experimental

For large amount of nuclear hydrogen production, the efficiency is important. In this paper, an experimental facility was designed to investigate the efficiency of direct pyrolysis of methane bubbling through liquid lead.

3.1 Facility design

The facility consists of argon gas buffer container, methane buffer container, inlet flow meter, outlet flow meter, heater, pyrolysis reactor, control unit, vacuum meter, vacuum pump, and filter bottle. Because both hydrogen and methane are explosive gases, in the experiment, the vacuum pump and argon are regarded as protective measures. At the beginning of the experiment the vacuum pump vacuumizes the pyrolysis reactor and then argon as protective gas flows into the reactor.

The pyrolysis reactor is made of corundum, with the inside diameter of 60mm and height of 900mm. Inside the reactor there is a lead pool which is also made of corundum. The lead pool's inside diameter is 50mm and height is 300mm. Methane gas flows into lead pool and bubbles. A thermocouple is used to detect the temperature of lead pool. Gas flux is measured by float flow meter. Gas produced is analyzed by chromatogram. The pyrolysis reactor structure is shown in Fig.2.

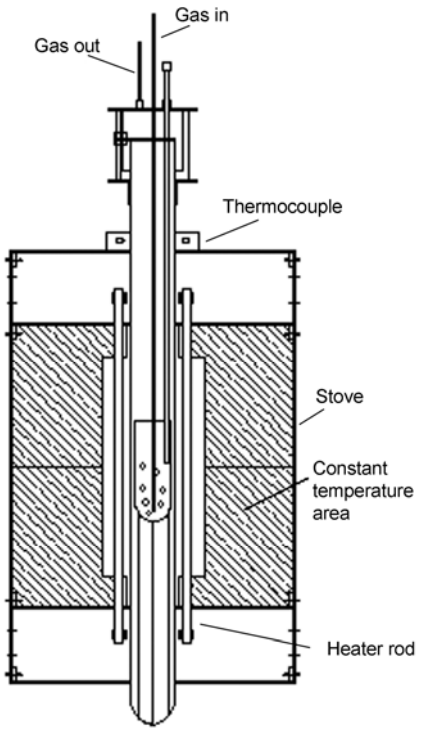

Fig.2 Scheme of pyrolysis reactor.

3.2 Experiment method and condition

The reaction is operated in 100kPa and height of liquid lead in the lead pool is 150mm. After excluding oxygen, methane flows into the reactor and is pyrolyzed in high temperature liquid lead. The temperature of reaction is around 800~1000℃ and flow rate of methane is about 7~21mL/min. Gases are collected at the end of the loop and analyzed by chromatogram. Liquid lead as heat exchange media provides heat for methane.

4 Results and discussion

On several different flow rate and temperature conditions, the end gases generated from the experiment are collected and analyzed. Hydrogen was generated. Carbon was found on the surface of lead pool, and also on the wall inside the reactor. No greenhouse gas was detected at the end of the loop. In this experiment, these considerable low conversion efficiencies are observed, even at a very high temperature.

The conversion efficiency of methane on different experimental conditions is calculated, as shown in Table 1.

Table 1 Conversion efficiency of methane %

Flow rate	Temperature		
(mL/min)	800℃	900℃	1000℃
7	1.09	4.23	22.00
14	0.93	3.18	19.02
21	0.14	2.91	15.59

4.1 Relation between efficiency and temperature

As shown in Fig.3, the conversion efficiency of methane increases dramatically as temperature increases. For instance, in flow rate of 7mL/min, at 800℃ the conversion efficiency is 1.09%, at 900℃ the conversion efficiency increases to 4.23%, and at 1000℃ the conversion is up to 22.00%. This is probably because high temperature causes methane more active and the reaction becomes easier.

However, in Fig.3, the theoretical curve[4,5] shows that, the conversion efficiency is rather high, even at low temperature. At 500℃ about 35% of methane is converted and at 1000℃ the conversion efficiency rises up to 95%. The experimental data are far below the theoretic results.

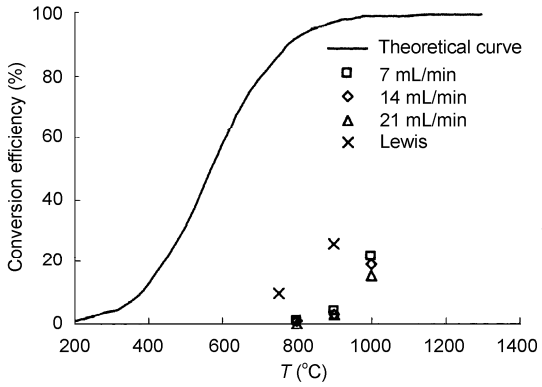

Fig.3 Conversion efficiency of methane as a function of temperature.

A similar experiment was done by Lewis[8] et al. The reaction temperature was set around 600~900℃. Some of their data was shown in Fig.3. At the same temperature, the conversion efficiency of methane is higher than that in this paper, which may be attributed to different experiment facility size and smaller flow rate of methane. But also, the same conclusion is drawn: H_2 yields increase with temperature and the efficiency is far below the theory for all the experimental conditions.

4.2 Relation between efficiency and flow rate

As shown in Fig.4, the most notable feature is that the methane conversion efficiency increases as the flow rate decreases, and this trend is more evident at high temperature. As one of the major experimental conditions, its influence on methane conversion efficiency is not as important as temperature's.

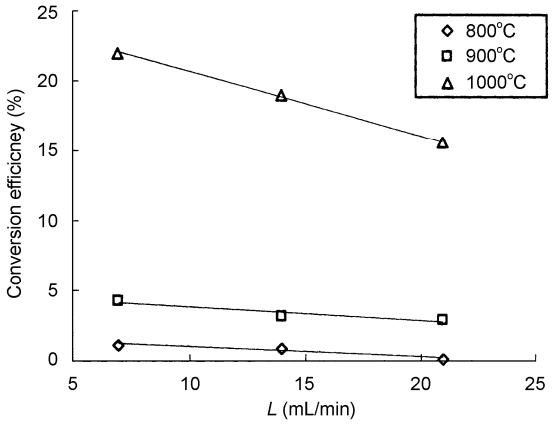

Fig.4 Conversion efficiency of methane as a function of flow rate.

Furthermore, the methane conversion efficiency is linearly related to the flow rate. For all three conditions, 800℃, 900℃ and 1000℃, we draw the same conclusion. A linear dependence of the conversion efficiency on the flow rate was formulated on different temperature conditions. Also, correlation coefficient is given for each line as follows:

800℃: $y = -0.0842x + 1.9881$, $R^2 = 0.9602$

900℃: $y = -0.0521x + 4.1033$, $R^2 = 0.9433$

1000℃: $y = -0.4721x + 25.723$, $R^2 = 0.9994$

4.3 Relation between efficiency and residence time

The decrease of the flow rate results in the increase of residence time of methane passing through the reactor, and the reaction time is extended. Therefore we did an extra analysis of the residence time of methane. The total time of gas passing through the reactor includes three parts: the time of gas getting through the downcome tube, the time of bubbling in the lead pool, and the time of gas staying above the pool. Because high temperature was kept, methane is decomposed along the whole path. Table 2 shows the residence time of methane in different experimental conditions.

Table 2 Residence time of methane min

Flow rate	Temperature		
(mL/min)	800℃	900℃	1000℃
7	33.1	30.3	27.9
14	16.5	15.1	14.0
21	11.0	10.1	9.3

The conversion increases as the residence time increases, especially at high temperature, as shown in Fig.5. The calculation of the resident time is based on the thermal-dynamic analysis, not detected in fact. More detailed data are needed for a precise analysis of the relation between conversion efficiency and residence time.

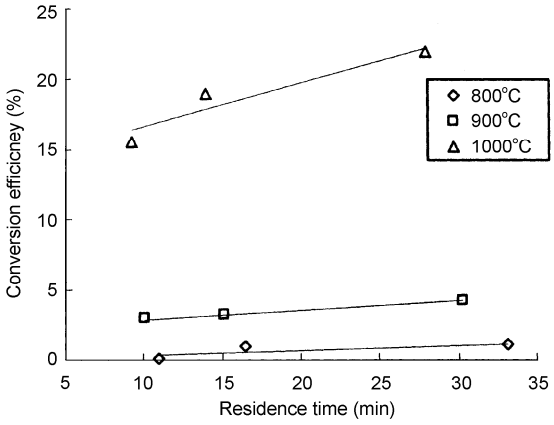

Fig.5 Conversion efficiency of methane as a function of resident time.

5 Conclusion

The DCP experiment shows that methane pyrolysis between 800~1000℃ yields only hydrogen and carbon. No greenhouse gases are generated. Conversion efficiency depends on temperature of the reaction and flow rate of methane. More hydrogen will be produced while temperature increases and methane

flow rate decreases, as well as the residence time increases. But the molecule of methane is very inactive without catalyzer. In this experiment the highest conversion efficiency is about 22% at 1000℃ with the methane flow rate of 7mL/min.

Both temperature and residence time are critical parameters of the reaction. According to preliminary results obtained, the efficiency of DCP is low, compared with other methods. For further investigation, some methods to get higher conversion efficiency in lower temperature are suggested, such as increasing the residence time of methane in the liquid lead by improving the reactor design, and increasing the contact area of methane or adding some catalyzers.

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