Hydrogen Production by Hydrocarbon Pyrolysis with Long DC Arc

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Abstract: Hydrogen production without direct CO_2 emission by hydrocarbon pyrolysis was successfully performed by long DC arc. The flow rate of the feedstock was changed to reveal the capability of H_2 production as well as decomposition and recombination mechanisms of hydrocarbon. High decomposition rate and high energy efficiency is achieved by long DC arc. Hydrocarbon pyrolysis with long DC arc is capable of being an alternative green technology for H_2 production.

Keywords: thermal plasmas, long DC arc, co-production, renewable energy

1. Introduction

Hydrogen is primarily used in the chemical industry such as ammonia synthesis and petroleum refining, and has recently received much attention in a view of the renewable energy [1]. The most common process for the H_2 production is a steam reforming from hydrocarbons. This process can produce large amounts of H_2 at low cost, however, CO_2 emission as a final product is unavoidable issue [2]. The electrolysis of water is an alternative H_2 production process without CO_2 emission, while it possesses the issues due to high cost and low productivity.

Thermal plasma pyrolysis of hydrocarbon is feasible for H_2 production because thermal plasma has many advantages; high enthalpy to enhance reaction kinetics, high chemical reactivity, rapid quenching rate, and selectivity of atmosphere in accordance with the required chemical reactions. Therefore, thermal plasma method can produce large amounts of H_2 at high production rate without direct CO_2 emissions. Furthermore, thermal plasmas enable to co-produce H_2 with useful carbon materials such as carbon black [3]. Although H_2 production by thermal plasma is disadvantageous in terms of energy efficiency, it has attracted attention because of the possibility of the solid carbon utilization as valuable resources.

Long DC arc is one of the most attractive thermal plasma sources because it has a long electrode gap distance of 300 mm. Therefore, long DC arc has larger plasma volume, and lower gas velocity compared with the conventional thermal plasmas. However, the investigation for hydrocarbon pyrolysis with the long DC arc has not been conducted yet. The purpose of this study is to decompose hydrocarbons by long DC arc and to synthesis H_2. Another purpose is to investigate decomposition mechanism of hydrocarbon.

2. Experiment

A schematic illustration of the long DC arc system used in this experiment is shown in **Fig. 1**. The setup consists of a power supply, a plasma torch, a gas chromatograph (GC), a pump, and a filter. Copper electrode was used for both the anode and cathode. Electrode gap distance was set to 230 mm. The feedstock was CH_4 as the main component of natural gas. Its flow rate was changed from 0.5 to 1.5 L/min. Argon was used as the plasma gas at 30 L/min. The arc current was set to 10 A.

Optical emission spectroscopy (OES) was applied to investigate decomposition and recombination mechanisms. The observed point was 60 mm just below the anode. The produced gases were analyzed by GC to investigate the gas composition and to estimate the decomposition rate of CH_4 and conversion rate of H_2. The decomposition rate and conversion rate were calculated from the following equations.

$$Decomposition\ rate[-] = \frac{Q_{CH_4}{}^{in} - Q_{CH_4}{}^{out}}{Q_{CH_4}{}^{in}} \quad (1)$$

$$Conversion\ rate[-] = \frac{2Q_{H_2}{}^{out}}{4Q_{CH_4}{}^{in}} \quad (2)$$

where $Q_{CH4}{}^{in}$ is the flow rate of the input CH_4 gas, and $Q_{CH4}{}^{out}$ and $Q_{H2}{}^{out}$ are the flow rates of the output CH_4 gas and H_2 gas, respectively.

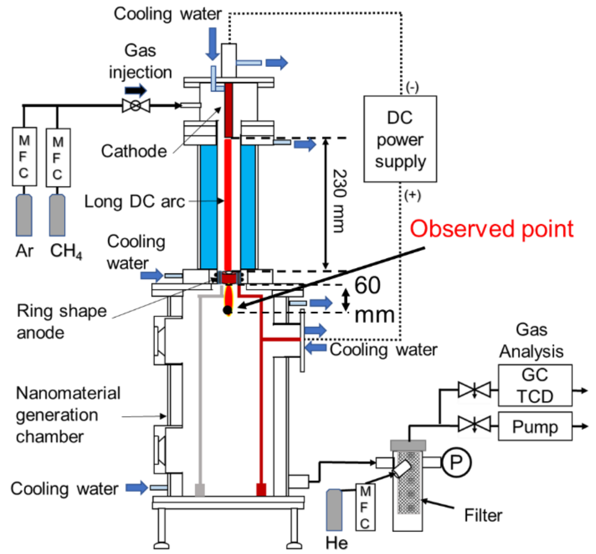

Fig. 1 Schematic diagram of long DC arc system.

3. Results and Discussion

The equilibrium composition of gas mixture of CH_4 and Ar under atmospheric pressure is shown in **Fig. 2**. Arc temperature in the core region of long DC arc is around 6,000 – 7,000 K [4]. In this temperature region, CH_4 is completely decomposed to C and H radicals. Outside the plasma region, H and C radicals recombine mostly to H_2 and solid carbon. Recombination temperature of H_2 is 3,750 K. Moreover, recombination temperature of CH_4, CH_3, CH_2, and CH is 3,180 K, 3,600 K, 3,540 K, 3,240 K, respectively.

Gas analysis revealed that H_2 was obtained as the main gaseous product of CH_4 pyrolysis. The effect of CH_4 flow rate on decomposition rate of CH_4 and conversion rate of H_2 are shown in **Fig. 3**. The decomposition rate is about 80% at all condition and the conversion rate is almost constant at all condition. This indicates that sufficient energy is supplied for CH_4 pyrolysis.

Hydrogen production rate and energy efficiency are shown in **Fig. 4**. Hydrogen production rate increased with an increase of CH_4 flow rate and the highest H_2 production rate was 2.0 L/min at CH_4 flow rate of 1.5 L/min. Energy efficiency also increased with an increase of CH_4 flow rate and the highest energy efficiency was 21.4 L-H_2/kWh at CH_4 flow rate of 1.5 L/min. This suggests the possibility of further increasing of feedstock supply.

Optical emission spectroscopy of the plasma jet was performed. Representative emission spectrum for CH_4 flow rate of 0.5 L/min is shown in **Fig. 5**. Emission from C_2 swan band and CH band were observed. C_2 swan band is due to C_2 radicals from complete decomposition of CH_4. CH band is due to CH radicals from incomplete decomposition of CH_4. The relative intensity of the CH band at 388.9 nm normalized by the intensity of C_2 band at 516.2 nm is shown in **Fig. 5**. The relative intensity decreased with an increase of CH_4 flow rate. This indicates that the number of CH_n radicals in the plasma increased with an increase of CH_4 flow rate.

4. Conclusion

Hydrocarbon pyrolysis with long DC arc plasma was successfully performed. High decomposition rate of hydrocarbon was achieved by long DC arc. The major gaseous product was H_2. OES results reveal that the number of CH_n radicals in the plasma increased with an increase of CH_4 flow rate. Long DC arc system is expected to play an important role in the H_2 production.

5. References

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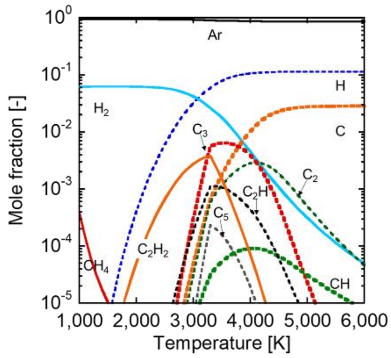

Fig. 2 Equilibrium composition of gas mixture of CH_4 and Ar system. Molar ratio of CH_4: Ar = 1.0: 30.

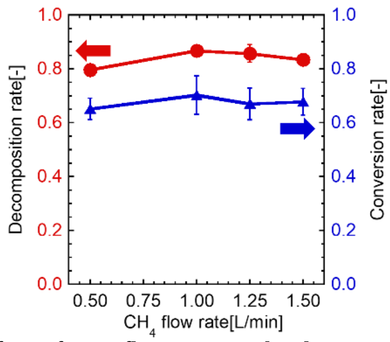

Fig. 3 Effect of CH_4 flow rate on the decomposition rate and conversion rate.

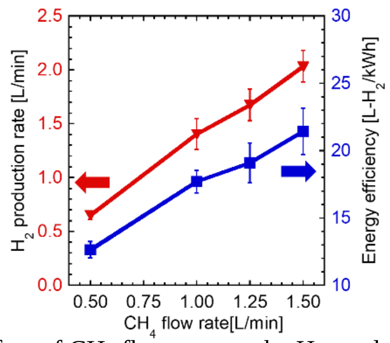

Fig. 4 Effect of CH_4 flow rate on the H_2 production rate and energy efficiency.

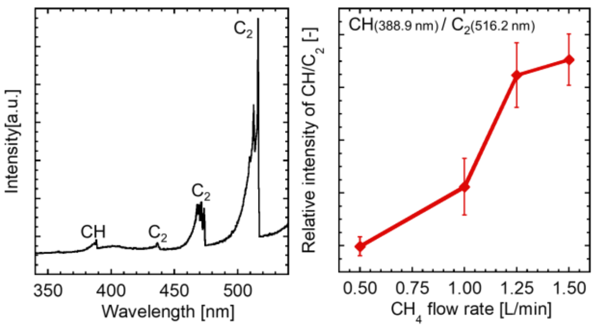

Fig. 5 Optical emission spectrum chart in CH_4 pyrolysis at CH_4 flow rate of 0.5 L/min and effect of arc current on relative intensity of CH normalized by the intensity of C_2 swan band.