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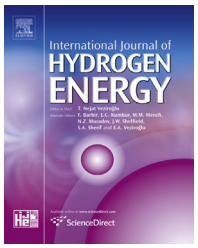

Experimental study of hydrogen production from reforming of methane and ammonia assisted by Laval nozzle arc discharge

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ABSTRACT

The production of hydrogen from hydrogen compounds for fuel cell or internal combustion engine applications is a potential method for responding to the energy crisis and environmental problems. In this work carbon dioxide reforming of methane and decomposition of ammonia using a Laval nozzle arc discharge (LNAD) reactor has been exploited at atmospheric pressure without external heating or catalysts. CH_4 (or NH_3) conversion and H_2 selectivity were observed to be negatively correlated with the concentration of CH_4 (or NH_3) and the flux of CO_2 (N_2) and positively correlated with voltage and the Laval nozzle throat radius. Power consumption increased with the concentration of methane at the same CO_2 flow rate, and the conversion of methane gradually increased with the content of water vapor in the gas mixture. A high conversion rate and fair H_2 selectivity were achieved, 51% and 37.5%, respectively, when the methane and carbon dioxide flow rates were 4 L/min and 14 L/min, respectively, and the minimum distance between the two electrodes was 2.5 mm. The LNAD reactor used in this study exhibited a good conversion rate and low energy consumption, which should be suitable for the industrial scale-up of the system.

Introduction

The formulation of solutions to the energy crisis and the environmental problems that we face today requires long-term efforts for sustainable development. The production of hydrogen or synthesis gas as a reliable alternative energy resource has become an effective way of addressing these issues, with the gas also serving as an important intermediate for the synthesis of various chemicals. However, the traditional method for producing hydrogen or syngas from coal, i.e., using natural gas and biomass, is not energy-efficient because it requires heating the reactants to a relatively high temperature [1]. For example, in the Koppers-Totzek coal gasification process, pulverized coal is rapidly partially oxidized with oxygen and steam at essentially atmospheric pressure and at a temperature of 1750 K [2].

Unlike in traditional thermal reforming to syngas, plasma reforming has become a novel approach because of its high energy, in particular, its ability to selectively distribute energy to active electronic species to induce a chemical reaction. Due to this characteristic of plasmas, the reaction apparatus can

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Table 1 – Comparison of several plasma treatment.

Plasma form	Feed flux (mL/min)	CH_4/CO_2	P(W)	Conversion (%)		Selectivity (%)			
				CH_4	CO_2	CO	H_2	C_2H_2	C_2H_4
Corona discharge [7,8]	25	1/1	8.4	56.3	22.8	9.1	–	15.0	1.9
DBD [9]	20	1/1	107.4	72.8	44.4	82	70	–	–
Microwave discharge [10]	200	3/2	60	70.8	68.8	75	–	17.8	4.1
Gliding arc discharge [11]	1000	1/1	190	40	31	62	50	12	–

be easily designed to be small, light-weight and low-cost and exhibit high fuel flexibility; indeed, even in the absence of a catalyst, the system can still achieve high efficiency.

Depending on its energy density level, temperature and electron density, a plasma can be classified as a thermodynamic non-equilibrium plasma or a thermodynamic equilibrium plasma. A thermodynamic non-equilibrium plasma is also called a cold plasma, in which the thermal kinetic energy of electrons is much greater than that of heavy particles. A thermodynamic equilibrium plasma is simply called a thermal plasma, in which the temperature of heavy particles is close to that of electrons, on the order of thousands of Kelvin. Currently, several types of plasmas have been tested in CH_4–CO_2 reforming [3–5], such as those formed by corona discharge, dielectric barrier discharge (DBD), microwave discharge, atmospheric pressure glow discharge (APGD) and gliding arc discharge [6]. For example, Liu et al. [7,8] studied CH_4–CO_2 reforming for hydrogen production by corona discharge, obtaining CH_4 and CO_2 conversion rates of 56.3% and 22.8%, respectively, using 0.1 g zeolite catalyst, a total flow rate of 25 mL/min and a CH_4/CO_2 ratio of 1/1. Wang et al. [9] used a coaxial DBD reactor to obtain CH_4 and CO_2 conversion rates of 72.8% and 44.4%, respectively, with syngas, C_2H_6 and trace amounts of other hydrocarbons as the main reaction products. Zhang et al. [10] employed a pulsed microwave plasma discharge reactor to reform CO_2–CH_4 at a flow rate of 200 mL/min (CH_4/CO_2 = 1.5:1) and peak microwave power of 120 W, obtaining CH_4 and CO_2 conversion rates of 70.8% and 68.8%, respectively. Antonius Indarto et al. [11] studied CH_4–CO_2 reforming by gliding arc discharge at a total feed-gas flow rate of 1000 mL/min, discharge power of 190 W and CH_4/CO_2 of 1:1; the authors obtained CH_4 and CO_2 conversion rates of approximately 40% and 31%, respectively, and H_2, CO and C_2H_2 selectivity's of approximately 50%, 62% and 12%, respectively.

A comparison of the reforming performance parameters of different plasmas is provided in Table 1. Previous research regarding plasma CO_2–CH_4 reforming shows that corona discharge and DBD are difficult to manage at a high flow rate because the electron density of the resulting plasmas is slightly lower than that of other types of plasma. Microwave discharge requires complex power supplies, including a high-frequency generator to form a high-frequency plasma. The feed flux associated with CH_4–CO_2 reforming by gliding arc discharge is much higher than that required by corona discharge and DBD. Moreover, the corresponding conversion rates are lower; however, gliding arc discharge still shows some potential for industrial application.

In this work, a novel gliding arc discharge plasma called a Laval nozzle arc discharge (LNAD) plasma was studied. LNAD not only combines the advantages of conventional gliding arc discharge and supersonic/subsonic discharge but also extends the discharge arc within a limited space by rotating the air flow. Lu et al. [12] studied the voltage–ampere (V–A) characteristics and movement of LNAD plasmas under various flow rates of working gas. The same plasma reactor was used by Du et al. [13] to investigate the reforming efficiency of bio-ethanol; the authors obtained a conversion rate and H_2 yield of 90% and 40%, respectively.

In addition to applying LNAD for CH_4–CO_2 reforming, NH_3 decomposition via LNAD was experimentally studied. At room temperature and a pressure of approximately 8 atm, NH_3 occurs in its liquid state and is easy to store. In addition, the hydrogen storage capacity (17.7 wt%) and energy density (3000 Wh/kg) of ammonia are higher than those of methanol and other fuels [14]. Ammonia decomposition is a mildly endothermic process, yielding hydrogen and nitrogen without any other co-products. Therefore, NH_3 decomposition is also an economical process for hydrogen production. Many papers have been published on the catalytic decomposition of ammonia for hydrogen production [14,15]. However, rarely has the process been applied in a plasma environment and without a catalyst.

Experimental section

Experimental apparatus

The LNAD reactor used in this study is similar to that described in previous work [12]. The plasma reactor, which features a chamber with dimensions of Φ 150 × 500 mm, is composed of a columnar cathode with dimensions of Φ 5 × 300 mm located in the middle and a Laval nozzle anode (with nozzle throat measuring 10 mm) wrapped around the periphery. The minimum distance between the two electrodes is 2.5 mm. The working gas is injected into the reactor through a tangential inlet (diameter 5 mm) situated at the bottom of the Laval nozzle, perpendicular to the cathode.

Fig. 1 shows the device system and a flow chart of the reforming process afforded by LNAD. A high-voltage AC gliding discharge is generated between electrodes connected to a 50-Hz and 220-V/10-kV high-voltage transformer. An oscilloscope (Tektronix TDS2024) is used to analyze the voltage signal from a Tektronix P6015 voltage probe and the current signal from a Tektronix TP301A current probe.

In a previous study [12], we observed that the ionization efficiency of LNAD decreases with increasing flow rate. Therefore, we set the total flow below 1.5 $m^3\ h^{-1}$ to obtain a