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Analysis on CO_2 reforming of CH_4 by corona discharge process for various process variables

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ABSTRACT

The CO_2 reforming of CH_4 to syngas by corona discharge at atmospheric pressure has been investigated for various process variables. The experiments were operated systematically in wide regions of process variables such as CO_2/CH_4 ratio, total flow rate, pulse frequency and applied peak voltage. The conversions of methane and carbon dioxide increase with increasing the applied peak voltage or pulse frequency and decrease with increasing the total flow rate. Selectivities of H_2 and CO increase with the increase of applied peak voltage, while increasing total flow rate and pulsed frequency does not affect H_2 and CO selectivities significantly.

Introduction

The reduction and utilization of greenhouse gases such as carbon dioxide and methane are becoming very important recently, due to the world concern of global warming. Carbon dioxide is a by-product of many industrial processes, for example, the emission gas from power plant contains a large amount of CO_2 [1–3]. Landfill gas commonly consists of 50% CH_4 and 50% CO_2 and decomposition of industrial wastewater also produces a mixture of CH_4 and CO_2. CO_2 reforming of methane, as a process to convert those greenhouse gases into synthesis gas, has attracted great attention in industry and academia [1–4]. Synthesis gas consists of hydrogen and carbon monoxide, and it can be used to produce higher hydrocarbons [5–7], liquid hydrocarbons and oxygenates [8]. Conventional catalytic methods of CO_2 reforming have two main disadvantages: the reaction is intensively endothermic (Eq. (1)) and requires considerable energy consumption due to high process temperature (700–850 °C), and the catalysts used in CO_2 reforming are vulnerable to deactivation due to coke deposition on the catalyst's surface [9–11].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \Delta H = 247\ \text{kJ/mol} \quad (1)$$

Therefore, a low temperature process for CO_2 reforming of methane is of great interest. Non-thermal plasmas can be a suitable process for CO_2 reforming of methane, because of its no equilibrium properties, low power requirement and capacity to induce physical and chemical reactions, resulting in conversion at relatively low temperature in comparison with the conventional catalytic processes [12–14]. The non-equilibrium characteristics of such plasmas could overcome thermodynamic barriers in chemical reactions (e.g. dry reforming) and enable thermodynamically unfavorable reactions to occur at atmospheric pressure and low temperature. The facilitation of reactions at lower reaction temperature, dry reforming of hydrocarbons in non-thermal plasma also has characteristics such as fast ignition of the reaction, the compatibility for a broad range of hydrocarbons, the insensitivity to impurities in the gas stream compared with thermal catalytic processes [15].

There have been several reports on the plasma-assisted methane reforming [16–21]. Huang et al. studied CO_2-reforming CH_4 reactions by glow discharge plasmas using a Y-type reactor [19]. The process was found effective in converting CH_4 and CO_2 into CO and H_2 with a small amount of hydrocarbons. Qi et al. applied novel plasma atmospheric pressure abnormal glow discharge to investigate synthesis gas production from reforming methane and carbon dioxide [20]. It was reported that the selectivity of CO and H_2 could be properly adjusted by changing the ratio of CH_4 and CO_2, and increasing content of CH_4 will cause serious carbon deposition on the electrodes. Zhang et al.

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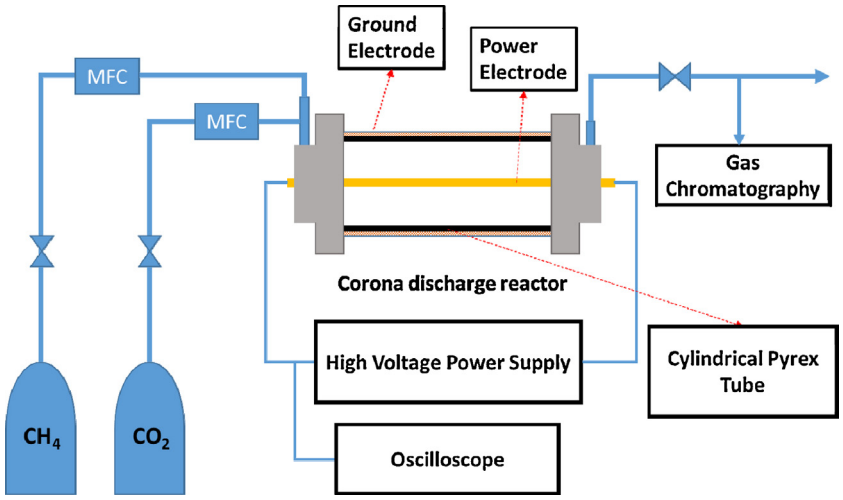
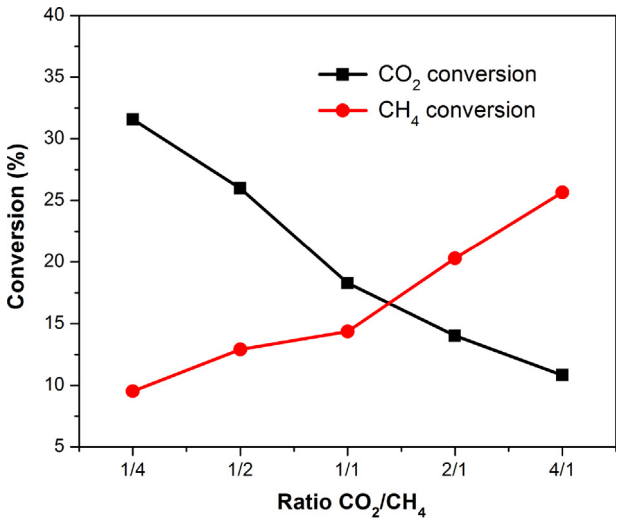


Fig. 1. Schematic of experimental setup for CO_2 reforming of CH_4 in corona discharge reactor.

investigated methane conversion in the presence of carbon dioxide under the conditions of dielectric-barrier discharge plasmas [21]. It was pointed out that the product of methane conversion contained gaseous hydrocarbons, syngas and oxygenates and also the surface of electrodes played an important role in the formation of acids and CO. From industrial viewpoint, corona discharge mainly has the chance to be applied to handle large gas volume, because it can be generated for near to or higher than atmospheric pressure at low temperature. Corona discharge has several industrial applications, such as reduction of NO_x and SO_x in flue gas, destruction of toxic compounds, and generation of ozone, etc. The electron temperature of corona discharge is in range of 3.5–6 eV and the electron density is about 10^{15}–10^{19} m^{-3} [15]. In comparison with other cold plasma processes, the advantage of corona discharge is that it can be established relatively easily. In this study, CO_2 reforming of CH_4 to syngas by corona discharge was studied systematically for various process conditions. The mixing ratio of CO_2/CH_4 in the feed, applied peak voltage, total flow rate, and pulse frequency were varied to determine experimentally the effects of these parameters on methane and carbon dioxide conversions, as well as on hydrogen and carbon monoxide selectivities. This study can be used as the stating data to design the industrial or pilot process and also to find the optimum process conditions for CO_2 reforming of CH_4 to syngas by corona discharge.

Experimental

Fig. 1 shows the experimental setup for CO_2 reforming of CH_4 by corona discharge plasma reactor. The corona discharge was generated in cylinder-wire type reactor, where the copper wire as discharge electrode was located at the center of the glass tube with the inner and outer diameters of 27 mm and 30 mm, respectively. The outside wall of the reactor was wrapped over by a stainless steel mesh which acts as a ground electrode. The corona discharge was generated by applying high voltage power into the reactor. The high voltage applied to the discharge electrode was measured by a 1000:1 high-voltage probe and a digital oscilloscope. The reactants, CH_4 (<99.9%) and CO_2 (<99.5%) in varied ratios of CO_2/CH_4, were well mixed and then flowed through the reactor at room temperature and atmospheric pressure. CO_2 and CH_4 flow rates were controlled by mass flow controllers (MFC). Each gas stream passed through the moisture trap (silica gel) to remove H_2O vapor. The concentrations of products at the outlet of reactor were measured by a gas chromatography (GC). The product gases were



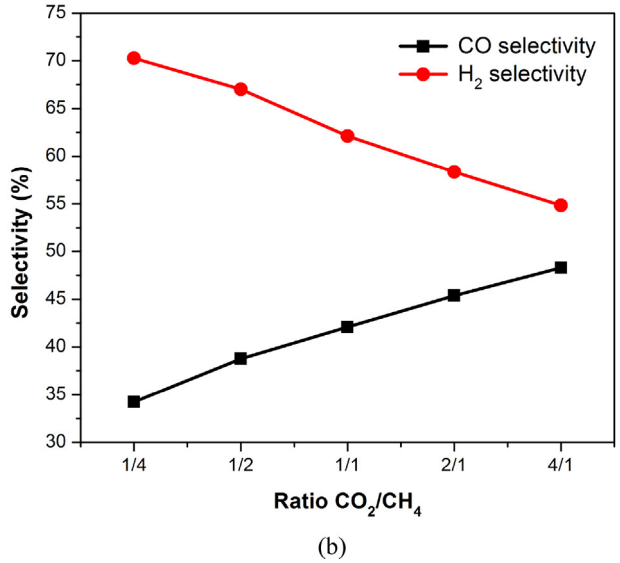


Fig. 2. CO_2 and CH_4 conversions (a) and CO and H_2 selectivities (b) for various ratios of CO_2 and CH_4.