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Short communication

Hydrogen production from dimethyl ether using corona discharge plasma

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Abstract

Dimethyl ether (DME), with its non-toxic character, high H/C ratio and high-energy volumetric density, is an ideal resource for hydrogen production. In this work, hydrogen production from the decomposition of DME using corona discharge has been studied. The corona discharge plasma decomposition was conducted at ambient conditions. The effects of dilution gas (argon), flow rate, frequency and waveforms on the DME decomposition were investigated. The addition of dilution gas can significantly increase the hydrogen production rate. The highest hydrogen production rate with the lowest energy consumption presents at the flow rate of 27.5 Nml min^{-1}. AC voltage is more favored than DC voltage for the production of hydrogen with less energy input. The optimal frequency is 2.0 kHz. The hydrogen production rate is also affected by the input waveform and decreases as following: sinusoid triangular > sinusoid > ramp > square, whereas the sinusoid waveform shows the highest energy efficiency. The corona discharge decomposition of DME is leading to a simple, easy and convenient hydrogen production with no needs of catalyst and external heating.

Keywords: Hydrogen production; Dimethyl ether; DME; Corona discharge; Cold plasma

1. Introduction

Hydrogen energy has attracted great attention worldwide. Especially, hydrogen for fuel cells is very promising since hydrogen conversion is clean without the emission of hazardous by-products like sulfur oxides and nitrogen oxides. Hydrogen is normally produced from reforming of natural gas, methanol, and gasoline via catalytic conversion thermally [1–3]. The reforming of natural gas and gasoline is usually operated at elevated temperatures (600–800 °C), which requires an intense energy input. Methanol was considered as a more favored option since it can be converted at relatively lower temperatures (150–300 °C). However, the toxicity of methanol limits its uses as hydrogen carrier. Various technologies are being explored to produce hydrogen from the point view of sustainable development. For example, solar energy is used to generate hydrogen via photocatalytic splitting of water or alcohols [4,5]. Biomass is used to replace fossil source as the reservoir of hydrogen [1,6]. However, much more efforts have to be made before any possible practical applications of these technologies. There are challenges and opportunities for the improvement of existing processes and for the development of new processes for hydrogen generation.

Dimethyl ether (DME) has been recently recognized as an alternative of diesel fuel and a potential fuel for power and domestic use. DME is relatively inert, non-corrosive, and non-carcinogenic. Its physical properties are similar to those of liquefied petroleum gas (LPG). It can be easily liquefied, stored and transported using the facilities providing LPG. DME is also an excellent resource for hydrogen production with its high H/C ratio and high-energy volumetric density. In 2001, Glvita et al. firstly reported the hydrogen generation from DME by steam reforming [7]. Then the studies on partial oxidation and steam reforming of DME increased quickly [8–13]. Several catalysts, including metal oxides and supported metals, have been investigated to improve the efficiency and to understand the reaction mechanism.

As addressed above, most of the established or developing processes for hydrogen production are conducted at elevated temperature with the presence of catalysts, which has some inherent drawbacks. These processes need a start-up stage and no hydrogen is produced before the temperature reaches the defined value. And, the catalysts inevitably suffer from deac-

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tivation. Therefore, it is very necessary to develop a simple, flexible and stable hydrogen production technology with quick responses that is specifically suitable for remote and domestic applications where temporary but instant hydrogen providing is needed.

Recently, plasma technologies, especially cold plasma ones, have been extensively used for chemical conversions. Cold plasma is characterized by highly energetic species (electrons, ions, excited atoms and molecules) and low gas temperature (as low as room temperature). The energy of those energetic species can be effectively transferred to other molecules through inelastic collisions. For example, stable chemical bonds like C–H in methane molecule are easily split with neither heating nor assistance of catalysts [14,15]. Therefore cold plasmas are highly effective to induce chemical reactions at ambient conditions. Dielectric barrier discharge plasma (a type of cold plasma) has been applied to produce hydrogen from water, methane and methanol [16–18]. Hydrogen is produced at room temperature but the energy efficiency has to be improved. We have utilized another kind of cold plasma, namely corona discharge plasma, to generate hydrogen from methanol with greatly improved energy efficiency [19]. This process is easily manipulated with quick response, showing great potential for practical applications. Since DME possesses many excellent natures, as addresses above, as an excellent source of hydrogen, we attempt to use the corona discharge plasma to produce hydrogen from DME in this work.

2. Experimental

Fig. 1 shows the experimental apparatus of corona discharge plasma system. Corona discharge was generated in a quartz tube with an inner diameter of 6 mm. A pin-plate electrode configuration was used with a pin electrode and a plate electrode inserted in the tube. The gap between the electrodes was 6 mm. The pin electrode was connected with high voltage and the plate electrode was grounded. The signal, with adjustable waveform and frequency generated by a signal generator (HP 33120A), was magnified by a high voltage amplifier (Trek, 20/20B) and transferred to the pin electrode. When the voltage was high enough, a bright corona discharge was formed. The discharge voltage and current were measured with a high voltage probe (Tektronix P6015) and a pulse current transformer (Pearson Electronics 411) and recorded with a digital oscilloscope (Tektronix 2440), respectively. The input power was measured with a digital multimeter (Keithley, 2000).

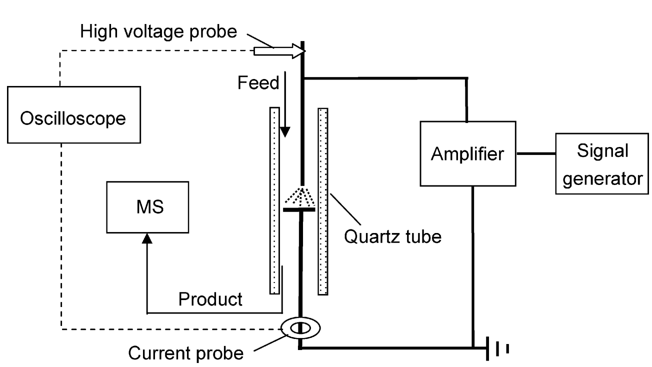

Fig. 1. Experimental apparatus of corona discharge plasma system.

DME was introduced into the discharge tube from the upper side of the discharge tube and decomposed in the plasma zone between electrodes. The flow rate was controlled by a mass flow rate controller. Argon with controlled flow rate was used as dilution gas in some cases. The composition of effluent gas was measured with an on-line MS (AVI-GmbH, Ominstar). The gas product includes H_2, CO and small amount of H_2O. Deposition of carbon was observed during the reaction and the amount of deposited carbon was measured with gravimetric analysis. The molar ratio of H_2/CO/C was 3/1/1. The total carbon balance was 97–102%. The total decomposition of DME is as following:

$$CH_3OCH_3 \rightarrow 3H_2 + CO + C$$

The conversion of DME was defined as following:

$$\text{Conversion}(\%) = \frac{\text{moles of DME consumed}}{\text{moles of DME introduced}} \times 100\%$$

The rate of H_2 production was measured with MS and was in good agreement with the value calculated as following:

$$\text{Rate of } H_2 \text{ production (Nml min}^{-1}) = \text{rate of DME consumed (Nml min}^{-1}) \times 3$$

The specific energy consumption (SEC) was defined as the energy consumed per Nml hydrogen:

$$\text{SEC (Wh Nml}^{-1}) = \frac{\text{power consumed (W)}}{\text{rate of } H_2 \text{ production (Nml min}^{-1}) \times 60}$$

3. Results and discussion

3.1. Effect of dilution gas

Fig. 2 shows the conversion of pure and diluted DME. The conversion of pure DME is relatively low and the presence of Ar can significantly improve the conversion. This indicates that the dilution gas Ar greatly improves the reaction through changing

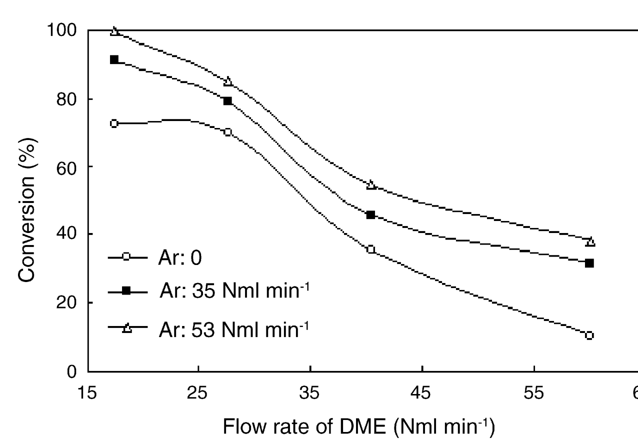

Fig. 2. Conversion of pure and diluted DME (input waveform: 2.0 kHz sinusoid).

the reaction pathway. When pure DME is introduced into the plasma zone, DME molecules are directly excited by highly energetic electrons through collisions.

$$CH_3OCH_3 + e^* \rightarrow CH_3OCH_3^* + e \quad (1)$$

where the asterisk means electrons or molecules with higher energy. The excited molecules are unstable and will be quickly decomposed if colliding with electrons or other excited species (M^*)

$$CH_3OCH_3^* + e^*(M^*) \rightarrow 3H_2 + CO + C \quad (2)$$

The efficiency of direct excitation is relatively low. On the contrary, the indirect excitation through Ar is more favorable because Ar is an excellent plasma-forming gas. When Ar atoms present in the plasma zone, they first collide with electrons and become excited:

$$Ar + e^* \rightarrow Ar^* \quad (3)$$

Then DME molecules get energy from the excited Ar atoms instead of electrons:

$$CH_3OCH_3 + Ar^* \rightarrow CH_3OCH_3^* + Ar \quad (4)$$

The excited DME molecules are further decomposed via collision with excited Ar atoms and other excited species:

$$CH_3OCH_3^* + Ar^*(M^*) \rightarrow 3H_2 + CO + C \quad (5)$$

3.2. Effect of flow rate

Fig. 2 also shows the effect of the flow rate of DME. The conversion decreases with the increase of flow rate of DME. However, Fig. 3a shows that the rate of H_2 production increases with the increasing flow rate and reaches the maximum at 27.5 Nml min^{-1}. For the pure DME plasma, the rate quickly decreases when the flow rate is further increased. Meanwhile a stable rate is obtained for the diluted plasma.

On the other hand, the increasing flow rate of DME will reduce the residence time of the reactant in the plasma zone, as the flow rate of argon remains unchanged. When the flow rate is low, the residence time is long enough for the decomposition of DME. If the flow rate is too high, the residence time becomes insufficient for the decomposition reaction. Therefore, the increasing flow rate cannot improve the reaction rate any more.

Fig. 3b presents the specific energy consumption for H_2 production. The lowest SEC is achieved with the flow rate of 27.5 Nml min^{-1}. The energy efficiency of the diluted plasma is obviously higher than that of pure DME plasma. The SEC of pure DME plasma is greatly dependent on the flow rate but the diluted plasma does not change much. This result is in good agreement with the result of Fig. 3a.

3.3. Effect of frequency

Corona discharge plasma can be ignited with DC or AC voltage. Fig. 4 shows the effect of frequency on the rate of hydrogen production. The reaction rate is very low when DC voltage (frequency = 0 Hz) is applied. AC voltage obviously leads to higher reaction rate. The conversion of DME is as high as 99.4% when the frequency rises to 10 kHz. Higher frequency is not studied due to the limitation of the voltage amplifier.

Table 1 shows the discharge parameters with various frequencies. Although the voltage and power consumed is very low for DC plasma, it exhibits a higher SEC because of the extremely low rate of H_2 production. AC plasma shows lower

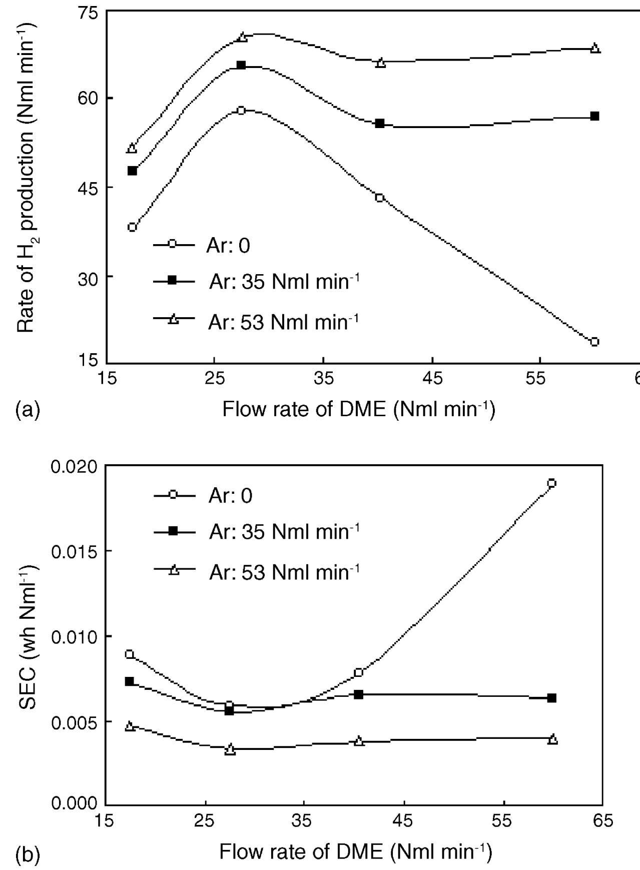

Fig. 3. Effect of flow rate of DME on (a) the rate of H_2 production and (b) SEC (input waveform: 2.0 kHz sinusoid).

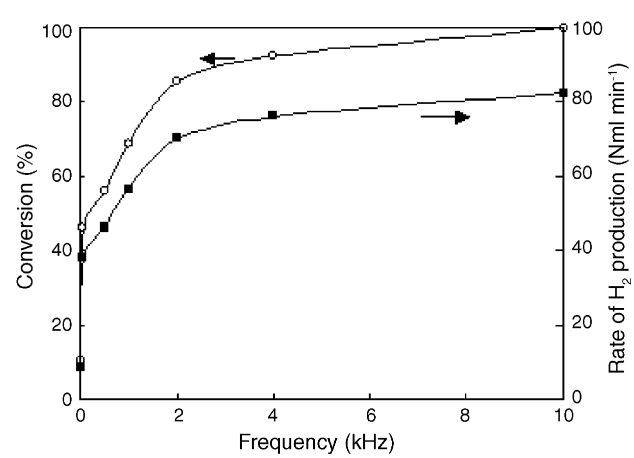

Fig. 4. Effect of frequency on the conversion of DME and rate of H_2 production (input waveform: sinusoid; feed: DME 27.5 Nml min^{-1}, Ar 53.0 Nml min^{-1}).

Table 1
Effect of frequency on the plasma DME decomposition to hydrogen (input waveform: sinusoid; feed: DME 27.5 Nml min^{-1}, Argon 53.0 Nml min^{-1})

Frequency (kHz)	Voltage (kV)	Current (mA)	Power (W)	SEC (Wh Nml^{-1})
0	0.08	38.0	3.0	0.0060
0.05	1.9	31.1	10.3	0.0045
0.5	1.3	46.8	12.6	0.0046
1	1.8	50.0	20.5	0.0061
2	1.6	40.6	14.1	0.0033
4	1.8	53.1	19.9	0.0044
10	1.9	53.1	17.3	0.0035

SEC despite the higher voltage and current presented, indicating its higher energy efficiency. No general rule on the effect of frequency is concluded. From the point view of energy efficiency, the optimal frequency is 2 and 10 kHz. The former is more practical because the cost is increased to output voltage with high frequency.

3.4. Effect of waveform

Four types of waveforms, sinusoid, sinusoid triangular, square and ramp, were investigated in the present work. As shown in Fig. 5, the sinusoid triangular waveform results in the highest reaction rate while the ramp waveform leads to the lowest value.

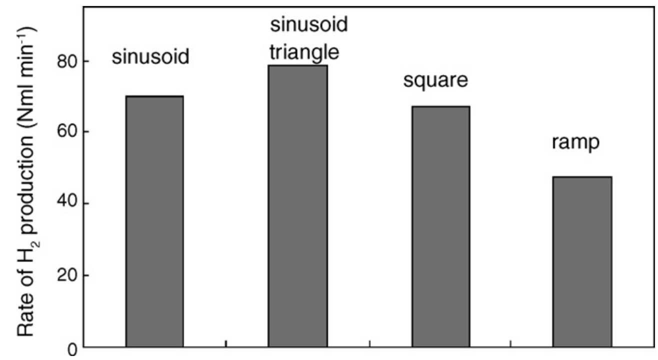

Fig. 5. Effect of waveform on the rate of H_2 production (frequency: 2.0 kHz; feed: DME 27.5 Nml min^{-1}, Ar 53.0 Nml min^{-1}).

Four types of voltage and current waveforms are shown in Fig. 6 and the discharge parameters are shown in Table 2. Although the input waveforms are different, the shape of discharge voltage and current curve is similar, especially for the former three. The current of sinusoid triangular is the highest and contains many pulses. The pulse in current is the characteristic of

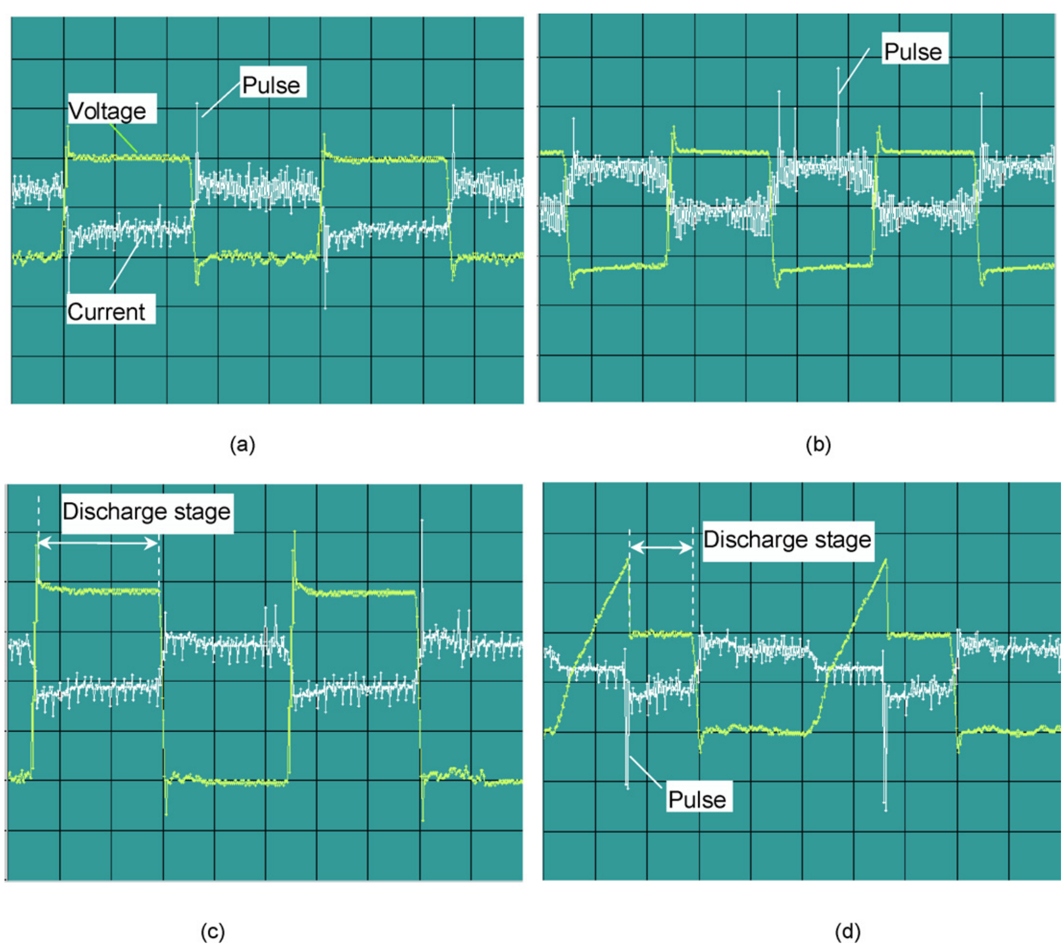

Fig. 6. Voltage and current waveforms of (a) sinusoid, (b) sinusoid triangular, (c) square and (d) ramp (frequency: 2.0 kHz; feed: DME 27.5 Nml min^{-1}, Ar 53.0 Nml min^{-1}).

Table 2
Effect of waveform on the plasma DME decomposition to hydrogen (frequency: 2.0 kHz; feed: DME 27.5 Nml min^{-1}, Ar 53.0 Nml min^{-1})

Input waveform	Voltage (kV)	Current (mA)	Power (W)	SEC (Wh Nml^{-1})
Sinusoid	1.6	40.6	14.1	0.0033
Sinusoid triangle	2.1	50.1	20.9	0.0044
Square	2.0	43.7	18.9	0.0047
Ramp	2.0	46.8	16.4	0.0057

pulsed streamer discharge that is very active for chemical reactions [14]. So the sinusoid triangular is most active and shows the highest hydrogen production rate of 78.7 Nml min^{-1}. The sinusoid and ramp waveforms also contain many pulses. In the case of ramp waveform, however, the duration of the discharge stage is only 61.1% in each cycle, which is much lower than the other three waveforms (81.0–92.9%). This ultimately decreases the activity and the rate of H_2 production is only 47.7 Nml min^{-1}. As to the energy efficiency, the sinusoid waveform shows the lowest SEC because it maintains a high current with low voltage, indicating that this waveform is more favorable for potential future applications.

4. Conclusions

The present investigation confirms that plasma DME decomposition using corona discharges is a simple and effective way for hydrogen production, which can be conducted at ambient conditions. No external heating, no complex equipment and no catalyst are required. The DME decomposition using corona discharge can be easily operated at flexible conditions, like cold start-up and transients. The addition of argon as dilution gas can significantly improve the reaction and decrease the energy consumption. And, the influence of flow rate presents a maximum on the DME decomposition to hydrogen. The highest hydrogen production rate with the lowest energy consumption presents at the flow rate of 27.5 Nml min^{-1}. AC voltage is more favored than DC voltage for the production of hydrogen with less energy input. The optimal frequency is 2.0 kHz. The hydrogen production rate is also affected by the input waveform and decreases as following: sinusoid triangular > sinusoid > ramp > square, whereas the sinusoid waveform shows the highest energy efficiency.

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