Novel Plasma Methanol Decomposition to Hydrogen Using Corona Discharges

Hui-qing Li, Ji-jun Zou,[†] Yue-ping Zhang,[†,††] and Chang-jun Liu*[†]
Key Laboratory for Green Chemical Technology, School of Chemical Engineering, Tianjin University, Tianjin 300072, P. R. China
[†]*ABB Plasma Greenhouse Gas Chemistry Laboratory, Tianjin University, Tianjin 300072, P. R. China*
[††]*Department of Chemistry, Tianjin University, Tianjin 300072, P. R. China*

(Received February 27, 2004; CL-040225)

We reported in this work a simple, effective, and efficient hydrogen production from plasma methanol decomposition using DC and AC corona discharges at ambient condition. The highest hydrogen production rate was achieved with AC corona discharges. The power consumption was normally less than 0.02 Wh/Ncm^3 H_2. A major advantage of methanol decomposition using corona discharge is that only a very small discharge space is enough for sufficiently high decomposition.

Hydrogen production from methanol is an interesting and promising option for the energy supply of fuel cells and other applications. Compared to the developed hydrogen storage technologies, the use of methanol as an effective storage of hydrogen is much safer and cheaper. The hydrogen production technologies from methanol include steam reforming,[1,2] partial oxidation,[3] oxidative steam reforming[4] and methanol decomposition.[5,6] The decomposition of methanol provides a better alternative for the hydrogen production. However, there are some drawbacks with the catalytic hydrogen production from methanol: 1) the present methanol reformers are mostly the packed bed reactors that suffer from problems such as the occurrence of hot and cold spots; 2) there are some problems during the cold start-up and transients; 3) the catalytic activity and stability still need to be improved.

Recently, there have been investigations on methanol decomposition using dielectric-barrier discharge (DBD)[7] and ferroelectric pellet packed-bed reactor (FPR).[8] These would be the first reports of plasma methanol decomposition to hydrogen and carbon monoxide, upon the knowledge of the author. A higher one-pass conversion rate can be achieved with this plasma way, compared to the catalytic decomposition. Especially, the DBD plasma methanol conversion is easier to be operated than the catalytic process, with an input power ranged from 0.27 to 6.40 Wh/(Ncm^3 H_2). The maximum CH_3OH conversion of 80% into H_2 was achieved with CO or CO_2 being the other major products in the absence or presence of water, respectively.[7] In this work, we will further simplify the discharge reactor system with a gas/gas corona discharge in order to increase the efficiency furthermore. A big difference between the DBD and corona discharge is the electrode configuration. The DBD has a dielectric layer between two electrodes, while no such dielectric-barrier within corona discharge, which contains a tip electrode below or above a normal plate electrode. This means that the two electrodes with the corona discharge will be expose directly to plasma phase and induces a significant change in discharge physics and chemistry.[9,10]

Figure 1 shows the corona discharge reactor applied in this work. This reactor is similar to the one previously used for plasma methane conversion via corona discharges.[10,11] The reactor is a quartz tube with the inner diameter of 6 mm. There is a cylindrical furnace placed around the reactor for the reaction temperature control. This discharge reactor consists of two electrodes, a top metal wire electrode and a lower hollow electrode as the grounded one. The gap between the electrodes can be adjusted to fit the reactive conditions. The high voltage amplifier (Trek 20/20B), connected with a HP33120A signal generator, supplied a high voltage with DC or AC (at different waveforms) signal to the top wire electrode. The voltage and current were measured with a high voltage probe (Tektronix P6015 A) and a pulse current transformer (Pearson Electronics 411) via a digital oscilloscope (LeCroy Model LC 334A). The discharge power was measured via a digital multimeter (Keithley 2000).

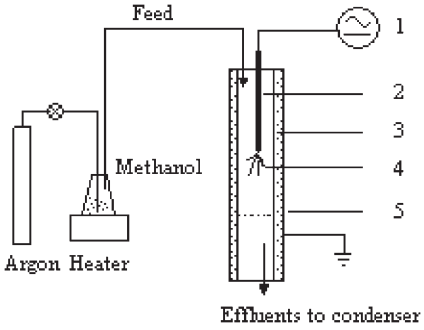

Figure 1. Schematic representative of corona discharge reactor 1: High voltage generator; 2: High voltage electrode; 3: Quartz tube; 4: Gas discharge gap; 5: Grounded electrode.

Argon was used as the carrier gas and pure methanol was saturated into the carrier gas when argon was flowing through the liquid methanol. The composition of methanol in the feed gas was controlled by heating the liquid methanol. The flow rate of argon was adjusted by a mass flow controller. The feed gas passed through the gap in the corona discharge reactor and methanol was converted within the discharge zone. The discharge reaction was terminated at the end of discharge region.

The composition of the feed and products were analyzed with a GC (Agilent 4890D) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). A mass selective detector (HP 5971) was used to identify the liquid products. Liquid products were collected in a cold trap cooled with a mixture of ice and water.

As a measure of energy efficiency for corona discharge reactor, specific energy density (SED) is used, where power denotes the plug-in power.

$$\text{SED (kJ/L)} = \text{power (kW)/total flow rate of Ar and } CH_3OH \text{ (L/s)} \quad (1)$$

Figure 2 presents a relationship among residence time, SED and methanol conversion. In Figure 2, DC-pos represents the positive direct current (DC) corona discharge and DC-neg means the negative DC corona discharge, while AC-sin denotes the alternative current (AC) corona discharge with sinusoid waveform. In general, the conversion of CH_3OH increases with increasing SED, upon Figure 2a. At the same residence time the SED decreases in the order as: AC-sin > DC-neg > DC-pos. It results in higher methanol conversion with AC-sin corona. AC corona discharge exhibits a different discharge performance from DC corona discharge. As the AC discharge is applied, each electrode performs alternately as anode or cathode. Therefore, it is easier to sustain AC corona discharge than to DC corona discharges.[11] The amount of active species within AC corona is larger than that within DC corona discharges.

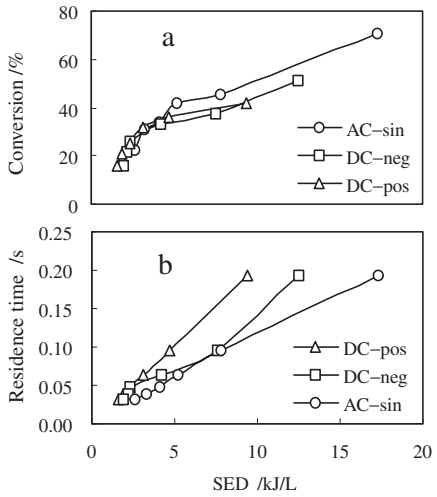

Figure 2. Relationship between SED, conversion of CH_3OH and residence time. a) SED vs conversion of CH_3OH, b) SED vs residence time (Ar flow rate: 40 NmL/min, CH_3OH feed concentration: 20%).

Figure 3 shows an effect of methanol feed concentration on plasma methanol decomposition using AC and DC corona discharges. Upon this figure, no significant difference between AC and DC corona discharges is observed at the low and high methanol feed concentrations. However, AC corona discharge leads to a better decomposition than DC one at the methanol feed concentration ranged from 20 to 75%. In addition, a maximum decomposition rate has been observed at 57.4% of methanol feed concentration. The maximum decomposition rate reaches 1.12 mmol/min with the minimum power consumption of 0.004 Wh/Ncm^3 H_2, using AC corona discharge. Meanwhile they are 0.78 mmol/min and 0.005 Wh/Ncm^3 H_2 with DC corona discharge.

One of principal advantages of methanol decomposition using corona discharges is that the energy request is relatively little. In addition, a significant advantage of methanol decomposition using corona discharge is that only a very small discharge space is enough for sufficiently high decomposition. This is very suitable to the use of automobiles. Further investigation would lead to a practical application of methanol decomposition using corona discharges.

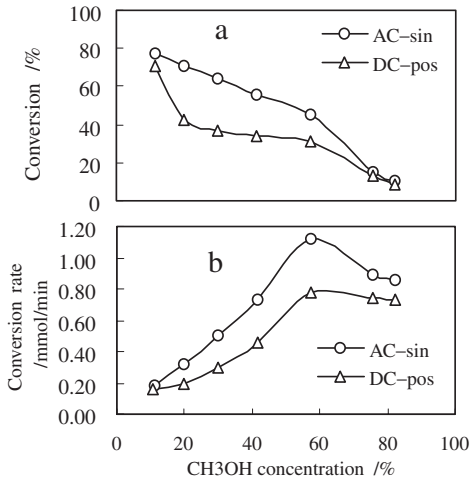

Figure 3. Effect of CH_3OH feed concentration on a) conversion of CH_3OH. b) conversion rate (Ar flow: 40 cm^3/min; frequency for AC-sin: 2000 Hz; applied average voltage: 0.8 kV; average input power: 12 w).

The supports from the Key Fundamental Research Project of Ministry of Science and Technology of China (under contract number #G1999022402) and ABB Switzerland Ltd. are very appreciated.

References

1 B. A. Peppley, J. C. Amphlett, and L. M. Kearns, *Appl. Catal., A*, **179**, 31 (1999).
2 P. J. de Wild and M. J. F. M. Verhaak, *Catal. Today*, **60**, 3 (2000).
3 J. H. Liu, W. Xing, H. Yang, and T. H. Lu, *Chin. Chem. Lett.*, **13**, 489 (2002).
4 S. Velu, K. Suzuki, and M. Okazaki, *J. Catal.*, **194**, 373 (2000).
5 W. H. Cheng, *Acc. Chem. Res.*, **32**, 685 (1999).
6 Y. Y. Liu, K. Suzuki, and S. Hamakawa, *Chem. Lett.*, **2000**, 486.
7 S. Tanabe, H. Matsuguma, K. Okitsu, and H. Matsumoto, *Chem. Lett.*, **2000**, 1116.
8 H. Kabeshima , H. Einaga, and S. Futamura, *IEEE Trans. Ind. Appl.*, **39**, 340 (2003).
9 S. Masuda and H. Nakao, *IEEE Trans. Ind. Appl.*, **26**, 374 (1990).
10 C. J. Liu, R. Mallinson, and L. Lobban, *Appl. Catal., A*, **178**, 17 (1999).
11 C. J. Liu, A. Marafee, B. Hill, G. H. Xu, R. Mallinson, and L. Lobban, *Ind. Eng. Chem. Res.*, **35**, 3295 (1996).

Published on the web (Advance View) May 24, 2004; DOI 10.1246/cl.2004.744