

## A TWO-STEP CONVERSION OF SYNGAS VIA DIMETHYL ETHER

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**ABSTRACT** In this presentation, we present some of our experimental results of a two-step conversion of syngas into more valuable chemicals or high performance fuel additives. In the first step, dimethyl ether (DME) is formed from syngas. With the second step, the formed DME is applied for the further synthesis via an "electronic" catalysis. The conversion of DME by this way can reach a high-energy yield. The products of such conversion include oxygenates and/or alkanes. The two-step conversion of syngas via DME could lead a new synthesis from syngas. Especially, the conversion of DME in the second step can be operated at ambient condition. The synthesis reported here could lead to a new application of DME.

**KEYWORDS:** DME, electronic catalysis, plasma

### INTRODUCTION

The formation of Dimethyl Ether (DME) from syngas conversion has recently attracted more and more attention. DME is becoming a major product, especially for the gas reserves at remote sites or coalbed methane. It is important for us to seek for more applications of DME. DME is a useful chemical intermediate for the synthesis of many important chemicals, including dimethyl sulfate, lower olefins and methyl acetate.<sup>[1-3]</sup> DME has also been proposed as an aerosol propellant to replace chlorofluoro carbons, which were found to have destroying effect on the ozonosphere.<sup>[4]</sup> In addition, DME is a promising alternative fuel to diesel.<sup>[5]</sup> Brown *et al.* had a detailed discussion on the possible fuels or fuel precursors from DME<sup>[6]</sup>. They also described some possible methodologies for the use chemically of DME, including oxidative coupling, vinylation/hydrogenation, oxidative coupling (with MTBE) and carbonylation. Compared to the utilization of DME as fuel, propellant and so on, the use of DME as a chemical intermediate is particularly attractive and needs to be investigated extensively. Especially, DME has been recognized as an alternative to methanol as a chemical building block.

Here we report a conversion of DME in a dielectric-barrier discharge (DBD) plasma reactor at ambient condition, as a two-step of conversion of syngas. The DBD used in these experiments is a high pressure, non-equilibrium discharge which is initiated when alternating voltages of sufficiently high amplitudes are applied between two electrodes separated by a non-conducting medium (dielectric barrier) in addition to a gas space. The frequency of the ac electric field can vary over a wide range from line frequency to several MHz. Glass, quartz or ceramics can be used as dielectric materials. When the amplitude of the applied ac electric field reaches a critical value, breakdown is initiated in the gas and current flows through the gas space from one electrode to the other. Once breakdown is initiated at any location within the discharge gap, charge accumulates on the dielectric resulting in an opposite electric field. This opposite electric field locally reduces the external electric field in the gap and interrupts the current flow within a few nanoseconds. By this mechanism individual current filaments called microdischarges are formed. Their duration depends on the pressure and the properties of the gases involved and the dielectrics used. A large number of such microdischarges will be generated when a sufficiently high ac voltage is applied. The principal advantages of the DBD are that non-equilibrium plasma conditions can be established at atmospheric pressure and that the entire electrode area is effectively used for discharge reactions. The unusual "electronic" catalysis of DBD for the conversion of DME at ambient condition has been confirmed in this investigation. This could lead to a two-step utilization of syngas. In the first step, dimethyl ether (DME) is formed from syngas. With the second step, the formed DME is applied for the further synthesis via such electronic catalysis. Due to the limited space, we only focus on the second step in this paper and leave the first step for the future discussions.

### EXPERIMENTAL

Figure 1 illustrates the reactor system. The gas flow (pure DME) is subjected to the action of the DBD in an annular gap formed between an outer stainless steel tube maintained at constant temperature and an inner quartz tube. The radial width of the discharge space was 1 mm, its length 50mm ~ 150 mm. This reactor system is very similar to the DBD reactor for methane conversion described elsewhere.<sup>[7,8]</sup> All the experiments were conducted at atmospheric pressure. The feed and exhaust gases were analyzed by a gas chromatograph (HP 4890) with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The exhaust gas from the reactor was first introduced into a condenser to separate the condensable product from the gas. A high voltage generator working at about 25 kHz applies the power. The power can be varied by

adjusting the voltage amplitude, which causes a slight change of frequency. The voltage and current measurements were conducted using a high voltage probe (Tektronix P6015) and a current probe (Tektronix CT-2) with a digital oscilloscope (Tektronix TDS 210).

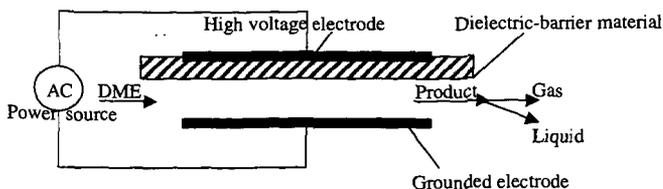
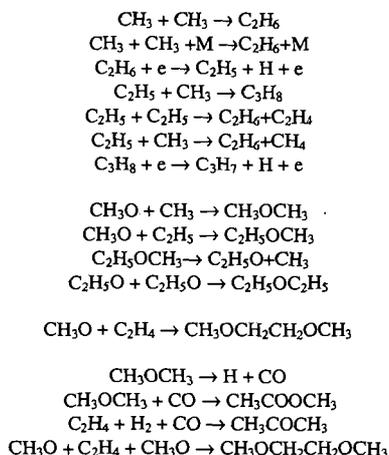


Figure 1. Schematically representative of the DBD reactor system

## RESULTS AND DISCUSSION

A surprising high DME conversion has been achieved in the present reactor design. The C-O bond breakdown in a DME molecule does not require a high energy and this leads to the high DME conversion. The bond strength of C-O in DME molecule is only 81 kcal/mol at 298 K.  $\text{CH}_3$  and  $\text{CH}_3\text{O}$  radicals can be easily obtained within DME plasmas. Hydrocarbons and ethers are expected to be formed from chain reactions initiated by  $\text{CH}_3$  and  $\text{CH}_3\text{O}$  radicals.

Table I shows the composition of gaseous products observed at 60°C and different gas flowrates. The gaseous product is a mixture of hydrocarbons, ethers,  $\text{H}_2$  and CO. Methane, ethane, propane, methyl ethyl ether, acetone, methyl isopropyl ether, ethyl ether, 1,2-dimethoxy ethane and dimethoxy methane were detected. Most of methoxy-containing hydrocarbons have been detected in the liquid phase. The composition of gaseous products changed greatly with the variation of gas flowrate. Experimental results showed that most of gaseous products were  $\text{H}_2$  and  $\text{C}_1$ - $\text{C}_3$  alkanes. The amount of oxygenates was very little in the gaseous phase but abundant in liquid product. Table I also shows the composition of lower alkanes in the gaseous phase increases with the decreasing flowrates. This is a typical characteristic of chain reactions. A mechanism has been presented to explain the observed phenomena.  $\text{CH}_3$  and  $\text{CH}_3\text{O}$  radicals are first generated in the DBDs via electronic dissociation or other plasma reactions. Some of chain reactions have been proposed as the following to explain the production of part of hydrocarbons:



In addition, the experiment has shown a formation of some paraformaldehyde, that could be induced from the reaction:  $\text{CH}_3\text{O} + \text{H} \rightarrow \text{HCHO} + \text{H}_2$ .

The DBD conversion of DME leads to a selective production of liquid product, that is a mixture of various ethers. Figure 2 shows the results of DME conversion and the ratio of liquid production to the total production. It is clear that higher DME conversion accompanies with more liquid products produced. More than 93% of the product is liquid at a gas flowrate of 20

ml/min. This suggests that DBDs could easily convert DME to liquid chemicals at ambient conditions. A more surprising phenomenon with this DBD DME conversion is that no carbon deposit has been observed on the dielectric, while a serious carbon deposit has been formed during plasma conversion of methane or other lower alkanes<sup>[8,9,10]</sup>. It has been considered that some aerosols would have been formed during DBD conversion of DME. It is the aerosol inhibits the formation of carbon deposit. Further investigations are being conducted.

Table 1: Effect of gas flow rate on the composition of gas product

Composition / mol%	Gas flow rate / ml/min			
	60	45	30	20
H <sub>2</sub>	9.15	10.83	20.49	31.26
CO	4.29	4.20	8.56	17.70
CH <sub>4</sub>	4.46	5.54	9.82	12.50
C <sub>2</sub> H <sub>6</sub>	2.66	3.19	5.36	6.02
C <sub>3</sub> H <sub>8</sub>	0.22	0.28	0.59	1.22
DME	76.48	72.87	50.63	26.71
C <sub>2</sub> H <sub>5</sub> O CH <sub>3</sub>	1.32	1.51	2.37	1.83
CH <sub>3</sub> CO CH <sub>3</sub>	0.04	0.05	0.10	0.20
C <sub>2</sub> H <sub>5</sub> (OCH <sub>3</sub> )CH <sub>3</sub>	0.04	0.04	0.09	0.10
C <sub>2</sub> H <sub>5</sub> O C <sub>2</sub> H <sub>5</sub>	0.02	0.03	0.05	0.07
CH <sub>3</sub> O CH <sub>2</sub> OCH <sub>3</sub>	0.19	0.22	0.32	0.23
CH <sub>3</sub> O CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	0.14	0.15	0.14	0.07
others	1.00	1.09	1.49	2.10

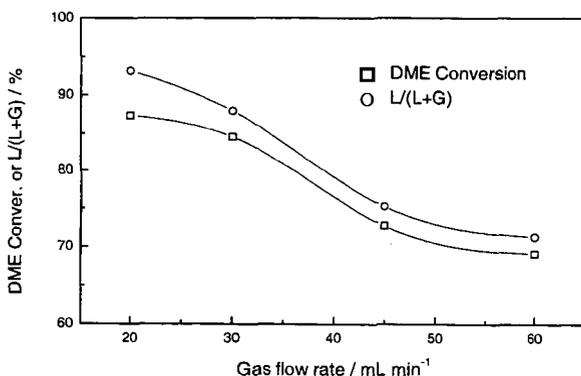
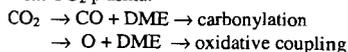


Figure 2. Effect of gas flow rate on experimental results

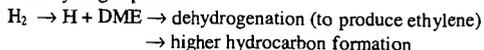
## CONCLUSIONS

The potential of plasma conversion of DME has been demonstrated in this work. The present product from this DME conversion can be used as the high performance fuel additive. Moreover, further investigation is being conducted to produce selectively other valuable hydrocarbons. Some other potential pathways for the DME conversion via electronic catalysis are as the following:

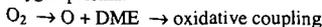
With CO<sub>2</sub> plasma:



With hydrogen plasma:



With oxygen plasma:



With lower alkane (methane, ethane or propane) plasma:

lower alkane plasma + DME  $\rightarrow$  high performance fuels or fuel precursors

With steam plasma:

steam plasma + DME  $\rightarrow$  special oxygenated hydrocarbons

With syngas plasma:

syngas plasma + DME  $\rightarrow$  carbonylation and others

These pathways open more doors to produce series of valuable chemicals. Especially, one of advantages of such electronic catalysis of DME plasma is her high efficiency that is able to convert DME into some special chemicals, that may be difficult to be produced using the conventional technologies. Since the plasma is a complex reactive system that contains a mixture of electrons, ions, radicals, photons, and so on. The control of plasma reactions needs special skills so that a selective conversion of DME can be achieved. We have confirmed that DBD can perform as excellent electronic catalyst for DME conversion. There are some other plasma phenomena, like corona discharge, arc discharge, gliding arc discharge and microwave discharge, that could also be useful for the DME conversion. To compare with the conventional catalysis, the controlling parameters of electronic catalysis are electron temperature, electron density, radical energy and density and so on. The gas temperature and pressure have a little influence on electronic catalysis. More fundamental investigations are necessary to understand the mechanisms. The feasibility of the two-step conversion of syngas via DME using electronic catalysis is being confirmed in our further investigations.

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#### REFERENCES

- 1 T. Shikada, K. Fujimoto, M. Miyauchi and H. Tominaga. *Appl. Catal.*, **1983**,7, 361.
- 2 W. W. Kaeding and S. A. Butter. *J. Catal.*, **1980**,61,155.
- 3 Guangyu Cai, Zhongmin Liu and Renmin Shi *et al.* *Appl. Catal.*, A **1995**,125, 29.
- 4 K. Guenter, S. Guenter and T. Dieter. DE Patent 4313584
- 5 Alkeos C. Sofianos and Mike S. Scurrell. *Ind. Eng. Chem. Res.*, **1991**,30, 2372.
- 6 D.M. Brown, B.L. Bhatt and T.H. Hsiung *et al.* *Catal. Today*, **1991**, 8, 279
- 7 Chang-jun Liu, Gen-hui Xu and Timing Wang. *Fuel Processing Technology*, **1999**,58, 119.
- 8 Balduur Eliasson, Chang-jun Liu and Ulrich Kogelschatz. *Ind. Eng. Chem. Res.*, **2000** (to be published).
- 9 Chang-jun Liu, R.G. Mallinson and L. Lobban. *J. Catal.*, **1998**, 179,326.
- 10 Chang-jun Liu, R.G. Mallinson and L. Lobban. *Appl. Catal. A*, **1999**, 178,17.