Conversion of Dimethyl Ether to Diesel Fuel Additives via Dielectric Barrier Discharges

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(Received January 15, 2001; CL-010036)

A high-efficient conversion of dimethyl ether (DME) to diesel fuel additives at ambient condition via dielectric-barrier discharges has been performed. The conversion of DME reaches a high value of 66.56% at a gas flow rate of 30 mL·min^{-1}. The liquid obtained is a cetane number promoter of diesel fuels. The selectivity of liquid product is more than 40%.

Dialkoxyalkane (DAAK) chemicals are a broad class of oxygen-containing chemical family. The best known compound in this family is probably dimethoxymethane (DMMT). Other compounds in this family include dimethoxyethane (DMET) and dimethoxypropane (DMPP), etc. DMMT has been proposed as a cetane number improving additive for diesel fuel because of the possibility of suppressing smoke emission.[1] DMET can also be used as a diesel fuel additive to reduce soot and smoke emission. Another purpose of adding DMET to diesel fuel is to increase the oxygen level of diesel fuel.[2]

DMET is usually obtained from the oxidative coupling of dimethyl ether (DME) (via $2CH_3OCH_3 + 1/2O_2 \rightarrow CH_3OCH_2CH_2OCH_3 + H_2O$).[3] It is well known that DME is a useful chemical intermediate for the synthesis of many important chemicals.[4–6] The special properties of DME allow it to be used as a chemical building block for oxygenated hydrocarbons with higher molecular weight. However, the oxidative coupling of DME has to be conducted at high temperature and pressure, with which the complete oxidation of DME is more thermodynamically favored. Here we report a non-oxidative conversion of DME in a dielectric-barrier discharge (DBD) reactor at ambient condition. DBD is one of non-thermal plasma phenomena, which has been considered very promising for organic chemical reactions because of its non-equilibrium properties, low discharge power requirement and its capacity to induce physical and chemical reactions within gases at relatively low gas temperatures.[7]

Figure 1 illustrates the reactor system. This tubular reactor is composed of an outer steel cylinder and an inner quartz tube. The outer steel cylinder serves as the ground electrode. A metal wire located in the center of quartz tube serves as the high voltage electrode. The gas flow of pure DME is subjected to the action of the DBD in an annular gap formed between the outer stainless steel tube maintained at constant temperature and the inner quartz tube. The radial width of the discharge space was 1 mm, its length 250 mm. This reactor system is very similar to the DBD reactor for methane conversion described elsewhere.[8] 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). Deviation of carbon balance was within ±3%. The exhaust gas from the reactor was first introduced into a condenser to separate the condensable product from the gas. The power was supplied by a high voltage generator working at about 25 kHz. 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).

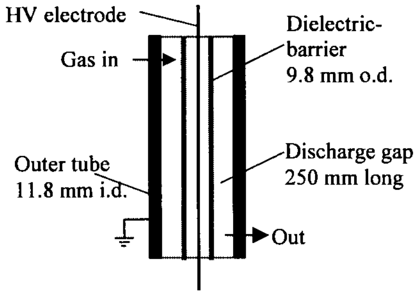

Figure 1. Schematically representative of the DBD reactor.

A high DME conversion has been achieved in the present reactor design. Figure 2 presents the effect of discharge power on conversion of DME. It can be seen that the conversion of DME increases from 17.43% to 66.56% when discharge power increases from 35 W to 100 W. Figure 2 also shows a slightly decrease in selectivity of liquid product and an increase in liquid yield with the increasing power.

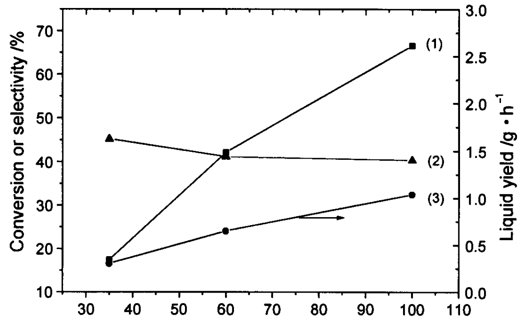

Figure 2. Effect of discharge power on DME conversion ((1) DME conversion, (2) liquid selectivity, (3) liquid yield; Reaction temperature 100 °C; gas flowrate of DME 30 mL·min^{-1}).

The DBD conversion of DME leads to a selective production of liquid product. The liquid product is a mixture mainly comprising DAAK chemicals including DMET, DMPP, 1,2,3-trimethoxypropane (TMPP) and some esters. From results in Table 1, one can see that the content of DMET reached 23%.

Table 1. Effect of gas temperature on DME conversion[a]

Temperature /°C	Composition of liquid/mol%					DME conversion /%	Liquid yield /g·h^{-1}
	DME	DMET	DMPP	TMPP	Esters		
80	47.83	17.27	4.09	1.02	29.79	27.85	0.43
100	40.26	23.37	5.66	1.48	29.22	42.14	0.65

[a] DME flow rate 30 mL·min^{-1}, discharge power 60 W.

A diesel fuel composition has been reported, which is consisted of moderate amounts DMPP and DMET blended into a conventional diesel fuel.[2] DMET has a very high cetane number of 105. It is a cetane number promoter when added to diesel fuel at concentrations above approximately 25 volume %. Adding DMET to diesel fuel can also increase the oxygen level of the diesel fuel so that the effect of oxygen level on emissions could be determined.

The gaseous product of such DBD conversion of DME is a mixture of hydrocarbons, ethers, H_2 and CO. Table 2 shows the composition of gaseous products observed at 60 °C and different gas flow rates. The gaseous products include methane, ethane, propane, methyl ethyl ether, acetone, methyl isopropyl ether, diethyl ether, dimethoxymethane and 1,2-dimethoxyethane. The composition of gaseous products changed greatly with the variation of gas flow rate. Experimental results showed that most of the gaseous products were H_2, CO and C_1–C_3 alkanes. The amount of oxygenates was very little in the gaseous phase but large in liquid product. Table 2 also shows the composition of lower alkanes in the gaseous phase increases with the decreasing flow rates.

Table 2. Effect of gas flow rate on conversion of DME[a]

Composition of gas effluent/mol%	Gas flow rate /mL·min^{-1}			
	60	45	30	20
H_2	4.37	5.26	9.86	20.38
CO	2.05	2.04	4.01	11.54
CH_4	2.13	2.69	4.87	8.15
C_2H_6	2.38	2.91	4.99	7.36
C_3H_8	0.29	0.37	0.76	2.19
DME	84.04	81.32	67.28	40.04
$C_2H_5OCH_3$	2.36	2.75	4.41	4.48
CH_3COCH_3	0.07	0.09	0.18	0.48
$(CH_3)_2CHOCH_3$	0.08	0.10	0.19	0.31
$C_2H_5OC_2H_5$	0.05	0.06	0.10	0.20
$CH_3OCH_2OCH_3$	0.42	0.50	0.78	0.70
$CH_3OCH_2CH_2OCH_3$	0.38	0.40	0.41	0.26
others	1.38	1.53	2.15	3.93
DME conversion /%	14.43	19.15	24.46	42.86
Liquid yield /g·h^{-1}	0.26	0.28	0.36	0.42

[a] Temperature 60 °C, discharge power 60 W.

It is clear that higher DME conversion accompanies with more liquid products produced in this DME conversion. More than 40% of the product is liquid at a gas flow rate of 30 mL·min^{-1}. This suggests that DBDs could easily convert DME to liquid chemicals at atmospheric pressure and low temperature. 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.[8–10]

It is interesting to note that 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. [$CH_3\cdot$] and [$CH_3O\cdot$] radicals can be easily obtained within DME plasmas. Hydrocarbons and oxygenated hydrocarbons are expected to be formed from chain reactions initiated by [$CH_3\cdot$] and [$CH_3O\cdot$] radicals.

The potential of plasma conversion of DME has been demonstrated in this work. Further investigation is being conducted to improve the selectivity of desired product.

The support from The Research Fund for the Doctoral Program of Higher Education in China is very appreciated. The assistance from Mr. Yang Li, Dr. Zhen-hua Li, Dr. Chun-de Yao and Dr. Ming-fa Yao in Tianjin University is also appreciated.

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