

# CONVERTING OF CARBON DIOXIDE INTO MORE VALUABLE CHEMICALS USING CATALYTIC PLASMAS

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## ABSTRACT

Experiment has confirmed that the CO<sub>2</sub> plasmas can generate a plentiful of active oxygen species and other active plasma species for further reaction with other reactants, like methane, low alkanes and others. These reactions leads to a formation of more valuable chemicals, like ethylene, propylene and oxygenates. The characteristics of CO<sub>2</sub> plasma reactions have been addressed therefore in this paper. To be our surprised, the experiment has shown that the CO<sub>2</sub> plasma is an excellent "catalyst" for the conversion of low alkanes to alkenes (esp., ethylene and propylene). To the knowledge of authors, this is the first report of this kind of experiments that could lead to a novel method for the utilization of CO<sub>2</sub> and low alkanes. The present yield of alkenes achieved has been competitive to that from the conventional catalytic dehydrogenation of low alkanes.

## INTRODUCTION

Any success in research and development of a feasible utilization of carbon dioxide will signify the attainment of objectives of slowing down a build-up of greenhouse gases in the atmosphere and better carbon resource utilization. Due to the difficulty in the utilization of carbon dioxide via the conventional catalysis, plasma approaches for the CO<sub>2</sub> utilization have been paid more and more attentions<sup>[1-10]</sup>. Within these plasma CO<sub>2</sub> utilization, an indirect utilization (via syngas) and a direct utilization have been investigated<sup>[11]</sup>. The plasma CO<sub>2</sub> utilization is being demonstrated to be an efficient method. In addition, the plasma flue gas treatment has become an industrialized operation. If more valuable chemicals can be directly produced from such plasma CO<sub>2</sub> utilization, the CO<sub>2</sub> emission control will become compensable. In this presentation, the recent progresses in converting of CO<sub>2</sub> into more valuable chemicals using dielectric-barrier discharge (DBD) plasmas has been reported. It has been found that CO<sub>2</sub> is a very good reactant within gas discharge plasmas for organic synthesis.

## EXPERIMENTAL

The 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 input power requirement and its capacity to induce physical and chemical reactions within gases at relatively low gas temperatures<sup>[1,4,6]</sup>. Figure 1 illustrates the reactor system. The feed gas flow 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 ~ 300 mm. This reactor system is very similar to the DBD reactor for methane conversion described elsewhere<sup>[4,6]</sup>. All the experiments were conducted at atmospheric pressure. The feed and exhaust gases were analyzed by gas chromatograph (MTI M200H and 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

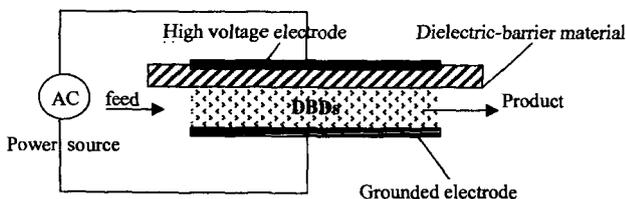


Figure 1 Schematically representative of DBD reactor system

the condensable product from the gas. The power is applied 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).

## RESULTS

We have previously reported a direct liquid fuel synthesis from methane and carbon dioxide via DBDs.<sup>1,4</sup> During this liquid fuel synthesis, the formation of ethylene and propylene, that is very important chemicals, have been observed. Upon the feed ratio of carbon dioxide/methane, a significant amount of oxygenates has also been detected. Figure 2 shows the effect of feed ratio of  $\text{CO}_2/\text{CH}_4$  on the conversions and selectivities. It is clear that a lower  $\text{CO}_2/\text{CH}_4$  feed ratio leads to a higher selectivity of ethylene and propylene. The highest selectivity of ethylene and propylene presents under the feed of pure methane. However, the methane conversion with the pure methane feed is low. The addition of carbon dioxide significantly increases the methane conversion but reduces the selectivity of alkenes. A mixture of oxygenates including methanol, DME, formaldehyde and so on has thereby been produced. Table 1 shows a summary of selectivities based upon the oxygen balance. The higher  $\text{CO}_2$  amount in the feed will induce a larger selectivity of oxygenates. Further investigations are being conducted to improve the selectivity of desired oxygenate, e.g. methanol. To get a higher selectivity of alkenes, a lower  $\text{CO}_2$  feed amount is suggested. In addition, the use of zeolite within the DBDs and changes in other plasma reaction condition can increase the selectivity of alkenes. We will report it in the near future.

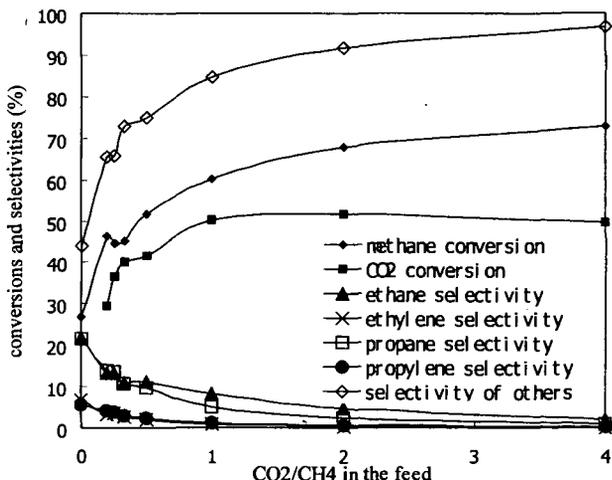
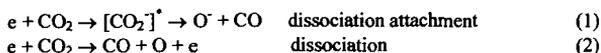


Figure 1 Effect of  $\text{CO}_2/\text{CH}_4$  feed ratio on the selectivities based on the carbon balance (input power: 500w; feed rate: 150 ml/min; gas temperature: 150°C; gas pressure: 1 bar)

Table 1. Effect of  $\text{CO}_2/\text{CH}_4$  feed ratio on the selectivities based on the oxygen balance

$\text{CO}_2/\text{CH}_4$	Selectivity (%)		
	CO	H <sub>2</sub> O	Oxygenates
0			
1/4	61.5	24.2	14.3
1/3	59.9	21.1	19.1
1/2	64.1	22.3	13.5
1/1	47.8	15.7	36.4
2/1	43.3	12.7	44.0
4/1	41.1	9.2	49.7
0	100.0		

It is generally accepted that the ethylene and propylene are from the secondary reactions of ethane and propane. The initiation reactions are thought to be the DBD-induced plasma dissociation of CO<sub>2</sub> and CH<sub>4</sub> to generate various radicals, like methyl, ethyl, propyl radicals and so on. A hydrocarbon chain growth reaction is thereby induced to produce ethane, propane and other higher hydrocarbons. Especially, the DBDs can generate a significant amount of active oxygen species from the following plasma CO<sub>2</sub> reactions:



The oxygen species O and O<sup>+</sup> are being of excited state or metastable state. These plasma species are very active for the dehydrogenation of alkanes and lead to the formation of ethylene and propylene. Experimental investigations have confirmed there are at least two kind of oxygen species produced in the DBDs from carbon dioxide: one leads to the formation of alkenes and oxygenated hydrocarbons and the other induces the complete oxidation of hydrocarbons. A comparative investigation has been conducted to study the decomposition of pure carbon dioxide. It has been found that the plasma decomposition of pure carbon dioxide in some of our reactor designs is higher than that of carbon dioxide and methane or other alkanes (ethane and propane conducted in this investigation) at the same reactive conditions. For example, a CO<sub>2</sub> conversion is 18% with pure CO<sub>2</sub> feed, while the CO<sub>2</sub> conversion reduces to 10% with a mixture feed of carbon dioxide and low alkanes. It can be considered that the CO<sub>2</sub> plasma could be a good catalyst for the conversion of alkanes. A high conversion has been achieved. The challenge, however, is that plasma is a complex mixture of electrons, radicals, ions, photons and others. Especially, the products (alkenes or oxygenates) from plasma CO<sub>2</sub> utilization using alkanes as hydrogen sources are easily to be destroyed by plasma species. It is very necessary to exploit how to control the activity of each plasma species. A special "quenching" has been successfully applied in our investigation on the conversion of low alkanes (ethane and propane) with CO<sub>2</sub> plasma and a selective production of alkenes has been achieved. The high selectivity of alkenes (as high as 80%) can be competitive to the conventional catalytic conversion of low alkanes. Table 2 shows a result of effect of CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> feed ratio on the selectivity of propylene. The products from this DBD conversion of carbon dioxide and propane only contain propylene, water, carbon monoxide and a small amount of iso-butane. Compared to hundreds of components produced<sup>[4]</sup>, this is a significant improvement in the organic synthesis via non-thermal plasmas and could lead to a practical application of plasma synthesis of more valuable chemicals from low alkanes and carbon dioxide.

Table 2 Effect of carbon dioxide/propane ratio in the feed on the selectivities

CO <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	conversions (%)		selectivities (%)		
	CO <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	CO	iso-C <sub>4</sub> H <sub>10</sub>
1/3	15.6	7.7	73.4	17.6	8.9
1/2	11.0	7.3	77.2	16.3	6.5
1/1	10.9	9.2	72.9	19.7	7.4

## CONCLUSION

The potential of the utilization of CO<sub>2</sub> plasma has been demonstrated in this investigation. Due to the low price of present oil market, the synthesis of liquid fuel<sup>[4]</sup> from methane and carbon dioxide would not be a good option. The production of more valuable chemicals, like ethylene and propylene, is a better choice for the utilization of carbon dioxide, together with the utilization of low alkanes, especially methane, ethane and propane. It can be considered this as an important innovative alternative technology to produce ethylene and propylene.

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