Conversion of Methane to Higher Hydrocarbons in Pulsed DC Barrier Discharge at Atmospheric Pressure

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Abstract—Conversion of methane to C_2/C_3 or higher hydrocarbons in a pulsed DC barrier discharge at atmospheric pressure was studied. Non-equilibrium plasma was generated in the barrier discharge reactor. In this plasma, electrons which had sufficient energy collided with the molecules of methane, which were then activated and coupled to C_2/C_3 or higher hydrocarbons. The effect of the change of applied voltage, pulse frequency and methane flow rate on methane conversion, selectivities and yields of products was studied. Methane conversion to higher hydrocarbons was about 25% as the maximum. Ethane, propane and ethylene were produced as primary products, including a small amount of unidentified C_4 hydrocarbons. The selectivity and yield of ethane as a main product came to about 80% and 17% as the highest, respectively. The selectivities of ethane and ethylene were influenced not by the change of pulse frequency but by the change of applied voltage and methane flow rate. However, in case of propane, the selectivity was independent of those condition changes. The effect of the packing materials such as glass and Al_2O_3 bead on methane conversion was also considered, showing that Al_2O_3 played a role in enhancing the selectivity of ethane remarkably as a catalyst.

Key words: CH_4, Plasma, Barrier Discharge, Methane Conversion, Natural Gas

INTRODUCTION

Natural gas is one of the most useful resources in the world because of its abundance and extent of distribution, and with reserves of oil being depleted, the value of natural gas as an alternative fuel is ever increasing. However, 60-90% of the natural gas wells discovered to date are located far away from where needed. Therefore, unless this useful gas can be liquefied or converted into other chemicals for easy transport in large-scale through pipe-lines to the consumers directly, this resource may be of no use in spite of its great amount. This is why so many researchers have been trying to convert methane, which is the main component of natural gas, to liquid fuel or other useful chemicals. But there are many difficulties in doing so because of the chemical stability of methane.

Natural gas can be indirectly converted to liquid fuels or other chemicals by way of synthesis gas, or directly transformed to C_2 hydrocarbon or methanol. Most commercial natural gas converting processes convert methane to synthesis gas with steam reforming, and then synthesize methanol or gasoline by using this synthesis gas as an intermediate. Since the process producing synthesis gas with steam reforming of natural gas requires much endothermic heat, it needs a great deal of energy and high temperatures over 800 °C, and another process to synthesize methanol from the synthesis gas. To overcome these problems, there have been many studies on the direct conversion method. Oxidative coupling [Sofranko et al., 1987; Zhang et al., 1988; Lin et al., 1988; Ito et al., 1988; Bae et al., 1999], thermal coupling [Holmen et al., 1995], plasma [Fraser et al., 1985; Oumghar et al., 1995; Savinov et al., 1999; Cho et al.,

1998] and so on are used for direct methane conversion.

Oxidative coupling reaction converts methane directly to ethane or ethylene over catalysts, and then transforms those C_2 hydrocarbons into liquid hydrocarbon fuels such as gasoline. Until now, there have been many studies on oxidative coupling. Oxygen is to be supplied with methane for methane oxidative coupling reaction so that Gibbs' free energy change may become negative. In this case, it is more likely for methane combustion to occur than methane coupling in view of thermodynamics and kinetics. To resolve this problem, therefore, it is necessary to develop effective catalysts capable of enhancing the methane coupling. Although some catalysts such as Li/MgO, Sm_2O_3, La_2O_3, PbO/MgO and so forth have been developed, the yield of C_2 has not exceeded 25%. Furthermore there is still the disadvantage that the reaction has to be performed at high temperatures over 600 °C to obtain reasonable methane conversions and C_2 selectivity [Zhang et al., 1988; Lin et al., 1988; Ito et al., 1988].

Thermal coupling converts methane directly to C_2 hydrocarbons at very high temperatures. Fischer and Pichler [1932] and Wheeler and Wood [1928] reported first that products other than hydrogen and carbon could be obtained by controlling residence time [Holmen et al., 1995]. Hereafter, there were many studies on the thermal coupling reaction of methane, especially on the production of acetylene. Recently, the synthetic processes for producing acetylene and ethylene together have been under study. Nonetheless, a thermal coupling reaction occurring at extremely high temperatures over 1,200 °C has limited applications because its main product acetylene is not used widely.

Methane conversion with plasma is being widely researched nowadays as an alternative in order to avoid these difficulties. Methane activation with plasma is very effective not only in that methyl rad-

icals could be easily made by the high energy of plasma, but also in that various kinds of chemical reactions could be induced through the high energy. Marafee et al. [1997] reported on a methane conversion reaction with glow discharge at a vacuum of 1-2 mmHg. Ethane, ethylene, acetylene, hydrogen and carbon layer deposited on the reactor wall were main products, and methane conversion was 98%. Another study with glow discharge also showed a methane conversion over 90% [Savinov et al., 1999]. But glow discharge does not seem to be economical because it must be operated under vacuum. Consequently, technologies using atmospheric pressure plasma, especially corona discharge, have been vigorously investigated [Liu et al., 1996; Chang et al., 1991]. In glow discharge one molecule of methane can get enough energy due to the rarity of molecules under vacuum state. However, it is very difficult to provide enough energy to one molecule of methane in corona discharge owing to the relatively high density of molecules at atmospheric pressure. This is why many researchers have applied corona discharge over metal oxide catalysts at a reaction temperature of 400-600 °C to convert methane [Liu et al., 1997, 1998; Marafee et al., 1997]. Nevertheless, the conversion of methane did not go beyond 30%.

In this study, barrier discharge at atmospheric pressure was used to overcome these limits of corona discharge. For barrier discharge, one or both of the surfaces of two electrodes should be surrounded with dielectrics such as glass, so that direct discharge may not occur in the gap between the two electrodes under high voltage. The difference between dielectricities of gas and solid gives a strong electric field to the gas, and high energy-level plasma may be generated. In addition, a more uniform discharge zone can be formed in barrier discharge than in corona discharge. Eventually, it is more possible for electrons, which have enough energy to break the carbon-hydrogen bond in the methane molecule, to collide with methane molecules and generate methyl radicals. Arc generation, which is much more likely to happen in corona discharge, can also be minimized due to the dielectric barrier between electrodes [Lee et al., 1994].

Using this barrier discharge which has many merits over corona discharge, methane conversion, the selectivities and yields of ethane, propane, ethylene as main products were investigated under different experimental conditions such as methane flow rate, applied voltage and pulse frequency, etc. The effect of packing materials on methane conversion and the product selectivities was also observed.

EXPERIMENTAL DETAILS

The experimental setup for methane conversion reaction with barrier discharge is shown in Fig. 1. Only methane with a purity of 99.99% was used as a feed gas, and the flow rate of methane was controlled with a Mass Flow Controller (Bronkhosrt, Type-5534 FA). Stainless steel wire with a diameter of 0.45 mm was installed in a Pyrex cylinder with an inner diameter of 25 mm, a thickness of 1.7 mm, and a length of 240 mm. The cylinder was surrounded by a copper plate with a thickness of 0.2 mm for ground. The reactor is represented in detail in Fig. 2. Silicon rubber was used to seal both ends of the reactor. A DC pulse generator (LG Industrial Systems, Co., Ltd., Model ASM-20K250A) with 20 kV and 1.5 kHz
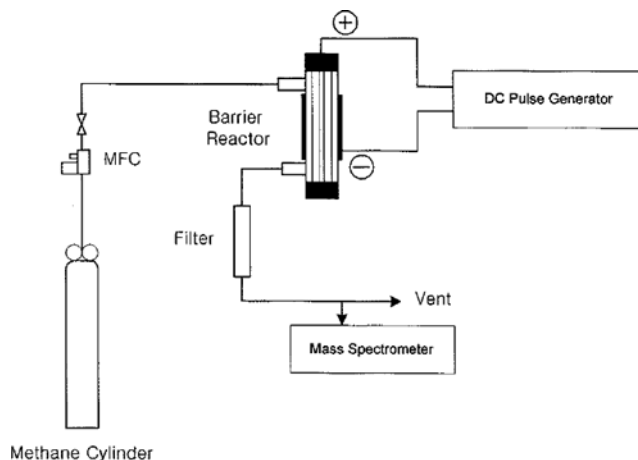

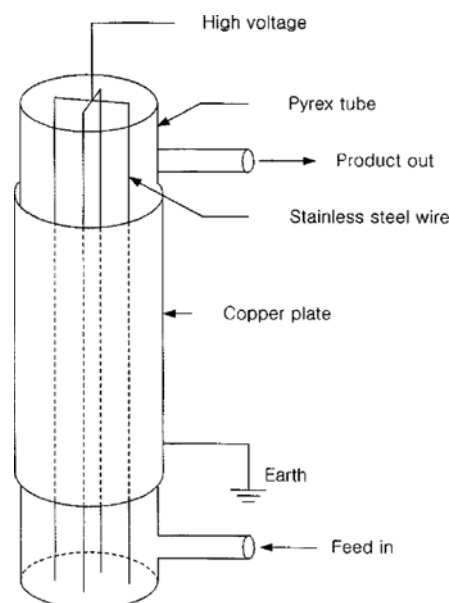Fig. 1. Schematic diagram of methane conversion system with barrier discharge.

Fig. 2. Details of cylinder-to-wire barrier discharge reactor.

pulse was employed for generating plasma. In comparison with continuous DC (or AC), the energy efficiency can be improved by preventing energy loss by heat. The gaseous products were measured qualitatively with mass spectrometer (Balzers Co., QMS 200), and analyzed quantitatively by correlating their concentrations to their component peak responses derived from the calibration data based on the mass spectrum of the binary mixture.

Variables in experimental conditions were methane flow rate, the structure of the wire electrode, applied voltage and pulse frequency, with or without packing materials. The flow rate of methane was varied at 20, 40 and 60 ml/min. The voltage was applied from 8 kV, at which a breakdown occurred in the gap between wire electrode and glass barrier, to 10 kV at the fixed pulse frequency of 1.5 kHz, and the products were analyzed. At the same flow rate, the pulse frequency was varied from 0.5 kHz to 1.5 kHz with applied voltage fixed at 10 kV.

The effect of packing material in the reactor was tested with glass

Table 1. Effect of the number of wires on methane conversion

No. of wires	1	2	4	8
Methane conversion [%]	13	23	25	21

(Experimental conditions; 10 kV, 1.5 kHz, CH_4 20 ml/min).

and Al_2O_3 bead at the diameter of 8 mm and 4 mm, respectively. The methane conversion, the selectivities and yields of the products according to the flow rate change were tested with the packing materials. The applied voltage and pulse frequency were fixed at 10 kV and 1.5 kHz, respectively. The main products from the barrier discharge reactor were ethane, propane and ethylene, including a few C_4 hydrocarbons. The maximum voltage supplied by the power source is 20 kV. If the applied voltage was over 10 kV, the reaction temperature increased sharply and the methane molecules were completely decomposed into carbon. This carbon deposited on both the wire electrode and the inside wall of the reactor, making the reactor efficiency decrease considerably.

RESULTS AND DISCUSSION

1. Effect of Reactor Structure on Methane Conversion

To optimize the reactor structure for experiment, methane conversion was measured with a number of wires inside the reactor. Table 1 shows how the number of wires from 1 to 8 affected the methane conversion. With the number of wires increased from 1 to 4, methane conversion was also increased because the plasma area became widened. When the number of wires was 8, methane conversion was rather decreased. This is because there's no uniform plasma distribution around 8 wires and no plasma around some wires, which caused a part of the methane to pass through the reactor without being affected by plasma. Therefore, the experiments were conducted with a 4-wire reactor that showed the highest conversion of methane.

2. Effect of Applied Voltage

The magnitude of the external applied voltage is related to the strength of the internal electric field, which is the most important parameter in the plasma reaction. Therefore, the effect of applied voltage was first considered. At methane flow rate of 20 ml/min, the changes of methane conversion, the selectivities and yields of
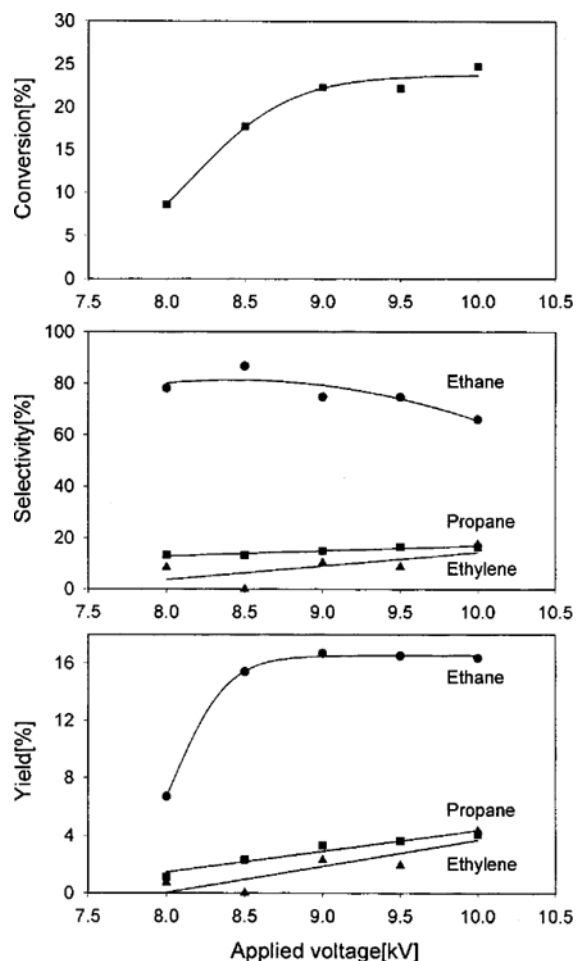
Fig. 3. Effect of applied voltage on methane conversion, selectivities and yields of products (frequency=1.5 kHz, methane flow rate=20 ml/min for selectivities and yields).

the products according to the change of applied voltage are represented in Fig. 3. The methane conversion increased with the increase of the applied voltage. The increase of the external applied voltage produced more energetic electrons, and the possibility of breaking the C-H bond in the methane molecule was enhanced. When the

Table 2. Comparison of conversion and selectivity to other plasma processes

Method	Feed	Flow (ml/min)	P (Torr)	V (kV)	Freq. (Hz)	CH_4 conversion (%)	Selectivity (%) C_2H_6	Selectivity (%) C_2H_4	Catalyst	Ref.
	CH_4	20	760	11	50	25	40	3	-	
	CH_4	20	760	6.5	50	14	40	3	-	
Parallel-plate barrier discharge	CH_4+He (3:1)	20	760	6.5	50	11	-	-	-	b
	CH_4+He (1:1)	20	760	6.5	50	29	-	-	-	
	CH_4+C_2H_6 (9:1)	20	760	6.5	50	24	-	3.5	-	
	CH_4+C_2H_6 (8:1)	20	760	6.5	50	23	-	5	-	
DC-corona discharge	CH_4+O_2 (4:1)	100	760	5	-	9	43[a]		-	c
	CH_4+O_2 (4:1)	100	760	5	-	21	44[a]		Sr/La_2O_3	
	CH_4+O_2 (2:1)	100	760	5	-	5	25[a]		-	
	CH_4+O_2 (2:1)	100	760	5	-	36	27[a]		Sr/La_2O_3	

a: C_2 total, b: Thanyachotpaiboon et al., 1998, c: Marafee et al., 1997.

Table 3. Comparison of conversion and selectivity to oxidative coupling processes

Ref.	Feed	Flow (ml/min)	T (°C)	CH$_4$ conversion (%)	Selectivity (%)		Catalyst	Remark
					C$_2$H$_6$	C$_2$H$_4$		
a	CH$_4$+O$_2$+He (29:15:56)	50	720	38	46.5^e		7% Li/MgO	
	CH$_4$+O$_2$+He (4:1:95)			29	58^e			
b	CH$_4$+O$_2$+He (28:15:57)	55	725	39	38.3^e		15% Na/CaO	
	CH$_4$+O$_2$+He (15:5:80)			26	51.5^e			
c	CH$_4$+O$_2$	100	800	2.3	23.9	31.8	15% Mn/SiO$_2$	Cumulative
				30	13.9	36.5		Instantaneous
d	CH$_4$+O$_2$+He (10:5:85)	50	750	28	24.6	28.7	0.18% Li/ZnO	

a: Ito et al., 1988, b: Lin et al., 1988, c: Sofranko et al., 1987, d: Zhang et al., 1988, e: C$_2$ total.

residence time of methane was long enough at a flow rate of 20 ml/ min, methane conversion was practically unchanged over 9 kV.

The ethane selectivity was from 60% to 80% at a methane flow rate of 20 ml/min. This value is fairly high compared to the average 30-40% with oxidative coupling [Sofranko et al., 1987; Zhang et al., 1988; Lin et al., 1988; Ito et al., 1988], and about 40% with the parallel plate barrier discharge at similar conditions by Marafee et al. [1997] and Thanyachotpaiboon et al. [1998]. The results of other studies are summarized in Tables 2 and 3. They reported that the selectivities of the products are independent of applied voltage. However, in this experiment the selectivity of ethane decreased slightly, that of propane was nearly constant, and that of ethylene increased a little with the increase of applied voltage. The production rate of methyl radicals increased at higher voltage, which resulted in increasing the production rate of ethane. At the same time, these ethane molecules collided with hydrogen radicals or methyl radicals to form ethyl radicals, from which hydrogen radicals were removed to produce ethylene molecules. The increase of ethane production rate meant the increase of ethane decomposition rate, which caused ethane concentration to decrease. The rate of ethane decomposition was probably higher than that of ethane production with the increase of applied voltage, so the selectivity of ethane was decreased.

As described above, the ethane was produced first, then ethylene was formed. Hence, the decrease of ethane meant the increase of ethylene. Propane molecule was formed from the collision of methyl radical and ethyl radical. The increase of methane conversion caused the available methyl radicals and ethyl radicals to increase, so the propane production is enhanced. But at the same time, since there was more chance to form C$_4$ hydrocarbon, propane forming was restricted [Marafee et al., 1997]. The propane selectivity remained constant in this system because these mutual offsetting effects were almost the same. The yields of the products increased as the applied voltage increased. The yields were calculated by multiplying the conversion by the selectivities of the products, and the change of conversion was mainly responsible for the changes in yields.

3. Effect of Pulse Frequency

The effect of pulse frequency on the conversion of methane was investigated at a constant electric field. Fig. 4 represents the changes of methane conversion, the selectivities and yields of the products with the change of pulse frequency at a methane flow rate of 20 ml/ min. Methane conversion increased with an increase of the pulse
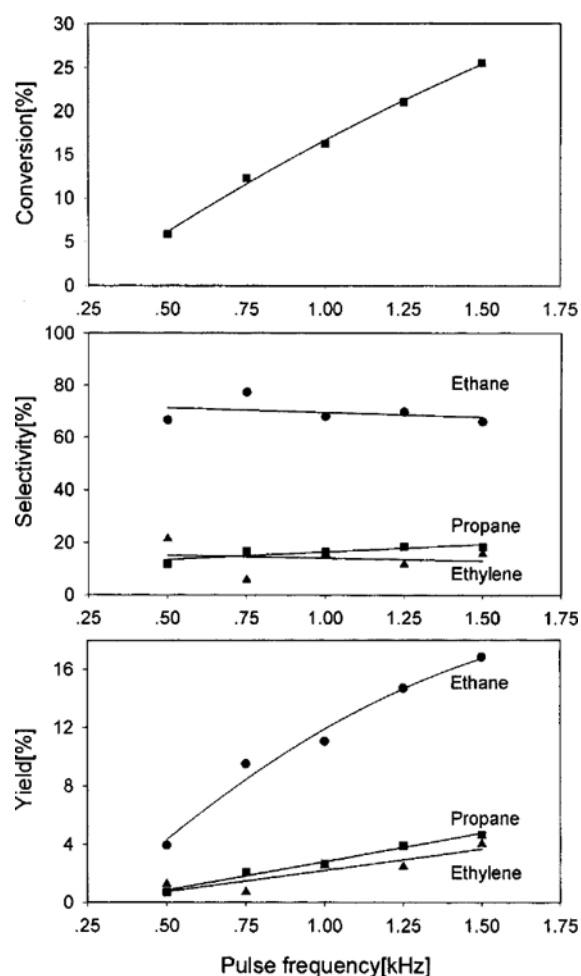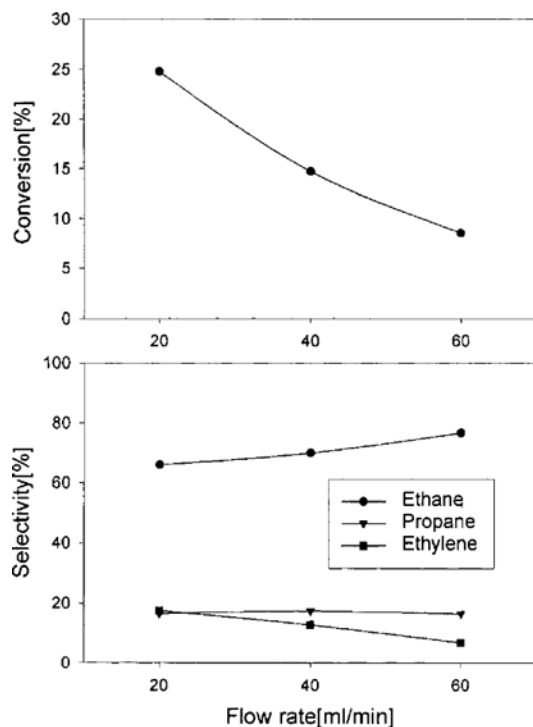

Fig. 4. Effect of pulse frequency on methane conversion, selectivities and yields of products (voltage=10 kV, methane flow rate=20 ml/min for selectivities and yields).

frequency. The energy supplied to the internal electric field per unit time was increased with the increase of pulse frequency, and the possibility of destroying C-H bond of methane molecule became higher. There was no significant change in the selectivities of the products, unlike the case when applied voltage was changed.

4. Effect of Methane Flow Rate

The effect of methane flow rate, in other words, the residence time of methane in the reactor was examined. Fig. 5 shows the
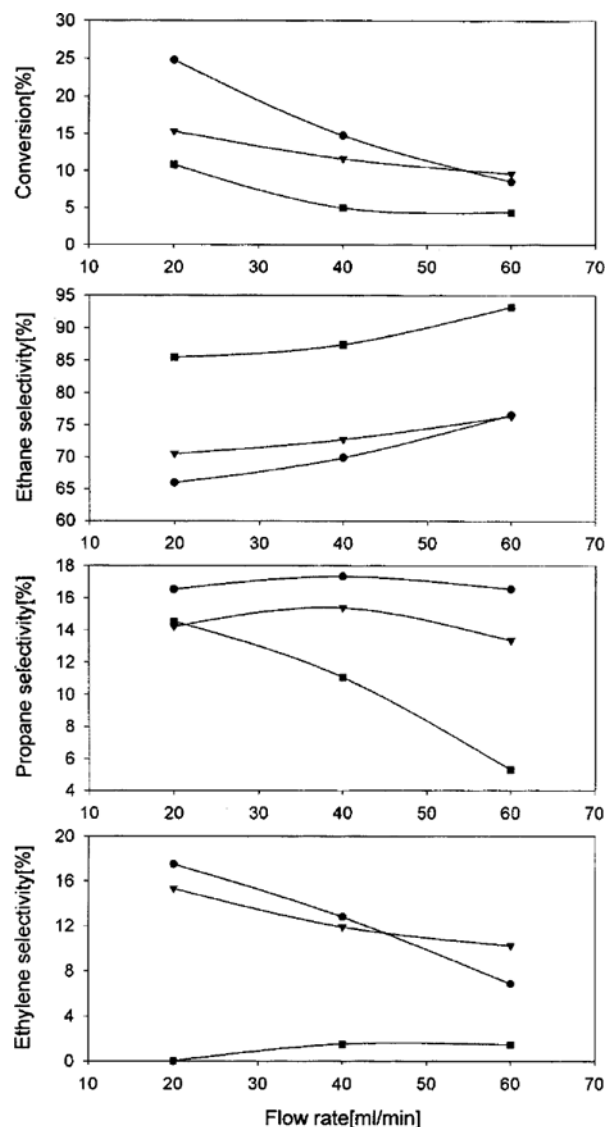
Fig. 5. Effect of flow rate on the selectivities and yields of products (voltage=10 kV, frequency=1.5 kHz).

changes of methane conversion, the selectivities and yields of the products according to the various flow rates at the applied voltage of 10 kV and pulse frequency of 1.5 kHz. Methane conversion decreased rapidly with the increase of methane flow rate, while the selectivity of ethane increased, that of ethylene decreased, and that of propane was almost constant. The increase of flow rate reduced the residence time of methane in the reactor, which resulted in reducing the chance of methane molecules to collide with electrons which had enough energy to destroy the C-H bond. This effect caused the production of methyl radicals to decrease.

5. Effect of Packing Materials

Many researchers [Liu et al., 1997, 1998; Marafee et al., 1997] have considered the plasma process with various packing materials as catalysts to enhance methane conversion and the selectivities of the products. To check the effect of these packing materials, glass beads and Al_2O_3 were packed in the reactor. The methane conversion and selectivity and yield of the products were observed according to the methane flow rate as shown in Fig. 6. Glass beads and Al_2O_3 with a diameter of 9 mm and 5 mm, respectively, were packed into 90% of the reactor volume. The mean residence time of methane without packing material was about 5 minutes, that with glass bead about 2.5 minutes, and that with Al_2O_3 about 2 minutes.

Methane conversion with packing materials was lower than without packing materials, and the difference between conversions became smaller as the methane flow rate increased. The trends were due to the decrease of the chance of methane molecules to collide with the electrons, which resulted from the shorter mean residence time in the packed bed than in the blank bed. The selectivity of ethane in Al_2O_3 was the highest, and improved by about 30% compared to that in the blank bed. The selectivity of propane in the glass beads and in the blank bed was independent of the change of meth-

Fig. 6. Effect of packing materials on methane conversion and product selectivities (voltage=10 kV, frequency=1.5 kHz; λ blank, τ glass bead, ∨ Al_2O_3 bead).

ane flow rate, but it decreased sharply in Al_2O_3. When Al_2O_3 was packed in the reactor, the selectivity of ethylene was very small.

From this result, it was thought that Al_2O_3 acted as a catalyst to improve the selectivity of ethane. The trends of the product selectivity were almost the same in glass beads and blank bed as shown in Fig. 6. The methane conversion of the glass bead packed bed at a flow rate of 20 ml/min corresponded to that of the blank bed at 40 ml/min. It can be confirmed at this point that glass beads in the reactor had no role other than they reduced the residence time of methane.

The methane conversion of the glass bead packed bed is higher than that of a blank bed at 60 ml/min of methane flow. This must be due to the effect of mixing at high flow rate. The plasma intensity is very high near the wire, and it becomes weak at long distance from wire. The molecules at high flow rate in the blank bed pass the reactor without contacting the strong plasma zone, so the conversion is low. The glass beads enhance the mixing of the mol-

ecules and more molecules contact the strong plasma zone, so the conversion becomes high.

CONCLUSIONS

In this study, it was verified that conversion of methane to C_2 or higher hydrocarbon under the barrier discharge at atmospheric pressure could be an alternative to the process using catalytic reaction or conventional corona discharge in view of the methane conversion and the product selectivity.

Using the cylinder-to-wire atmospheric barrier discharge reactor with the applied voltage of 10 kV, the pulse frequency of 1.5 kHz and the methane flow rate of 20 ml/min, the methane conversion was about 25%. The products are ethane, propane and ethylene including a few C_4 hydrocarbons, and the yield of ethane was about 17%. The ethane selectivity was some 60%, which is quite good compared to about 40% of Caldwell et al. [1998]. This was a much encouraging result in terms of commercial applications. The production of olefins like ethylene was extremely restricted in comparison with that of paraffin such as ethane and propane. This was because a large amount of hydrogen produced from methane decomposition inhibited the olefin production.

Increasing the applied voltage increased the strength of the internal electric field which produced more energetic electrons, and promoted the activation of methane molecules into forming more C_2/C_3 hydrocarbons, so methane conversion was improved. With the increase of the applied voltage, ethane selectivity was decreased, and ethylene selectivity increased. On the other hand, the selectivity of propane was independent of the increase of the applied voltage. Although the increase of pulse frequency elevated the density of the energetic electrons, the selectivities of the products were almost unchanged because of the equilibrium between the production and decomposition reaction. The increase of methane flow rate decreased the methane conversion, and the selectivities of the products showed the reverse trend to the case in which applied voltage was increased. At an applied voltage of 10 kV, pulse frequency of 1.5 kHz, and methane flow rate of 20 ml/min, the methane conversion in the Al_2O_3 packed bed was lower than that in the blank bed. However, the ethane selectivity was enhanced by about 30% to over 90%. This fact assured that Al_2O_3 played a part in improving ethane selectivity as a catalyst.

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