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A DIRECT CATALYTIC CONVERSION OF NATURAL GAS TO C2+ HYDROCARBONS BY MICROWAVE PLASMA

Wonihl Cho, Youngsoon Baek†, Hyosun Pang and Young Chai Kim*

Division of Gas Utilization, KOGAS R&D Center, Ansan City, Kyunggi-Do, 425-150, Korea
*Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea
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Abstract – Methane, the major constituent of natural gas, was converted to higher hydrocarbons by a microwave plasma. The yield of C2+ products increased from 29.2 % to 42.2 % with increasing plasma power and decreasing flow rate of methane. When catalysts were used in the plasma reactor, the selectivities of ethylene and acetylene increased, while the yield of C2+ remained constant. Among various catalysts used, Fe catalyst showed the highest ethylene selectivity of 30 %. And when the actual natural gas was introduced, more C2+ products were obtained (46 %). This is due to the ethane and propane in the natural gas. Applying electric field inductance for evolving the high plasma, we obtained high C2+ products of 63.7 % when Pd-Ni bimetal catalyst was used.

Key words: Microwave Plasma Catalysis, Electric Field Inductance, C2+ Products, Methane Conversion, Natural Gas

INTRODUCTION

Natural gas, 90 % methane, is an inexpensive and abundant energy resource that has been extensively studied to find an effective and economic process to obtain higher hydrocarbons, methanol and synthesis gas. Demand for ethylene and methanol, which are the objective products of this study, is increasing. Consequently, producing ethylene from methane has attracted intensive industrial and academic interest [McCarthy, 1954; Suib and Zerger, 1991; Wan, 1993].

However, methane activation is difficult due to the strong stable bond between carbon and hydrogen. Most previous studies, such as on reaction with super-acids, coordination to metal complexes, and selective oxidation by metal oxides, have concentrated on producing higher hydrocarbons by oxidative coupling reaction on metal oxide catalysts [Wan, 1986; Suib and Zerger, 1993; Ioffe et al., 1995]. Heterogeneous catalysts in oxidative coupling and partial oxidation processes show low selectivity and non-selective activation of methane.

In this study, plasma technology was accommodated to activate methane. The aim of this work was to produce more valuable chemicals such as ethane, ethylene, and acetylene by a microwave plasma and catalyst.

A plasma can be defined as an electrically conducting gas. Gas-phase species in the plasma state are electrons, and ground-state and excited-state molecules on ions. The commercial applications of plasma are in coatings, semiconductor manufacture, and chemical vapor deposition [Kizling and Järås, 1996].

We investigated a plasma system coupled with catalyst to increase yield and selectivity. Methane was dissociated in a plasma reactor to methyl radicals and hydrogen atoms and then subsequently recombined to produce ethane, ethylene, acetylene and hydrogen. Another possible mechanism is a direct reaction of methane to ethylene, ethane and acetylene.

Selectivities and conversions are reported as functions of pressure, flow rate, and plasma power.

†To whom all correspondence should be addressed.
E-mail: YSBAEK@KOGAS.RE.KR

EXPERIMENTAL

A microwave (2.45 GHz, ASTEX Co.) was used to generate plasma of methane. The maximum microwave power is 120 W. A schematic diagram of a microwave plasma reaction system is shown in Fig. 1. A mass flow controller controlled the flow rate of methane (99.99 %, Methanson Co.) and natural gas into the plasma reactor. Before reaction, the system was evacuated by a turbo-molecular pump down to 10^{-7} torr. The plasma reactor consisted of a quartz tube of 25 mm O.D. connected to a microwave cavity. Forward and reflected powers of microwaves were monitored during the experiments. The plasma was initiated with a Tesla coil. Metal catalysts such as Fe (KGC1), Pt (KGC2) and Ni (KGC3, 4, 5) were used and about 1.0 g of catalyst was placed in the middle of the reactor for each experiment when the catalyst was used. For analysis, the C2+ products were collected in a liquid nitrogen trap during the reaction and then vaporized into a bulb of known volume at room temperature. Eq. (1) was used to calculate the conversion or C2+ productivity.

$$\text{Conversion (or C2+ productivity)} = \frac{2M_{C2+}}{M_{CH_4}} \quad (1)$$

where M_{C2+} is the mole of the C2+ products and M_{CH4} is the mole of the input methane. Amounts of product were evaluated by a gas chromatograph (HP 6890) with a Porapak N column. The column temperature was 50 °C, injection temperature was 100 °C, and detector (TCD) temperature was 150 °C.

Three kinds of reactor were tested: the first model was a series connection of the plasma generator and the catalyst

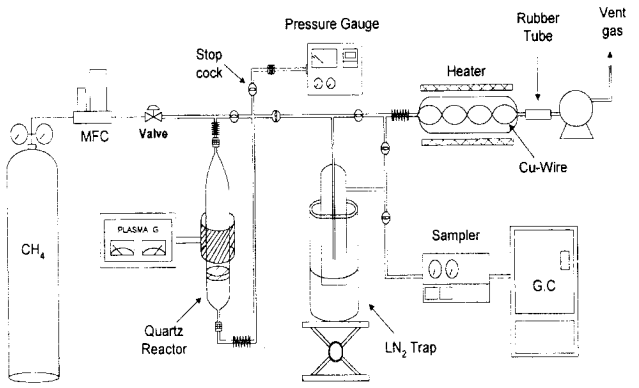

Fig. 1. Schematic diagram of the microwave plasma catalysis system.

reactor up-side down; the second one was the reverse of the first model; and the third model was a high density plasma reactor, which was composed of three parts (plasma generator, electric field inductance, and catalyst reactor).

Typical reaction conditions are 10 torr of pressure, 40-120 W of power, and 2-40 ml/min of flow rate. The reactions without catalyst were also carried out under the same experimental conditions.

RESULTS AND DISCUSSION

1. Products and Selectivity

The conversion of methane was increased from 29.9 % to 48.3 % with increasing power of microwave plasma in the absence of catalyst. It was observed that the conversion decreased with increasing flow rate (Fig. 2) with a maximum value of 48.3 % at 120 W and 2 ml/min. Polymeric carbon and coke formed on the wall of the reactor in all of experiments, but the amount of the deposit was negligible compared to the gaseous products.

In the case of higher plasma power (~2 kW), higher C2+ productivity and more carbon was observed.

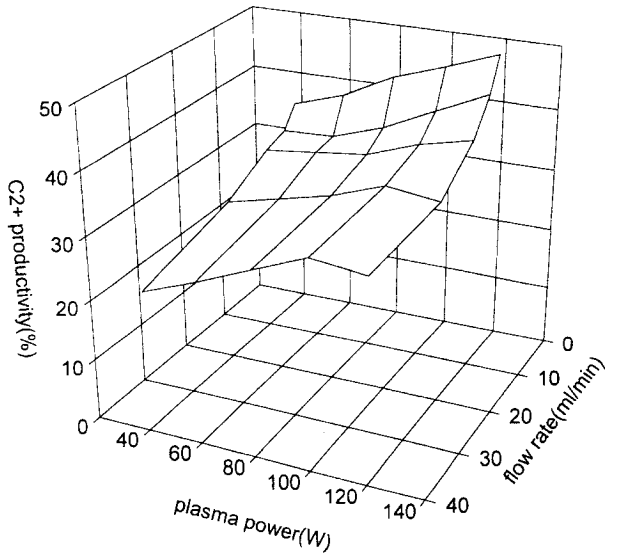

Fig. 2. Plot of C2+ productivity from methane as a function of the flow rate and the plasma power.

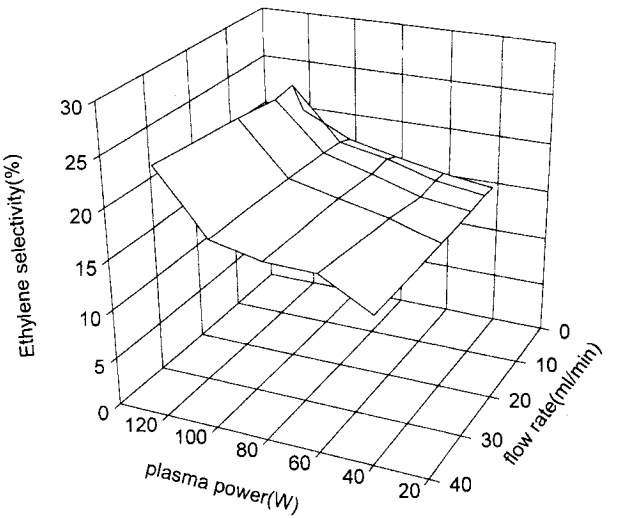

Fig. 3. Plot of ethylene selectivity as a function of the flow rate and the plasma power.

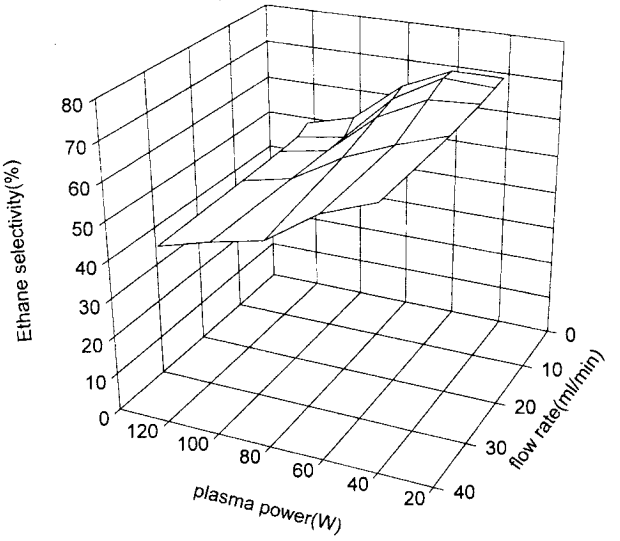

Fig. 4. Plot of the ethane selectivity as a function of the flow rate and the plasma power.

In every experiment with different flow rates, the selectivity of ethylene was increased with an increase in the power (Fig. 3), while the selectivity of ethane decreased (Fig. 4). The C-H bonds of methane are dissociated by microwave plasma and recombine with unsaturated hydrocarbons. Radicals were produced by methane plasma and then recombined with each other [Suib and Zerger, 1993; Huang and Suib, 1994];

$$2CH_4 \rightarrow 2\alpha CH_3 \cdot + \alpha H_2,\ 2\beta CH_2 \cdot + 2\beta H_2,\ 3\gamma CH \cdot + 3\gamma H_2 \quad (2)$$

$$CH_3 \cdot + CH_3 \cdot \rightarrow C_2H_6 \quad (3)$$

$$CH_2 \cdot + CH_2 \cdot \rightarrow C_2H_4 \quad (4)$$

$$CH \cdot + CH \cdot \rightarrow C_2H_2 \quad (5)$$

Therefore, the stoichiometric equation of the methane reaction is:

$$2CH_4 \rightarrow \alpha C_2H_6 + \beta C_2H_4 + \gamma C_2H_2 + (\alpha + 2\beta + 3\gamma)H_2 \quad (6)$$

where, $\alpha+\beta+\gamma=1$. The values of α, β, γ are the selectivity of the ethane, ethylene, and acetylene, respectively, and they are changed with the intensity of plasma power. Fig. 5 shows the relationship beween the flow rate and the plasma power on the selectivity. The selectivities of ethylene and acetylene are constant with the change of the flow rate and they increased with the increasing plasma power. This is due to more free radicals like acetyl (CH:) and ethyl (CH2:) produced at higher plasma power. At lower power, free radicals like methyl (CH3 ·) and ethyl are produced. The flow rate, however, does not affect the selectivity.

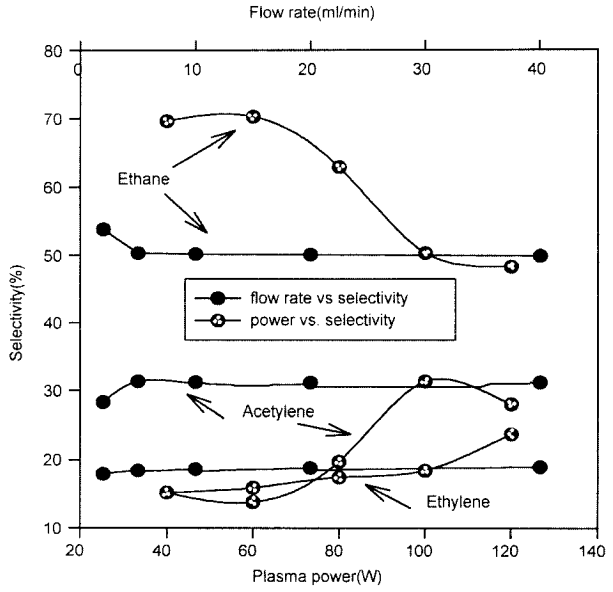

Fig. 5. The effect of the flow rate and the plasma on the selectivity.

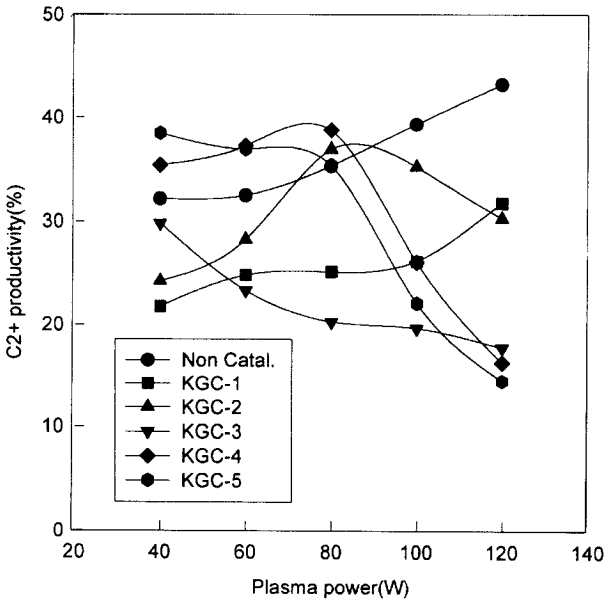

Fig. 6. Plot of C2+ productivity of methane according to various catalysts.

Fig. 6 shows plot of C2+ productivity of methane according to various catalysts and plasma power. In the presence of catalysts, the C2+ productivity increased and/or remained constant with increasing plasma power up to 80 W, and it decreased rapidly over 80 W in the case of the Ni-series. The productivity may be an intermediate power zone (80 W). This result is consistent with Suib's [1993] below 60 W. Radical recombination occurs on the catalysts through the steps of Eq. (3) and (4) (Fig. 7 and Fig. 8). The change of selectivity depends on the nature of the catalyst and the plasma state. In this work, ethane was also dissociated, then recombined with the microwave plasma to produce ethylene and acetylene.

2. The Effective C2+ Production

The C2+ productivity increased with plasma power in the

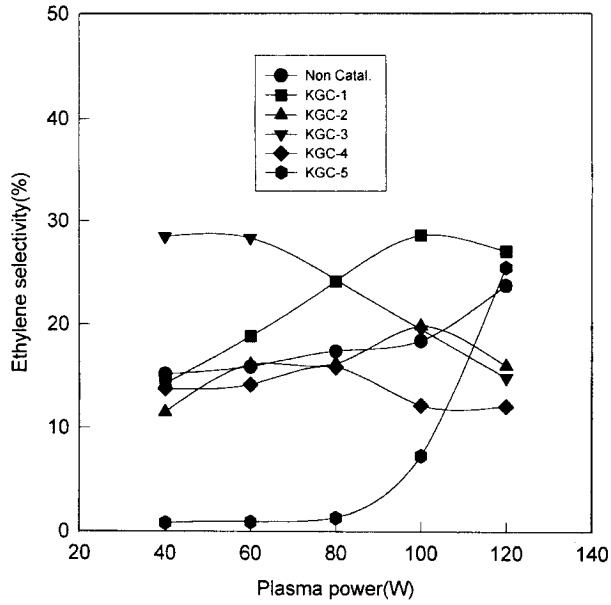

Fig. 7. Comparison of ethylene selectivity on various catalysts.

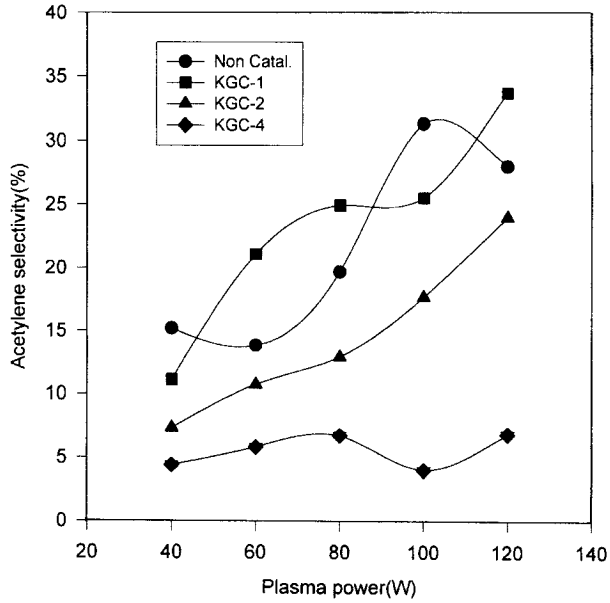

Fig. 8. Comparison of acetylene selectivity on various catalysts.

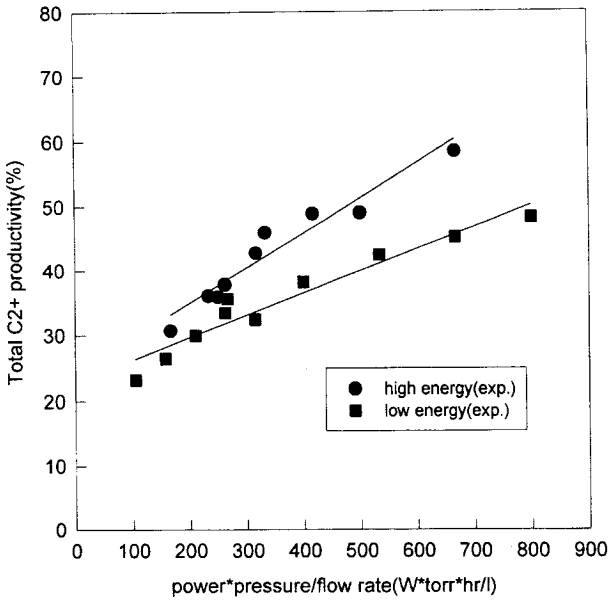

Fig. 9. Plot of C2+ productivity vs [power*pressure/flow rate].

absence of catalyst. We suggest the following equation [Eq. (7)] with experimental parameter at Fig. 9:

$$\text{Conversion} = A \times \text{power} \times \text{pressure/flow rate} + B \quad (7)$$

where A are found to be 0.05 and 0.034 at higher and lower power density, respectively, and B is a minimun productivity under this reaction condition as a range of 40-120 W plasma power and 2-40 ml/min flow rate. The productivity is linearly proportional to the flow rate of methane as shown in Fig. 5. In the case of the dependence of methane conversion to ethane, ethylene and acetylene, the analysis with these experimental parameters is more complex than that of the total methane conversion. At this point, it is contrived as more of an experimental parameter to analyze the microwave plasma and catalysis.

3. Natural Gas Conversion

Instead of methane, natural gas was treated as a reactant.

Table 1. Comparison of the plasma reaction between methane and natural gas in the absence of catalyst (plasma power: 80 W, flow rate: 20 ml/min, pressure: 5 torr)

Components	Productivity (%)	Selectivity (%)		
		Ethylene	Ethane	Acetylene
Methane	33.3	21.8	47.7	30.5
Natural Gas	46	29.2	46.7	24.1

Actually when the plasma power of 80 W and the flow rate of 20 ml/min were adopted, the conversion was increased up to 46 % as shown in Table 1. Also the selectivity of ethylene was increased up to 29.2 %. This is thought to be due to inclusion of more active hydrocarbons (ethane ;~8 %, and propane ;~1-2 %) in the natural gas. The variation of selectivity and conversion as a function of flow rate and plasma power was observed to be very similar to that of methane gas. From the viewpoint of C2+ productivity, natural gas appeared to be a more active reactant than methane gas.

In Table 2, the C2+ productivities and selectivities are summarized at various conditions. In particular, we used the electric field inductance (EFI) in order to evolve a high density of microwave plasma. The EFI locates near the plasma region. With a Pd-Ni catalyst, C2+ productivity reaches to 63.7 % in conversion at a voltage of 8 V, current of 2A, natural gas flow rate of 20 ml/min and plasma power of 100 W. When a dehydrogenation catalyst of Pt-Sn was used, the conversion was 52.8 %, which was lower than that of a redox catalyst of Pd-Ni.

In the catalytic activity, the natural gas conversion was represented as 16.8 % for Pt-Sn catalyst and 27.8 % for Pd-Ni catalyst. The selectivity of C2+ was shown to be 91.3% of ethane for Pt-Sn and 84 % of ethane, 3 % of acetylene for Pd-Ni catalyst as shown in Table 2. It is noteworthy that the best catalytic activity of natural gas conversion is the redox catalyst of Pd-Ni rather than the dehygenation catalyst of Pt-Sn.

In this system, catalysts in the plasma process played a role of sorbing any produced radicals with C-H bond and acted

Table 2. Summary of microwave plasma and catalysis

Catalyst	Reactors	Plasma power (W)	DC power	Productivity (%)	Selectivity (%)		
					Ethylene	Ethane	Acetylene
	Plasma	100		46	29.2	46.7	24.1
Pt-Sn	Catalyst			16.8	-*	91.26	-*
	Plasma+Catalyst	80		46.3	22.3	50.4	27.3
	Catalyst+Plasma	80		48.2	25.7	54.3	20
	Plasma+EFI	100	8V, 2A	45.5	28.9	49.6	21.5
	Plasma+EFI+Catalyst	100	8V, 2A	49.4	32.4	33.2	34.4
	Catalyst+EFI+Plasma	100	8V, 2A	52.8	24.3	47.4	28.3
Pd-Ni	Catalyst			27.8	0.5	84	3
	Plasma+Catalyst	80		51.1	30.2	45.9	23.9
	Catalyst+Plasma	80		52.7	27.2	48.7	24.1
	Plasma+EFI	100	8V, 2A	45.5	28.9	49.6	21.5
	Plasma+EFI+Catalyst	100	8V, 2A	58.9	42.1	44	13.9
	Catalyst+EFI+Plasma	100	8V, 2A	63.7	37.4	40.2	22.4

*; NOT detected.

as a helper at surfaces for producing the ethyl and acetyl radical but restrained the methyl radical on the catalyst surface. Therefore, ethane was converted to the formation of ethylene and acetylene in a microwave plasma catalysis.

CONCLUSIONS

Methane was activated to produce C2+ products by microwave plasma and catalysis at room temperature. C2+ products were obtained much more to be due to the production of many free radicals at low plasma power. Therefore, we expect improvement of the energy efficiency. Selectivity toward ethylene and conversion can be enhanced by the redox catalyst of Pd-Ni rather than the dehydrogenation catalyst of Pt-Sn. The role of the catalyst in the plasma process is activated to produce the C2+ products. Hydrogen and hydrocarbon radicals adsorbed on the catalyst and produced C2 products. Natural gas was a more active reactant and produced higher C2+ products such as ethane, ethylene and acetylene in a microwave plasma-catalyst system.

The study should be continued to elucidate the reaction mechanism and to improve the selectivity and the natural gas conversion by means of plasma and various catalysts. Also, there is need for improvement in the reactor design and development of an effective process of separation of C2+ and hydrogen.

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