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Short communication

Conversion of methane by an electric barrier-discharge plasma using an inner electrode with discharge disks set at 5 mm intervals

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ABSTRACT

In this study, we investigated the effect of inner electrode structure on methane conversion (X_{CH_4}) and product selectivity using dielectric barrier-discharge plasma. We used two types of inner electrodes: those with discharge disks set at 5 mm intervals (Type A) and those with discharge disks set at 0 mm intervals (Type B).

When electric power (Pw) was increased, the methane conversion (X_{CH_4}) of Type A and Type B increased. However, the X_{CH_4} of Type A reactor was lower than that of Type B reactor, irrespective of Pw. When the total thickness of the discharge disks set at 0 mm intervals was the same as that in Type A, X_{CH_4} was lower than the X_{CH_4} for Type A or Type B. This result shows that the presence of discharge disk intervals can result in increased X_{CH_4}. The primary product was ethane when using electrodes with/without intervals under various conditions. When Pw was increased in Type A, the product carbon selectivity (PCS) of propane and C4+ hydrocarbon increased with increased Pw and the PCS of ethylene decreased. When Type B was used, the PCS of acetylene also increased with an increase in Pw. These results show that Type A reactors can promote homologation and Type B reactors can promote dehydration. When the flow rate (F_0) was varied at a Pw of 3 or 32 W, X_{CH_4} decreased with increased F_0. Ethane was again the primary product, and the F_0 value did not dramatically affect the PCS.

1. Introduction

Methane is a major component in natural gas and is thermodynamically very stable. In general, methane conversion (X_{CH_4}) is achieved by pyrolysis with/without a catalyst, partial oxidation or by a plasma technique. Of these methods, the plasma technique has a characteristic reaction when converting methane. It is well known that acetylene is produced primarily by microwave plasma (Onoe et al., 1997) and ethane is produced primarily by spark discharge plasma (Kado et al., 2004; Li et al., 2008), corona discharge plasma (Kado et al., 2004) or electric barrier-discharge (DBD) plasma (Kado et al., 2004; Li et al., 2004; Indarto et al., 2008; Konno et al., 2010).

The structure of a dielectric barrier discharge (DBD) reactor generally consists of inner and outer electrodes with a dielectric barrier, as shown in Fig. 1. Using a DBD reactor

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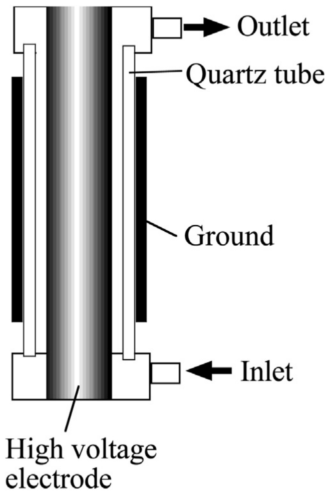


Fig. 1 – Typical DBD reactor.

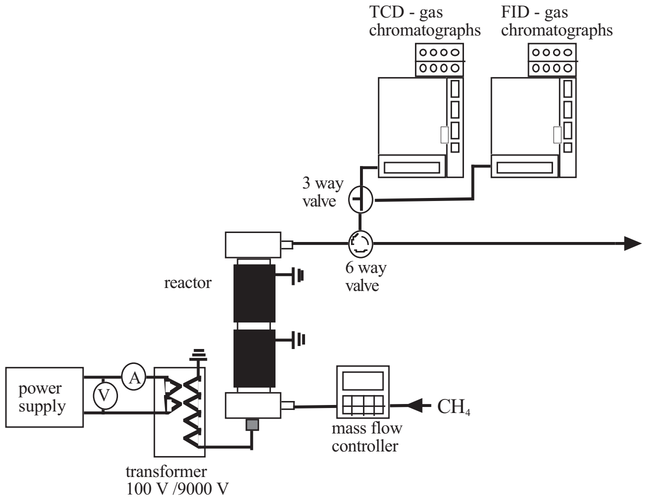


Fig. 2 – DBD apparatus.

similar to the one shown in Fig. 1, Kado et al. reported a X_{CH_4} of 23% and a selectivity for ethane and C3+ hydrocarbon of 35% (electric power: 17 W, methane flow rate: 30 ml/min, frequency: 70 kHz) (Kado et al., 2004). Li et al. reported a X_{CH_4} of 8% and an ethane selectivity of 55% (electric power: 15 W, methane flow rate: 15 ml/min, frequency: 50 Hz) (Li et al., 2004). In a previous study, we used the original inner electrode with discharge disks comprising 40 sheets set at 5 mm intervals to obtain a X_{CH_4} of 4.3% and an ethane selectivity of 58% (electric power: 16 W, methane flow rate: 50 ml/min, frequency: 10 kHz) (Konno et al., 2010). Recent studies have used DBD reactors to investigate the conversion of methane with respect to the partial oxidation of CO_2 (Wang et al., 2013) or O_2 (Kolb et al., 2013).

When converting methane using our DBD reactor, we obtained slightly higher ethane selectivity than that obtained by previous studies that used conventional DBD reactors. We consider this difference to be caused by the different structure of the high voltage electrodes, which primarily affect X_{CH_4} and product selectivity, although the electric power, methane flow rate and frequency also differed between this study and previous experiments. Our aim is to produce low levels of molecular hydrocarbon (ethane, propane, etc.) from methane using electric barrier-discharge plasma. In this study, we investigate the effect of the structure of the inner electrode on X_{CH_4} and product selectivity, using an electric barrier-discharge plasma reactor whose inner electrodes are constructed from discharge disks set at 0 mm intervals (Type A reactor) and at 5 mm intervals (Type B reactor).

2. Experimental

Fig. 2 shows a schematic of the experimental apparatus of the DBD plasma, which consists of five sections including the gas supply, high voltage power supply, radiator, plasma reactor and analysis equipment. The plasma reactor is illustrated in detail in Fig. 3. We used a Pyrex tube (25 mm i.d. and 300 mm length) as the dielectric barrier between the outer and inner electrodes. Aluminium was pasted on the outer wall of the reactor tube to serve as the outer electrode. The inner electrode consisted of a stainless steel rod (φ6.0 mm × 200 mm length) with discharge disks. Discharge occurred in the gap between the edge of the disks and the inside wall of the tube. In the plasma reactor, the inner and outer electrodes were separated into upper and lower sides. In Type A, the lower

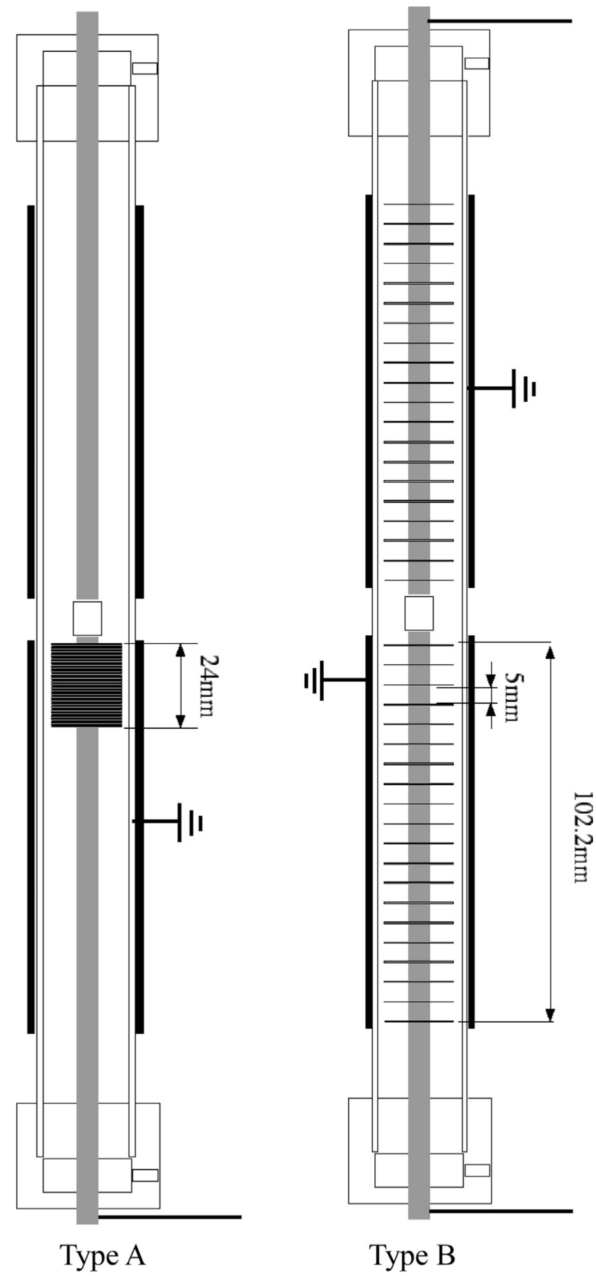


Fig. 3 – Details of a DBD.

side electrode functioned and the lower side inner electrode had a discharge disk of 40 sheets set at 0 mm intervals. The total thickness of the array of discharge disks was 24 mm. In Type B, both lower and upper side electrodes functioned and each of the inner electrodes had a discharge disk of 20 sheets placed on rods and set at 5 mm intervals. The discharge disks consisted of a total of 40 sheets, and the total thickness of the discharge-disk array was 24 mm.

We varied the power level of the primary and secondary voltages from 0 to 100 V and 9.0 kV, respectively. Voltage and current values were measured using a high voltage probe and a current probe with an oscilloscope, respectively. Very low levels of electric power (3–32 W) were required to achieve a discharge with this reactor. All experiments were conducted under atmospheric pressure.

We used high-purity CH_4 gas (99.9999%) as the sole reactant gas. The reactant gases were supplied to the DBD reactor at a total feed rate of 6.25–50 ml/min.

After we applied the discharge for 240 s in the plasma state, we sampled and analyzed the outlet gas using gas chromatography (SHIMADZU, GC-14B) with a thermal conductivity detector and a flame ionization detector using a SHINCARBON S (φ2 m × 3 mm) and a SHINCARBON T (φ6 m × 3 mm) as the separation columns, respectively.

We defined the conversion of the reactant methane as follows:

$$\text{Methane conversion} \quad (X_{CH_4}, \%) = 100 \times \frac{(\text{carbon moles of methane consumed})}{(\text{carbon moles of methane introduced})}.$$

We defined the selectivity of the products as follows:

$$\text{Product selectivity} \quad (\%) = 100 \times \frac{(\text{carbon moles of the product})}{(\text{total carbon moles of all products excepting methane})}.$$

3. Results and discussion

3.1. The effect of electric power

3.1.1. X_{CH_4}

Fig. 4 illustrates the relation between X_{CH_4}s and Pw for Type A and Type B reactors; X_{CH_4} of Type A and Type B reactors was almost the same at Pw levels of 10 W or less. However, the X_{CH_4} of Type B was higher than that of Type A at Pw levels equal to or greater than 25 W. The X_{CH_4} of Type B was 6.9% when the Pw was 30 W and that of Type A was 3.6%. The rod consisted of a 40-sheet discharge disk with a total thickness of 24 mm, irrespective of the reactor type. Therefore, our results show that the presence of an interval between discharge disks can improve X_{CH_4} for Pw levels of 20 W or higher.

This result supports the need for an efficient supply of energy to the methane in Type B reactors. A discharge generally occurs at the gap between the inner electrode and the dielectric barrier in DBD reactors such as that shown in Fig. 1. Therefore, for a Type A reactor, discharge also occurred at the gap between the discharge disks and dielectric barrier. It is not necessarily the case that all discharge disks do not function and result in low spike density. When discharge disks are placed on the rod at intervals of 5 mm, discharge is assumed

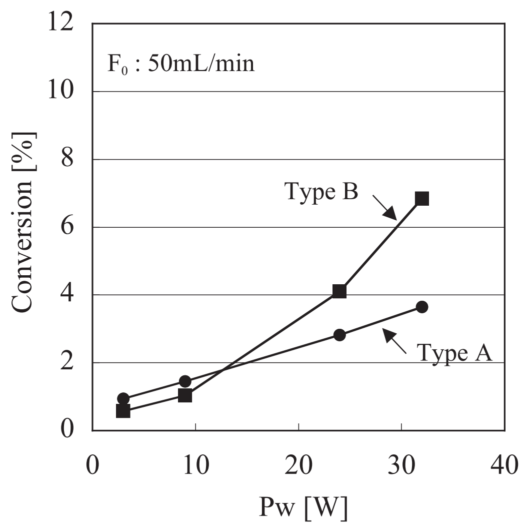


Fig. 4 – Comparison of X_{CH_4} of Type A and Type B reactors.

to occur at the gap between the discharge disks and dielectric barrier; however, when the discharge disk is efficiently used, the spike density increases in comparison to reactors without intervals between the discharge disks. Therefore, we believe that high X_{CH_4} may be obtained by using a Type B reactor.

3.1.2. *Product carbon selectivity (PCS)*

Fig. 5 shows the relation between Pw and PCS obtained with Type A and Type B reactors. Ethane was produced primarily for a Pw range of 3–32 W with Type A and Type B reactors.

When we used Type A, the PCS of ethylene decreased, and the PCS of acetylene, C_4 hydrocarbon and other hydrocarbons increased with increased Pw.

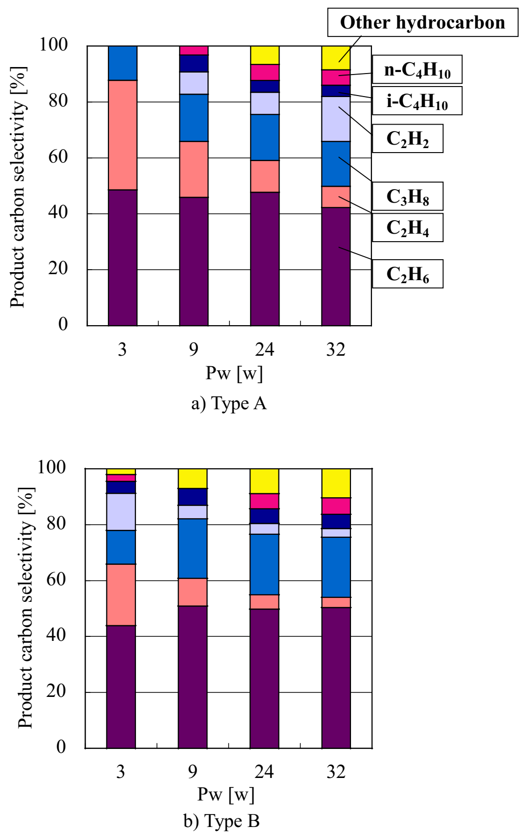


Fig. 5 – Comparison of PCS for Type A and Type B reactors (F_0: 50 ml/min).

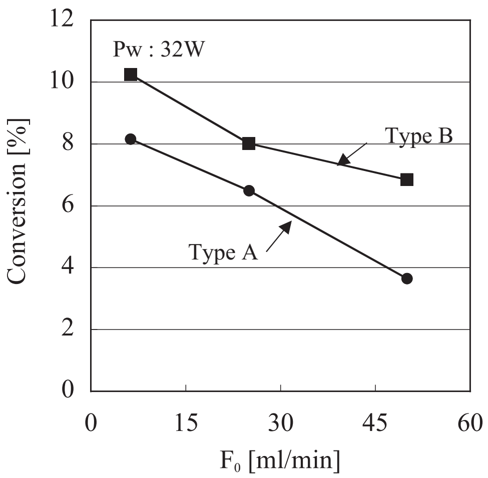


Fig. 6 – Comparison of X_{CH_4} of Type A and Type B reactors.

When we used Type B, the PCS of acetylene was low at a Pw of 9 W and slightly decreased with an increase in Pw of more than 9 W. The PCS of ethylene also decreased with increased Pw. The PCS of propane, C_4 hydrocarbon and other hydrocarbons increased with increased Pw.

Comparing PCS levels obtained at a Pw of 32 W, the PCS of ethane was approximately the same value. The obtained PCS of propane and C_4 and higher hydrocarbons with the Type B reactor was higher than that obtained with Type A. The PCS of acetylene obtained with the Type B reactor was lower than that obtained with Type A reactor.

These results show that the Type B reactors promoted homologation and Type As promoted dehydration. This suggests that the discharge disk intervals between the 40 sheets affect PCS, because both reactors have a total discharge-disk-array thickness of 24 mm. In Type A, methane was decomposed by the discharge through the gap between dielectric barrier and the discharge disks without intervals, thus promoting successive dehydration. However, in Type B, discharge occurs only in the gap between the discharge disks and dielectric barrier, and no discharge occurs in the remaining area. Therefore, the non-discharge area can promote the homologation of propane, C_4 hydrocarbon and other hydrocarbons. We consider that CH_3, C_2H_5 and C_3H_7 obtained from methane or other products in the gap between the discharge disk and dielectric barrier reacts to C_3H_8 and C_4H_{10} in the non-discharge area of Type B reactors.

3.2. *The effect of flow rate*

3.2.1. *X_{CH_4} and PCS at 32 W*

Fig. 6 presents the comparison of X_{CH_4} when using Type A and Type B reactors when F_0 is varied and the Pw level is maintained at 32 W. The X_{CH_4} of both reactors decreased with an increase in F_0, and the X_{CH_4} of Type B was higher than that of Type A, irrespective of F_0. We consider that the interval of the discharge disks can improve X_{CH_4} of Type B reactors because the total thickness of the discharge disk array of both reactors was 24 mm. The X_{CH_4} of the Type B reactor decreased owing to the low level of supplied energy because the available time for discharge in the gap between the discharge disks and dielectric barrier is short for increasing F_0. In turn, the short discharge time may be a result of the highly efficient discharge of the divided discharge disk in the gap between the discharge disks and dielectric barrier. In contrast, the Type

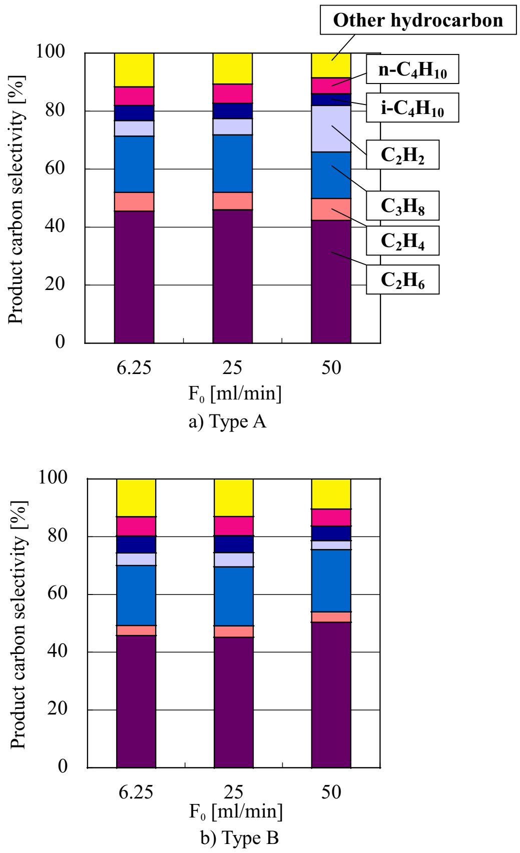


Fig. 7 – Comparison of PCS for Type A and Type B reactors (Pw: 32 W).

A discharge at the connected discharge disks resulted in less efficient discharge.

Fig. 7 shows the relation between F_0 and PCS at a Pw of 32 W. In both reactors, the primary product was ethane, irrespective of the F_0. At an F_0 of 25 ml/min or less, the PCS was not affected by changes in the F_0 in either reactor. When using the Type A reactor, the PCS of acetylene increased and the PCS of C_2 and higher hydrocarbons decreased at an F_0 of 50 ml/min.

When using Type B, the PCS of ethane slightly increased, while that of acetylene, propane and C_4 hydrocarbon decreased at an F_0 of 50 ml/min.

Comparison of the PCS obtained by both reactors shows that the PCS was not affected by reactor type at an F_0 of 25 ml/min or less. At an F_0 of 50 ml/min, the PCS of acetylene obtained by Type A was higher than that obtained by Type B. We found that the interval of the discharge disks has no effect on the PCS when F_0 is varied.

The mechanism of methane decomposition in plasma discharged between electrodes has been proposed by Kado et al. and involves the reaction of atomic carbon decomposed from methane reacting with H or C to form CH and C_2. This reaction can result in a high level of C_2H_2 production because the spike of electron energy in the plasma can be higher than that in the DBD reactor.

We propose that the mechanism of methane decomposition in a DBD reactor proceeds in a stepwise dehydrogenation to form CH_3, CH_2 and CH, and these ionized hydrocarbons couple to form C_2H_6, C_2H_4 and C_2H_2 because the PCS of C_2H_2 increases with increased voltage. C_4H_{10}, C_3H_8 and other hydrocarbons are formed from C_2H_5, C_2H_3 and C_2H decomposed from the obtained hydrocarbons (C_2H_6, C_2H_4, C_2H_2). We consider that the presence of the interval enhances the

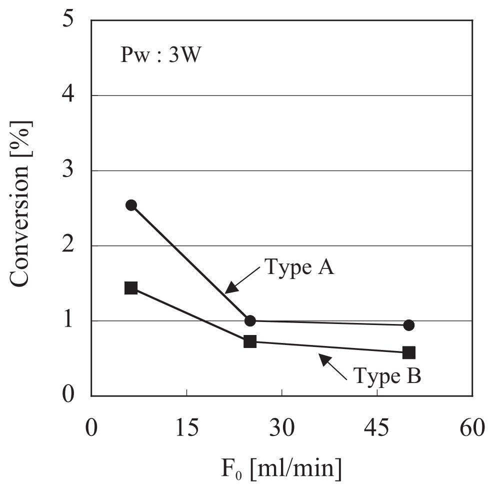
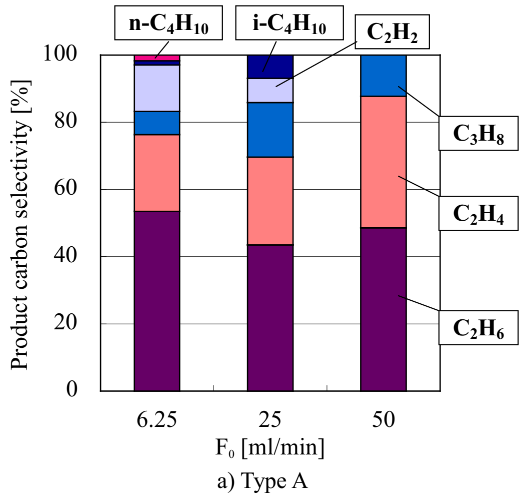


Fig. 8 – Comparison of X_{CH_4} of Type A and Type B reactors.



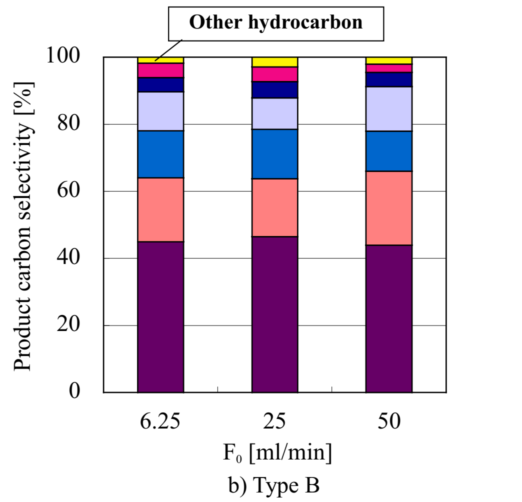


Fig. 9 – Comparison of PCS for Type A and Type B reactors (Pw: 3 W).

decomposition of products and the coupling of the C_2H_5, C_2H_3 and C_2H. Therefore, in Type A reactors, the increase of the PCS of C_2H_2 occurs because there is no chance for the CH to react with other hydrocarbons in the gap between dielectric barrier and the discharge disks when the flow rate is increased and there is no interval between the discharge disks.

3.2.2. *X_{CH_4} and PCS at 3 W*

Fig. 8 shows the comparison of X_{CH_4} of Type A and Type B reactors when the F_0 was varied and the Pw was maintained at 3 W. The X_{CH_4} also decreased with an increase in F_0, irrespective of the type of reactor. This tendency is similar to the result reported in Section 3.2.1, but the X_{CH_4} of Type A was higher than that of Type B for all F_0 values.

We assume that discharge is more difficult to achieve in the gaps of Type B than that in Type A when the Pw is low.

Fig. 9 shows the relation between F_0 and the PCS of Type A and Type B reactors, when Pw is maintained at 3 W. Ethane is the primary product for various F_0 values in both reactors. When using Type A, the PCS of ethylene increased and ethane, ethylene and propane were obtained only for F_0 values of 50 ml/min. We consider that dehydration of acetylene is difficult to promote because the supplied energy is low as F_0 increases. This is because the time available for discharge through the gap between the electrode and the dielectric barrier is short. Type A yields a continuous supply of energy for CH_4 through the gap between the electrodes. However, the results of varying F_0 at 3 W are different from those at 32 W in Type A. This may be due to the different range of energy supplied to methane. Dehydration of methane is promoted with increased energy levels, as is the homologation to C_3 and other hydrocarbons, which require high energy to dehydrate C_2H_6, C_2H_4 and C_2H_2. Therefore, the PCSs of C_4 and other hydrocarbons are high at a Pw of 32 W and an F_0 of 6.25 ml/min at high energy levels, and the PCSs of ethane and acetylene are high at a Pw of 3 W and an F_0 of 50 ml/min at low energy levels. Using the Type B reactor, the PCSs of C_4 and other hydrocarbons decreased, in comparison with those obtained at a Pw of 32 W. Using a low power of 3 W, slight homologation may occur because of presence of small amounts of C_2H_5, C_2H_3 and C_2H obtained from the experiments.

4. Conclusion

To clearly identify the characteristics of X_{CH_4} by electric barrier-discharge plasma using an inner electrode with discharge disks set at 5 mm intervals, we compared its X_{CH_4} with that when using an inner electrode with discharge disks with no intervals. Our results are as follows:

When the 5 mm-interval discharge disks were placed on the rod, the maximum value of X_{CH_4} was obtained at a Pw of 32 W and an F_0 of 6.25 ml/min. The interval of the discharge disks slightly affects the PCS of ethane as the primary product. In the minor products, the presence of an interval between the discharge disks increased the PCS of propane and C_4 and higher hydrocarbons but decreased the PCS of ethylene. These findings indicate that the presence of an interval between the discharge disks can improve X_{CH_4} and support the homologation reaction.

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