



# A single step methane conversion into synthetic fuels using microplasma reactor

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## ABSTRACT

Direct conversion of natural gas into synthetic fuels such as methanol attracts keen attention because direct process can reduce capital and operating costs of high temperature, energy intensive, multi-step processes. We report a direct and selective synthesis of organic oxygenates such as methanol, formaldehyde, and formic acid via methane partial oxidation at room temperature using non-thermal discharge microreactor. Heat generated by methane partial oxidation is removed efficiently in the microreactor configuration: liquid components are condensed on the reactor wall and separated from O<sub>2</sub>-rich reactive plasma, enabling selective synthesis of oxygenates while high methane conversion is achieved in a single reactor. As a result, organic oxygenates were synthesized with one-pass yield of 5–20% with 70–30% selectivity. In addition to oxygenates, syngas was produced with selectivity of 40% and H<sub>2</sub>/CO = 1. Assuming one step catalytic DME synthesis as a post-discharge process, one-pass liquid yield of 30% with 80% selectivity is feasible.

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## 1. Introduction

Direct conversion of natural gas (main component is methane) into synthetic fuels such as methanol attracts keen attention because direct process can reduce capital and operating costs of high temperature, energy intensive, multi-step processes via syngas production [1]. Although tremendous effort has been made on direct CH<sub>4</sub> conversion to oxygenates in homogeneous gas phase reaction and over solid catalysts [2–5], the yield for desired products was below an economical value [6]. More recently, atmospheric pressure non-thermal discharge is highlighted as a viable synthesis method because high energy electron impact initiate methane partial oxidation, enabling a single step CH<sub>4</sub> conversion into various oxygenates. Nevertheless, one-pass yield for useful oxygenates was unsatisfactory [7–9]. Nozaki et al. proposed non-thermal discharge generated in a microreactor which enabled a moderate methane oxidation at room temperature, and selectively produced methanol (CH<sub>3</sub>OH), formaldehyde (HCHO), and formic acid (HCOOH) with one-pass yield of more than 10% [10–12]. Performing non-thermal discharge in a microreactor brings unconventional thermochemical conditions to materials processing, enabling better control over process parameters to selective synthesis of desirable products [13–16]. The principle of microplasma technology is as follows: a flammable CH<sub>4</sub> and O<sub>2</sub> mixture was activated by high energy electrons produced by dielec-

tric barrier discharge (DBD), which initiates oxidative destruction of chemically stable methane independently of reaction temperature. Microreactor configuration removes heat generated by methane partial oxidation efficiently. Low temperature synthesis is essential because oxygenates are condensed on the microreactor wall which realizes product separation from O<sub>2</sub>-rich reactive plasma. Furthermore, pulsed water injection mechanically washes out condensed oxygenates and suppresses successive destruction of reactive oxygenates, enabling selective synthesis of oxygenates while high methane conversion is achieved in a single reactor. The given microplasma reactor is benign, simple, and does not require hazardous or expensive materials such as palladium, platinum, ionic liquid, or mercury. Furthermore, current technology greatly reduces the operating temperature, making the process more economically attractive. In this paper, we describe the principle of room temperature methane partial oxidation using DBD. Subsequently, microplasma reactor combined with pulsed water injection is described for practical methane partial oxidation. Given microplasma reactor also produces relatively large amount of syngas. Assuming one step catalytic dimethyl ether (DME) synthesis as a post-discharge reaction, one-pass liquid yield of 30% with 80% selectivity is feasible. Finally, concluding remarks are presented.

## 2. Principle

### 2.1. Thermodynamic equilibrium

Equilibrium calculation was performed by STANJAN software that solves adiabatic equilibrium state of gas mixture based on

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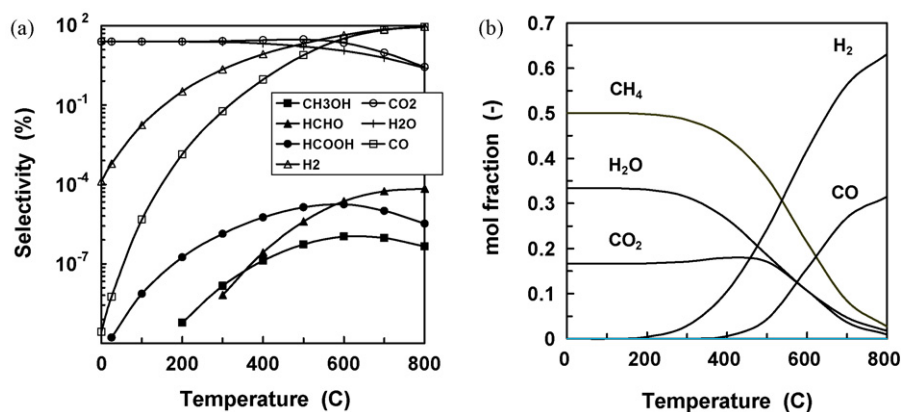
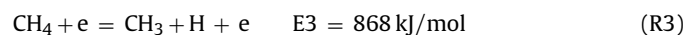
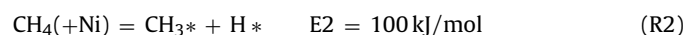
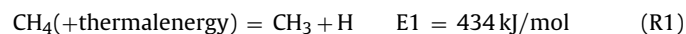


Fig. 1. Equilibrium composition of CH<sub>4</sub>, O<sub>2</sub>, and oxidative products at 101 kPa with O<sub>2</sub>/CH<sub>4</sub> = 0.5. (a) Product selectivity and (b) mol fraction.

JANAF thermochemical database [17]. Fig. 1 shows equilibrium composition of CH<sub>4</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, HCHO, CH<sub>3</sub>OH, HCOOH, assuming initial O<sub>2</sub>/CH<sub>4</sub> = 0.5 at atmospheric pressure (101 kPa). These components were considered based on experimental results. According to thermodynamic equilibrium, O<sub>2</sub> is fully consumed even at room temperature. Correspondingly, 50% of methane is converted, producing full combustion products such as H<sub>2</sub>O and CO<sub>2</sub> when the temperature is well below 300 °C. As temperature increases, fraction of CO and H<sub>2</sub>, i.e. syngas, increases and remaining methane is gradually consumed. Eventually, H<sub>2</sub>/CO ratio approaches 2 as temperature approaches 800 °C. This reaction scheme expresses typical multi-step methane reforming for syngas production. On the other hand, liquid components were negligibly small all the way through the temperature considered. Fig. 1 emphasizes several important facts: first, to achieve highest selectivity for useful oxygenates, abrupt termination of methane oxidation at desired moment must be realized before thermodynamic equilibrium is established [5,18]. Catalysts have a capability of accelerating specific reaction pathway preferentially for better selectivity of the process; however, results were not satisfactory by now [6]. Non-thermal discharge would provide a totally different methane activation route with different kinetics in unusual temperature range, realizing a better feasibility of partial chemistry instead of going to equilibrium.

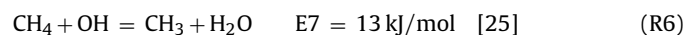
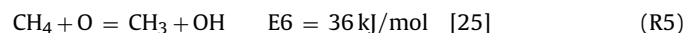
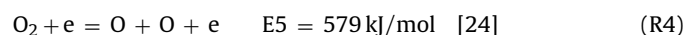
## 2.2. Methane activation via active oxygen

The rate-determining step of CH<sub>4</sub> conversion is to dissociate strong C–H bond. Here, three different approaches are compared: R1, homogenous gas phase reaction; R2, heterogeneous surface reaction; R3, plasma-enhanced reaction.



E1–E3 express activation energy and superscript “\*” denotes chemisorbed fragments. Activation energy for R3 was estimated from collision cross section of methane [19]. Activation energy for methane pyrolysis (R1) is 434 kJ/mol [20] that requires high temperature thermal energy (>1000 °C). Activation energy as well as reaction temperature is greatly reduced by the use of transition metal catalyst (R2) [21]. Peculiarity of non-thermal discharge is that chemically stable methane is dissociated by electron impact almost independently of reaction temperature; however, inelastic electron collision requires large activation energy. Comparing to endothermic enthalpy of CH<sub>4</sub> dissociation (440 kJ/mol at 298 K), approximately 50% of electronic energy fed into methane is

inevitably wasted via molecular collision. Consequently, energy efficiency of electronic methane dissociation is generally low. Furthermore, due to large activation energy, electronic CH<sub>4</sub> dissociation is essentially slow reaction. Detailed kinetic modeling on CH<sub>4</sub> activation is described in separate reference [22,23]. According to R3, CH<sub>4</sub> conversion is increased as electron density increased; however, high electron density plasma is characterized as arc discharge where high temperature thermal energy (>10,000 K) plays a more important role than electronic dissociation of CH<sub>4</sub>. Also, product distribution is likely governed by thermodynamic equilibrium under high temperature situation. It is indispensable to take advantage of radical chain reaction in order to enhance CH<sub>4</sub> conversion with minimum energy consumption. In this context, CH<sub>4</sub> activation by oxygen-related species would be promising solution:



Even a trace amount of active oxygen induces exothermic chain reaction. In addition to ground state atomic oxygen (R4), five ionic species (O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, O<sup>-</sup>, O<sub>2</sub><sup>-</sup>, O<sub>3</sub><sup>-</sup>), several excited neutrals (O<sup>\*</sup>, O<sub>2</sub><sup>\*</sup>, O<sub>3</sub><sup>\*</sup>), and ozone (O<sub>3</sub>) are produced [24]. Activation energy for electronic dissociation and ionization of O<sub>2</sub> is relatively large; however, electron attachment and electronic excitation of O<sub>2</sub> are possible with much smaller threshold energy. Although detailed methane oxidation chemistry involving those species are not fully understood, various oxygen-related reactive species are considered to be an essential chain reaction promoters at low temperature. Once oxidative methane fragmentation is initiated by active oxygen, additional oxidative agents such as OH creates another chain reaction pathway. In this experiment, production of CH was identified by optical emission spectroscopy (432 nm band lines) [10]; however, other radical species such as CH<sub>3</sub>, CH<sub>2</sub>, and active oxygen were not readily identified. Extensive work such as laser absorption spectroscopy is needed to diagnose plasma-generated reactive species; it is beyond the scope of the present study.

## 3. Experimental

A schematic diagram of microplasma reactor is presented in Fig. 2. A microplasma reactor consists of quartz tube (I.D. 1.5 mm, O.D. 2.7 mm, length: 50 mm) equipped with internal twisted wire electrode (0.5 mm stainless steel) and external grounded electrode. A bipolar pulsed high voltage with peak intensity of 10 kV and fixed frequency at 10 kHz was applied between metallic electrodes. This type of discharge is defined as dielectric barrier discharge (DBD) where a number of transient filamentary discharges with

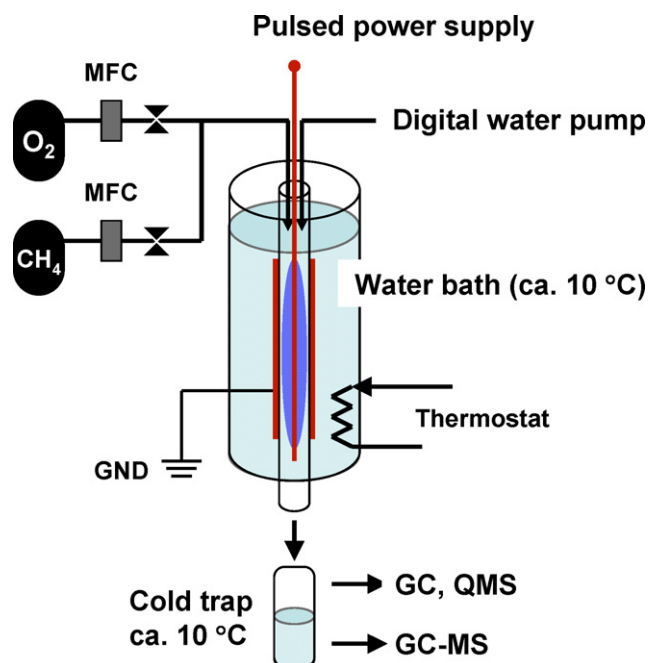


Fig. 2. Schematic diagram of microplasma reactor and experimental setup.

nanosecond duration are randomly generated inside glass tube [26]. Because gas breaks down temporarily with nanosecond duration, average gas temperature only slightly increases [27,28], while high energy electrons activate methane and oxygen, initiating methane partial oxidation at room temperature. The microplasma reactor was immersed into the water bath maintained near room temperature (10 °C): microreactor configuration enhances removal of heat generated by methane partial oxidation. Low temperature operation enhances condensation of liquid components on the cooled reactor wall, realizing product separation from O<sub>2</sub>-rich reactive plasma. Product separation is extremely important because organic oxygenates are much more reactive than methane, and readily decomposed during methane activation.

A flammable CH<sub>4</sub> and O<sub>2</sub> mixture was introduced into a microplasma reactor. Total flow rate was varied so that reaction time of gas flow becomes between 100 ms and 500 ms, while O<sub>2</sub>/CH<sub>4</sub> ratio was varied at 0.2, 0.5, and 1.0. In addition to feed gas, distilled water was injected intermittently from the top of the reactor (1.2 cm<sup>3</sup> min<sup>-1</sup> for 10 s and 2 min interval). Liquid water washed out condensed oxygenates from the microreactor. Carbon balance was deteriorated without pulsed water injection because successive destruction of condensed oxygenates took place, forming tar-like products on the reactor wall: carbon balance was smaller than 80% without water injection. On the other hand, liquid water covers twisted wire electrode temporarily, suppressing DBD formation. Therefore gaseous products were accumulated in a sampling bag over 30 min, then average value was analyzed by gas chromatography equipped with FID and TCD (Shimadzu, GC-8A). Liquid components were determined by gas chromatography–mass spectrometry (SHIMADZU, QP2010Plus) after cold-trapping.

#### 4. Results and discussion

##### 4.1. Effect of reaction time and initial O<sub>2</sub>/CH<sub>4</sub> ratio

Fig. 3 shows CH<sub>4</sub> conversion with respect to reaction time. The initial O<sub>2</sub>/CH<sub>4</sub> ratio was also varied. CH<sub>4</sub> conversion increases linearly with reaction time. Tar-like products were observed and carbon balance was below 80% when O<sub>2</sub>/CH<sub>4</sub> = 0.2; there-

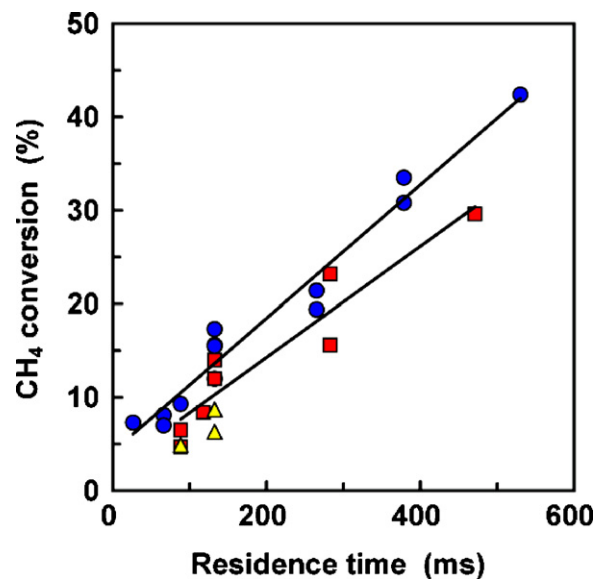


Fig. 3. CH<sub>4</sub> conversion vs. reaction time. O<sub>2</sub>/CH<sub>4</sub> = 0.2 (▲), 0.5 (■), 1.0 (●).

fore, experiments were conducted mostly with O<sub>2</sub>/CH<sub>4</sub> = 0.5 and 1.0. Fig. 4 shows ratio of reacted CH<sub>4</sub> and O<sub>2</sub> with respect to O<sub>2</sub>/CH<sub>4</sub> ratio. Interestingly, nearly the same amount of CH<sub>4</sub> and O<sub>2</sub> were reacted when sufficient amount of oxygen was supplied (O<sub>2</sub>/CH<sub>4</sub> > 0.5). Data is rather scattered when O<sub>2</sub>/CH<sub>4</sub> = 0.2 due to formation of tar-like products. Methane steam reforming is also anticipated because water vapor exists as a result of pulsed water injection. However, a trace amount of methane was converted in the absent of oxygen: electronic H<sub>2</sub>O dissociation to produce OH, which is a viable radical chain propagator, is very unlikely took place. D<sub>2</sub>O was injected to trace D<sub>2</sub>O (i.e. H<sub>2</sub>O) dissociation pathway; however, either HD or D<sub>2</sub> were not identified by quadrupole mass spectrometry (Prisma-100; Pfeiffer Vacuum Technology AG) (data is not shown). Liquid water mechanically washes out condensed oxygenates, but it does not participate in methane oxidation. Liquid components were quantitatively analyzed by GC–MS, showing methanol (CH<sub>3</sub>OH), formaldehyde (HCHO), and formic acid (HCOOH) were the main components.

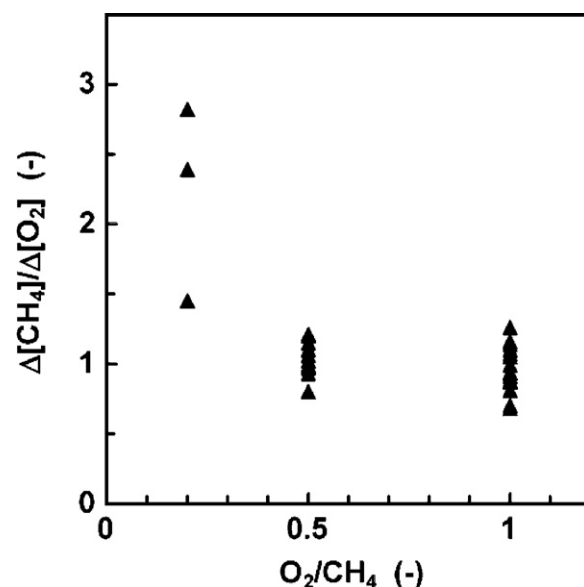


Fig. 4. Ratio of reacted CH<sub>4</sub> and O<sub>2</sub> vs. O<sub>2</sub>/CH<sub>4</sub> ratio.

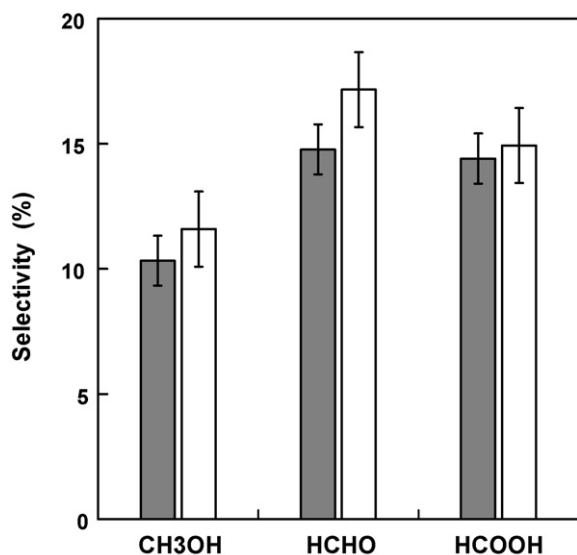


Fig. 5. Selectivity for oxygenates. (■) CH<sub>4</sub>:O<sub>2</sub> = 20:20 cm<sup>3</sup> min<sup>-1</sup> (CH<sub>4</sub> conv = 12.0%); (□) 30:15 cm<sup>3</sup> min<sup>-1</sup> (8.4%); reaction time, 130 ms.

Selectivity for three components is described in Fig. 5. Total liquid selectivity was 40–50% and almost independent of initial O<sub>2</sub> content. The fact implies that product separation due to liquid condensation effectively suppressed excessive oxidation of organic oxygenates. Selectivity for liquid oxygenates and syngas were 5–6 orders of magnitude greater than thermodynamic equilibrium shown in Fig. 1, implying that methane oxidation is successfully terminated before thermal equilibrium is established.

#### 4.2. Syngas production and DME synthesis as post-discharge reaction

In addition to oxygenates, relatively large amount of syngas is produced. Syngas is beneficial by-product because it is readily converted into synthetic fuels at moderate conditions using well-established catalysts. Specifically, we focus on dimethyl ether synthesis (DME; CH<sub>3</sub>OCH<sub>3</sub>) as a desirable post-discharge process. DME is widely recognized as viable alternative liquid fuel because it is readily liquefied at moderate conditions; –23.6 °C at 100 kPa or 25 °C at 610 kPa. One step catalytic DME synthesis has been commercialized from syngas with H<sub>2</sub>/CO = 1 (R7) [29], while syngas with H<sub>2</sub>/CO = 0.8–1.2 is obtainable using given microplasma reactor when initial O<sub>2</sub>/CH<sub>4</sub> ratio was properly selected. It is worth mentioning that methanol synthesis requires H<sub>2</sub>-rich syngas (H<sub>2</sub>/CO = 2) that requires additional H<sub>2</sub> moderator in the post-discharge process. Integration of given microplasma reactor and one step DME synthesis is desirable combination to give highest liquid yield.



Eventually, the overall liquid selectivity,  $S_{\text{total}} = S_{\text{liq}} + S_{\text{DME}}$ , would be feasible:

$$S_{\text{liq}} = [\text{CH}_3\text{OH}]_{\text{sel}} + [\text{CHOH}]_{\text{sel}} + [\text{HCOOH}]_{\text{sel}} \quad (1)$$

$$S_{\text{DME}} = \frac{2}{3} \times [\text{CO}]_{\text{sel}} \quad (n > 1) \quad (2)$$

$$S_{\text{total}} = S_{\text{liq}} + S_{\text{DME}} \quad (3)$$

Fig. 6 shows CO and CO<sub>2</sub> selectivity and Fig. 7 represents H<sub>2</sub>/CO ratio. CO selectivity gradually increases with CH<sub>4</sub> conversion. Correspondingly, liquid selectivity decreases with CH<sub>4</sub> conversion (see Fig. 8; ●), implying that oxidation of liquid products yield CO. Note CH<sub>4</sub> conversion is most influenced by reaction time and there is a

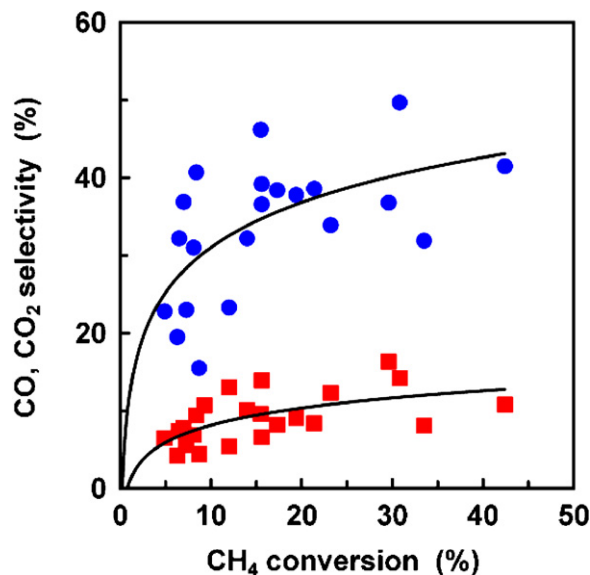


Fig. 6. Selectivity for CO and CO<sub>2</sub> at various conditions.

small dependence on O<sub>2</sub>/CH<sub>4</sub> ratio as shown in Fig. 3. In contrast, H<sub>2</sub>/CO ratio is independent of CH<sub>4</sub> conversion, but it is determined by initial O<sub>2</sub>/CH<sub>4</sub> ratio, implying there is a parallel reaction pathway. As mentioned previously, liquid products are condensed and separated from reactive plasma zone. Therefore liquid selectivity is less affected by O<sub>2</sub>/CH<sub>4</sub> ratio. On the other hand, H<sub>2</sub> remains in the gas phase and it is likely oxidized as O<sub>2</sub>/CH<sub>4</sub> ratio increased. Small amount of oxygen, such as O<sub>2</sub>/CH<sub>4</sub> = 0.2, produced hydrogen rich syngas ( $n = 1.8$ ); however, formation of tar-like product was recognized on the reactor wall. Note solid carbon formation was eliminated because of low temperature synthesis and absence of metallic catalyst. When O<sub>2</sub>/CH<sub>4</sub> = 1, CH<sub>4</sub> conversion exceeded 40%, while liquid selectivity was only slightly decreased. As discusses in Section 4.3, we assume DME synthesis from syngas with H<sub>2</sub>/CO > 1 as a post-discharge reaction. Initial O<sub>2</sub>/CH<sub>4</sub> = 0.5, which produced syngas with H<sub>2</sub>/CO = 1.2, is desirable.

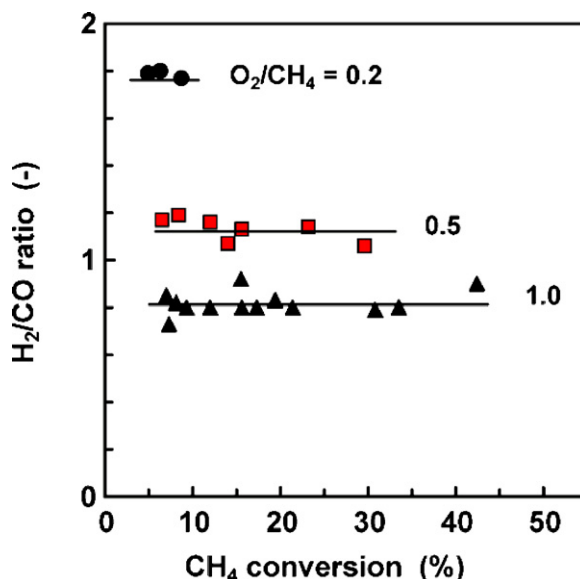
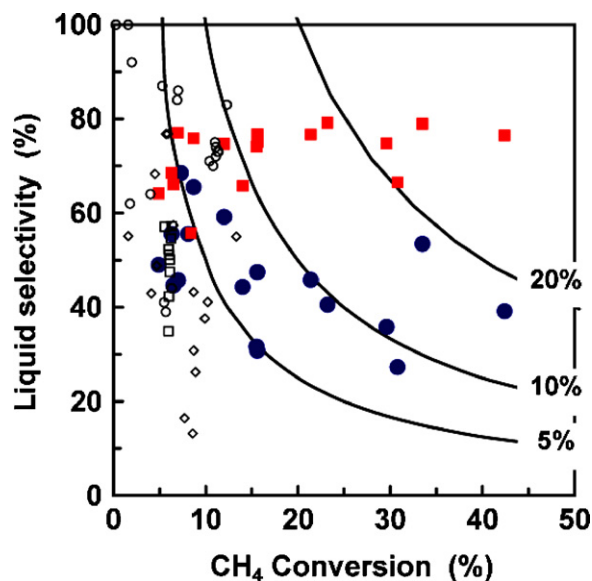


Fig. 7. H<sub>2</sub>/CO ratio vs CH<sub>4</sub> conversion. (●) O<sub>2</sub>/CH<sub>4</sub> = 0.2, (■) 0.5, (▲) 1.0.



**Fig. 8.** Liquid selectivity (●:  $S_{liq}$  and ■:  $S_{total}$ ) vs.  $CH_4$  conversion. Conditions,  $O_2/CH_4$ , 0.5 and 1.0; reaction time, 130–530 ms. Three curves represent constant yield lines. Hollow symbols express cited literature; (□) Bjorklund and Carr [2], (○) Feng et al. [3], (◇) Yarlagadda et al. [4].

#### 4.3. Liquid selectivity vs. methane conversion

Fig. 8 shows selectivity of liquid components ( $S_{liq}$  and  $S_{total}$ ) with respect to  $CH_4$  conversion obtained by wide spectrum of operating conditions. Results are compared with three literatures that used thermochemical methods. In conventional methods, thermal energy is added to initiate methane oxidation, while small amount of oxygen, typically 10% at most, was introduced so that heat generated by methane oxidation does not create high temperature hot spots. Effective cooling method, such as water bath used in this study, could not be taken because low temperature situation does not initiate methane oxidation. As a result,  $CH_4$  conversion beyond 10% was hardly achieved. Although  $CH_4$  conversion increased by increasing either  $O_2$  content or reaction temperature, selectivity for useful oxygenates sharply dropped. Unlike conventional technology, liquid product selectivity is slightly decreases with  $CH_4$  conversion, implying that liquid product separation worked effectively in the given microplasma reactor. Although one-pass liquid yield beyond 15% is obtainable with given microplasma reactor, liquid selectivity was below 60% (●). Assuming post-DME synthesis with given syngas ( $H_2/CO=1$ ), the overall liquid selectivity is enhanced up to 80% (■). Selectivity for methanol, formaldehyde, and formic acid slightly decreased with  $CH_4$  conversion, which in turn produces syngas (Fig. 6). Therefore, overall liquid selectivity,  $S_{liq} + S_{DME}$ , is kept constant around 80%.

## 5. Concluding remarks

Newly developed non-thermal discharge microreactor enabled a single step, non-catalytic, and selective synthesis of synthetic fuels (methanol, formaldehyde, and formic acid) via room temperature methane partial oxidation. Low temperature synthesis is essential because low temperature situation promotes condensation of liquid components on the microreactor wall; as a result, reactive oxygenates are separated from  $O_2$ -rich plasma zone. Furthermore, pulsed water injection mechanically washes out condensed oxygenates, and thus suppresses successive destruction of reactive oxygenates, enabling one-pass  $CH_4$  conversion of 40% while selectivity for useful oxygenates was 30%–50%.

In addition to oxygenates, given microplasma produces relatively large amount of syngas with 40% selectivity and  $H_2/CO=1$ . Assuming one step catalytic DME synthesis as a post-discharge reaction, overall liquid yield of 30% with 80% selectivity is feasible. Further increase in oxygenate selectivity is important issue. In addition, effective integration of microplasma technology and existing catalytic processes is an attractive option that realizes economically and technologically viable material conversion process.

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