

## CARBON DIOXIDE REFORMING OF METHANE BY CATALYTIC-PLASMA REACTOR OVER Cu/Zn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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**Abstract.** In the current study, the influence of input power for conversion of CH<sub>4</sub> and CO<sub>2</sub> into syngas was investigated in both Dielectric Barrier Discharge (DBD) plasma and catalytic-plasma cylindrical reactors. It was observed that for both reactors, higher input power favored fragmentation reactions rather than recombination of light intermediates into heavier hydrocarbons, thus improving H<sub>2</sub> yield. Meanwhile, the presence of Cu/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst enhanced the H<sub>2</sub> yield from 16.5% to 19.1%, while the H<sub>2</sub>/CO ratio remained almost constant near unity, thus indicating the suitable ratio for Fischer-Tropsch (FTS) processes.

*Keywords:* Plasma; catalytic; hydrogen; DBD

**Abstrak.** Dalam kajian semasa, pengaruh kuasa input untuk penukaran CH<sub>4</sub> dan CO<sub>2</sub> ke gas sintetik disiasat di dalam kedua-dua reaktor silinder plasma DBD dan reaktor plasma pemangkin. Diperhatikan bahawa untuk kedua-dua reaktor, input kuasa yang lebih tinggi menyokong tindak balas pemecahan dan bukannya penggabungan semula perantaraan ringan kepada hidrokarbon yang lebih berat, meningkatkan hasil H<sub>2</sub>. Sementara itu, kehadiran pemangkin Cu/Zn/Al<sub>2</sub>O<sub>3</sub> mempertingkatkan pengeluaran H<sub>2</sub> daripada 16.5% kepada 19.1%, manakala nisbah H<sub>2</sub>/CO kekal hampir malar berhampiran nilai 1, nisbah yang sesuai untuk proses FTS.

*Kata kunci:* Plasma; plasma pemangkin; hidrogen; DBD

### 1.0 INTRODUCTION

Numerous attempts have been directed at limiting greenhouse gases especially CO<sub>2</sub> and CH<sub>4</sub> emissions to halt global warming [1]. Using hydrocarbon

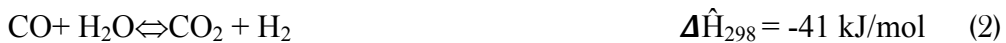
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feedstock from fossil fuels, generally natural gas, for syngas production has given a promising hope to mitigate green-house gases. However, the traditional approach for syngas production, i.e steam reforming of methane, discharges notable quantity of CO<sub>2</sub> to the environment [1-3]. Furthermore, the ratio of H<sub>2</sub>/CO in the syngas is between 2 to 3, which is very high to be directly used to produce oxygenated chemicals and olefins, unless adjusting the H<sub>2</sub>/CO ratio to the required value. On the contrary, simultaneous utilization of CH<sub>4</sub> and CO<sub>2</sub> which is known as CO<sub>2</sub> reforming of methane or dry reforming of CH<sub>4</sub>, produces syngas with an appropriate H<sub>2</sub>/CO ratio. Dry reforming is a highly endothermic reaction that requires a temperature beyond 700°C to yield a reasonable amount of H<sub>2</sub>. The main reaction which may occur along with dry reforming of CH<sub>4</sub> (Eq. 1) is water-gas shift reaction (Eq. 2).



Nevertheless, only a few industrial processes have been established for simultaneous utilization of CH<sub>4</sub> and CO<sub>2</sub> as feedstock into higher-value added chemicals due to several factors. CO<sub>2</sub> is an inert and stable molecule while strong C-H bonds exist in CH<sub>4</sub>. The chemical equilibrium analysis demonstrated thermodynamic constraints [4-6] on the CH<sub>4</sub>-CO<sub>2</sub> reactions. In addition, coke and solid carbon formation led to fast catalyst deactivation, reactor clogging and high operational cost [7]. Many studies have embarked on activation of CO<sub>2</sub> as reactant together with CH<sub>4</sub> [8].

Plasma is one of the cost-effective technologies that has attracted much attention due to its effective activation of CO<sub>2</sub> [9]. Among the various types of plasmas, non-thermal plasma has been more appreciated as a sustainable alternative for syngas production for greenhouse gas conversion at ambient temperatures. The presence of highly active species such as ions, photons and radicals in the plasma is beneficial for the purpose of initiation and improving all types of reactions [10]. Among non-equilibrium plasmas, dielectric barrier discharge is the most suitable for plasma chemical processing due to their ability to initiate reactions that thermodynamically would not occur at low gas temperature and atmospheric pressure, providing relatively equal performance and sometimes higher than commercial reaction processes [11]. The advantage of Dielectric Barrier Discharge (DBDs) is easy scale-up from a bench scale in the laboratories

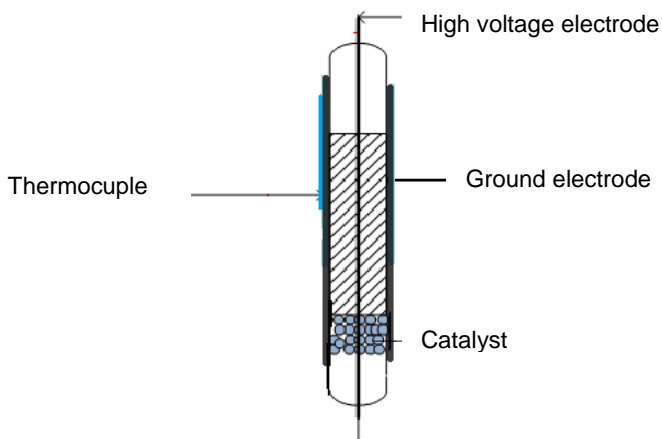
to a large-scale installation in industry with input power in the order of several megawatts [12]. The incentive of combining catalyst plasma techniques was derived from this fact that the interaction of catalytic surfaces with non-equilibrium plasmas can lead to a suitable performance and activity at much lower temperature, as compared to the conventional lower temperatures processes [9]. In a combined catalytic-plasma reactor, the catalyst activity can be improved in the plasma medium as well as the plasma properties by the function of the catalyst [13].

Until now, although the interactions of plasma with the catalyst have received much attention, exploring for a highly selective and cost-effective catalyst towards  $H_2$  while improving the reactor performance and using lower input power is an extreme challenge. In the present work, the effect of power on the product yields and reactant conversion for non-catalytic plasma and catalytic-plasma reactor were investigated. The catalyst packed in the gas gap of the DBD plasma reactor was  $Cu/Zn/\gamma-Al_2O_3$ .

## 2.0 EXPERIMENTAL

### 2.1 Plasma Reactor

The experiments were carried out in a high temperature and frequency resistant quartz tube reactor with the inner and outer diameter dimensions being 10 and 12 mm, respectively and length of 38 cm. Fig. 1 displays a schematic diagram of the reactor used for the experiments. A 6 mm diameter of a special alloy wire was inserted in the symmetric axis of the quartz tube functioning as a high-voltage electrode. A 15 cm elongated aluminum cylindrical screen shell partially surrounded by the quartz tube played the role of a grounded electrode. For that part of the experiments in hybrid catalytic-plasma reactor, the end part of the plasma discharges media was loaded by catalysts, otherwise it was left empty. Reactants, including  $CH_4$  and  $CO_2$  entered through the reactor with the molar ratio of unity and a constant total volume flow rate of 40 ml/min. A high-voltage pulse AC generator (PVM500-DIDRIVE10) supplied the required high voltage with the pulse waveform at a frequency of 18-20 KHz. The voltage and frequency measurements were conducted using an oscilloscope (Tektronix-2440) equipped with a high-voltage probe (Tektronix-p 6015 A) and a current transformer.



**Figure 1** Schematic diagram of the experimental catalytic-plasma reactor

## 2.2 Materials

The commercial catalyst of MK-21 (43 wt % Cu and 20 wt % Zn supported on  $\gamma$ - $\text{Al}_2\text{O}_3$ ) were procured from BIPC (Bandar Imam Petrochemical Complex) which was manufactured by Haldor Topsoe S/A (Denmark). Firstly, the catalyst was crushed to take a non-uniform size and shape; then was reduced for 3 hr by 80 ml/min of 50%  $\text{H}_2$ / 50% He before being used in the catalytic-plasma experiments. The gas products were analyzed using a gas chromatograph (Agilent-6890N) equipped with Temperature Conductivity Detector (TCD) and Molecular Sieve 5A and Poraplot Q columns for the separation of  $\text{CH}_4$ , CO,  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$  and  $\text{CO}_2$ . A cold trap containing dry ice was placed after the plasma reactor before directing to the GC in order to condense all condensable liquid products.

## 2.3 Formula Definition

The conversions ( $X$ ) of  $\text{CH}_4$  and  $\text{CO}_2$ , selectivities ( $S$ ) of  $\text{H}_2$ , CO and  $\text{CO}_2$  were defined as:

$$\text{Conversion of } CH_4 \text{ (or } CO_2)\% = \frac{\text{Mole of } CH_4 \text{ (or } CO_2)\text{Converted}}{\text{Moles of } CH_4 \text{ (or } CO_2)\text{in the feed}} * 100\% \quad (3)$$

The selectivity and yields of the products were calculated based on carbon atoms:

$$\% \text{Selectivity of } H_2 = \frac{0.5 * \text{moles of } H_2 \text{ produced}}{\text{mole of } CH_4 \text{ converted}} * 100\% \quad (4)$$

$$\% \text{Selectivity of } CO = \frac{\text{Moles of } CO \text{ produced}}{\text{moles of } CH_4 \text{ converted} + \text{moles of } CO_2 \text{ converted}} * 100\% \quad (5)$$

$$\text{Yield of } H_2\% = CH_4 \text{ Conversion} * H_2 \text{ selectivity} * 100\% \quad (6)$$

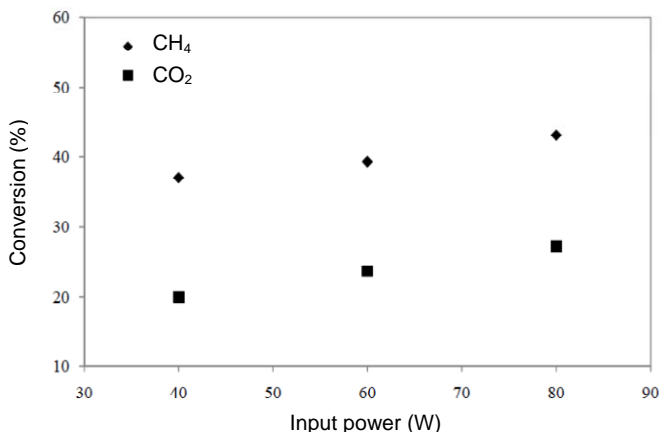
### 3.0 RESULTS AND DISCUSSION

#### 3.1 Effect of Exerted Electrical Power on the Reactant Conversion

Supplying high-energy electrons in order to decompose  $CH_4$  and  $CO_2$  molecules is dependent on the source of the voltage. The experiments were conducted in order to understand the effect of the power variation on the reactant conversion in a discharge  $CO_2/CH_4$  mixture of unity, a total reactant flow rate of 40 mL/min at a constant frequency of 20 kHz and atmospheric pressure. The results of the experiments are depicted in Fig. 2. Obviously, the conversions of  $CH_4$  and  $CO_2$  increased from 37% and 20% to 43.1% and 27.3%, respectively, when the power was increased from 40 to 80 W.

High-energy electrons produced by the DBD attacked  $CO_2$  and  $CH_4$  molecules to initiate the reactions. It has been reported that the conversions of  $CH_4$  and  $CO_2$  increased with increasing discharge voltage or input power, as the input power is directly proportionate to the voltage [4, 9, 14-16]. In fact, the reason can be expressed as increasing the external voltage caused an increase in the internal electrical field across the region between the ground and high voltage electrode, which then, makes the number of the energetic electrons and the gas temperature go up. This phenomenon, therefore makes more collisions between reactant molecules and those energetic electrons take place and the degree of the  $CH_4$  and  $CO_2$  dissociation and conversion increase. It seems that the formation of some intermediates and species can assist in  $CH_4$  and  $CO_2$  conversions.  $CH_4$  is

decomposed more easily than CO<sub>2</sub> either individually or in the mixture of CO<sub>2</sub> and CH<sub>4</sub>, although the electron energy for methane is higher than CO<sub>2</sub> [16, 17].



**Figure 2** Effect of the input power on the reactant conversion, flow rate=40 ml/min; CO<sub>2</sub>/CH<sub>4</sub> ratio= 1; frequency=20.5 KHz; discharge length=15 cm

### 3.2 Effect of Exerted Electrical Power on the Product Distribution

The selectivity of H<sub>2</sub> and CO increased with input power from 31 % and 21 % to 38.2 % and 24.3 %, respectively; since the discharge energy is enough for CO<sub>2</sub> dissociation to CO and O radicals, but not sufficient for CO dissociation, it is assumed that CO<sub>2</sub> can be reduced to CO easily in the presence of CH<sub>4</sub> [9]. Meanwhile, the selectivity of the by products of C<sub>2</sub>-C<sub>4</sub> (C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>) decreased with the input power due to the preference for the fragmentation reactions over the recombination ones [18, 19]. The value of H<sub>2</sub>/CO ratio slightly increased which is in accordance with the previous studies [14, 16, 20].

More created energetic species such as O radicals and O<sup>•</sup> can oxidize CH<sub>4</sub> to CH<sub>3</sub> radicals which are the building blocks intermediates for alkanes production. Eqs. 6 to 12 illustrate the proposed channel for reactant conversion into products.





Higher power or voltage destroyed heavier hydrocarbon ( $\text{C}_2\text{-C}_4$ ) which were converted to other lighter products. In other words, the amount of the electron energy is proportional to discharge voltage, thus more active species might be generated at higher input power or discharge voltage.

Contrary to the conventional thermal  $\text{CO}_2$  reforming of  $\text{CH}_4$  in which formation of carbon black and polymerized hydrocarbon film on the reactor wall is a principal drawback, only a small amount of coke was formed on the surface of the high-voltage electrode and the quartz tube which most probably aroused from  $\text{CH}_4$  decomposition (Eq. 13). The generated carbon, subsequently, is partially removed with the oxygen species obtained by dissociation of  $\text{CO}_2$  (Eq. 7) according to the Eq.14.

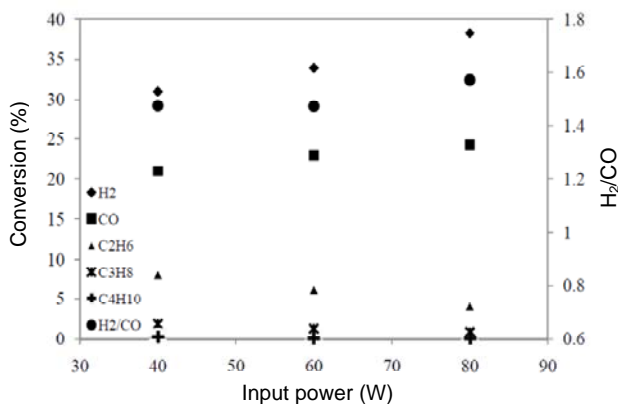


### 3.3 The Effect of Catalyst on the Reactor Performance

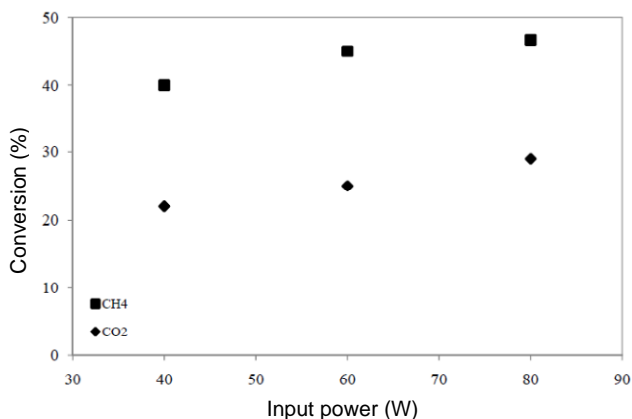
Transition metals can be exploited in the plasma reactions as efficient catalysts due to the change of their oxidation states. The copper (Cu) particles along with ZnO have been understood to be the active sites for the oxidation of  $\text{CH}_4$  [21]. When the Cu/Zn/ $\text{Al}_2\text{O}_3$  catalysts were packed in the gap distance of the plasma reactor, both  $\text{CO}_2$  and  $\text{CH}_4$  conversions increased. The reduced-Zn site was suggested to activate  $\text{CO}_2$  [22].

Comparing Fig. 2 with Fig. 4 and Fig. 3 with Fig. 5, one realizes that the reactant ( $\text{CO}_2$  and  $\text{CH}_4$ ) conversions and product ( $\text{CO}$  and  $\text{H}_2$ ) selectivities in the catalytic-plasma reaction follow the same behavior with the non-catalytic plasma reactor regardless of the conversion and selectivity values. Conversion of  $\text{CH}_4$  attained 46.7 % from 40 %, while that of  $\text{CO}_2$ , to 29 % from 22 % with increasing input power from 40 to 80 W. These results are comparable with the preceding

research by Li *et al.* [20] in which conversions of the  $\text{CO}_2$  and  $\text{CH}_4$  in hybrid catalytic-plasma reactors did not change considerably relative to plasma reactors, similarly to the results reported for catalytic- DBD plasma reactor loaded with zeolites [4, 23]. The decrease of the  $\text{C}_2\text{-C}_4$  selectivities with increasing input power opposite to the increasing trend of  $\text{H}_2$  and  $\text{CO}$  verify a preferable fragmentation reactions of molecules rather than recombination of the lighter molecules to form heavier products such as  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ .

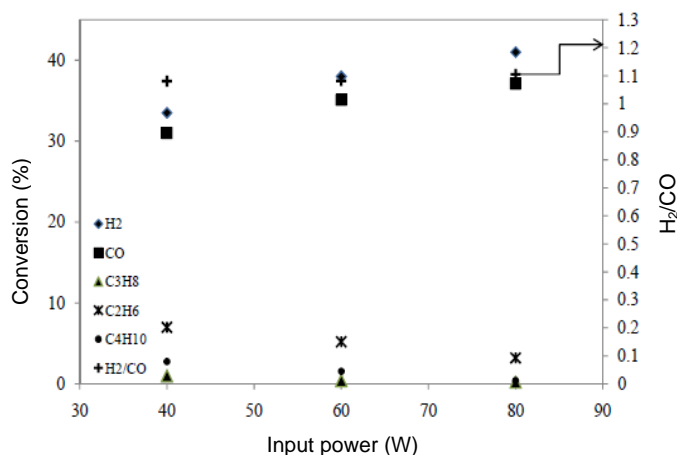


**Figure 3** Effect of the input power on the product selectivity. Flow rate=40 ml/min;  $\text{CO}_2/\text{CH}_4$  ratio=1; frequency=20.5 kHz; discharge length=1.5 cm



**Figure 4** Effect of the input power on the reactant conversion. Flow rate=40 ml/min;  $\text{CO}_2/\text{CH}_4$  ratio=1; frequency=20.5 kHz; discharge length=1.5 cm and 2 gram catalysts loaded in the gap distance





**Figure 5** Effect of the input power on the product selectivity. Flow rate=40 ml/min;  $\text{CO}_2/\text{CH}_4$  ratio=1; frequency=20.5 kHz; discharge length=15 cm and 2 gram catalysts loaded in the gap distance

It has been approved that the surface properties of the catalysts can be modified and developed by cold plasma-formed active and excited species at even ambient temperature. Such plasma-modified catalysts will affect the chemisorptions and desorption processes of the reactants and generated intermediates which occur on the surface of a catalyst during the reaction, thus change product selectivity [16, 24]. In other words, there is a two-fold interaction between a gas discharge and catalyst activity so that the gas discharges can promote the catalyst activity and catalyst enhances the non-equilibrium characteristics of a plasma environment.

Table 1 demonstrates the differences of experimental results between non-catalytic plasma reactor, and the one loaded with catalyst. As one can see the  $\text{CH}_4$  and  $\text{CO}_2$  conversions for the catalytic-plasma reactor is slightly greater than those for the non-catalytic plasma reactor but CO selectivity is significantly higher for the catalytic-plasma reactor. This phenomenon can be described by the superior ability of the catalytic plasma reactor for  $\text{CO}_2$  decomposition to CO, O and O at greater input power, leading to higher CO selectivity.

In fact, in such a catalytic-plasma reactor with a high dielectric barrier, electrical field can be formed on the dielectric surface after polarization of the catalyst particles and accumulation of the charges on the dielectric surface. An intense electrical field is formed around each catalyst particle, leading to micro-discharges

formation between the catalysts. Micro-discharges in the packed-bed reactor generate many electrons rather than ions, which are responsible for greater reactants ( $\text{CO}_2 + \text{CH}_4$ ) conversion and more fragmentation reactions. Also, these micro-discharges make significant enrichment of electrons which are necessary for creating capable and sustainable plasma.

**Table 1** Comparison of the reactant conversion and product selectivity for the only plasma and catalytic-plasma reactors at the input power of 80 W

	$\text{XCH}_4$	$\text{XCO}_2$	$\text{SH}_2$	$\text{SCO}$	$\text{H}_2/\text{CO}$	$\text{YH}_2$	$\text{SC}_2\text{H}_6$	$\text{SC}_2\text{H}_4$	$\text{SC}_3\text{H}_8$	$\text{SC}_4\text{H}_{10}$
<b>Without catalyst</b>	43.1	27.3	38.2	24.3	1.58	16.46	4.1	0	0.9	0.057
<b>With catalyst</b>	46.7	29	41	37.1	1.11	19.15	3.2	0	0.22	0.012

It is noted that no carbon could be detected on the surface of the catalyst or on the reactor wall as the catalyst did not turn into black or gray.

## 4.0 CONCLUSION

In the current study,  $\text{CO}_2$  reforming of  $\text{CH}_4$  was investigated exploiting both DBD non-catalytic plasma reactor and a combined plasma reactor with  $\text{Cu/Zn/Al}_2\text{O}_3$  as catalyst. Experimental results illustrated a synergistic effect of plasma-catalysis on the reactant conversion and syngas selectivity. Loading 2 g of  $\text{Cu/Zn/Al}_2\text{O}_3$  catalyst enhanced the  $\text{H}_2$  yield from 16.1 to 19, while the  $\text{H}_2/\text{CO}$  ratios almost remained constant near unity which is the suitable ratio for FTS processes. Higher input power is in favor of fragmentation reactions rather than recombination of light intermediates into heavier hydrocarbons leading to greater  $\text{H}_2$  production.

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