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DECOMPOSITION OF CARBON DIOXIDE IN THE THREE-PASS FLOW DIELECTRIC BARRIER DISCHARGE PLASMA REACTOR

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ABSTRACT

Carbon dioxide (CO_2) as one of the greenhouse gas emissions was decomposed to Carbon Monoxide (CO) and Oxygen (O_2) in the three-pass flow Dielectric Barrier Discharge (DBD) plasma reactor, a new designed reactor that having special configuration of its reactant gas flow. This configuration can simultaneously cools the High Voltage Electrode (HVE) during the reaction process; and preheats the gas feed flow before entering plasma zone as well. This article explains the result of a preliminary research which aims to observe the performance of this reactor in utilizing CO_2, mixed with CH_4 to produce synthesis gas CO and H_2, in a CO_2 reforming process. This research was conducted using 3 (three) different reactor lengths, they were 36, 24 and 12 cm (Re1, Re2 and Re3), to observe the results of CO_2 decomposition performance in the difference reactor lengths, and to observed the occurrence of reverse reaction inside the Re1 reactor. Other parameters were feed flow rates and the reactor voltage. Applied CO_2 flow rates were 500, 1000 and 1500 SCCM/minute and applied reactor voltage were 5.4; to 9.5 kV. Results show that the conversion of CO_2 was increased with the increasing of reactor voltage and longer reactor. The highest conversion was achieve at the lowest feed flow rate 500 SCCM/minute, this mean in the longest residence time. However, CO_2 was only reaching the maximum conversion value on the reaction time of 2.1 minute, and dropped off after that. It is possibly caused by occurring of the reversed reaction due to the high temperature plasma reaction. At that point, the Specific Energy (SE) was 270 kJ/mol. This value is lower compare to the previous research results, as well as compare to its energy bonding, that shows the more energy efficient performance of this reactor.

Keywords: CO_2 decomposition; Dielectric barrier discharge; Synthesis gas; Three-pass flow plasma reactor

1. INTRODUCTION

The increase of CO_2 emission since the industrial revolution is an important issue that is believed to cause climate change. Some efforts have been done and planned to reduce the CO_2 emission and one of the effort that can be considered is to decompose it into CO and O_2. The CO, along with H_2 is known as synthesis gas (syngas), that can be produced using a mixture of feed gas consist of CO_2 and CH_4, through the CO_2 reforming process. Compare to the steam reforming process, the CO_2 reforming process has advantage that it utilizes the CO_2 gas, as well as can reduce the consumption of CH_4 gas in producing CO gas.

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Reaction of steam reforming process can be seen in Equation 1 below that need 1 mol CH_4 gas to form 1 mol CO, whereas reaction in the CO_2 reforming process is written in Equation 2 produce 2 mol of CO by using 1 mol CH_4. It is mean that in CO_2 reforming process is only need 0.5 mol of CH_4 to form 1 mol CO (Tao et al., 2011).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (2)$$

The reaction products CO and H_2, as syngas is a main component of industry gas, which plays a significant role in producing various chemicals, such as urea, methanol, inorganic and organic carbonate, polyurethane and polycarbonate.

One of the considerations in the selection of CO_2 utilization, related to climate change issue, is the longer life time of the products. For example, the lifetime of urea and methanol are only about 6 months, while polyurethane and polycarbonate are until centuries.

Moreover, the utilization of CO_2 as feedstock of polyurethane can also replace the use of phosgene as raw material in polyurethane production process, whereas phosgene is an extremely hazardous chemical (Davidson, 2005).

The syngas utilization in producing several useful chemicals can be seen in Figure 1, as follows.

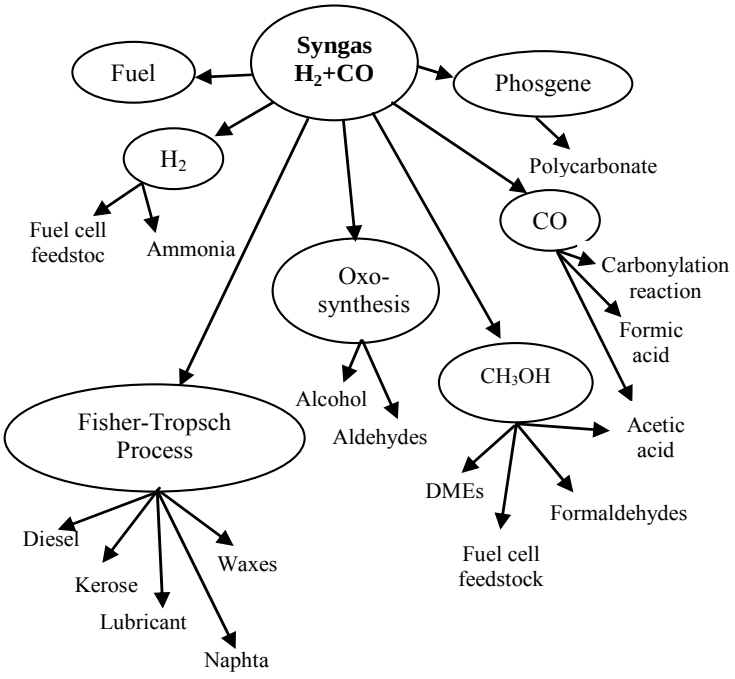

Figure 1 Utilization of Syngas (Gallon, 2010)

Plasma technology has been used in this experiment because it has a tremendous capability to activate chemicals, where high-speed electrons being generated by high voltage electricity can break chemical bonds such as, covalent, ionic and hydrogen bonds. Chemical bonds that are very hard to split in normal conditions, such as CO_2 gas can be broken by non-thermal plasma

or cold plasma at low pressures and low temperatures (Yamamoto & Okubo, 2007). Without plasma, CO_2 as a very stable gas requires high temperature or high pressure to decompose. According to Srivastava and Kobayashi (2010), CO_2 can be decomposed at a temperature between 2,600–11,000K or at 50 atm and 300^oC (Yamamoto & Okubo, 2007). It also found that CO_2 is a very good plasma gas reactant for organic chemicals synthesis (Chang-Jun Liu, et. al., 2005). Dielectric Barrier Discharge (DBD) is one of the types of non-thermal plasma reactor that has a huge potential for organic and in-organic chemical reactions (Istadi, 2006).

The main goal of this research is observe performance of the three-pass flow DBD plasma reactor performance using CO_2 as feed gas, mixed with CH_4 to produce synthesis gas CO and H_2. This research is a preliminary study of the research that aims to observe the decomposition of CO_2 into CO and O_2 using a new prototype of three-pass flow DBD non-thermal plasma (TPFD non-thermal plasma) reactor, that having special configuration of its reactant gas flow.

2. METHODOLOGY

The material used in this research was Carbon Dioxide with the purity written in the label was greater than 99.97%. After analyzed by GC, the content of this gas was CO_2 99.69% and CO 0.3%. This gas produced by PT. Industrial Gasses Indonesia.

As an engineering design test for a new type of DBD Plasma reactor, this experiment used three units of TPFD non-thermal plasma reactors, named Re1, Re2 and Re3. They have the same diameter and have various reactor lengths of 36 cm, 24 cm and 12 cm and therefore various volumes of 83.5; 55.4, and 27.7 ml, respectively. The objective of the use these three reactors is to observe the CO_2 decomposition performance inside the longest reactor (Re1) and to observe if there was a reverse reaction happened inside the Re1 reactor, because the previous CO_2 decomposition experiment indicated the occurrence of reversed reaction inside the reactor (Fatrian, 2010). As it was impossible to sampling the gas resulted at several point inside the Re1 reactor, therefore this experiment was designed to use shorter length of reactor, i.e. 12 cm (Re3) and 24 cm (Re2) to represent the reaction performance of Re1 reactor at point 12 and 24 cm. The schematic of the three-pass flow DBD plasma reactor is as follows:

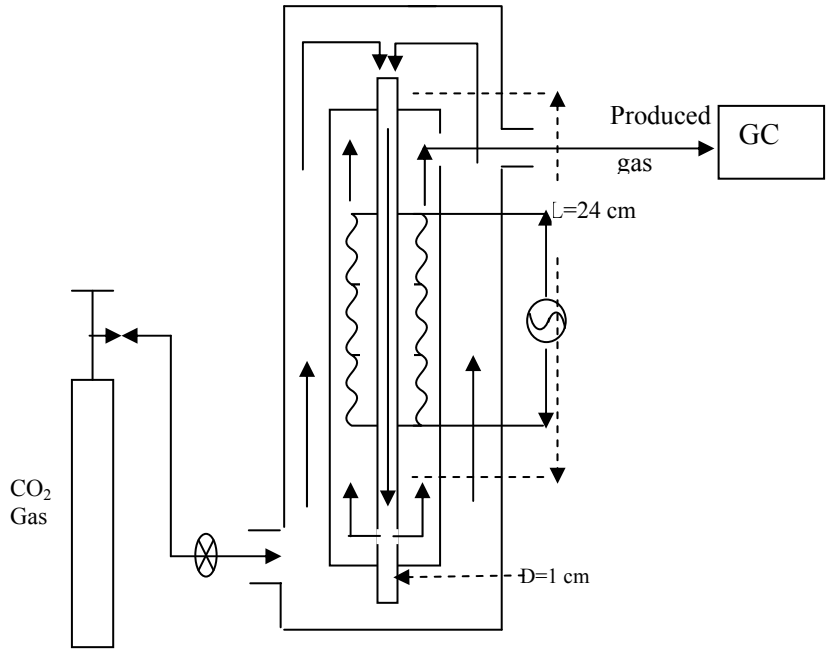

Figure 1 Schematic of the TPFD non-thermal plasma reactor

The design of three-pass gas flow in the reactor gives the advantage that this reactor can simultaneously cools the High Voltage Electrode (HVE) during the reaction process, and also preheats the gas feed flow before entering the plasma zone, where the plasma reaction actually happened. So, the existence of this cooling process that taken place inside the reactor made this reactor does not need to have a separate cooling device in its operation.

The research was studied the performance of the TPFD non-thermal plasma reactor using parameters feed flow rates and plasma reactor voltages.

Observations were made on feed flow rate, plasma reactor voltage, electric current and produced gas composition; and were measured using flow meters, voltmeter and ampere meter, respectively, While the composition of the produced gas was analyzed by gas chromatography (GC).

The experiment was carried out at reaction time of 2.1, 4.2, 6.3 and 8.4 minutes, to follow the previous experiment, that the reaction has reached steady state after the second minutes. At the beginning, several data were taken in various reaction time intervals in order to have data repetition and to have the clear and not overlap GC curve. The feed flow rate in this experiment was 500, 1000 and 1500 SCCM/minute. The plasma voltage parameters was between 5.44 to 9.5 kV, because there was not any reaction taken place under 5.44 kV yet, while above 9.5 kV, there was already seen the reactor sparks and caused reactor burnt.

2.1. Calculation of the Conversion and Specific Energy

CO_2 conversion (X) was calculated using Equation (3), where $F_{(CO2)o}$ and F_{CO2} are the flow rate of CO_2 before reaction (feed) and after reaction in mmol/minute. Specific energy (SE) was calculated using Equation (4), where P is the energy consumption in the reactor that were calculated using the observation data of electric voltage (V) and electric current (mA) in the reactor.

$$X_{CO_2} = \frac{F_{(CO_2)_0} - F_{CO_2}}{F_{(CO_2)_0}} \quad (3)$$

$$SE = \frac{P\ (kW)}{F_{CO}(mole/sec)} \quad (4)$$

3. RESULTS AND DISCUSSION

The result of the reaction in the reactor was CO and O_2. The reaction mechanism in the plasma reactor during the decomposition is took place through the radical reaction phase that can be seen in Equations 5, 6 and 7. These have been reprocessed based on the results of this experiment and several previous experiments (Fotouh & Liu, 1996; Istadi & Amin, 2006; Indarto, 2007), as follows:

$$CO_2 \rightleftharpoons CO^* + O^* \quad (5)$$

$$CO^* \rightarrow CO \quad (6)$$

$$2O^* \rightarrow O_2 \quad (7)$$

Detail results of the experiment will be explained below.

3.1. Effect of Reaction Times and Plasma Voltages against the CO_2 Conversion

The CO_2 conversion (%) for feed flow rate 1,000 SCCM/minute in Re1, Re2 and Re3 reactors for various plasma electric voltage against reaction times of 2.1, 4.2, 6.3 and 8.4 is shown in Figures 2, 3 and 4. It represent that the CO_2 conversion was still low and reached the maximum conversion of about 7%. It may be caused by the use very high feed flow rate for this experiment, even though it used low energy consumption as much as 12.6 Watt with the ratio of energy toward the feed flow rate was only 0.0126. This ratio is very low compared to the previous experiments (Wang, 2009; Song, 2004) that applied the ratio of energy towards feed flow rates of about 5.37 and 4.33, respectively, in which it reached the CO_2 conversion of 44.4 and 30.95%.

Figures 2, 3 and 4 also indicate that the CO_2 conversion increased as reaction started and it reached the maximum conversion at 2.1 minute and dropped off after that time. The decrease of the CO_2 conversion might be due to the reverse reaction. In some cases, the decrease of the conversion even reached to -0.3, these indicated that the CO content in the feed gas was also converted back to CO_2.

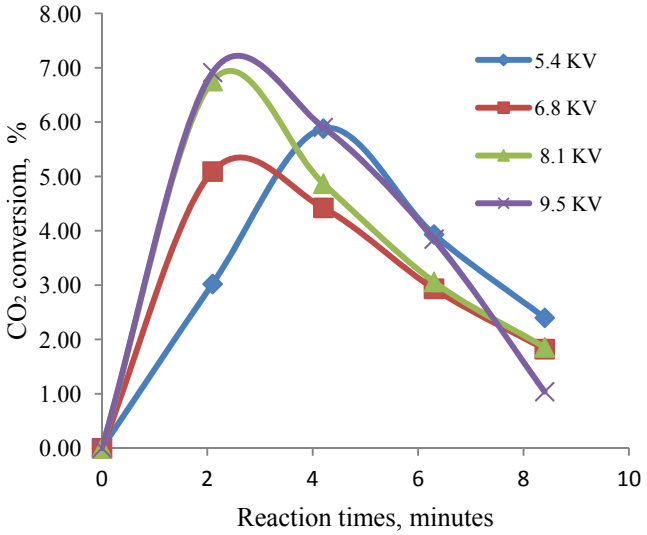

Figure 2 CO_2 conversions for Re1 in feed flow rate of 1,000 SCCM/minutes for various voltages and reaction times

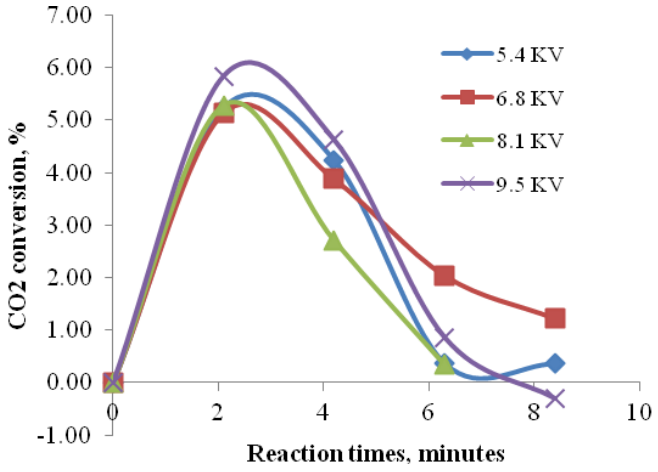

Figure 3 CO_2 conversions for Re2 in feed flow rate of 1,000 SCCM/minutes for various voltages and reaction times

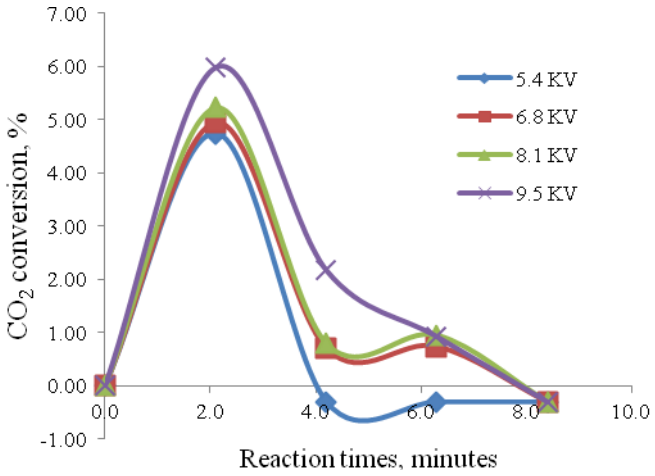

Figure 4 CO_2 conversions for Re3 in feed flow rate of 1,000 SCCM/minutes for various voltages and reaction times

As mention in the previous experiments (Istadi, 2006), the advantage of using non-thermal plasma reactor is that the gas temperature can be kept remain in the room temperature, although the electron temperature may reach 10,000–100,000K (1–10 eV). The very high electron temperature may lead to increase the reaction temperature inside the plasma reactor that may cause a reverse reaction or decrease in the rate of the CO_2 decomposition reaction (Istadi, 2006; Aresta et al., 2010). Other research showed that there was no reaction happened at all at temperature above 300^{o}C (Gleit, 1969).

The increased of plasma voltage causes the increased of bulk gas temperature in the reaction zone that can increase the conversion (Istadi & Amin, 2007). This phenomenon was also took place in this experiment as can be seen in Figures 2, 3, and 4 that indicated the CO_2 conversion for all reactors were increased by the increasing of plasma voltage.

3.2. Effect of the Reactor Length on the CO_2 Conversion

Experiment results presented in Figure 5 was for feed flow rate 1.000 SCCM/minute and at the highest reactor voltage 9.5 kV. In this condition, residence time in Re1 was 5.0 seconds, for Re2 was 3.3 seconds and for Re3 was 1.7 seconds. Data were taken for reaction times of 2.1, 4.2 and 8.4 minutes.

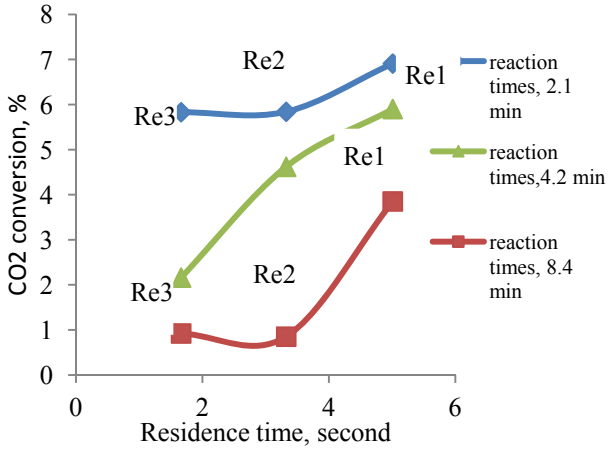

Figure 5 The effect of reactor length to CO_2 conversion for feed flow rate 1,000 SCCM/minutes in the plasma voltage of 9.5 kV

Reaction results show that conversion was higher with the longer residence time for all reaction times. This indicated that there is no reversed reaction took place inside the reactor until the residence time of 5.0 seconds. The reversed reaction was occurred after reaction times 2.1 minutes, which was possibly due to high electron temperature that could lead to increase the reaction temperature inside the plasma reactor as mention above.

3.3. Effect of Feed Flow Rate against the CO_2 Conversion

The effect of feed flow rate against the CO_2 conversion can be seen in Figure 6 as follows.

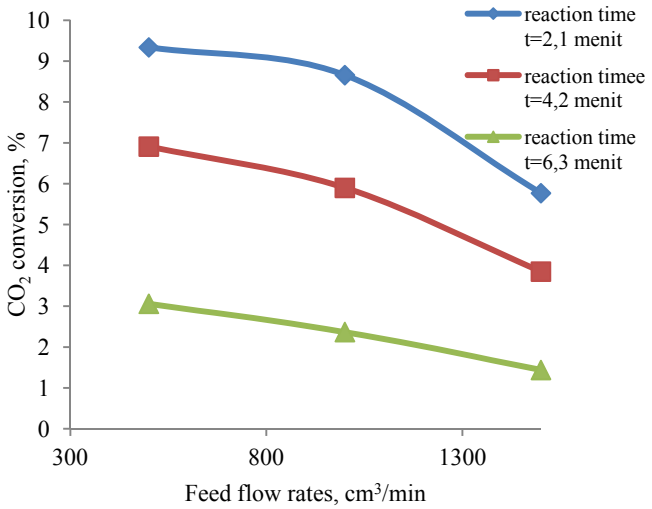

Figure 6 Effect of feed flow rates to the CO_2 conversion in the voltage 9.5 kV for Re3 reactor

Experiment result on the effect of feed flow rates against the CO_2 conversion using Re3 reactor, at 9.5 kV plasma voltages, were represented in Figure 6. It indicated that the conversion of CO_2 has increased by the decreasing of the feed flow rates. The best conversion was took place in the lowest feed flow rates of 500 SCCM/minutes. This happened due to the lower feed flow rates that will lead to a longer residence time, so that there will be a longer opportunity for the CO_2 gas feed to react inside the reactor.

3.4. Specific Energy (SE)

In conducting the decomposition of CO_2, it is important to reach the high. But, decomposition process needs energy, that in the plasma process, the energy is provided by electricity, and generating the electricity will release CO_2 (Tao et.al, 2010). Therefore, the energy efficient is necessary, i.e. the energy require in the decomposition process should not release CO_2 emission higher than the amount of CO_2 will be decomposed. The energy required in the plasma reaction can be identified by calculating the specific energy.

As mention above, the specific energy (SE) is the amount of energy required to form one mol of CO gas produced per minute of reaction. SE was calculated using the Equation (2).

In this experiment, it was resulted that the Specific Energy (SE) in the reaction time of 2.1 minutes was more efficient than the previous experiment. Experiment with the condition of the feed flow rate of 1,000 SCCM/minute, plasma voltage 9.5 kV and electric current 90 mA, produced CO gas 2.37 mmole/minute and it has the SE value of 270 kJ/mole. Compared to the previous experiment (Zheng, 2004), that has the SE value 529.8 kJ/mole, this experiment was resulted in the lower specific energy. It means that this experiment was more energy efficient.

The value of SE of this experiment was even lower than the value of CO_2 energy bonding 803.33 kJ/mole.

4. CONCLUSION

The decomposition of CO_2 producing CO and O_2 in TPFD non-thermal plasma reactor for all feed flow rates and electrical voltages reached the maximum conversion at the reaction time 2.1 minute, and then dropped off after that. This was caused by the reversed reaction due to the high temperature of plasma reaction.

There is no reversed reaction took place in the longest reactor lengths. The CO_2 conversion increased with the increasing of plasma voltage and residence time and with decreasing the feed flow rate.

The best feed flow rate was noted at 500 SCCM/ minute, where the reaction has the specific energy (SE) of 270 kJ/mole, which is much lower and more efficient than the previous experiment as well as lower than the CO_2 energy bonding.

5. ACKNOWLEDGEMENT

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