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Carbon Dioxide Conversion to Synthesis Gas when Combined with Methane using a New Designed of Non-thermal Plasma Reactor

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ABSTRACT

The aim of this study in to investigate the performance of a three-pass flow configuration of a dielectric barrier discharge non-thermal plasma, as a new designed of non-thermal plasma reactor, to convert greenhouse gas emission, CO_2 and combined with CH_4 to produce synthesis gas, CO and H_2 in a CO_2 reforming process. This new designed reactor has a special configuration of its reactant gas flow that can provide several advantages, namely simultaneously cools the High Voltage Electrode (HVE) during the reaction process, extends the gas feed residence time and preheat the gas feed flow before entering the plasma zone, where the plasma reaction actually happens. The cooling process inside the reactor makes this reactor does not require a separate cooling device for its operation and the longer of residence time that can improve the feed gas conversion. Furthermore, the preheating of gas feed flow can improve the efficient use of energy for the process. Gases were converted in a 180 mA of 12.27 kV. The feed flow rates applied were 9.19, 19.45 and 85.43 cm^3 min^{-1} and the reaction was carried out for a time on stream of 140 min. Results showed that the highest CO_2 and CH_4 conversions were 36.73 and 35.52%, respectively, obtained at a feed flow rate of 9.19 cm^3 min^{-1}. The reaction produced not only synthesis gas but also C_2H_6 and C_3 gas component with a proportions in terms of the molar flow rate were 28-53 and 0-26%, respectively. These gasses form were increased with an increasing feed flow rate. The most efficient Specific Energy (SE) was obtained at 2,333.5 kJ $mole^{-1}$ which was reached at a feed flow rate of 85.45 cm^3 min^{-1}. This value was lower and more efficient than previous experiments by Wang (7,289 kJ mol^{-1}) but still higher comparing with the standard enthalpy needed for CO_2 reforming 61.75 kJ mol^{-1}.

Key words: Carbon dioxide, dielectric barrier discharge reactor, new designed non-thermal plasma, synthesis gas, three-pass flow

INTRODUCTION

The increasing greenhouse gas emission is an important factor in global warming. Industrial sectors and power generation account for a significant portion of CO_2 emission in the use of fossil fuel and production processes.

One effort to reduce CO_2 emission is to use CO_2 as a raw material in chemical industries through direct or indirect utilization. Direct utilization is directly using CO_2 in industries related to urea,

inert agents, water treatment, precipitated calcium carbonate and methanol. Indirect utilization is using CO_2 in a reforming process with the addition of $CH_4$to synthesis gas, CO and H_2, according to the following chemical reaction (Eq. 1):

$$CO_2+CH_4 \rightarrow 2CO+2H_2 \quad (1)$$

Synthesis gas is known as a main component of industry gas that is useful in the production of various chemicals, such as methanol, alcohols, aldehydes, acetic acid, formic acid, diesel, kerosene, naphtha, lubricants, waxes and fuel cell feed stock (Gallon, 2010).

One of the considerations in the selection of the utilization of CO_2 is the "lifetime" of the product. For example, the lifetimes of urea and methanol are only 6 months while those of polyurethane and polycarbonate can be on the scale of centuries. In addition, CO_2 can be used as a raw material instead of phosgene, an extremely dangerous chemical, to produce polyurethane (Metz *et al*., 2005).

CO_2 is a very stable gas and its decomposition thus requires high temperature or high pressure i.e., temperature between 2600 and 11,000 K or pressure of 50 atm at 300°C (Yamamoto and Okubo, 2007). This condition could be solved by using plasma technology. Plasma technology has the tremendous capability to activate chemicals; high-speed electrons generated by high-voltage electricity can break covalent, ionic and hydrogen bonds. Chemical bonds that are very hard to split in normal conditions, such as those of CO_2 gas, can be broken by non-thermal plasma at low pressures and low temperatures (Yamamoto and Okubo, 2007). CO_2 is a very good plasma gas reactant for the synthesis of organic chemicals (Liu *et al*., 2006).

Figure 1 shows various possible reaction mechanisms of CO_2 and CH_4 in the non-thermal plasma reactor.

CO_2 reforming process is an attractive process, because it can not only utilize CO_2, as a greenhouse gas but also can reduce methane consumption comparing by using steam reforming process. However, the CO_2 reforming reaction is a highly endothermic reaction that needs high energy consumption in its reaction process (Tao *et al*., 2011).

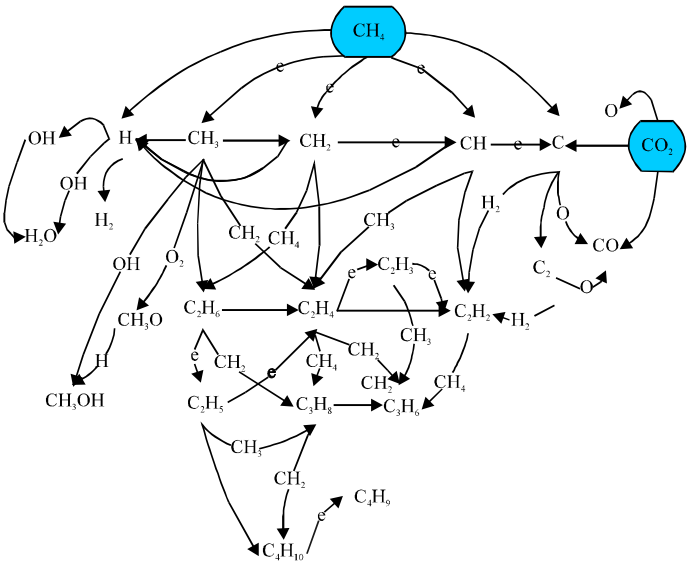

Fig. 1: Possible reaction mechanisms in a non-thermal plasma reactor

Reaction of steam reforming process can be seen in Eq. 2 below. It is needed 1 mol CH_4 gas to form 1 mol CO, whereas reaction in the CO_2 reforming process is written in Eq. 1 produce 2 mol of CO by using 1 mol CH_4. It means that in CO_2 reforming process only needed 0.5 mol of CH_4 to form 1 mol CO (Eq. 2):

$$CH_4+H_2O\rightarrow CO+3H_2 \quad (2)$$

Dielectric Barrier Discharge (DBD) reactor is one type of non-thermal plasma reactor that has huge potential for organic and inorganic chemical reactions (Istadi, 2006). In the DBD plasma reactor, the electron temperature is very high, reaching thousands of degrees Kelvin, while the neutral gas can be at room-temperature range (Istadi and Amin, 2007). Several researches on CO_2 reforming process have been conducted by several researchers; however, the conversion of reactants is low in most cases (Tao *et al*., 2011).

To increase the conversion of the reactant as well as to reduce the energy consumption in the reaction process it was developed the new designed of the DBD three pass flow configuration of the Non-Thermal Plasma (NTP) reactor. This new designed reactor was continuing the development of the DBD double-pass plasma reactor that has been proved to be able to increase the conversion of the reactant, comparing with the single pass reactor, due to the longer residence time of reaction (Bismo, 2000). Besides that, the three-pass flow configuration of the reactant's gas flow has also other advantages that can simultaneously cool the High Voltage Electrode (HVE) during the reaction process and can preheat the gas feed flow before entering the plasma zone, where the plasma reaction actually happens. The cooling process inside the reactor makes this reactor does not require a separate cooling device for its operation. Moreover, the preheating of gas feed flow can improve the efficient use of energy for the process.

The present study investigates the performance of this new designed DBD three-pass flow configuration of the Non-Thermal Plasma (NTP) reactor, in terms of the conversion of CO_2 and CH_4, the selectivity of the gas produced and the Specific Energy (SE) of the reactor in the CO_2 reforming process.

MATERIALS AND METHODS

The material used in this research was the mixture gas carbon dioxide and methane with the composition of CO_2 and CH_4 were 51.07 and 48.93%, respectively. This gas produced by PT. Aneka Gas Industri, Bekasi, Indonesia.

The new-designed of NTP reactor used in this research was a cylindrical reactor having a length of 24 cm and diameter of 1 cm. The schematic diagram of the reactor is in the Fig. 2.

The feed flow rate was regulated with a mass flow controller and checked using bubble soap. The electric voltage and current were measured using a voltmeter and ampere meter, respectively. The feed and reactant gas compositions were analyzed by thermal conductivity detector gas chromatography (GC-TCD), using activated carbon and Porapak-Q GC columns. Conversions and selectivity were obtained by analyzing the peak area data of the GC. The reaction produced H_2, CO, C_2H_6 and other unidentified gases.

Feed flow rates in the experiment were determined from the results of experiments conducted by Wang *et al*. (2009) and Song *et al*. (2004), in which a certain ratio of energy consumption for process reaction in the reactor over the feed flow rate was required to achieve high conversion of the gas reactants. Wang *et al*. (2009) used a ratio of 5.37 and Song *et al*. (2004) used a ratio of

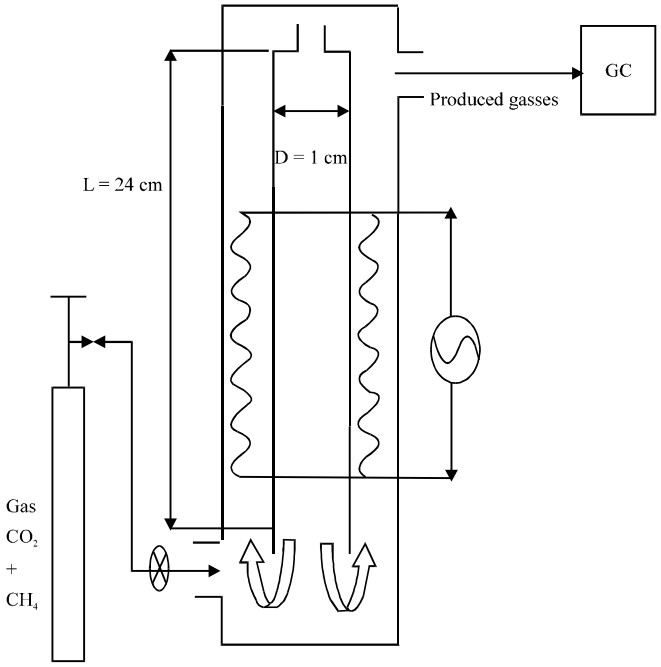

Fig. 2: Schematic diagram of the new designed of NTP reactor

4.33. To prevent burning of the reactor, the present experiment was conducted at a maximum voltage of 12.27 kV with electric current of 180 mA which means that the maximum power of the reactor was 25.2 W. According to the ratios used by Wang *et al.* (2009), the present experiment required a feed flow rate of 4.7-6.8 cm^3 min^{-1} to achieve high conversion.

However, in the present experiment, a very low flow rate would lead to very weak cooling inside the reactor. Very low feed flow rates thus lead to very high temperature inside the reactor and it was feared that the reactor would burn in such a case. Therefore, the flow rate was set by the mass flow controller to be a minimum of 10 cm^3 min^{-1} which was in fact 9.19 cm^3 min^{-1} when checked with bubble soap. At this feed flow rate, the ratio of energy consumption over the feed flow rate was 2.74. The experiment was also carried out at higher feed flow rates of 19.45 and 85.43 cm^3 min^{-1} with ratios of energy consumption for process reaction in the reactor over feed flow rate of 1.3 and 0.29. To further prevent overheating that may burn the reactor, a fan was utilized as an additional cooler of the reactor during the reaction processes.

The observation was carried out for a Time of Stream (TOS) of 140 min. To validate the data, the observations were repeated three times for each feed flow rates and then results were averaged.

Calculation of the conversion and selectivity: The conversion of CO_2 and CH_4 in the plasma reactor (X_{CO_2} and X_{CH_4}) and selectivity of CO and H_2 as reaction products (S_{CO} and S_{H_2}) were calculated using the following Eq. 3-6:

$$X_{CO_2} = \frac{F_{(CO_2)_0} - F_{CO_2}}{F_{(CO_2)_0}} \times 100\% \quad (3)$$

$$X_{CH_4} = \frac{F_{(CH_4)_0} - F_{CH_4}}{F_{(CH_4)_0}} \times 100\% \quad (4)$$

$$S_{CO} = \frac{F_{CO}}{(F_{(CH_4)_0} - F_{CH_4}) + (F_{(CO_2)_0} - F_{CO_2})} \times 100\% \quad (5)$$

$$S_{H_2} = \frac{F_{H_2}}{2\,(F_{(CH4)_0} - F_{CH_4})} \times 100\% \quad (6)$$

Here, $F_{(CO_2)_0}$ and $F_{(CH_4)_0}$ are the molar feed flow rates of CO_2 and CH_4 and F_{CO_2} and F_{CH_4} are the molar flow rates of CO_2 and CH_4 after the reaction (mol min^{-1}).

Calculation of SE: The SE is the energy required (in kW) to produce 1 mol sec^{-1} of CO and H_2 gas product and can be calculated using the following Eq. 7 (Tao *et al*., 2011):

$$SE = \frac{P}{[CO + H_2]} \quad (7)$$

Here, P is the total electrical energy used in the reactor during the process in kW.

RESULTS AND DISCUSSION

The results of the experiment show that the produced gases were not only synthesis gas (i.e., H_2 and CO) but also C_2H_6 and a C_3 gas component. In terms of molar flow rates, CO_2 and CH_4 feed gas was converted to synthesis gas, C_2H_6 and the C_3 gas component in proportions of 21-53, 47-53 and 0-26%, respectively.

Effect of the feed flow rate: Figure 3 shows that the conversion of CO_2 and CH_4 decreases with an increase in the feed flow rate.

This is possibly due to the higher feed flow rate reducing the residence time of CH_4 and CO_2 in the reactor which would reduce the chance of the two molecules colliding each other and with electrons that have enough energy to break carbon-hydrogen and carbon–oxygen bonds to further form the produced gases (Istadi and Amin, 2007; Song *et al*., 2004). The highest conversions of CO_2 (36.73%) and CH_4 (35.52%) were obtained for the feed flow rate of 9.19 cm^3 min^{-1}. Comparison between the CO_2 and CH_4 conversion results of this experiment and the previous experiment by Wang *et al*. (2009) and Song *et al*. (2004) is shown in Table 1.

Table 1 shows that the use of the ratio of energy consumption over the feed flow rate (P/V) in this experiment was mostly much lower (2.74, 1.3 and 0.29) than previous experiments by Wang *et al*. (2009) and Song *et al*. (2004) which were 5.37 and 4.33%, respectively. However, the conversion results were mostly not much lower. Even the CO_2 conversion for feed flow rates of

Table 1: Comparison of CO_2 and CH_4 conversion with previous experiment

Observations	Feed flow, V (mL min^{-1})	Energy, P (Watt)	Ratio P/V	Conversion CO_2 (%)	Conversion CH_4 (%)
This study (2013)	9.19	25.2	2.74	36.73	35.52
	19.45	25.2	1.30	34.15	30.19
	85.43	25.2	0.29	28.50	22.92
Wang *et al*. (2009)	20.00	107.4	5.37	44.40	72.80
Song *et al*. (2004)	30.00	130.0	4.33	30.95	55.71

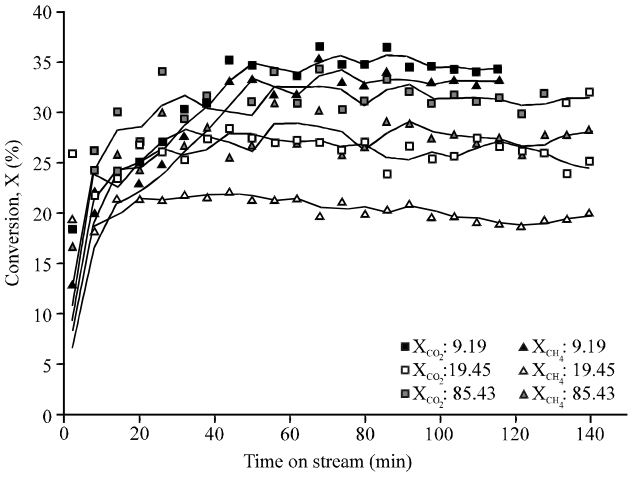

Fig. 3: Conversion of CO_2 and CH_4 at feed flow rates of 9.19, 19.45 and 85.43 cm^3 min^{-1}

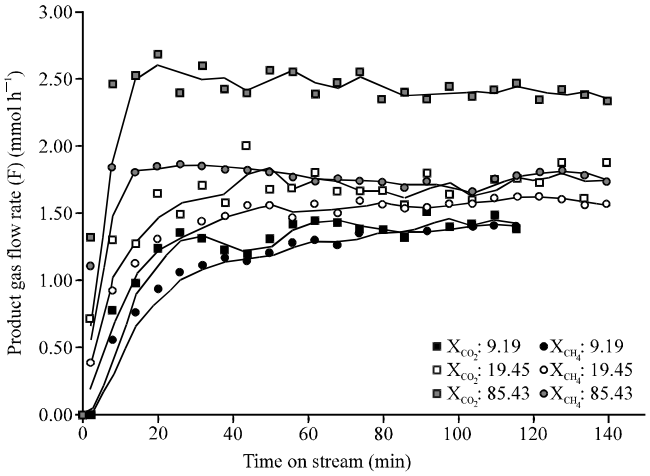

Fig. 4: Mole flow rates of synthesis gas CO and H_2 for feed flow rates of 9.91, 19.45 and 85.43 cm^3 min^{-1}

9.19 and 19.45 cm^3 min^{-1} which has the value of 36.73 and 34.15 % were higher than the Song's experiment. So, if it is seen from the energy consumption, this research achieved relatively higher conversion than the previous experiment by Wang *et al.* (2009) and Song *et al.* (2004).

Moreover it also can be seen that the conversion did not fall too significant with the sharply increase of the feed flow rate. The feed flow rate 9.19 cm^3 min^{-1} achieved the highest conversion of CO_2 that was 36.73%, while at the feed flow rate of 85.43 cm^3 min^{-1} still could reach 28.5%. This may indicate that the plasma reaction is not only influenced by energy consumption in the reaction processes but also by other factors, such as electrical voltage, electrical frequency and plasma density. The plasma density is influenced by the discharge gap of the plasma reactor, plasma temperature and plasma reactor configuration. These influenced factors needs to be studied further.

Figure 4 shows the effects of the feed flow rate (9.91, 19.45 and 85.43 cm^3 min^{-1}) on the molar product flow rate of CO and H_2 and Fig. 5 shows the effect on the molar product flow rate of C_2H_6 and C_3 component for the TOS until 140 min.

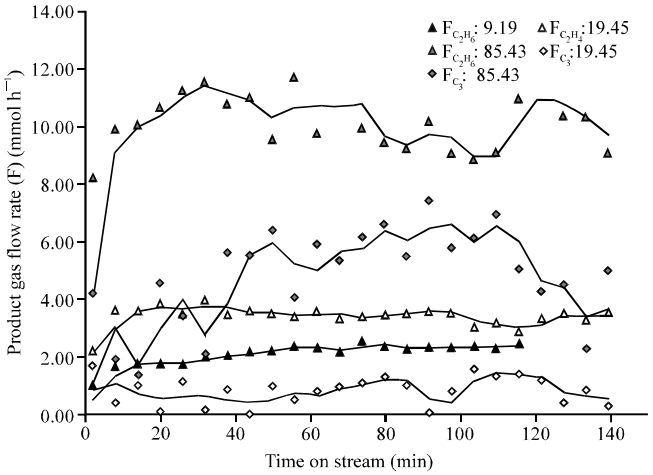

Fig. 5: Mole flow rates of C_2H_6 and C_3 gas for feed flow rates of 9.91, 19.45 and 85.43 cm^3 min^{-1}

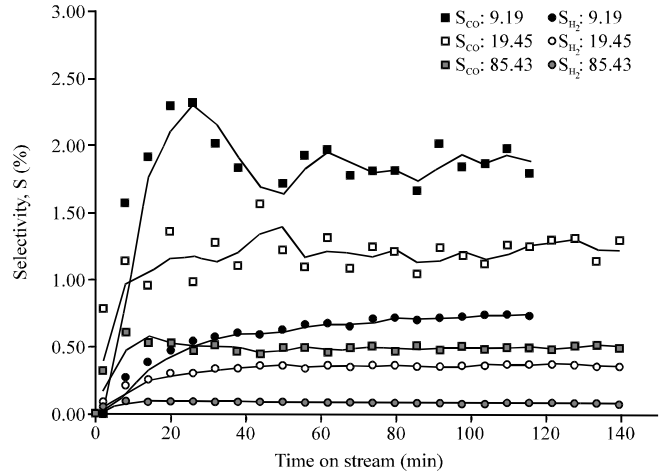

Fig. 6: Selectivity of synthesis gases CO and H_2 at feed flow rates of 9.19, 19.45 and 85.43 cm^3 min^{-1}

Figure 4 indicates that the total molar flow rate of the synthesis gas was higher for a higher feed flow rate. This was also happened with the C_2H_6 and C_3 gas component products as seen in Fig. 5. The total molar flow rate of the C_2H_6 product reached the significant value and also increased with an increasing feed flow rate. Additionally, the C_3 gas component did not form for the lowest feed flow rate of 9.19 cm^3 min^{-1} but did form for the higher feed flow rates of 19.45 and 85.43 cm^3 min^{-1}. The amount of this gas increased with increasing feed flow rate.

Although, the total flow rate of products were increased by the increasing of feed flow rates, the selectivity of the product that can be seen in Fig. 6 and 7 shows the different tendency. The selectivity of synthesis gas CO and H_2, as well as C_2H_6 were decreased with the increasing of the feed flow rates. Only the selectivity of C_3 increased with an increasing feed flow rate. The cause is probably as follow: The increased of the feed flow rate means greater cooling in the reactor and hence lower temperature inside the reactor. The amount of synthesis gas CO, H_2 and C_2H_6 as lower product gas components decreased with the decreasing temperature inside the reactor, whereas the

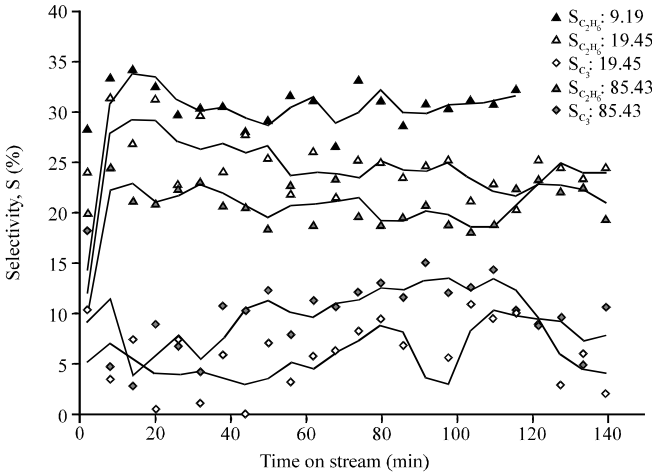

Fig. 7: Selectivity of C_2H_6 and C_3 at feed flow rates of 9.19, 19.45 and 85.43 cm^3 min^{-1}

amount of the C_3 gas component as higher chemical product-component increased. This may be due to the higher temperature producing a higher degree of ionization that produces more electrons and free radicals. The higher temperature would thus tend to produce lower gas components. This phenomenon is corroborated by the experimental results of Istadi and Amin (2007) that lower-temperature non-equilibrium streamer discharge favoured the formation of higher hydrocarbons.

Effect of TOS: The effect of the TOS on the molar flow rate is shown in Fig. 4 and 5. Most of the gas products increased in amount until a reaction time of about 20-40 min. Afterward, most of the gas products reached a steady state with quite stable mole flow rates; the exceptions were the fluctuations of the amounts of C_2H_6 and the C_3 component for a feed flow rate of 85.43 cm^3 min^{-1}. Similar fluctuation was also seen for the C_3 gas component at a feed flow rate of 19.45 cm^3 min^{-1}. These fluctuation of the products may have been unstable because of the unstable plasma reaction inside the reactor after a longer reaction time.

Effects of the TOS on the conversion and selectivity are shown in Fig. 2, 6 and 7. Figure 2 shows that a higher feed flow rate requires a shorter time to achieve the highest conversion which is 44 min for a feed flow rate of 9.19 cm^3 min^{-1}, 38 min^{-1} for a feed flow rate of 19.45 cm^3 min^{-1} and 20 min for a feed flow rate of 85.43 cm^3 min^{-1}. After that time, the trend of conversion was relatively stable and reached a steady state.

Figure 6 and 7 illustrates that the selectivity of the gas produced, except that of H_2, slightly decreased after reaching a peak and was unstable thereafter; i.e., the plasma reaction inside the reactor was no longer stable after a certain time. This might be due to the unstable temperature inside the reactor after a longer reaction time, leading to an unstable reaction.

Specific Energy (SE): SE in this experiment was calculated using Eq. 6. The CO_2 reforming reaction is an endothermic reaction that needs energy to produce syngas as shown in Eq. 8 (Wang *et al.*, 2009).

$$CO_2+CH_4 \rightarrow 2CO+2H_2$$

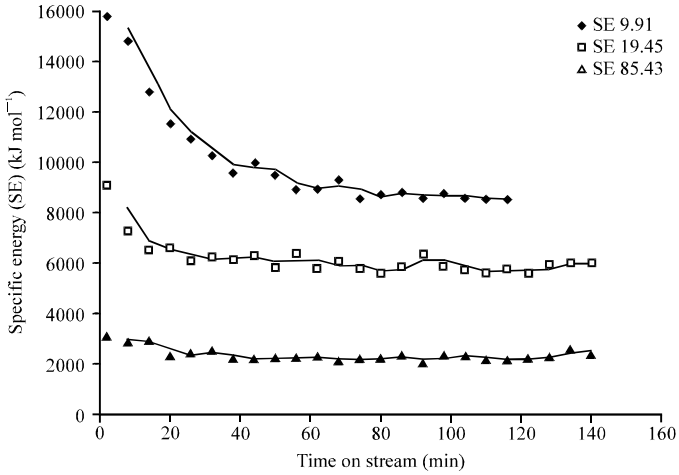

Fig. 8: SE for feed flow rates of 9.91, 19.45 and 85.43 cm^3 min^{-1}

$$\Delta H=247 \text{ kJ mol}^{-1} \quad (8)$$

Equation 8 shows that the standard enthalpy needed for the CO_2 reformation is 247 kJ mol^{-1} of CH_4. Therefore, a minimum SE of 61.75 kJ mol^{-1} is needed to produce 1 mol sec^{-1} of CO and H_2 (Tao *et al*., 2011).

Figure 8 presents the results for SE in this experiment. It shows that the reaction is most energy efficient for the highest feed flow rate of 85.43 cm^3 min^{-1}, as indicated by the lowest SE of 2,333.5 kJ mol^{-1}. SE increases with a decreasing in the feed flow rate which means the reaction becomes less energy efficient. The SE for feed flow rates of 19.45 and 85.43 cm^3 min^{-1} is, respectively 8,990 and 6,051 kJ mol^{-1}.

The SE for feed flow rates of 19.45 and 85.43 cm^3 min^{-1} indicates better energy efficiency than that in the previous experiments of Wang *et al*. (2009) which had an SE of 7,289 kJ mol^{-1}. However, none of the SE results of this experiment are efficient when compared with the standard enthalpy of 61.75 kJ mol^{-1}.

CONCLUSION

The feed gases used for the NTP reactor, CO_2 and CH_4, were converted to synthesis gas, C_2H_6 and C_3 gas component with molar proportions of 21-53, 28-53 and 0-26%, respectively. The amount of C_2H_6 product increased with an increasing feed flow rate and the flow rate of synthesis gas increased with a decreasing feed flow rate. The conversion of CO_2 and CH_4 increased with a decrease in the feed flow rate owing to the shorter residence time by increasing the feed flow rates. The conversions of CO_2 and CH_4 were highest (36.73 and 35.52%, respectively) for a feed flow rate of 9.19 cm^3 min^{-1}. The reactions in the present experiment achieved a steady state after TOS of 20-40 min. The most efficient specific energy was achieved at the highest feed flow rate 85.45 cm^3 min^{-1} (SE of 2,333.5 kJ mol^{-1}). Based on the SE, the reaction in this experiment is more efficient than that in Wang's experiment (SE of 7,289 kJ mol^{-1}) but it is inefficient when the SE is compared with the standard enthalpy of 61.75 kJ mol^{-1}.

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