Methane conversion to H_2 and higher hydrocarbons using Non-thermal plasma dielectric barrier discharge reactor

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Abstract

The use of Non-Thermal Plasma (NTP) reactors has been proposed as an alternative solution to the World's stranded gas challenge due to their ability to perform reactions, such as direct conversion of methane to H_2 and higher hydrocarbons ($>C_1$), at room temperature. An optimisation study varying plasma power (10-50 W) and residence time (3.82 -19.08 s) was performed using a DBD reactor with no catalyst. The effects of additives including water vapour, nitrogen, and hydrogen were also explored. The optimum conditions for methane conversion (36.5 %) without additives at ambient temperature (20 °C) were found to be maximum at 50 W and 19.08 s, resulting in a H_2 yield of 13.9 %. The key finding from the additive study was that the addition of 10 % N_2 resulted in an increase in conversion (37.6 %) and an increase in H_2 yield (14.5 %), at 50 W and 19.08 s.

1. Introduction

NTPs are a possible small-scale solution for stranded gas valorisation as they can convert methane into H_2 and valuable hydrocarbons at ambient conditions [1]. NTPs are plasmas with

electron temperature (energy) greater than the temperature of the background plasma's gas. Electrons temperatures typically range from 10^4 - 10^5 K (1 – 10 eV) at ambient gas temperature [2]. This high energy means the electrons produced can dissociate strong molecular bonds via collision with reactant molecules. The plasma generates highly reactive radicals at room temperature, which drives the reactions.

Depending on the energy used, the electrons can dissociate CH_4 directly into CH_3, CH_2, CH, and C [3]. In many previous studies, conversion of methane to H_2 and higher hydrocarbons was investigated. It was observed that plasma power and residence time played an important role in the conversion of methane [4]. It was reported that conversion of methane started to increase when increasing power and residence time [5]. Moreover, the distribution of products was also dependent upon above mentioned parameters. Therefore, the suitable selection of these two parameters is very important during the non-thermal plasma conversion of methane to valuable products.

Researchers have also investigated the effects of numerous noble gas additives. With improving membrane separation technology, these additives could in principle be separated from the main product stream and reused many times. Jo *et al.* (2013) investigated the use of He, Ne and Ar and found that conversion of methane was higher with Ar compared to the other gases [6]. In a subsequent study, it was found that Xe and Kr had even better conversions than the previous noble gases, due to increased electron temperature and density [7]. In these publications, there was no direct comparison with pure methane. Another gas that can be used as an additive is nitrogen. Increasing the volume % of N_2 from 0-70 %, has been shown to increase CH_4 conversion, with drastic conversion increases after 70 % concentration of nitrogen [8].

The Dielectric Barrier Discharge (DBD) reactor is particularly affective for electron generation at ambient conditions because of the flexibility of its configuration [9]. DBD discharges electrons across a narrow gap between two electrodes. The dielectric barrier between the electrodes distributes discharges and prevents spark formation [10]. Discharges occur when the electric field induces breakdown and distributed in the discharge gap, and distribution improves the conversion [11]. Extensive research has concentrated on Dielectric Barrier Discharge (DBD) NTP reactors, with a particular focus on packed bed and regular DBDs. Little attention has been paid to using additives. This project aimed to maximise yield of H_2 and higher hydrocarbons through an optimisation study; varying power and residence time. Building upon these optimum conditions, an additive study showed the effect of water vapour, hydrogen and nitrogen, on conversion and yield.

2. Methodology

The methane, nitrogen and hydrogen gases were supplied to the system by BOC Industrial gases U.K. The overall gas composition and flow rates (20-100 ml/min) is controlled by mass flow controllers on each gas supply. Before the feed reaches the reactor, it passes through a stainless steel pressure gauge, which ensures the pressure remains atmospheric. Water vapour was sent to DBD reactor at relative humidity of 40 % (at 20 ^{o}C and ambient pressure) by passing dry methane through a water bubbler.

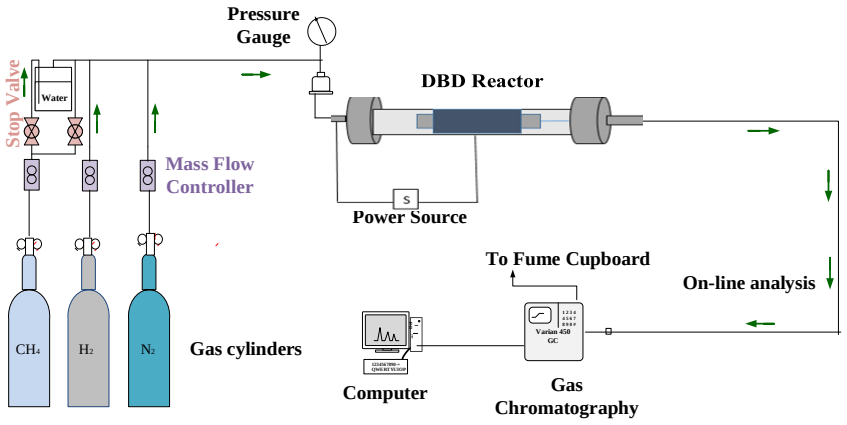


Fig. 1 The schematic diagram of the experimental setup

Figure 1 shows the schematic diagram of the experimental setup. The DBD reactor used was cylindrical and consisted of two 316 stainless steel electrodes: a mesh (10 cm) outside the outer cylindrical glass quartz tube (inner diameter 15 mm and outer diameter 18 mm) and a sheet inside the inner tube (outer diameter of 12 mm). The one end of the inner tube is closed to allow the flow through annular space. The discharge gap was 1.5 mm and inner tube was held in place using quartz wool to keep constant discharge gap. Plasma was generated in the gap between these cylindrical tubes and it volume was 6.36 cm^3. The residence time was obtained by dividing the plasma volume with flow rate. Power was supplied to the reactor by a plasma power source, attached via clips. The power source operated at a fixed frequency of about 20 kHz and power varied from10 to 50 W. Products leaving the reactor where analyzed using a Varian-450 Gas Chromatograph (GC).

The following equations were used to analyze DBD performance,

$$\text{Conversion (\%)} = \frac{\text{Moles of } CH_4 \text{ Converted}}{\text{Moles of } CH_4 \text{ In}} \times 100$$

$$\text{Yield } C_n \text{ (\%)} = \frac{n \times \text{Moles of } C_n \text{ Produced}}{\text{Moles of } CH_4 \text{ in}} \times 100$$

$$\text{Yield } H_2 \text{ (\%)} = \frac{\text{Moles of } H_2 \text{ Produced}}{2 \times \text{Moles of } CH_4 \text{ in}} \times 100$$

$$\text{Yield } H_2 \text{ (\%)} = \frac{\text{Moles of } H_2 \text{ Produced}}{(2 \times \text{Moles of } CH_4 \text{ in}) + \text{Moles of } H_2O \text{ In}} \times 100$$

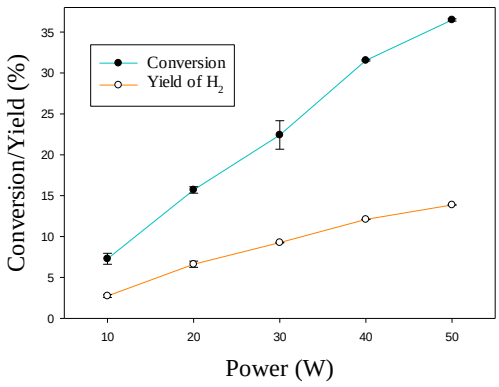
$$\text{Energy efficiency(EE) (mol/J)} = \frac{\text{Converted moles of } CH_4 \text{ per unit time}}{\text{Power}}$$

$$\text{Specific input energy (SIE) } \left(\frac{\text{kJ}}{\text{L}}\right) = \frac{\text{P (W)} \times 60/1000}{\text{Flow rate total (L/min)}}$$

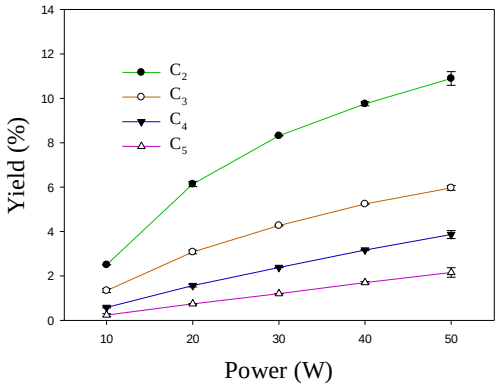
3. Results and Discussion

3.1 Power

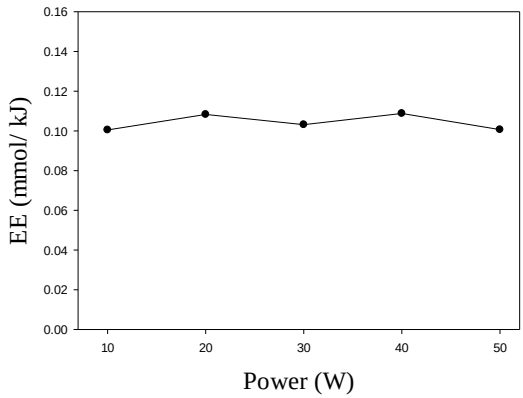
Dissociation of methane into CH_3 and H by NTP forms a mixture of products, and composition of this mixture heavily depends on the process conditions. Increasing power increases conversion, H_2 yield, and higher hydrocarbons yield [4]. Increasing power induces a stronger electric field which in turn, increases electron temperature, resulting in a higher proportion of electrons with sufficient energy for methane dissociation. It also increases the electron density which increases the number of collisions. Both these effects explain the increase in conversion.



(a)



(b)



(c)

Fig. 2 Effect of power on (a) the conversion of CH_4 and yield of H_2 (b) yield of higher hydrocarbons (C) energy efficiency (EE). Reaction conditions: residence time=19.08 s; flow rate of methane= 20 ml/min; and SIE=30-150 kJ/L

Therefore, from Figure 2 (a), conversion increases linearly with power from 7.3 % at 10 W to 36.5 % at 50 W. It can also be seen that the yield of H_2 exhibits the same trend: increasing with increasing power. The electron collides with methane, transferring its energy and leading to the dissociation of methane into radicals as shown in equation 1. The hydrogen radicals can combine to produce H_2 via combination reactions (equation 9). Furthermore , it was reported that the most important mechanism for H_2 formation also occurred via electron impact dissociation (equation 2) [8].

$$e^- + CH_4 \rightarrow CH_3 + H + e^- \qquad (1)$$

$$e^- + CH_4 \rightarrow CH_2 + H_2 + e^- \qquad (2)$$

From Figure 2 (b), the product yield increases with increasing power, as expected because of the high number of energetic electrons at high power. The Maxwellian electron energy distribution function (EEDF) tells the more the average electron energy is, the high number of electrons with more energy will be formed [12]. The EEDF depends on gas composition and electric field (depends on power) [13]. Therefore, increasing power affects the EEDF and increases energetic electrons due to stronger electric field at high power. It has been reported that electron impact dissociation contribute a dominant role in the conversion of methane to produce radicals (CH_3, CH_2, and CH) [4]. These radicals re-combine to produce higher hydrocarbons. Hence, high power favoured the recombination of reactive radicals and increased the yield of heavy hydrocarbons [14]. In another study it was reported that high power increased the product's yield during the dry reforming of CH_4 [15].Fig. 2 (c) shows the effect

of power on the energy efficiency. It can be seen that the energy efficiency does not change considerably with the increase in discharge power. This is possible because the conversion increases in the same way as the power increases.

The electron impact reactions play a key role for the conversion of methane in non-thermal plasma process to produce CH_3 (equation 1). These radicals can combine to produce C_2 hydrocarbons (equation 3). The electrons impact can also produce C_2H_5 from C_2H_6, which further combines with CH_3 or C_2H_5 to produce C_3H_8 and C_4H_{10} hydrocarbons (equation 5 and 6). The production of C_5H_{12} hydrocarbons may be occurred due to combination of C_3H_8 and C_2H_5. The formation of alkene can also possible due to abstraction of two hydrogen atoms from alkanes.

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad (3)$$

$$C_2H_6 + e^- \rightarrow C_2H_5 + H \quad (4)$$

$$C_2H_5 + CH_3 \rightarrow C_3H_8 \quad (5)$$

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \quad (6)$$

$$C_3H_8 + e^- \rightarrow C_3H_7 + H \quad (7)$$

$$C_3H_7 + C_2H_5 \rightarrow C_5H_{12} \quad (8)$$

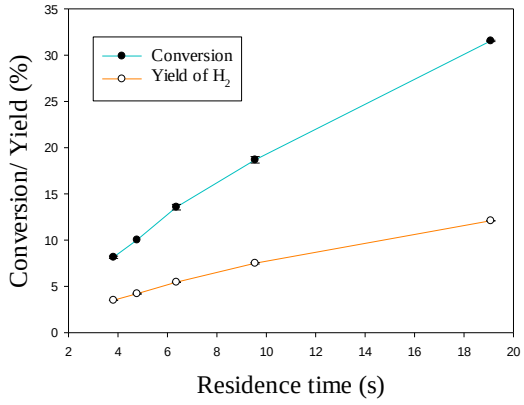
$$H + H \rightarrow H_2 \quad (9)$$

In current study, the formation of yellow wax was observed inside the reactor. It is possible that the yellow wax was formed through an oligomerisation mechanism in which number of monomers join together to form a macromolecular complex. This wax requires further analysis to determine, but it is very likely hydrocarbon in nature. The carbon balance was performed using the data of CH_4 converted to C_1-C_5 hydrocarbons and it decreased from 84 % to 71 % with increasing the power from 10 to 50 W. Carbon balance also decreased with increasing

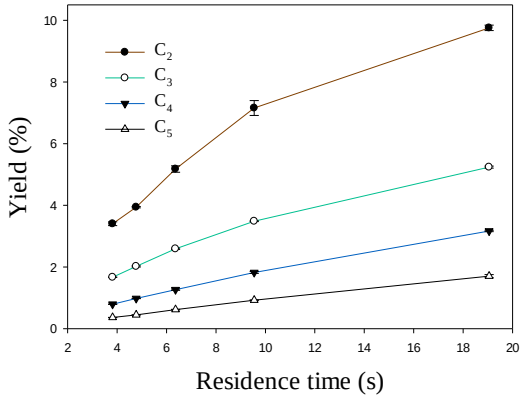
residence time from 82% to 72%. It seems that the selectivity towards undetected hydrocarbons also increases with power and residence time, and due to this there are likely >C_5 hydrocarbons present. Finally, the GC chromatograms showed small peaks that had a longer retention time than C_5. Components could not be identified from these peaks but their presence further indicates the possibility of >C_5 hydrocarbon formation. The missing carbon was due to the production of wax and heavier carbon species >C_5. In previous study, the formation of carbon deposits on the electrode was also reported and carbon balance remained in the range of 70 - 75 % [6].

3.2 Residence Time

Increasing the residence time has the same effect as increasing power in their respective publications [4, 14, 16-21]. This is because increasing the residence time increases the chance that the feed gas molecules collide with high energy electrons and free radicals [14, 22, 23].



(a)



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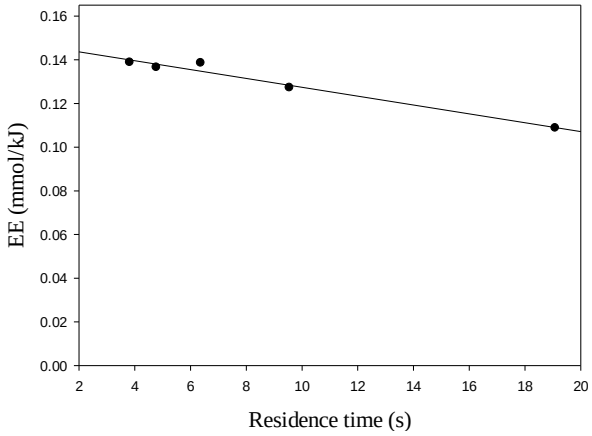
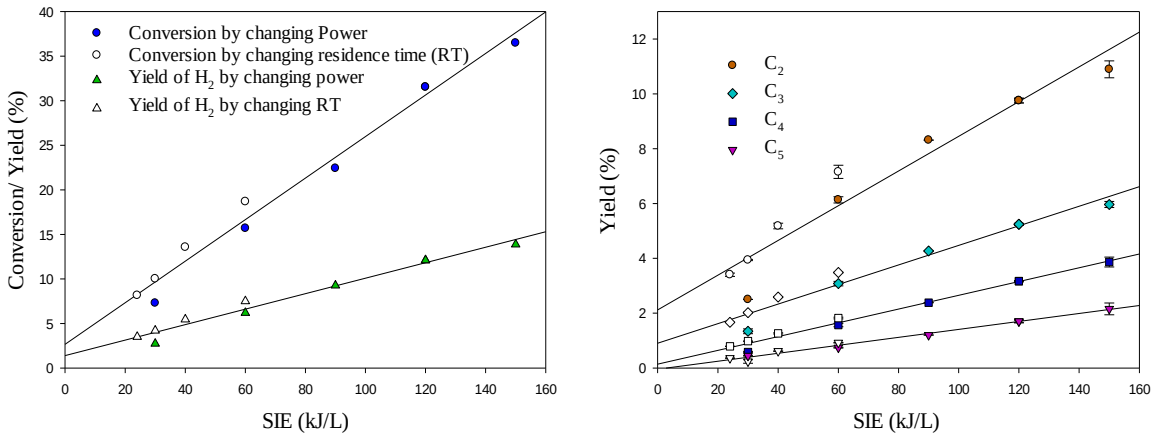


(c)

Fig. 3 Effect of residence time on (a) the conversion of CH4 and yield of H_2 (b) yield of higher hydrocarbons (c) energy efficiency (EE). Reaction conditions: Plasma power= 40 W; flow rate of methane= 20-100 ml/min

From Figure 3 a), increasing residence time, linearly increases conversion from 8.15 % at 3.82 s to 31.54 % at 19.08 s. Figure 3 (a) also shows an increase in H_2 yield from 3.5 % to 12 % when residence time increases from 3.82 s to 19.08 s. The residence time is directly related to the methane flow rate, and to increase residence time flow rate needs to be lowered. Therefore, the molecules of CH_4 gas spend more time in the plasma discharge zone when increasing residence time, which produces more H radicals. These H radicals may contribute to increasing the yield of H_2 and higher hydrocarbons (> C_1) by reacting with intermediates. As can be seen from Figure 3 (b), increasing the residence time has the same overall effect as power on yield of higher hydrocarbons. This is because the longer residence time increases the collision frequency of intermediates with high energy electrons or energetic radicals. The effect of residence time on the energy efficiency is shown in fig.3 (c). It can be observed that the energy efficiency decreases with increasing the residence time.



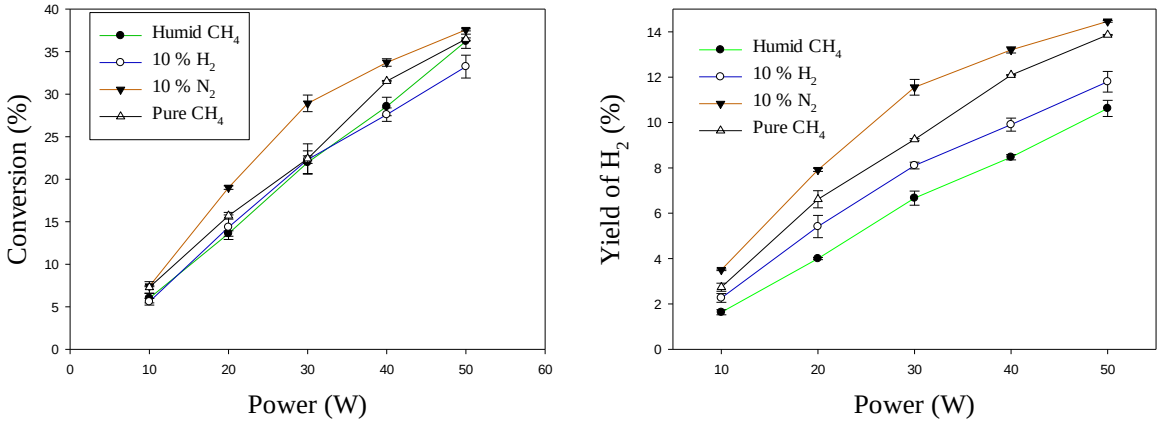
(a) (b)

Fig. 4 Effect of specific input energy (SIE) on (a) the conversion of CH_4 and yield of H_2 (b) yield of higher hydrocarbons. Reaction conditions: Plasma power= 10-50 W; flow rate of methane= 20-100 ml/min

Figure 4 (a) clearly shows that there is an increase in conversion and H_2 yield with increasing SIE. Conversion increases with SIE, which is expected as increasing SIE increases the average input energy. Figure 4 (b) shows the same trends as in the power and residence time experiments.

3.3 Additive Study

Figure 5 (a) shows that conversion of CH_4 is highest for addition of 10 % N_2 with a rise in conversion from 7.41 % at 10 W to 37.6 % at 50 W, an improvement on the conversion with pure CH_4. In a previous study, the effect of He, Ne and Ar additives has been studied on the conversion of methane, with addition of Ar having the greatest effect. It was observed that the electron temperature and electron density was higher in the mixture of Ar and methane [6]



(a) (b)

Fig. 5 Effect of power on (a) the conversion of CH_4 in different additives (b) the yield of higher hydrocarbons using different additives. Reaction conditions: Residence time= 19.08 s; flow rate of methane= 20 ml/min: SIE= 30-150 kJ/L

Therefore, it may be possible that the dilution of CH_4 with N_2 caused an increase in conversion due to high proportion of excited N_2 molecules [24]. Upon collision with high energy electrons, the N_2 molecules become excited and rise to a higher energy state. These excited N_2 molecules can then collide with CH_4, causing dissociation. It was reported that the collision of methane with singlet and triplet metastable states of N_2 contributed to higher conversion. The methane dissociation occurs via Penning dissociation reactions due to collision with the metastable N_2, which leads to energy transfer, and subsequent dissociation of the molecule [8]. Carbon balance also increased up to 93% when N_2 was added as additive due to presence of metastable excites species.

The addition of water vapours does not affect the conversion of methane significantly. The addition of H_2 also lowered conversion of methane, with an increase of only 5.59 – 33.24 % from 10 – 50 W. It was reported that the most important formation reaction is combination of CH_3 and H radicals [8]. So the decrease in conversion upon H_2 addition is indeed the result of an increase in this reaction rate due to an increase of the H radical density.

Figure 5 (b) shows that a mixture of methane and 10 % N_2 has a higher yield of H_2 than pure methane and other additives. It was reported that the excited species of N_2 played a key role during the non-thermal processes [24]. Yu *et al*. reported that the excited species of nitrogen showed major role in non-thermal plasma reactions than the direct impact of electron [25, 26]. Therefore, in the current study, the mixture of methane with 10 % N_2 showed the highest conversion and product yield. The carbon balance also increased up to 93% with N_2 due to presence of metastable excites species.

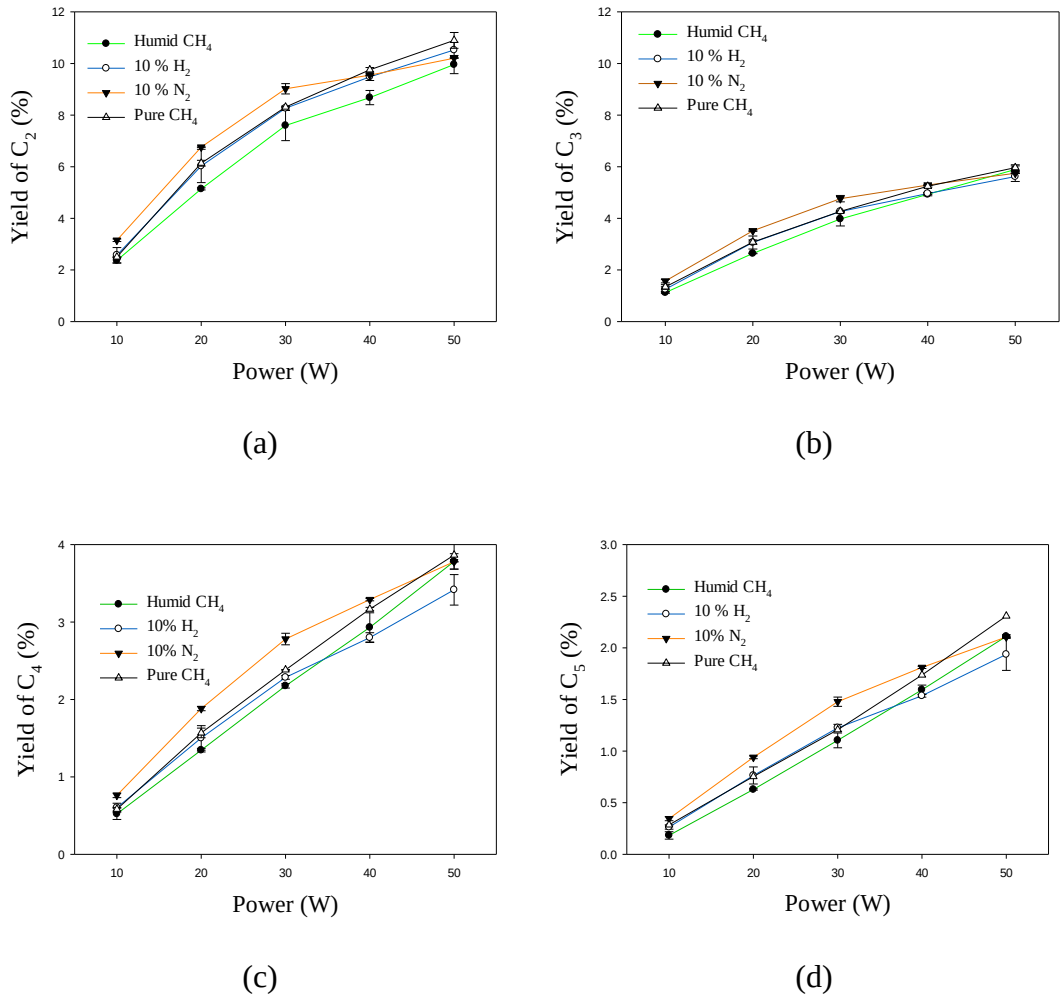


Fig. 6 Effect of power on (a) the yield of of C_2 in different additives (b) the yield of C_3 in different additives (c) the yield of C_4 in different additives (d) the yield of C_2 in different additives. Reaction conditions: Residence time= 19.08 s; flow rate of methane= 20 ml/min: SIE= 30-150 kJ/L

Figures 6 (a) to (d) show that the yield of C_2-C_5 hydrocarbons is higher with N_2 additive below 40 W. At high power, the yield of products converges due to presence of high energetic electrons. Increasing power increases the number of reactive species and electrons in all carrier gases. Consequently, chances of electron impact dissociation involving excitation, dissociation and ionization of carrier gases can be increased. Subsequently, high number of active species can be produced in the plasma discharge which gives high yield in all carrier gases. The addition of 10 % hydrogen shows slightly higher yield of hydrocarbons as compared to humid methane. It was reported that formation of C_2-C_5 hydrocarbons was a hydrogen consuming process and selectivity of C_2-C_5 lower hydrocarbons increased when adding hydrogen in the background gas [27].Therefore the presence of excess H radicals promote the formation of C_2-C_5 hydrocarbons.

Conclusions

In this study, the performance of a DBD reactor was investigated at various plasma powers (10-50 W), residence times (3.82-19.08 s), and additives (N_2, H_2O, H_2). In conclusion, a number of main findings are made from this project:

(i) The conversion of methane increased when increasing plasma power and residence. The maximum conversion of methane was 36.48 % at 50 W and 19.08 s. However, this can be further increased by controlling these two parameters.

(ii) The products were H_2 and higher hydrocarbons (>C1). Their yield increased with respect to power and residence time. The maximum yield of H_2 was 13.85% at 50 W and 19.08 s.

(iii) In the study of possible additives, the addition of 10 % N_2 increased conversion of methane, H_2 yield, and higher hydrocarbons yield more than the other additives (H_2O and H_2) below 40 W.

(v) The addition of 10 % H_2 reduced conversion, but increased higher hydrocarbons yield than humid methane.

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