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# Plasma-assisted removal of methanol in N<sub>2</sub>, dry and humidified air using a dielectric barrier discharge (DBD) reactor†

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In this work, a non-thermal plasma dielectric barrier discharge (DBD) was used to remove methanol from ambient air. The effects of carrier gases (N<sub>2</sub>, dry and humidified air), power (2–10 W), inlet concentration (260–350 ppm), and residence time (1.2–3.3 s) were investigated to evaluate the performance of the plasma DBD reactor in terms of removal efficiency, product selectivity and reduction of unwanted by-products at ambient temperature and atmospheric pressure. It was found that the conversion of methanol increased with power and residence time regardless of the carrier gas used. However, the removal efficiency decreased with the increasing concentration of CH<sub>3</sub>OH. Almost complete removal of methanol (96.7%) was achieved at 10 W and a residence time of 3.3 s in dry air. The removal efficiency of methanol followed a sequence of dry air > humidified air > N<sub>2</sub> carrier gas. This was due to the action of the O radical in dry air, which dominates the decomposition process of the plasma system. The introduction of water vapour into the DBD system decreased the removal efficiency but had a number of significant advantages: increased CO<sub>2</sub> selectivity and yield of H<sub>2</sub>, it significantly reduced the formation of O<sub>3</sub>, CO and higher hydrocarbons. These influences are probably due to the presence of potent OH radicals, and the conversion pathways for the various effects are proposed. It is important to note that no solid residue was formed in the DBD reactor in any carrier gas. Overall, this research indicates that methanol can be almost completely removed with the correct operating parameters (96.7% removal; 10 W; 3.3 s) and shows that humidification of the gas stream is beneficial.

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## 1. Introduction

Volatile organic compounds (VOCs) emitted by the chemical processing industries, agricultural operations, and indoor sources have sparked widespread concern in recent years, owing to their harmful influence on human health and the environment.<sup>1</sup> VOCs are precursors for the formation of ground-level ozone, organic aerosols, and photochemical smog.<sup>2</sup> Some VOCs are toxic and carcinogenic, while others can cause unpleasant odours.<sup>3</sup> Methanol is one of the most common alcohols and is a key product in the chemical industry. It is mainly used to produce other chemicals such as acetic acid, formaldehyde, and polymers.<sup>4</sup> It is classified as highly volatile alcohol and has been widely used as a solvent in the chemical processing industries.<sup>5</sup> Methanol is one of the most frequent

odorous VOCs.<sup>5</sup> Methanol production has almost doubled in the past decade. The production rate could rise to about 500 Mt per annum by 2050, which can lead to an increase in methanol emission.<sup>4</sup> Long-term exposure to methanol can cause nausea, headaches, blurred vision and neurological damage.<sup>5</sup> As a result, reducing methanol emissions is a significant concern and a critical research area worldwide.

Non-thermal plasmas (NTPs) reactors are a promising method for removing VOC emissions from gas exhausts at relatively low temperatures and atmospheric pressure.<sup>6,7</sup> NTP technology has received much attention in recent years as a promising method for removing low and high concentrations of VOC emissions from industrial exhausts.<sup>8</sup> The term non-thermal plasma, or “cold plasma”, refers to an ionised gas consisting of bulk gas molecules and atoms, electrons, ions and excited species. NTPs are not in thermal equilibrium, and the temperature differs significantly between the electrons and other species such as atoms, molecules and ions. The gas temperature can be at room temperature, whereas the energy of the electrons is significantly high, with an average electron temperature of 10 000 to 100 000 K (1 to 10 eV).<sup>9</sup> An NTP is typically generated by applying an electric field to a neutral gas, and if the breakdown field strength is exceeded, the plasma forms a gas discharge. Reactive species in NTP systems are

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generated through the impact of highly energetic electrons with gas molecules.<sup>10</sup>

Dielectric barrier discharge (DBD) technology is one of the most studied NTP techniques for removing odorous VOCs among different NTP reactors.<sup>11</sup> DBD plasma is of practical interest due to its simple design, moderate cost, flexibility, operation under ambient conditions, and rapid attainment of a steady-state allows for fast start-up and shutdown.<sup>9,12</sup> Previous researchers have studied the use of DBD plasma reactors to decompose odorous VOCs such as methanol. Sato *et al.*<sup>13</sup> investigated methanol decomposition in a DBD reactor at a 16–20 kV voltage using an air carrier gas. Although a high removal efficiency was achieved, they did not report the product's composition. It's unknown what the hydrogen concentration and yield were in their studies. Wang *et al.*<sup>14</sup> reported the direct conversion of methanol into value-added chemicals and fuels in a DBD reactor using N<sub>2</sub>. They reported a removal efficiency of 74% at 50 W and a constant concentration of CH<sub>3</sub>OH in N<sub>2</sub> flow rate of 250 ml min<sup>-1</sup>. They demonstrated that increasing the power increased the methanol removal efficiency and product selectivity. Wang *et al.*<sup>2</sup> studied methanol oxidation in a DBD reactor using an air carrier gas. They reported that for NTP alone system, the removal efficiency of methanol increased from 14.1% to 43.9% when power increased from 0.3 to 0.9 W. Their findings showed the formation of a high O<sub>3</sub> concentration (about 773 ppm), which is an undesirable by-product that can limit the practical application of NTP-DBD reactors. Futamura *et al.*<sup>15</sup> observed a low methanol conversion (between 8–26%) at 1 mol% inlet concentration and gas flow rate of 100 ml min<sup>-1</sup> using N<sub>2</sub> in two different configurations of the DBD reactor. In another study, Tanabe *et al.*<sup>16</sup> used a DBD reactor to decompose methanol to hydrogen using argon carrier gas at a low voltage of 2–6 kV. They obtained a maximum removal efficiency of 80%, and the yield of H<sub>2</sub> increased with increasing plasma power in the absence of humidity. The yield of H<sub>2</sub> of more than 100% was obtained in the presence of H<sub>2</sub>O. The primary decomposition product was hydrogen. In the absence or presence of water in the system, CO or CO<sub>2</sub> was the other main product. Norsic *et al.*<sup>17</sup> investigated methanol oxidation using dry and humidified air carrier gases. They reported a removal efficiency of 60% in dry air plasma, which decreased to 43% when water vapour with a relative humidity of 35% was introduced to the DBD system. Their findings showed that high humidity had an inhibitive influence on methanol decomposition and hindered the formation of secondary products. The water vapour influences the features of the plasma discharge and the chemistry of the plasma in the gas stream, which has a substantial impact on the removal efficiency. Excess humidity restricted the current at constant applied voltage due to the alteration of the dielectric's surface resistance and lowered the transferred charges between the electrodes, limiting the plasma volume.<sup>18</sup> Rico *et al.*<sup>19</sup> reported the formation of coke during the conversion of CH<sub>3</sub>OH into CO and H<sub>2</sub> using a DBD reactor. Solid residue formation can cause fouling problems to the DBD reactors over a long operation time.

However, there have been a variety of drawbacks associated with NTP-alone systems, including low selectivity and low

removal efficiency,<sup>18,19</sup> high energy consumption, and formation of unwanted by-products, *e.g.*, high ozone concentration,<sup>2</sup> and solid deposition.<sup>19</sup> In addition, rapid deactivation of catalysts by poisoning and sintering,<sup>20</sup> and high ozone emission in plasma catalytic systems limit their practical applications in VOC abatement.<sup>2</sup> Catalyst lifetime is severely limited, which suggests that optimising non-catalytic DBD methanol treatment may be advantageous due to the reduced maintenance and ongoing consumable costs associated with replacing catalysts.

Therefore, there is a strong need to improve the performance of an NTP-alone system by investigating the effect of various operating parameters on the removal efficiency of methanol, product selectivity and the elimination of unwanted by-products. Furthermore, understanding the methanol decomposition pathways in the plasma-alone system using different carrier gases is critical for the practical application/scale-up of the NTP-DBD technology.

Methanol is selected as model VOC in this study since it is odorous volatile alcohol that has been mainly used industrially as a solvent, alternative source of fuel and pesticide. Therefore, ingestion or inhalation of methanol can cause neurological damage, blurred vision, headache, and dizziness. As a result, in this work, an NTP-DBD reactor is developed to remove methanol from ambient air. It is studied in N<sub>2</sub>, dry and humidified air environments at ambient temperature and atmospheric pressure. These carrier gases were chosen because they can aid in the development of pathways for methanol decomposition using NTPs. The effect of various operating parameters such as carrier gases, plasma power, inlet concentration and residence time were evaluated based on removal efficiency, product selectivity and elimination/reduction of unwanted by-products. In addition to the optimisation of the operating parameters, for example, solid residue formation is a big challenge in the application of plasma-assisted VOC decomposition. The air-cleaning technology developed in this study provided a solution to the major drawback associated with non-catalytic plasma-assisted VOC conversion by eliminating the solid residue formation in the DBD reactor, increasing the removal efficiency and product selectivity and reduced O<sub>3</sub> concentrations.

Furthermore, the technology also converted methanol to higher hydrocarbons such as C<sub>2</sub>–C<sub>4</sub>. In addition, pathways for the decomposition of methanol in the NTP-alone system using different atmospheric gases has been explored. Overall, the study reports a technology for the reduction of methanol in gaseous effluents based on a low cost, low energy non-thermal plasma technology, so pertains to indoor and outdoor air quality control.

## 2. Materials and methods

### 2.1 Experimental set-up

Fig. 1 shows a schematic of the experimental set-up. The experiment was carried out at ambient temperature and atmospheric pressure. The non-thermal plasma was generated using a cylindrical dielectric barrier discharge (DBD) reactor consisting of two coaxial quartz tubes. The plasma DBD reactor



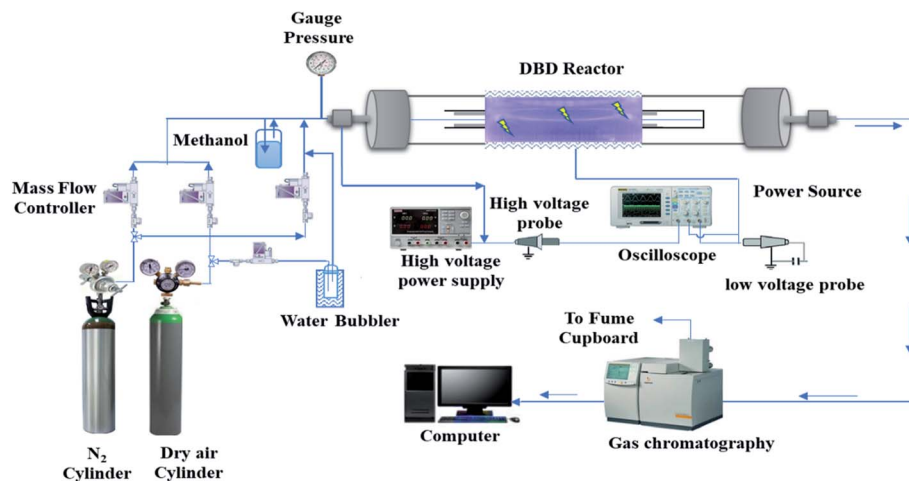


Fig. 1 Schematic of the experimental set-up for NTP-assisted removal of methanol.

consists of two 316 stainless steel grade electrodes: one outside a cylindrical glass quartz tube (length 330 mm, inner diameter 15 mm, and outer diameter 18 mm) and the other inside the tube. The other electrode was inserted into the domed inner tube (outer diameter of 12 mm). Both the outer and inner electrodes were made of the same material. The discharge gap was 1.5 mm, and the inner tube was secured with quartz wool to keep the discharge gap uniform. Plasma was generated between the annular spaces of the cylindrical quartz tubes.

The length of the external mesh was 60 mm, leading to a discharge volume of 3.82 cm<sup>3</sup>. A variac AC transformer was used to control the power supplied to the DBD reactor from the power source. The discharge zone is where the two electrodes overlap; so the residence time was calculated using the discharge volume. A P6015A high voltage probe was used to measure the voltage signal/waveform applied to the DBD plasma reactor, and a PEM CWT003X/B current probe was used to measure the plasma current signal/waveform. The current and voltage signals were recorded by a Tektronix TPS 2014 four-channel optical storage oscilloscope. The power was determined by integrating the current signal  $I(t)$  and voltage  $U(t)$  recorded by the oscilloscope, as shown in eqn (1). The power dissipated to the DBD reactor was varied from 2 to 10 W at a frequency of about 20 kHz in this study.

$$P = \frac{1}{T} \int_0^T U(t)I(t)dt \quad (1)$$

Pure nitrogen ( $\geq 99.9\%$ ) and air (zero grade) were purchased from BOC industrial gases, U.K. The overall gas composition and total flow rates of the carrier gases (70–160 ml min<sup>-1</sup>) were regulated by computer-controlled Bronkhorst F201 mass flow controllers (MFC). To investigate the effect of humidity, water vapour-containing air with a relative humidity of 24% (at 20 °C and atmospheric pressure) was introduced into the DBD reactor by passing dry airflow through a water bubbler kept in a water bath (20 °C). Furthermore, to saturate with the desired amount of methanol, the carrier gas was passed through a bubbler

containing anhydrous methanol ( $\geq 99.9\%$  – Sigma-Aldrich). The methanol bubbler was placed in an ice bath to reduce the influence of diurnal fluctuations in ambient temperature on the rate of evaporation of methanol. The mixture of methanol vapour and the carrier gas then passed through the DBD reactor.

The composition of the product gases and methanol concentration was measured using a Varian 450 gas chromatograph equipped with a thermal conductivity detector (TCD) for the measurement of CH<sub>4</sub>, H<sub>2</sub>, CO and CO<sub>2</sub>, and a flame ionisation detector (FID) for measuring the inlet and outlet concentrations of methanol, and hydrocarbons.

## 2.2 Definitions

The removal efficiency of methanol ( $\eta_{\text{methanol}}$ ) is defined as:

$$\eta_{\text{methanol}}(\%) = \frac{[\text{CH}_3\text{OH}]_{\text{in}} - [\text{CH}_3\text{OH}]_{\text{out}}}{[\text{CH}_3\text{OH}]_{\text{in}}} \times 100\%$$

where  $[\text{CH}_3\text{OH}]_{\text{in}}$  and  $[\text{CH}_3\text{OH}]_{\text{out}}$  are the inlet and outlet methanol concentrations (ppm).

The following formulae were used to determine the selectivity of different gas products:

$$C_mH_n \text{ selectivity}(\%) =$$

$$\frac{\sum \text{moles of } C_mH_n \text{ produced (mol min}^{-1}) \times m}{\text{moles of CH}_3\text{OH converted (mol min}^{-1})} \times 100$$

where  $m$  is the number of carbon atoms in the product.

$$\text{H}_2 \text{ yield}(\%) =$$

$$\frac{\text{moles of H}_2 \text{ produced}}{2 \times \text{moles of } [\text{CH}_3\text{OH}]_{\text{in}} + \text{moles of H}_2\text{O}_{\text{in}}} \times 100$$

$$\text{CO}_2 \text{ selectivity}(\%) = \frac{\text{moles of CO}_2 \text{ produced}}{\text{moles of } [\text{CH}_3\text{OH}] \text{ converted}} \times 100$$

$$\text{CO selectivity}(\%) = \frac{\text{moles of CO produced}}{\text{moles of } [\text{CH}_3\text{OH}] \text{ converted}} \times 100$$



The specific input energy (SIE) is defined as:<sup>21</sup>

$$\text{Specific input energy (SIE)} (\text{kJ L}^{-1}) = \frac{P(\text{W})/1000}{Q(\text{L min}^{-1})} \times 60$$

### 3. Results and discussion

#### 3.1 Effect of carrier gases and power

The effect of power on the removal efficiency of methanol in N<sub>2</sub>, dry, and humidified air is shown in Fig. 2. The input power significantly affects the performance of the reaction regardless of the carrier gas used. In N<sub>2</sub> carrier gas, methanol decomposition increases from 27.6% to 71.3% when the input power is increased from 2 W to 10 W (SIE = 1.7–8.6 kJ L<sup>-1</sup>). This is generally expected because as the input power increases, the number of the energetic electrons increases, increasing the number of excited species, ions, and free radicals due to the collision between these energetic electrons and gas molecules.<sup>22</sup> Therefore, the reaction probability between the reactive species and CH<sub>3</sub>OH molecules in the discharge zone increased.<sup>2</sup>

The maximum methanol removal efficiency of 96.7% was achieved in dry air, followed by humidified air (77.7%) and N<sub>2</sub> (71.3%) at 10 W and 3.3 s. This was due to the action of the O radical in dry air, which dominates the plasma system's decomposition process. The average electron temperature of dry air is 4.14 eV, which is higher than the 3.85 eV mean electron energy of pure nitrogen.<sup>23</sup> It is well known that the decomposition of dilute volatile organic compounds in dry air plasmas is initiated by the direct electron impact dissociation of N<sub>2</sub> and O<sub>2</sub> to form chemically reactive species such as N, N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>), O, and O(<sup>1</sup>D) for the conversion of VOCs and intermediates into H<sub>2</sub>O, CO, CO<sub>2</sub>, and other by-products.<sup>5</sup> Therefore, the generation of higher discharges in dry air plasma can lead to the formation of excited species such as O-radicals,

excited N<sub>2</sub> and metastable N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>).<sup>13</sup> This resulted in a more significant increase in the conversion of methanol.

Fig. 3 below shows the selectivity to (a) CO<sub>2</sub>, (b) CO, (c) C<sub>2</sub>–C<sub>4</sub>, (d) CH<sub>4</sub>, and (e) H<sub>2</sub> yield as a function of carrier gas and input power.

Carbon dioxide, carbon monoxide, methane, ethane, *n*-butane and butene, and hydrogen were produced in all carrier gases. Previous investigations reported only the production of CO, CO<sub>2</sub> and H<sub>2</sub> as the major products formed in dry or humid air carrier plasma.<sup>16</sup>

As presented in Fig. 3(a)–(e), increasing the input power increases product selectivity, indicating that the high input power appears to directly enhance the product selectivity due to the high number of energetic electrons. The relationship between electron energy distribution function (EEDF) and electron energy indicates that the higher the mean electron energy is, the more electrons with higher energy will be generated.<sup>24</sup> Electron impact dissociation has been reported to play a significant role in decomposing VOCs to produce CH<sub>3</sub> radicals, which recombine to produce higher hydrocarbons.<sup>25</sup> These findings indicate that the presence of O<sup>•</sup> in dry air favoured the formation of CO and suppressed hydrocarbon formation.

Fig. 3(c) and (d) also show that higher input power resulted in higher selectivity to C<sub>2</sub>–C<sub>4</sub> and CH<sub>4</sub> in all the carrier gases. For instance, C<sub>2</sub>–C<sub>4</sub> selectivity increased from 5.1% to 16.6% in N<sub>2</sub>, and CH<sub>4</sub> selectivity increased from 9.7% to 17.9% in dry air. The selectivity to C<sub>2</sub>–C<sub>4</sub> (C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub> and C<sub>4</sub>H<sub>8</sub>) is higher in N<sub>2</sub> plasma than in dry and humidified air, especially at higher input power. This is because the presence of the O radical in dry air opens up routes to CO formation instead. The maximum selectivity to C<sub>2</sub>–C<sub>4</sub> was observed in N<sub>2</sub> plasmas. This was due to enrichment in CH<sub>3</sub> radicals, compared to other carrier gases tested here, which can be converted to CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>4</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub> (see Section 3.4). In N<sub>2</sub> plasma, the probability of collision between CH<sub>3</sub>OH and various excited N<sub>2</sub> species (*e.g.* metastable state nitrogen N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>)) are higher, leading to more CH<sub>3</sub> radicals at higher residence time. The CH<sub>3</sub> can be dimerised to form C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub> can be generated through the hydrogenation reaction of CH<sub>3</sub>, as shown in R(4) and R(5).<sup>26</sup> However, the selectivity to C<sub>2</sub>–C<sub>4</sub> is lower in dry and humidified air when compared with N<sub>2</sub> plasma. This is because the presence of O and OH radicals in dry and humidified air oxidises the intermediate species to CO and CO<sub>2</sub>.<sup>5</sup> At the same time, the excited N<sub>2</sub>, metastable N<sub>2</sub>, can be quenched/consumed by oxygen species to form ground state N<sub>2</sub> and NO<sub>x</sub> (NO + NO<sub>2</sub>). It is significant to note that NO<sub>x</sub> was not detected in the present study. Furthermore, as the input power increases, methanol decomposition leads to a higher yield of H<sub>2</sub> through recombination reaction of H-radicals or dissociation of CH<sub>3</sub>OH.<sup>27,28</sup>

In humid air, this route is joined by other routes based on the OH radical formed from the dissociation of H<sub>2</sub>O, which promotes CO<sub>2</sub> formation. In addition, O and OH radicals can also oxidise hydrocarbon species and CO leading to higher CO<sub>2</sub> selectivity.<sup>29</sup>

The presence of water vapour reduces the methanol removal efficiency. This is probably due to the opening up of the reverse

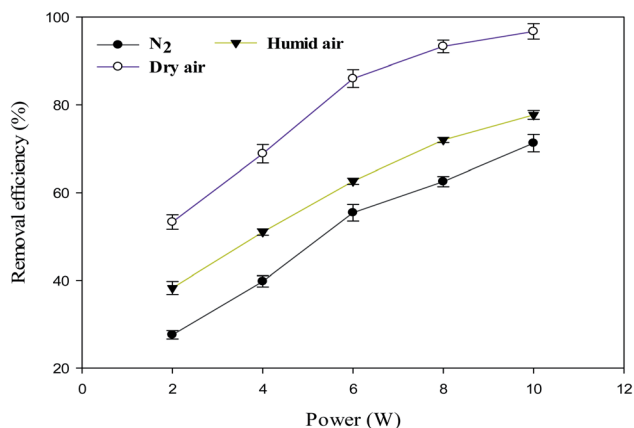
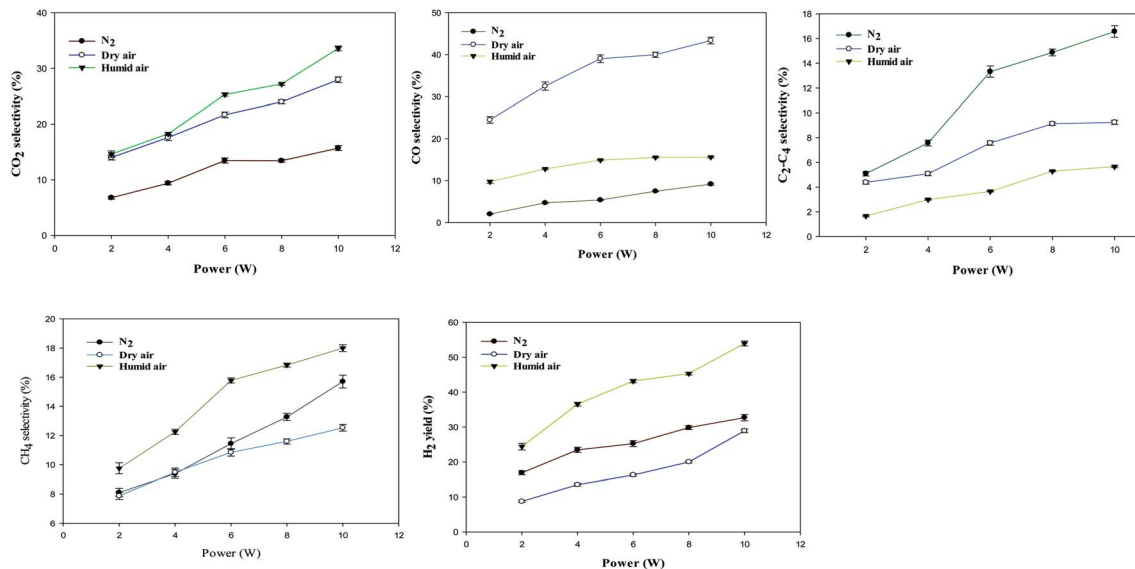


Fig. 2 Effect of power in different carrier gases as a function of removal efficiency of methanol (reaction conditions: temperature = ambient; concentration = 260 ppm; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 1.7–8.6 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation ± σ for 3 measurement results).





**Fig. 3** (a) Effect of power in different carrier gases as a function of selectivity to CO<sub>2</sub> (reaction conditions: temperature = ambient; concentration = 260 ppm; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 1.7–8.6 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (b) Effect of power in different carrier gases as a function of selectivity to CO (reaction conditions: temperature = ambient; concentration = 260 ppm; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 1.7–8.6 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (c) Effect of power in different carrier gases as a function of selectivity to C<sub>2</sub>–C<sub>4</sub> (reaction conditions: temperature = ambient; concentration = 260 ppm; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 1.7–8.6 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (d) Effect of power in different carrier gases as a function of selectivity to CH<sub>4</sub> (reaction conditions: temperature = ambient; concentration = 260 ppm; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 1.7–8.6 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (e) Effect of carrier gases and power on yield of H<sub>2</sub> (reaction conditions: temperature = ambient; concentration = 260 ppm; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 1.7–8.6 kJ L<sup>-1</sup>, relative humidity = 24%, Error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results).

reaction OH + CH<sub>3</sub> to CH<sub>3</sub>OH. Also, greater humidity reduces the transfer of charges between the electrodes, leading to a decrease in effective plasma volume,<sup>30</sup> which led to a greater reduction of the plasma electric field,<sup>31</sup> which would also decrease the removal efficiency.

However, water addition increased the selectivity to CO<sub>2</sub> and CH<sub>4</sub> and the yield of H<sub>2</sub>, rather than CO and longer hydrocarbons. The increase in CO<sub>2</sub> selectivity is due to the more rapid oxidation of CO to CO<sub>2</sub> by the OH radical, than by the O<sup>•</sup> (dry air) or N<sub>2</sub><sup>•</sup> (in nitrogen only). Clearly, introducing water vapour to the NTP-alone system could (i) reduce CO generation, (ii) reduce O<sub>3</sub> concentration, (iii) increase the yield of H<sub>2</sub>, (iv) increase CO<sub>2</sub> selectivity. Detailed mechanisms of the methanol decomposition pathways are presented in Section 3.4.

The formation of solid residues during the decomposition process is a source of concern because they can foul the DBD reactor over time and are undesirable by-products. Solid residue formation must be reduced or eliminated for DBD plasma techniques to be more effective and efficient.<sup>32,33</sup> In this work, no solid residue was formed in the DBD reactor in all the tested carrier gases. This could be due to the influence operating conditions, reactor configuration or nature of the model VOC (*i.e.* CH<sub>3</sub>OH), which produced more OH<sup>•</sup> radicals through the dissociation of methanol during the decomposition process. In the NTP decomposition of VOCs, reactive species such as OH, O and H radicals can be generated due to the impact of energetic

electrons on the VOC molecules and the carrier gases. The electrons have mean energy in the range of 1–10 eV.<sup>30</sup> Therefore, in methanol decomposition, OH radical can easily be generated from the electron impact dissociation of CH<sub>3</sub>OH. It has been reported that OH and O radicals are potent oxidants produced in the non-thermal plasma technique.<sup>34</sup> The OH, H and O radicals generated in the plasma reactor can convert methanol and its intermediates to CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O, resulting in the elimination of solid residue in the DBD reactor. Another reason for the elimination of solid residue is the shorter discharge gap used in this study. The shorter discharge gap can significantly increase the electric field strength, which could enhance the energy in the plasma discharge zone, which increase the removal efficiency and CO<sub>2</sub> selectivity.<sup>35</sup> The shorter discharge gap (1.5 mm) can facilitate the generation of more OH radicals from electron impact dissociation of CH<sub>3</sub>OH, increasing the removal efficiency and fast oxidation of carbon species to CO and CO<sub>2</sub>.

### 3.2 Effect of CH<sub>3</sub>OH concentration

Fig. 4 shows the effect of CH<sub>3</sub>OH concentration on the removal efficiency in N<sub>2</sub>, dry, and humidified air. The inlet concentration of CH<sub>3</sub>OH was varied over the range of 260–350 ppm with a total gas flow rate of 70 ml min<sup>-1</sup> (residence time of 3.3 s) and input power of 6 W at ambient temperature and atmospheric pressure. Fig. 4 shows that the removal efficiency of methanol



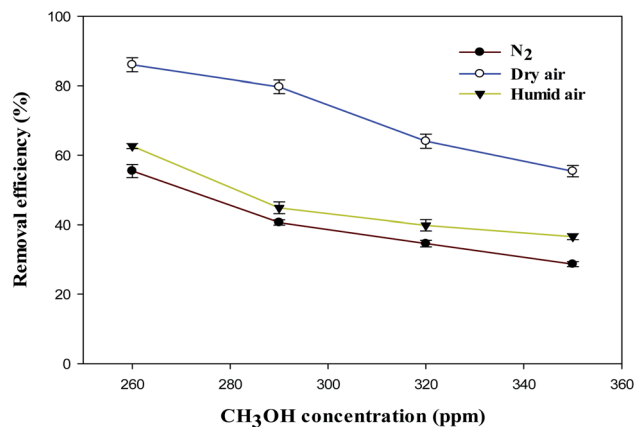


Fig. 4 Effect of concentration on removal efficiency of methanol in N<sub>2</sub>, dry and humidified air (reaction conditions: temperature = ambient; power = 6 W; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 5.1 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results).

decreased with increasing the inlet concentration of CH<sub>3</sub>OH regardless of the carrier gas used.

For instance, the removal efficiency of methanol in N<sub>2</sub>, dry and humidified air plasmas are 55.4%, 86.0% and 62.6% at an inlet concentration of 260 ppm, respectively. However, these values decreased to 28.6%, 55.4% and 36.5% when the inlet concentration increased to 350 ppm. This is because the

number of methanol molecules flowing into the DBD reactor increases while discharge length, input power, and residence time remain fixed. As a result, the undecomposed VOC molecules have a greater probability of leaving the DBD reactor discharge area unreacted.

Fig. 5 shows the selectivity to (a) CO<sub>2</sub>, (b) CO, (c) C<sub>2</sub>–C<sub>4</sub>, (d) CH<sub>4</sub>, and (e) H<sub>2</sub> yield as a function of carrier gases and CH<sub>3</sub>OH inlet concentration.

The selectivity to CO<sub>2</sub> decreased with increasing CH<sub>3</sub>OH inlet concentration. For example, increasing CH<sub>3</sub>OH inlet concentration from 260 ppm to 350 ppm resulted in a considerable decrease in CO<sub>2</sub> selectivity from 25.3% and 10.1% in dry air plasma. The selectivity to CO increased as the CH<sub>3</sub>OH inlet concentration increased from 260 ppm to 320 ppm in all the carrier gases and then decreased when methanol concentration increased to 350 ppm. In humidified air plasma, an increase in CH<sub>4</sub> selectivity from 15.8 to 17.9% was observed when methanol concentration increased from 260 to 320 ppm, as shown in Fig. 5(c). It was observed that selectivity to C<sub>2</sub>–C<sub>4</sub> decreases as the CH<sub>3</sub>OH inlet concentration increases, as more CH<sub>3</sub> radicals are produced, which react with H-radicals to form CH<sub>4</sub> (see mechanisms in Section 3.4).

The H<sub>2</sub> yield decreases as the CH<sub>3</sub>OH inlet concentration increases from 260 to 350 ppm. This is because, at higher concentrations, the number of energetic electrons, excited species, and gas-phase radicals is reduced per methanol molecule, resulting in a greater reduction in the yield of H<sub>2</sub> in the

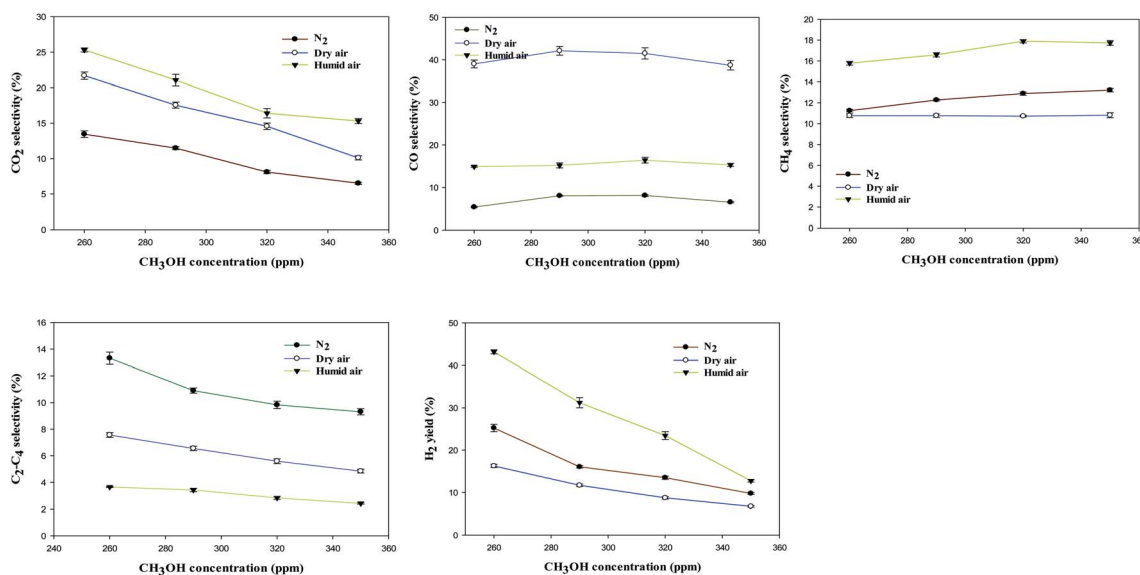


Fig. 5 (a) Effect of concentration on selectivity to CO<sub>2</sub> in N<sub>2</sub>, dry and humidified air (reaction conditions: temperature = ambient; power = 6 W; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 5.1 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (b) Effect of concentration on selectivity to CO in N<sub>2</sub>, dry and humidified air (reaction conditions: temperature = ambient; power = 6 W; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 5.1 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (c) Effect of concentration on selectivity to CH<sub>4</sub> in N<sub>2</sub>, dry and humidified air (reaction conditions: temperature = ambient; power = 6 W; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 5.1 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (d) Effect of concentration on selectivity to C<sub>2</sub>–C<sub>4</sub> in N<sub>2</sub>, dry and humidified air (reaction conditions: temperature = ambient; power = 6 W; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 5.1 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (e) Effect of concentration on yield of H<sub>2</sub> in N<sub>2</sub>, dry and humidified air (reaction conditions: temperature = ambient; power = 6 W; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s, SIE = 5.1 kJ L<sup>-1</sup>, relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results).



decomposition process. Furthermore, more VOC molecules were subjected to the discharge zone at higher concentrations, while the concentration of energetic electrons, excited species, and gas-phase radicals remained constant.<sup>14,17,36,37</sup>

### 3.3 Effect of residence time

Fig. 6 shows the effect of residence time on the removal efficiency of methanol in  $N_2$ , dry, and humidified air carrier gases. As presented in Fig. 6, the removal efficiency of methanol significantly increased from 29.6%, 32.4%, 50.8% at 1.4 s to 55.4%, 62.6%, and 86.1% at 3.3 s in  $N_2$ , humidified and dry air carrier gases, respectively. Clearly, the removal efficiency of methanol significantly increases with increasing residence time in all carrier gases.

The VOC molecules have more time to interact with the reactive plasma-generated species at higher residence times, increasing removal efficiency.<sup>37,38</sup> The maximum removal efficiency of methanol achieved was 86.1% at 3.3 s in dry air plasma.

Fig. 7 shows selectivity to (a)  $CO_2$ , (b) CO, (c)  $C_2-C_4$ , (d)  $CH_4$  and (e)  $H_2$  yield as a function of carrier gases and residence time.

The product selectivity and  $H_2$  yield increased with residence time. The  $CO_2$  selectivity and  $H_2$  yield increased from 17.3%, 14.4% to 25%, and 43.2% as the residence time increased from 1.4 to 3.3 s in humidified air. The selectivity to  $CO_2$  and yield of  $H_2$  increased due to more reaction/collision time between the energetic electrons, gas-phase radicals ( $OH^\bullet$ ,  $O^\bullet$  and  $H^\bullet$ ) and the methanol molecules in the plasma zone.

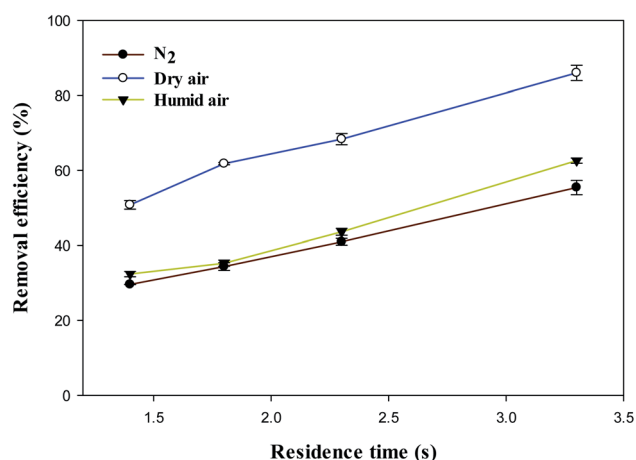


Fig. 6 Effect of residence time on the removal efficiency of methanol in  $N_2$ , dry and humidified air (reaction conditions: temperature = ambient; concentration = 260 ppm; flow rate = 70–160  $ml\ min^{-1}$ ; power = 6 W, SIE = 2.3–5.1  $kJ\ L^{-1}$ , relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results).

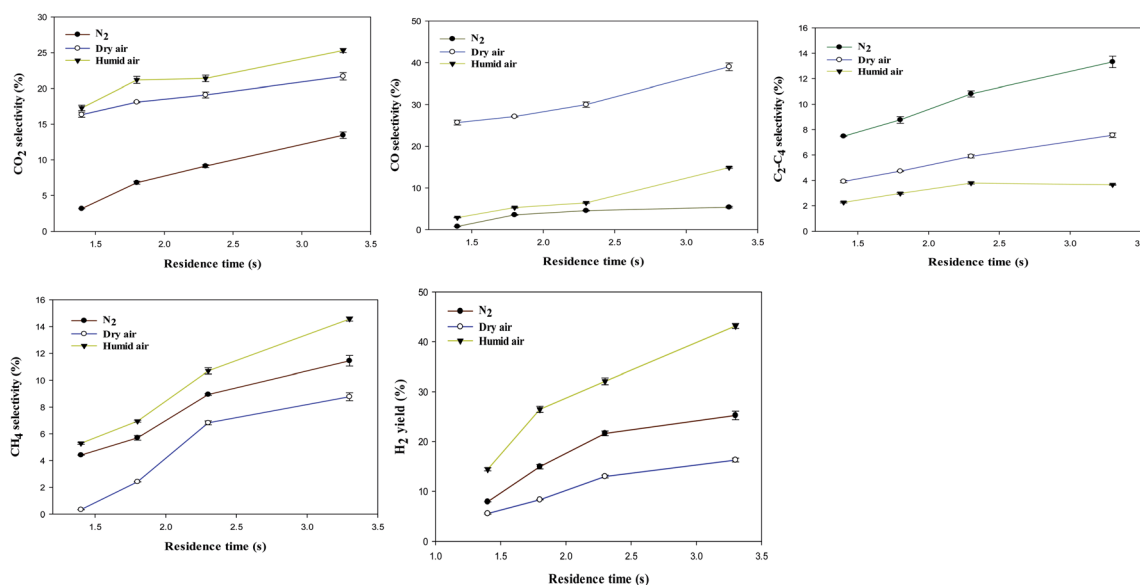


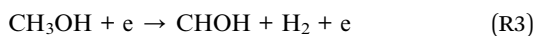
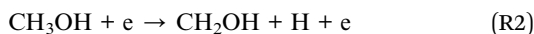
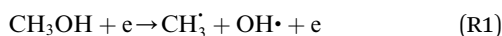
Fig. 7 (a) Effect of residence time on selectivity to  $CO_2$  in  $N_2$ , dry and humidified air (reaction conditions: temperature = ambient; concentration = 260 ppm; flow rate = 70–160  $ml\ min^{-1}$ ; power = 6 W, SIE = 2.3–5.1  $kJ\ L^{-1}$ , relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (b) Effect of residence time on selectivity to CO in  $N_2$ , dry and humidified air (reaction conditions: temperature = ambient; concentration = 260 ppm; flow rate = 70–160  $ml\ min^{-1}$ ; power = 6 W, SIE = 2.3–5.1  $kJ\ L^{-1}$ , relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (c) Effect of residence time on selectivity to  $C_2-C_4$  in  $N_2$ , dry and humidified air (reaction conditions: temperature = ambient; concentration = 260 ppm; flow rate = 70–160  $ml\ min^{-1}$ ; power = 6 W, SIE = 2.3–5.1  $kJ\ L^{-1}$ , relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (d) Effect of residence time on selectivity to  $CH_4$  in  $N_2$ , dry and humidified air (reaction conditions: temperature = ambient; concentration = 260 ppm; flow rate = 70–160  $ml\ min^{-1}$ ; power = 6 W, SIE = 2.3–5.1  $kJ\ L^{-1}$ , relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results). (e) Effect of residence time on selectivity to  $C_2-C_4$  in  $N_2$ , dry and humidified air (reaction conditions: temperature = ambient; concentration = 260 ppm; flow rate = 70–160  $ml\ min^{-1}$ ; power = 6 W, SIE = 2.3–5.1  $kJ\ L^{-1}$ , relative humidity = 24%, error bars represent the standard deviation  $\pm \sigma$  for 3 measurement results).



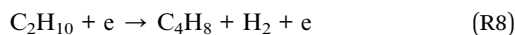
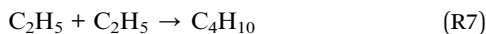
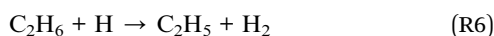
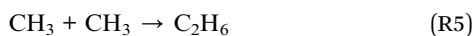
### 3.4 Mechanisms of methanol decomposition using NTP-plasma

In a dielectric barrier discharge (DBD) plasma, discharge occurs in three stages: breakdown, quasi-equilibrium, and non-equilibrium.<sup>39</sup> Non-equilibrium plasmas cause the formation of excited species, ions and radicals. The average electron energy in the DBD system is between 1 and 10 eV.<sup>30</sup> The excited species such as  $N_2$ ,  $N_2(A)$ ,  $N_2(A^3\Sigma_u^+)$ ,  $O_2$  and radicals (O, H and OH) could be generated through continuous collision with the energetic electrons produced in the DBD plasma reactor.<sup>37</sup> The plasma-assisted decomposition of VOCs in  $N_2$ , dry and humidified air carrier gases can be initiated in three pathways: electron-impact decomposition reactions  $e^*$ , collisions with excited species such as  $N_2$  and  $O_2$ , and reactions with gas-phase radicals, such as O, H or OH. The C–O, C–H, and O–H bond dissociation energies of  $CH_3OH$  are 3.638 eV, 4.291 eV, and 4.768 eV, respectively.<sup>40</sup> Therefore, electrons, excited species, and gas-phase radicals with energies above 3.638 eV could break the strong C–O bond in methanol, generating intermediates that are further converted to gaseous products such as  $CO_2$ , CO,  $CH_4$ ,  $H_2$ , and  $C_2$ – $C_4$  hydrocarbons.

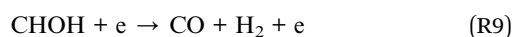
Methanol decomposes to species such as  $CH_3$ ,  $CH_2OH$ , and  $CHOH$  through electron-impacted reaction as shown in R(1)–R(3).<sup>41</sup>



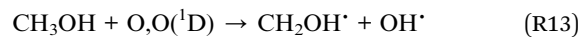
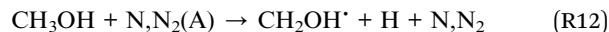
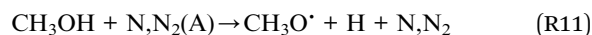
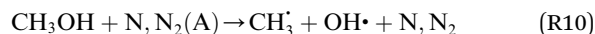
Once produced,  $CH_3$  can easily react with H radicals to form  $CH_4$  through hydrogenation reaction R(4).<sup>27</sup>  $CH_3$  can also dimerise to form longer hydrocarbons such as  $C_2H_6$ ,  $C_2H_5$ ,  $C_4H_8$ , and  $C_4H_{10}$  through hydrogenation and coupling reactions between the  $C_mH_n$  species at low temperatures, as shown between R(4)–R(8).



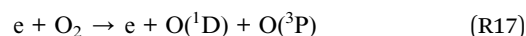
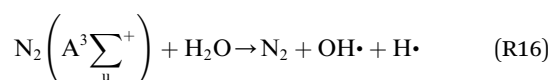
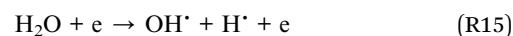
$CH_2O$  is unstable in NTPs,<sup>28</sup> and can be converted to CO and  $H_2$  via electron impact dissociation reaction, as shown in R(9).<sup>41</sup>



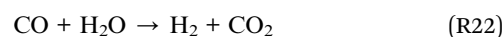
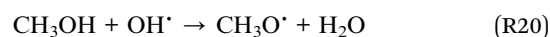
It has been proposed that the direct collision of methanol molecules with excited species and gas-phase radicals could open up a new decomposition pathway, as shown in R(10)–R(14).<sup>42</sup>



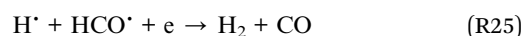
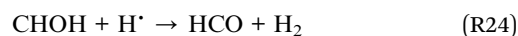
The addition of water vapour to non-thermal plasma DBD reactors provided new insights into the methanol decomposition pathway. Here, the radicals  $H$  and  $OH$  are generated through the electron impact dissociation and excitation reaction of  $H_2O$  molecules as shown in R(15)–R(18).<sup>3,43</sup>



The OH, O and H radicals generated can convert methanol to  $CO_2$ ,  $H_2$  and  $H_2O$  as shown in R(19)–R(22). It is important to note that the introduction of water vapour with a relative humidity of 24% at 20 °C increased  $CO_2$ ,  $CH_4$  and  $H_2$  and decreased CO and longer hydrocarbons selectivities as presented in Fig. 3(a)–(e).



The  $CH_3OH$  decomposition pathway R(21) is followed by  $H_2O$  gas shift reaction R(22) when water vapour is added to the DBD process, leading to increased  $CO_2$  selectivity and  $H_2$  yield.<sup>44</sup> The H radical produced through the dissociation of  $CH_3OH$  can recombined with the H radical generated from the dissociation of  $H_2O$  to form more  $H_2$ , as shown in R(23).



Another reason for the increased  $H_2$  is that during methanol conversion using non-thermal plasma,  $H_2$  is also produced through the reaction of  $CH_2O$  with H radical R(24), and HCO can further react with H radical to form  $H_2$  and CO R(25).<sup>27</sup> This agrees with this work's experimental findings, indicating that



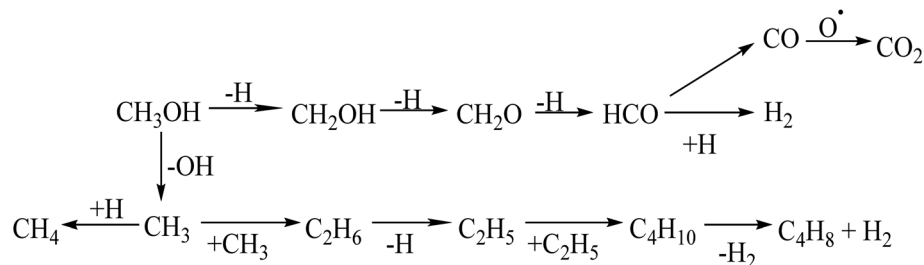
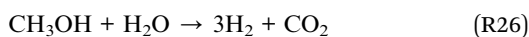


Fig. 8 Decomposition pathways of methanol.

H<sub>2</sub> yield increased with plasma power when water vapour with 24% relative humidity introduced the DBD system and CO decreased.

The interaction of H<sub>2</sub>O with CH<sub>3</sub>OH is also known to be a significant pathway for the production of H<sub>2</sub> and CO<sub>2</sub>.<sup>44</sup>



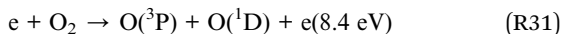
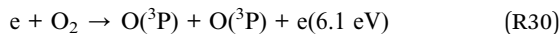
Tanabe *et al.*<sup>16</sup> also reported that, apart from methanol decomposition to H<sub>2</sub> and CO, as shown in R(21), there was another reaction pathway between H<sub>2</sub>O and CH<sub>3</sub>OH, leading to CO<sub>2</sub> and H<sub>2</sub> (see R(26)). In addition, water vapour increased the selectivity to CO<sub>2</sub>.<sup>45</sup> The O and OH radicals can oxidise CO to CO<sub>2</sub>, as shown in R(27) and R(28),<sup>46</sup> and hydrogen radicals can recombine to form H<sub>2</sub> (R29).<sup>47</sup>



Based on the analyses above, the methanol decomposition pathways are summarised in Fig. 8.

### 3.5 Ozone and NO<sub>x</sub> formation

Ozone is one of the main by-products formed in non-thermal plasma DBD abatement of VOCs using dry air. O<sub>3</sub> formation can be initiated in a DBD plasma *via* collisions between energetic electrons and oxygen molecules, as shown in R(30) and R(31).<sup>48</sup>



Furthermore, O<sub>3</sub> can also be generated through a three-body recombinations reaction of atomic oxygen O and molecular oxygen, as shown in R(32).<sup>49</sup> The third body M can be oxygen or nitrogen molecules in the dry air carrier gas.



Here, the influence of input power on ozone formation at constant CH<sub>3</sub>OH concentration (260 ppm) and residence time (3.3 s) in dry and humidified air carrier gases were studied. The

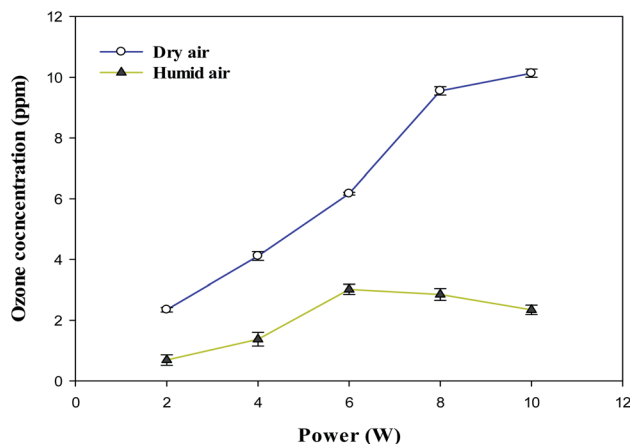
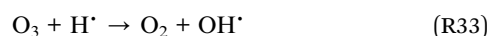
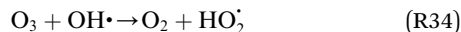


Fig. 9 Ozone concentration as function of input power (reaction conditions: temperature = ambient; concentration = 260 ppm; total flow rate = 70 ml min<sup>-1</sup>; residence time = 3.3 s; SIE = 1.7–8.6 kJ L<sup>-1</sup>; carrier gas = dry and humidified air, relative humidity = 24%, error bars represent the standard deviation ± σ for 3 measurement results).

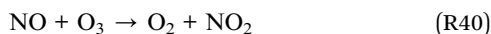
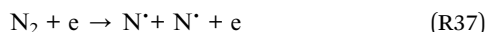
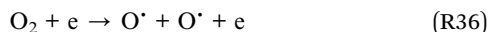
O<sub>3</sub> concentrations from the outlet of the DBD reactor were measured using the standard KI solution method as described by Yulianto *et al.*<sup>50</sup> The O<sub>3</sub> concentration as a function of input power using dry and humidified air carrier gases is presented in Fig. 9.

The ozone concentration increased with input power in dry air. The O<sub>3</sub> concentration increased from 2.4 ppm (2 W) to 10.2 ppm (10 W) at constant inlet methanol concentration (260 ppm) and residence time (3.3 s) in dry air. However, ozone concentration initially increases when the plasma power increases from 2 to 6 W and decreases when plasma power increases (8–10 W) in humid air plasma. The introduction of water vapour significantly reduced the ozone concentration at every point and kept it below 3 ppm. Water addition reduces the production of ozone due to the utilisation of O(<sup>1</sup>D) by H<sub>2</sub>O, the primary source of ozone formation.<sup>51</sup> H<sub>2</sub>O decreased the O<sub>3</sub> concentration by quenching the energetic electrons.<sup>52</sup> On the other hand, the O<sub>3</sub> concentration decreased due to an increase in direct interactions between O<sub>3</sub> and gas-phase radicals such as OH, H and HO<sub>2</sub> radicals. As a result, the O<sub>3</sub> destruction reactions can be summarised as follows: R(33)–R(35)<sup>51,53</sup>

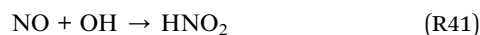




In the plasma-assisted decomposition of VOCs, the formation of  $\text{NO}_x$  is a significant health and environmental concern,<sup>54</sup> and decreased the efficiency of the abatement process.<sup>55</sup> In dry air plasma,  $\text{NO}_x$  can be formed *via* the electron impacted dissociation reaction of  $\text{N}_2/\text{O}_2$  as shown in R(36)–R(40).<sup>49,56</sup>



The excited  $\text{N}_2$  or metastable  $\text{N}_2$  species can be quenched/consumed by oxygen species to form ground state  $\text{N}_2$  and  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ).<sup>57</sup> In this work, the DBD outlet  $\text{NO}_x$  concentrations at steady state were measured using Gastec detector tubes (detection limit = 0.1 ppm).  $\text{NO}_x$  was not detected in any of the tested experimental conditions; hence, it is below 0.1 ppm and is therefore not at problematic levels. This could be due to more OH radicals in the decomposition process generated from the electron impact dissociation reaction of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ , which provides more OH radicals in the plasma discharge, resulting in the conversion of VOC intermediates to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2$ .<sup>49</sup> Furthermore, the OH radicals can oxidise NO to form  $\text{HNO}_2$  as shown in R(41).<sup>58</sup>



Since OH and H radicals can shut down the ozone containing pathway as shown R(33) and R(34), it is possible to eliminate or reduce  $\text{NO}_x$  concentrations to below 0.1 ppm by operating the DBD reactor at low flow rates and low plasma power or by the introduction of water vapour with a relative humidity of 24%. It is important to note that operating a DBD reactor at very flow rates and low plasma power can increase the specific input energy and residence time which can affect the product distribution.

## 4. Conclusions

A dielectric barrier discharge (DBD) plasma system was used to remove methanol from gas streams at ambient temperature and pressure. The system was studied with carrier gases of dry air, humidified air and nitrogen, to determine the respective roles of  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$ . The plasma power (2–10 W),  $\text{CH}_3\text{OH}$  inlet concentration (260–350 ppm), and residence time (1.4–3.3 s) were varied for each gas. The removal efficiency of methanol increased with input power and residence time regardless of the carrier gas used and decreased with increasing  $\text{CH}_3\text{OH}$  inlet

concentration. The methanol removal efficiency increased in the series:  $\text{N}_2 < \text{humidified air} < \text{dry air}$ . In dry air plasma, the findings suggest that the action of O radicals dominates the methanol decomposition. Methanol was converted to  $\text{CO}_2$ ,  $\text{H}_2$ , and various hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_4\text{H}_{10}$  and  $\text{C}_4\text{H}_8$ ). The  $\text{N}_2$  carrier gas exhibited the highest selectivity to  $\text{C}_2$ – $\text{C}_4$  hydrocarbons due to the absence of O and OH, which could decompose hydrocarbons.  $\text{CO}_2$  and CO production were lower in  $\text{N}_2$  than the other carrier gases, again because of the absence of O and OH radicals, which resulted in higher selectivity to hydrocarbons. The introduction of  $\text{H}_2\text{O}$  (RH = 24% at 20 °C) into the carrier gas reduced the removal efficiency, but significantly improved selectivity toward  $\text{CO}_2$  and  $\text{H}_2$ . There were various other benefits to the presence of  $\text{H}_2\text{O}$ , including significant reductions in both  $\text{O}_3$  and CO.

The reaction mechanisms for the various decomposition pathways of methanol have been hypothesised, including electron impact decomposition reaction, direct collision with excited species, and reaction with gas-phase radicals such as O, H or OH. The role of the OH radical can largely explain the effects of  $\text{H}_2\text{O}$  inclusion. Furthermore, no solid residue was formed in the DBD reactor in all the carrier gases. Overall, the dry air plasma exhibited the highest removal efficiency, but the humidification, although it decreased the removal efficiency, greatly reduced various typically unwanted species, including CO and  $\text{O}_3$ , whilst increasing the more desired (less toxic) species, such as  $\text{CO}_2$  and  $\text{H}_2$ .

## Conflicts of interest

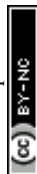
There are no conflicts to declare.

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