CO₂ Decomposition to CO in the Presence of up to 50% O₂ using a Non-Thermal Plasma at Atmospheric Temperature and Pressure

Kui Zhang, Adam Harvey

School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

Abstract

CO₂ can be converted to the more reactive species, CO and O, by non-thermal plasmas (NTPs) even in atmospheres containing significant quantities of O₂. The conversion of CO₂ was 15 - 21%, when the O₂ concentration was in the range 0 - 20% (remainder CO₂). At 20% the conversion began to decline, falling to ~10% at 50% O₂. These conversions would require a few thousand K in conventional “thermal” chemistry, in the absence of a catalyst, but here they were achieved at ambient pressure and temperature. The NTP reactor used was a dielectric barrier discharge (DBD) design, packed with BaTiO₃ spheres. The concentration of O₂ was varied between 0 and 50% in CO₂, at temperatures below 373K and atmospheric pressure, at a residence time of 4.2s. This discovery could open up new routes for direct CO₂ decomposition to CO and O₂, where the presence of O₂ would have been assumed problematic. This “activation” of CO₂ may open up a range of possible chemistries for the use and sequestration of CO₂ as CO is more reactive. It may also open up opportunities for the use of CO₂ as an oxidant, i.e. a source of the O radical.

Key words: Non-thermal plasma; CO₂ conversion; dielectric barrier discharge (DBD); BaTiO₃

1. Introduction

Carbon dioxide is the principal “greenhouse gas”. Anthropogenic CO₂ emissions, from combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, certain industrial processes and land-use change, are responsible for the concentration of CO₂ increasing in the atmosphere, particularly over the last 200 years.[1] In addition to the adverse environmental effects, CO₂ emission represents waste of a natural carbon source. The conversion of CO₂ to other high value products has been the subject of intensive study in recent decades[2-5]. However, the intrinsically low reactivity of CO₂ has made economically viable conversion to such products difficult. Therefore, the use of CO₂ as a chemical feedstock has been limited to a few industrial processes: synthesis of urea and its derivatives, salicylic acid and the production of certain carbonates (e.g. the carbonation reaction of CaO for CaCO₃ production in inorganic chemical process). As one of the key challenges in sequestering CO₂ by chemical means is that it is not very reactive, a more convenient initial step in the process for making a useful product from CO₂ is to convert it into CO and O₂.

$$(\Delta H_{298K} = +282.8\text{kJ/mol} ; \Delta G_{298K} = +257.2\text{kJ/mol})$$

However, this is a thermodynamically unfavourable reaction. It is endothermic and requires a high temperature for a significant equilibrium conversion and rate. Thermal decomposition of CO₂ is usually not significant until over 2000K according to thermodynamic equilibrium calculation.[6] It is difficult to decrease the temperature from over 2000K to low temperatures very quickly to quench the reverse reaction ($CO + 0.5O_2 = CO_2$) of CO₂ decomposition. Furthermore, the high temperature reaction processing (>2000K) for CO₂ decomposition to CO

and O₂ may lead to higher capital costs on the special material selection for high temperature reactor design/manufacture, process control, and maintenance.

However, this may be possible using non-thermal plasmas.

Non-thermal plasma (NTP) technology is a promising alternative to the conventional thermal/catalytic chemical process operating at high temperatures. The mean “electron temperature” in such systems is between 10,000 and 100,000 K (average electron energy: 1 - 10 eV), even though the actual gas temperature is near room temperature[7-9].

The energy of some electrons, due to the high energy tail of Maxwellian or Druyvesteyn electron energy distribution function (EEDF)) in a typical DBD plasma, will be higher than the chemical bond dissociation energy of the gas molecules (5.5eV for CO₂)[10]. Therefore, chemical reactions can be initiated at low temperatures. CO₂ decomposition to CO and O₂ has been investigated with various NTP systems[11]. CO₂ decomposition has been realized in microwave plasmas at various pressure[12-15]. In a microwave plasma, the dissociation of CO₂ is based on the excitation of the vibrational levels of CO₂[8, 15]. In a radio-frequency (RF) plasma at reduced pressure, the conversion of CO₂ to CO has been shown to reach about 90%, but the energy efficiency only reached a maximum of 3%[16]. In a DC corona plasma operated in both positive and negative polarities, the CO₂ conversion was lower in positive polarity discharge than that in negative polarity discharge[17]. DBD plasmas have been applied for CO₂ decomposition at low temperatures and ambient pressure[18-23]. In a DBD plasma, the dissociation of CO₂ is dominated by electron impact reactions[19, 24, 25]. The mean electron energy is an important factor affecting the activation of molecules (excitation, dissociation, or ionization) in a DBD plasma reactor[24]. In a conventional DBD plasma, the applied voltage, discharge gap and the gas density can affect the reduced electric field (Td) and the mean

electron energy[26]. An increase in the reduced electric field (Td) can lead to an increase in the mean electron energy, which can lead to higher CO₂ conversion.

Introducing barrier pellets (i.e., glass or BaTiO₃) into the discharge gap in a DBD plasma reactor creates a packed bed plasma reactor. The pellets can refract the electric field, making the local electric field non-uniform and stronger than the externally applied field by a factor of 10 to 250 depending on the shape, porosity, and permittivity of the beads[8]. The local electric field strength near the contact points between the beads, and the beads and quartz tubes can be 10-10⁴ times higher than that in the void between the beads, depending on the contact angle, curvature, and dielectric constant of the packing pellets[27-30]. An increase in the dielectric constant of the packing materials from 1 to 1000 can result in an increase in the electric field strength by a factor of 1-1.5. After this, any further increase in the permittivity of the packing materials does not enhance the electric field strength[30].

Packed bed plasma reactors have previously been applied for ozone generation and air pollution control technologies[30]. In a DBD plasma reactor packed with BaTiO₃ and glass balls (1 mm in diameter), Mei and co-workers demonstrated that adding BaTiO₃ beads into a DBD plasma enhanced the average electric field and mean electron energy (by a factor of 2) which contributed to the enhancement of CO₂ conversion[31]. The CO₂ decomposition was shown to be increased by: the increased permittivity of the packing material; the size of the packing beads, use of a stainless steel electrode to plasma, and the introduction of a Ni/SiO₂ catalyst into the BaTiO₃ packed bed[32]. Yu and co-workers[33] demonstrated that the dielectric properties and morphology of packing dielectric pellets (0.42-0.84 mm) played important roles in CO₂ decomposition due to their influence on the electron energy distribution in the plasma reactor. Recently, Xu et al^{34,35} reported that adding certain carrier gases (20% CO₂ + 80% N₂, or 20% CO₂ + 80% Ar) can enhance the average electron energy, and promote CO₂

decomposition in a BaTiO₃ packed bed plasma reactor. Previous studies demonstrate that the permittivity, size and the chemical property of packing materials, the reactor configuration, N₂ or Ar in gas mixture, and catalysts affect CO₂ decomposition in packed bed plasma reactors significantly at low temperatures and ambient pressure[21-23, 31-34]. Generally, BaTiO₃ beads can generate higher average reduced electric field (Td) than glass balls, and hence, higher mean electron energy and CO₂ conversion in the packed bed DBD plasma reactor.

In this research, the aim was to investigate whether the presence of significant levels of O₂ would affect the decomposition of CO₂, in an attempt to prove the theory that the back-reaction ($\text{CO} + \text{O} \rightarrow \text{CO}_2$) would be negligible, as the radicals would be mopped up by the $\text{O} + \text{O} \rightarrow \text{O}_2$ reaction. The “self-reaction” should be much faster, but the back reaction of the CO with the O₂ would not be significant at these temperatures (explained in more detail in 3.3).

2. Experimental section

Figure 1, below, shows a schematic of the experimental set-up. The coaxial DBD reactor used consists of two coaxial quartz tubes one inside the other. The outer quartz tube had a 32 mm inner diameter (ID) and was 300 mm in length. The inner tube had a 17 mm outer diameter (OD). The thickness of the quartz tubes was 1.5 mm. Hence, the gap between the two tubes was 7.5 mm. One stainless steel mesh electrode was fixed on the inner surface of the internal quartz tube, and the other was fixed on the external surface of the external quartz tube. The length of the stainless steel mesh electrodes was 17.3 mm, which gave a plasma volume of about 100 cm³ in the reactor. The discharge volume of the reactor was filled with 100 cm³ of BaTiO₃ balls (diameter: 3mm; permittivity: ~1000). The void volume of the discharge volume of the reactor was 35 cm³.

Figure 1 Set-up of the DBD Non-thermal Plasma Reactor

The plasma power source unit could provide 0-150W by adjusting the amplitude of the applied voltage. In the experiment, an alternating sinusoidal high voltage of up to 20 kV amplitude (peak-to-peak) and about 25 kHz frequency was applied to the two stainless steel mesh electrodes. The voltage signal was monitored using a high voltage probe (P6015A), and the current signal in the plasma was detected using a 1Ω resistor (100W) in the return circuit. A capacitor (46 nF) was connected into the return circuit for the determination of the charge signal. The plasma power dissipated in the discharge was calculated by integrating the product of voltage and current recorded by a TPS 2014 Four Channel Digital Storage Oscilloscope (Tektronix). In addition, the oscilloscope was also used to record the voltage-charge Lissajous diagrams. The temperature of the wall temperature of the BaTiO_3 packed plasma reactor was measured with a RS PRO Infrared Thermometer (resolution: 0.1K). The effluent gas temperature (measured by a thermocouple positioned 1 cm in the downstream of the plasma zone) was $<363\text{K}$ in the experiment.

The feed gases, CO₂ (purity: >99.99%, BOC Industrial gases, UK) and O₂ (purity >99.99%, BOC Industrial gases, UK), were introduced into the reactor from high pressure gas bottles via mass flow controllers (MFCs), admitting a total gas flow of 25 to 100 mL/min. A back pressure valve at the inlet of the DBD reactor was used to monitor the pressure in the reactor. The reaction products (CO and O₂) were analysed online using a Varian 450-GC equipped with a thermal conductive detector (TCD) and with 3 columns (column one: HAYESEP Q 0.5m x1/8" x 2.0 mm, Ultimetel (#CP81073); column two: HAYESEP T 0.5m x1/8" x 2.0 mm, Ultimetel (#CP81072); and column three: Mol sieve 13X 1.5m x1/8" x 2.0 mm, Ultimetel (#CP81071) to detect permanent gases (CO₂, CO and O₂). The Varian 450-GC was calibrated with standard gas samples (including various concentrations of CO₂, O₂, CO, and N₂) purchased from Scientific and Technical Gases Ltd. All measurements were carried out at stable reaction conditions and repeated 3 times.

The mass balance of the reaction was obtained by adding a constant flow of N₂ (6.0 mL/min) (oxygen free, purity >99.998, BOC Industrial gases, UK) as reference gas to the exit of the reactor in order to monitor the change of volume flow as a consequence of plasma chemical reactions. In this study, the carbon balance ($100 \times \text{moles of CO} / (\text{moles of CO}_2_{(in)} - \text{moles of CO}_2_{(out)})$) was always found to be higher than 98%.

The conversion of CO₂ is defined as:

$$CO_2 \text{ Conversion } (\%) = \frac{CO_{2(input)} \text{ (mol./s)} - CO_{2(output)} \text{ (mol./s)}}{CO_{2(input)} \text{ (mol./s)}} \times 100$$

An optical spectrometer (USB2000+, Ocean Optics) was used to quantify the ozone concentration in the effluent. The UV absorption peak at the wave number of 254 nm was

selected, and the ozone concentration was calculated according to the Beer-Lambert law. In this study, the cell length (l) was 1 cm. The obtained ozone concentration (mol/L) was converted into parts per million (ppm). All measurements were repeated twice.

The specific input energy (SIE) is defined as:

$$SIE \text{ (kJ/L)} = \frac{\text{Plasma power (kW)}}{\text{Feed gas flow rate (L/s)}}$$

In this study, for a 95% CO₂ and 5% O₂ gas mixture, at a constant total flow rate of 50 mL/min (residence time: 42 s), a power from 46 to 106 W was applied, resulting in the specific input energy (SIE) in the range of 55.2–127.2 kJ/L. Furthermore, at a constant input power of 86 W, the same gas mixture was used, with a flow rate between 50 and 100 mL/min (residence time: 42–21 s), the SIE was in the range of 51.6 – 103.2 kJ/L.

The energy efficiency of plasma assisted CO₂ decomposition in O₂ is defined as:

$$\text{Energy efficiency (mmol/kJ)} = \frac{CO_{2(input)} \text{ (mmol/s)} - CO_{2(output)} \text{ (mmol/s)}}{\text{Plasma power (kW)}} \times 100$$

3. Results and discussion

3.1 Influence of O₂ concentration

3.1.1 Effect of O₂ concentration on CO₂ reduction

Figure 2, below, shows the effect of O₂ concentration on CO₂ decomposition. Increasing O₂ concentration in the CO₂ stream resulted in a steady decrease in CO₂ conversion. However, the decrease in CO₂ conversion when increasing the O₂ from 0 to 20% was only from 16.1 to 15.1%, which was within experimental error. Clearly, the dependence is very different from conventional chemistry, where the equilibrium would be significantly shifted to the reactant side by such a significant increase in O₂. Beyond 20% a significant decrease was observed, but, even at 50% O₂ concentration in the CO₂ stream, a significant CO₂ conversion (11%) was achieved. Note that carbon formation was not observed, indicating that the Boudouard reaction ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) and the decomposition of CO to carbon and O₂ ($\text{CO} = \text{C} + 0.5 \text{O}_2$) were negligible.

Figure 2 Influence of O₂ concentration on CO₂ Conversion

(Total flow rate: 50 mL/min (residence time: 4.2 s); plasma power: 86W; pressure: 1 bar; wall temperature: ~373K; frequency: around 25 kHz; SIE: 103.2 kJ/L)

Carrier gases influence CO₂ conversion in plasmas, as they can essentially act as catalysts, via their promotion into excited electronic states. Previous experimental and computational studies have shown that introducing N₂ into the CO₂ gas stream can enhance the CO₂ conversion because the meta-stable N₂ molecules can promote the CO₂ decomposition in a DBD plasma reactor. [35] However, undesirable compounds, such as N₂O, NO and NO₂, are also produced at concentrations up to a few 100 ppm. In a BaTiO₃ packed plasma reactor, the CO₂ conversion has been shown to increase with an increase in the concentration of N₂ or Ar at the SIE of 36 kJ/L[34, 36]. The dilution of CO₂ with N₂ (20% CO₂ + 80% N₂) or Ar (20% CO₂ + 80% Ar) may reduce the breakdown voltage, which in turn affects the EEDF and average electron temperature in the plasma[34]. The dilution of CO₂ with Ar (20% CO₂ + 80% Ar) can increase the average electron temperature and the electron density, which can result in increased CO₂ dissociation[36]. In this study, we instead diluted the CO₂ with O₂, which is one of the reaction products of plasma-assisted CO₂ decomposition (as shown in R1). The effect of O₂ on CO₂ decomposition is different from that of N₂ or Ar. In addition to plasma-promoted CO₂ dissociation, plasma can excite and convert O₂ molecules into O radicals, which can increase the concentration of O radicals in the plasma reactor. Therefore, according to chemical kinetics, the reverse reaction of CO₂ dissociation (R6) could be promoted in the gas mixture of CO₂ and O₂ leading to a decreased CO₂ conversion by increasing the O₂ concentration. However, clearly this did not occur to a significant extent. The reasons for this are discussed in detail in section 3.3.

3.1.2 Effect of reaction time on O₃ concentration

In a gas mixture of CO₂ and O₂, NTP can lead to the formation of ozone. At the beginning of the reaction, higher O₃ concentrations were observed in the effluent at lower wall temperatures.

O₃ concentration increased with increasing O₂ concentration in the feed gas, as might be expected. However, the O₃ concentration decreased significantly with time, as the system stabilised and the wall temperature increased. After a stabilisation time of 10 min, the reactor wall temperature remained steady at about 373K, and the ozone concentration stabilised at a level below 100ppm.

Figure 3 depicts the effect of time on O₃ concentration and reactor wall temperature in a 20% O₂ + 80% CO₂ gas mixture. When the plasma was switched on (at 2 min), the O₃ concentration increased significantly (from 0 to about 6500 ppm). The wall temperature's response was much slower. Clearly, as the wall temperature rises, the O₃ drops significantly. Here, the O₃ concentration stabilized at about 40 ppm after 10 min, as the wall temperature of the reactor stabilized at 373K.

Figure 3 Influence of reaction time on ozone concentration

(Total flow rate: 50 mL/min (residence time: 4.2 s); O₂ concentration in feed gas: 20% (mol. %); plasma power: 86W; pressure: 1 bar; frequency: around 25 kHz; SIE: 103.2 kJ/L)

O₃ formation from DBD plasma-assisted CO₂ decomposition has been reported in DBDs[25, 37] and BaTiO₃ packed-bed plasma reactors[34, 36]. In a DBD-assisted CO₂ decomposition, CO, O₂, and O₃ were the main products. The CO:O₂ ratio was almost stoichiometric, at 2:1, indicating that there were no significant side reactions or by-products, and the ozone has been observed up to 750 ppm[37]. In a BaTiO₃ packed bed plasma reactor, the O₃ concentration has been shown to increase with increasing Ar concentration. The highest O₃ concentration (about 100 ppm) was achieved at an SIE of 18 kJ/L and Ar concentration of 80%.[34] Further increase in the SIE resulted in lower O₃ concentration. This study was carried at SIE of 103.2 kJ/L in the presence of O₂ (from 0 to 50%), which was higher than that (up to 36 kJ/L) reported by Xu et al[36]. Furthermore, the wall temperature increased from 293 to about 373K after running the reactor for 8 min. Although high concentrations of O₃ (up to 6500 ppm) were initially formed at the lower wall temperatures, the higher SIE and consequent higher wall temperature led to O₃ decomposition, and a much lower steady state O₃ concentration (~40ppm).

3.2 Influence of specific input energy (SIE)

The important variables in this system were plasma power and feed gas flow rate. Adjusting either plasma power or feed gas flow rate can alter the SIE in the plasma reactor. The gas flow rate not only affects the SIE at constant power, but also determines the residence time of the feed gas in plasma. Figure 4 shows the influence of SIE on CO₂ conversion by varying the input power and by varying the feed gas flow rate. It is important to mention that there is no significant difference in CO₂ conversion between the two cases. In general, an increase in the SIE leads to an increase in CO₂ conversion, indicating that CO₂ decomposition is an energy-dependent reaction in the presence of O₂ under these conditions.

Figure 4 Influence of specific input energy (SIE) on CO₂ Conversion

(Gas composition: 5% O₂ + 95% CO₂; pressure: 1 bar; reactor wall temperature: ~373K; frequency: around 25kHz)

In this reactor, an increase in the plasma power or SIE was realized by increasing the input voltage and discharge current at the constant gas flow rate (residence time 42s) and atmospheric pressure. [Increasing the SIE can result in an increase in the CO₂ conversion.](#) On the other hand, decreasing the gas flow rate can lead to an increase in SIE and the residence time at constant plasma power, which can lead to higher CO₂ conversion. In addition to this, it has been suggested that increasing the residence time may increase the charge transferred per half cycle of the applied voltage, which could promote the electron-induced CO₂ decomposition. [36] Based on the above discussion, in addition to SIE, the CO₂ conversion in the presence of O₂ could be further optimised by optimising the gas composition (add other gas, i.e, N₂, or Ar), residence time, plasma power and property(i.e., frequency, waveform), catalyst, and reactor configuration.

3.3 Mechanism of CO₂ conversion in O₂

In an NTP, chemical reactions are initiated by the electric field/energetic electrons rather than high temperatures. As mentioned earlier, the average electron energy is in the range of 1-10 eV in a DBD plasma[7, 9, 26]. Introducing BaTiO₃ balls into the discharge gap can reduce the breakdown voltage, enhance the electric field strength and mean electron energy in a packed bed DBD plasma reactor.[8, 30, 31] Especially, an increase in the average electron energy can increase the proportion of high-energy electrons in the tail of the Maxwellian EEDF. Xu et al reported that the average electron energy in CO₂ plasma was 5.9 eV at the reduced electric field of 200 Td in a BaTiO₃ packed bed plasma reactor, and it increased with increasing SIE. [34, 36] At the SIE of 36kJ/L, emission from electronically excited states of CO₂⁺ was detected by an optical emission spectroscopy (OES), which suggested that the electrons in the high energy tail (higher than the ionization energy of CO₂: 13.8 eV) of EEDF was non-negligible[34].

The effect of reduced electric field (E/N) and O₂ concentration on the average electron energy and electron energy distribution function (EEDF) was calculated using Bolsig+[38]. An increase in the reduced electric field (E/N) can lead to an increase in the average electron energy in the plasma (supporting material S-Figure 1). Adding O₂ can result in an increase in the average electron energy. For example, increasing the O₂ concentration from 0 to 50% in the gas mixture leads to an increase in the average electron energy from 3.66 to 4.03 eV at 100 Td (supporting material S-Figure 2). An increase in the average electron energy can increase the portion of high energy electrons as shown in the high energy tail of EEDF (supporting material, S-figure 3-4). This should increase the CO₂ conversion. However, this can also lead to the

activation of O₂ for the formation of excited state O₂ molecules and O (³P, ¹D) species at the same time, which can result in the reverse reaction of CO₂ decomposition.

The electrons in the higher energy tail (higher than the bond dissociation energy of CO₂: 5.5 eV) of the EEDF can initiate direct electron-impact dissociation of CO₂.

In addition to the electron impact CO₂ dissociation as described in R2, the CO₂ dissociation by electron impact ionization (R3) followed by electron-ion dissociative recombination(R4) could have contribution to the decomposition of CO₂. However, the contribution of this reaction channel (R3 and R4) to CO₂ decomposition is not significant because of its high ionization energy (13.8 eV).

The O radicals and CO species are formed by above processes during the discharge. The chemical kinetics of the following reactions will also influence the final CO₂ conversion and product distribution under the NTP reaction conditions.

$$(k_1 = 5.82 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}) [39]$$

$$(k_2 = 4.44 \times 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}) [40]$$

Where M represents the third body in the reaction.

As shown in R5 and R6, the O radical can either react with another O radical to form O₂, or react with CO to form CO₂, which would lower CO₂ conversion. The reactant (CO, O) concentrations and the rate constant are important factors affecting the reaction rate of above reactions (R5 and R6). In pure CO₂ dissociation, the concentration of O equals to the concentration of CO. The effective rate constant at the reaction temperature of 373 K for the 3 body reaction of O + O + M ($k_1 = 5.82 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$) [39] is 2 orders of magnitude larger than that of O + CO + M ($k_2 = 4.44 \times 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$) [40]. Therefore, the formation of O₂ from O radicals should prevail over that of CO₂ from O and CO.

When O₂ is added to the gas stream, O species in the electronically ground state O(³P) and excited state O(¹D) can be generated from the excited state of O₂ ($A^3\Sigma_u^+$, $B^3\Sigma_u^-$) in an NTP.[24] The energy threshold for the formation of O₂ ($A^3\Sigma_u^+$), which can produce O (³P) + O (³P), is about 6 eV, is lower than that for the formation of O₂ ($B^3\Sigma_u^-$) (8.4 eV) which can produce O (³P) + O (¹D). [8] Therefore, the concentration of O (¹D) is lower than that of O (³P) in this plasma reactor. Formation of these O(³P) and O(¹D) species may increase the overall concentration of O, and hence the reaction rate of R5, which lower CO₂ conversion at higher O₂ concentrations in the gas stream. Moreover, O₃ produced in the gas mixture may contribute to the oxidization of CO to CO₂.

3.3.1 Effect of O (¹D)

The excited state O(¹D) can oxidize CO to CO₂ by a 2nd order reaction (R7) leading to a lower CO₂ conversion:

$$(k_3 = 8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) [41]$$

However, the $O(^1D)$ species can be consumed/quenched by collisions with O , O_2 , and CO_2 in the plasma reactor (R8-R10). For the 2nd order reactions (R7-R10), the rate coefficient of R 8-R10 is comparable with that of R7. As show in Figure 2, the CO_2 conversion was 15.1% (gas composition: CO : 11.3 %, CO_2 : 64.2%, O_2 : 24.5%, O_3 : 41 ppm) when the O_2 concentration was 20% in the feed gas. The ratio of the reaction rate of R10 to R7 (R10:R7) is 17.9:1, and that of R9 to R7 (R9/R7) 1.04:1. Therefore, the probability of $O(^1D)$ participating in the oxidation of CO (R7) is significantly decreased due to the competing reactions (R8-R10).

$$(k_4 = 8.00 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) [42]$$

$$(k_5 = 3.83 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) [43]$$

$$(k_6 = 2.52 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) [41]$$

3.3.2 Effect of ozone

The O species ($O(^3P, ^1D)$) can react with O_2 molecules to form O_3 via a 3rd order reaction (R11). [8, 9, 24]

$$(k_7 = 5.8 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}) [39]$$

The reactor temperature and the concentration of O radicals influence O₃ stability/concentration significantly.[7, 8, 26] At 373K, the rate of O₃ decomposition (R12) is significantly faster than that of O₃ formation (R11).[8]

$$(k_8 = 6.5 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) [44]$$

Furthermore, the concentration of O radicals clearly affects O₃ formation. When the relative concentration of O/O₂ is higher than 0.3-0.5%, the energy efficiency of O₃ formation decreases significantly, because the O radical can decompose O₃ and convert it to O₂ (R13). [8]

$$(k_9 = 3.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) [45]$$

O₃ may also oxidize CO under plasma conditions. The reaction between O₃ and CO (R14) is a 2nd reaction.

$$(k_{10} < 4 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) [46]$$

However, the ratio of the effective rate constant for the thermal decomposition of O₃ (R12) ($k_8 = 6.5 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) to that for the O₃ oxidation of CO (R14) ($k_{10} < 4 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (R12:R14) is about 163:1 at 373 K. Moreover, the rate coefficient for the O radical-induced decomposition of O₃ (R13) ($k_9 = 3.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is 11 orders of magnitude larger than that of the O₃ oxidation of CO (R14) ($k_{10} < 4 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

¹). Hence, it is important to note that O₃ concentration at the stable reaction condition was only about 40 ppm (as depicted in Figure 3). Therefore, the contribution of CO oxidization by O₃ (R14) is very little due to the fast decomposition of O₃ and its low concentration under reaction conditions.

3.3.3 Effect of O radical

The reaction rate of R5 and R6 can be described as equation 1 and equation 2, respectively.

$$Rate_5 = 5.21 \times 10^{-35} \times e^{7480/RT} \times [O]^2[M] \quad (\text{Equation 1})[39]$$

$$Rate_6 = 5.43 \times 10^{-33} \times \left(\frac{T}{298}\right)^{-1.5} e^{-20950/RT} \times [CO][O][M] \quad (\text{Equation 2})[40]$$

(M represents the third body)

Temperature is an important factor affecting above reactions. At 373K, the reaction rate of R5 and R6 can be converted to:

$$Rate_5 = 5.82 \times 10^{-34} [O]^2 [M] \quad (\text{Equation 3})$$

$$Rate_6 = 4.44 \times 10^{-36} [CO][O][M] \quad (\text{Equation 4})$$

(M represents the third body)

In equation 1-4, the CO is from CO₂ dissociation, and the O species from CO₂ dissociation and O₂ decomposition under plasma conditions when O₂ is added to the CO₂ gas stream. An increase in O₂ concentration in the feed gas can lead to an increase in the O radical concentration in the plasma reactor. Therefore, an increase in O₂ concentration can increase the reaction rate of R6(equation4), which can result in lower CO₂ conversion. However, the

efficiency of the combination of O with CO (R6) is decreased due to the competing reaction(R5). As described in equation 5, the rate ratio of R5 to R6 (Rate₅/Rate₆) increases with an increase in O concentration (equation 5). Therefore, CO₂ conversion/reduction to CO and O₂ could be expected even at higher O₂ concentrations in the gas stream under NTP reaction conditions.

$$\frac{Rate_5}{Rate_6} = 1.31 \times 10^2 \times \frac{[O]}{[CO]} \quad (\text{Equation 5})$$

According to literature[8, 47], O(³P, ¹D) species might react with CO₂ to produce CO and O₂ (R15 and R16). However, we did not observe the obvious effect of these O(³P, ¹D) species on CO₂ decomposition/reduction. As show in Figure 2, the CO₂ conversion only increased slightly from 16.1 to 16.7% when the O₂ concentration was increased from 0 to 5% in a CO₂ stream, which was within the experimental error.

NTPs can circumvent the thermodynamic and kinetic limits of conventional “thermal” CO₂ decomposition/reduction in the presence of O₂ by opening up new reaction pathways via radicals and excited species etc This is apparent even at high concentrations of O₂ (up to 50% in this study). From a chemical kinetics point of view, the effectiveness of the reverse reaction of CO₂ decomposition (R6, R7, R14) i.e. formation of CO₂ form CO and O, which would lower

CO₂ conversion is reduced by a range of reactions (R5, R8-10, R12-13) competing for the O radical.

3.4 Energy Efficiency

As depicted in Figure 5, the energy efficiency of CO₂ decomposition to CO and O₂ in the presence of O₂ decreases with increasing O₂ concentration in the feed gas mixture. Previous research work demonstrated that introducing carrier gas (N₂ or Ar) into CO₂ can decrease the energy efficiency of CO₂ plasma decomposition in both DBD and BaTiO₃ packed bed plasma reactors, and the effect increases with increasing the fraction of the carrier gas, [34, 35, 49] which is similar to our results. These carrier gas molecules can be converted into active species (through electron excitation, ionization or dissociation) that promote CO₂ dissociation in plasma. However, in this study, the carrier gas (O₂) is one of the products of CO₂ decomposition. O(³P, ¹D) species and O₃ can be formed in the gas mixture, which can promote the reverse reaction of CO₂ reduction under plasma conditions. At the same time, the recombination of these O species and the decomposition of O₃, the de-excitation of O(¹D) species can reduce the efficiency of the reverse reactions of CO₂ decomposition. As shown in Figure 5, increasing O₂ concentration from 0-5% decreased the energy efficiency negligibly.

Figure 5. Influence of O₂ concentration on the energy efficiency of CO₂ reduction

(Total flow rate: 50 mL/min (residence time: 42 s); plasma power: 86W; pressure: 1 bar; frequency: around 25kHz; SIE: 103.2 kJ/L)

Energy efficiency is a major concern for any plasma-assisted reaction. Compared with the results in literature[15, 31-36], it is possible to further enhance the energy efficiency of CO₂ dissociation in the presence of O₂ by optimizing the DBD reactor configuration, the reaction parameters (such as plasma power, gas flow rate, wall temperature), and introducing a proper dielectric barrier material or catalyst into the plasma reactor. Furthermore, the energy efficiency of this method can be improved by harvesting and using the heat energy released from the DBD plasma reactor.

In a DBD plasma, in addition to being used in excitation, ionization, and dissociation of molecules, more than 60% of the plasma power converts to heat in plasma assisted steaming reforming of methane due to the dielectric heating, the recombination reactions and quenching

collisions [50, 51]. An energy balance analysis shows 2.2% of the input energy goes into CO₂ decomposition. Hence, most of the energy leaves the reactor in the form of heat, by convection (~71%) and radiation (~22%) from the outer surface, based on simple calculations. Approximately 5% of the input energy was consumed by the electric device.

It is suggested that the energy of some electrons, especially the lower energy fraction (<5.5 eV) of EEDF in the BaTiO₃ packed DBD plasma, do not make a significant contribution to the electron impact dissociation of CO₂. [10] A substantial fraction of energy supplied to the plasma reactor leads to vibrational excitation of CO₂ and carrier gas molecules (i.e., Ar, He, N₂, O₂). However, the contribution of those vibrationally excited molecules to CO₂ dissociation is limited because most of the energy transferred to vibrational excitation of those molecules converted to heat in DBD plasmas.[25] The accumulation of the heat can increase the wall temperature of the reactor, which can affect the reaction rate of the reactions involved in the plasma reactor leading to a lower CO₂ conversion (i.e., equation 1-2). Therefore, effective recovering/removing the thermal energy from the plasma reactor can not only prevent the reverse reaction of CO₂ decomposition but also harvest the thermal energy generated by DBD plasmas, which may significantly improve the energy efficiency of plasma assisted CO₂ decomposition at low temperatures and ambient pressure. Furthermore, the ever-increasing use of renewable energy sources (i.e., solar, wind, nuclear, geothermal, or hydroelectricity), which has meant an ever more distributed electricity supply could be a good fit with NTP-initiated chemical processes, particularly as a form of energy storage/usage when supply is too great and prices are very low (or even negative). A plasma process with higher energy efficiency can be achieved by a deep understanding and integration of plasma physics, chemistry, engineering reactor design and industrial process intensification (PI).

Thermal plasmas can be used for CO₂ decomposition, but require very high temperatures. The calculated theoretical thermal conversion of CO₂ increases from 1.5 to 47% when increasing the temperature from 2000 to 3500K [52]. However, although the energy efficiency of high temperature (“thermal”) plasmas can be higher than that of low temperature plasmas, it incurs substantial material costs to operate above 2000K, and numerous attendant operating and capital costs. It should also be noted that, at the energy efficiency of 4.4% (for thermal decomposition at 2000K in theory) the CO₂ conversion was only 1.5%, while at the energy efficiency of 2% (for DBD plasma at 373K in this study) the CO₂ conversion was as high as 16.1%.

High temperature decomposition of CO₂ follows thermodynamic equilibrium, and the equilibrium of this reaction strongly favours the reactants, and does not remove one of the products (i.e., CO or O₂) efficiently, as the non-thermal plasma route does. Performing this reaction in O₂ in these conditions would decrease the CO₂ conversion and energy efficiency. However, CO₂ decomposition in a DBD plasma reactor works at non-equilibrium reaction conditions at low temperatures and ambient pressure. Although the energy efficiency of DBD plasma is lower than that of high temperature reactions (i.e., thermal plasma arc), it can decompose CO₂ even in the presence of high concentrations of O₂.

3.5 Potential applications

This study may open up 2 possibilities for the use of CO₂. Firstly, it allows CO₂ to be “activated” by converting it to more reactive CO at low temperatures, even in high concentrations of O₂.

Secondly, O radicals are generated that could be used as oxidants “*in situ*” even in the presence of CO under NTP conditions at low temperatures and ambient pressure.

A typical composition of flue gas from gas-fired boilers is: CO₂: 7.4-7.7%, H₂O: 14.6%, O₂: 4.45%, N₂: 73-74%, CO: 200-300 ppm, and NO_x: 60-70 ppm; and that from coal-fired power plants: CO₂: 12.5-12.8 %, H₂O: 6.2%, O₂: 4.4 %, N₂: 76-77%, CO: 50 ppm, NO_x: 420 ppm, and SO₂: 420 ppm.[53] The NO_x and SO₂ can be removed by pollution control technologies. Normally, Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) technologies can capture CO₂ from these point sources, but they are typically energy intensive process. [54] When water is removed from the flue gases, the concentration of O₂ is about 5% in the dehumidified flue gases. As shown in Figure 2, an increase in the O₂ concentration from 0-10% does not decrease the CO₂ conversion apparently. Therefore, the current study may open up a novel approach for the direct CO₂ conversion/reduction to CO and O₂ from the dehumidified flue gases.

4. Conclusions

This study clearly demonstrated that CO₂ decomposition/reduction to CO and O₂ can be realized in the presence of high concentrations of O₂ in an NTP at low temperatures (gas temperature ~ambient; wall temperature: ~100 °C) and ambient pressure. The concentration of O₂ did not affect the conversion of CO₂ significantly until ~20% O₂, and was still significant (11%) at 50% O₂. The present study opens up the possibility of “activating” CO₂ at low temperatures by converting it to CO (even at high concentrations of O₂) which is more reactive, rendering conversion to value added chemicals or sequestered carbon easier. Furthermore, this

study may provide a novel approach for direct CO₂ conversion/reduction, to CO and O₂, respectively, for gas-stream such as the dehumidified flue gases of power plants.

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