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Full Length Article

Reaction engineering of carbon monoxide generation by treatment with atmospheric pressure, low power CO_2 DBD plasma

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ABSTRACT

One of the greatest challenges faced by humanity is the changing global environmental trends. Evidence points out to the increased greenhouse gas emission by humans as the main cause. One of the possible solutions to reduce CO_2 emissions is to produce value added products or the precursors which can be used as the feedstock for the former. In the current study CO_2 is converted to CO by dielectric barrier discharge (DBD)-corona hybrid plasma treatment while maintaining low power consumption. The kinetics of CO formation by CO_2 plasmolysis is studied and analysed in detail. A well mixed system kinetics model has been proposed to estimate the reaction time for the experimental studies. Optical emission spectroscopy has been used to study CO_2 plasma and mixtures of CO_2/N_2, CO_2/water vapour and CO_2/Ar plasma. A parametric study varying length of electrode, voltage, frequency, CO_2 flow rate and pressure in plasma chamber is conducted. CO formation was found to be favoured at 600 mL/min flow rate, 1 atm pressure, 4.8 kV voltage at 40 kHz of frequency with 9 cm electrode.

1. Introduction

Awareness of potential hazards of CO_2 emission and its reduction is a major issue of the current industrial age [25]. Studies show that 50–80% reduction in CO_2 emission level of the year 2000 is required in order to reduce the concentration of atmospheric CO_2 to a level of 250–400 ppm and keep net increase in global temperature to 2.0–2.4 °C [32].

There are several possible solutions for this problem, such as increasing process efficiency to utilize less power and hence net reduced emission of CO_2, renewable energies with zero CO_2 emission and CO_2 capture and geological storage [28]. However, one of the innovative approaches is to utilize the CO_2 as chemical feed stock and hence make process emissions neutral [19,26]. Carbon dioxide is not only the major greenhouse gas, but could also be used as an important resource. It is topical to explore all the possibilities of utilization of CO_2 as an industrial raw material although the possible market for this approach is not significant compared to the global emission of CO_2 [7].

Electrochemical reduction of CO_2 to many industrially important chemical feed stocks such as carbon monoxide, formic acid, ethylene and methane etc., has been envisaged [32]. Varghese et al. [30] has shown the production of CH_4 through photocatalysing CO_2 and water over the surface of titania nanotube arrays combined with nanoparticles of co-catalyst. Centi et al. [7] reported that CO_2 can be converted to liquid fuels (isopropyl alcohol, in particular) by using electrocatalytic conversion. Also, by the combination of the electrodes to a nanostructured titania photoanode, CO_2 could be captured and converted to long-chain alcohols and hydrocarbons by the usage of solar energy and water in “artificial energy trees”. Tao et al. [29] presented the study of the reforming of CH_4-CO_2 by using cold plasmas and thermal plasma to produce CO and H_2. A pure CO_2 decomposition was studied by using the combination of pulsed corona discharged and γ-Al_2O_3. From the report, CO yield could reach 15% [31].

Graves et al. [14] have recently shown the feasibility of recycling CO_2 by co-electrolysis of H_2O and CO_2 to produce gasoline or diesel. Electricity to fuel efficiency has been estimated to be around 70% and the price of synthetic fuel is found to be dependent mainly on the price of electricity which indicates that further margin of improvement if the electricity is produced by renewable energies such as wind or solar technology. It is interesting to note here that plasmolysis offers high specific productivity, is considered 1000 times more volumetrically scalable than electrolysis and is considered more selective [12]. Plasmolysis or plasma-chemical synthesis has traditionally been considered as an expensive. This is because of the requirement of high power in order to sustain plasma in large conventional plasma reactors. Large inter electrode gap is required to avoid recombination of active species

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by collision with reactor walls [21,24]. A discussion on the recombination on the surface and ambipolar diffusion is done in Section 2. The problem of having higher power to have sustainable plasma could be solved by reducing the inter-electrode distance to micron scale. Lozano-Parada and Zimmerman has shown the scope of producing ozone at lower power than the conventional plasmolysis by using a micro plasma reactor of diameter around 800 μm [21]. Also, Rehman et al. has shown the H_2 generation at lower costs than previously thought [5,23]. Hence plasmolysis of CO_2 alone or a mixture of CO_2 and H_2O could offer higher efficiencies in terms of producing synthetic fuel or chemical feed stock such as CH_3OH. Better control of the process is another advantage of micro plasma reactors along with their lower power requirement. The better control is the result of tailor made fluid dynamics of micro plasma reactors through high but brief field gradients which are spatially precise and electronically controlled [33].

Under typical non-thermal plasma conditions CO_2 dissociation could be represented by Eq. (1-1).

$$CO_2 + e \rightarrow CO + \frac{1}{2}O_2 + e \quad \Delta H_r^{\theta} = 283\ \text{kJ/mol} \tag{1-1}$$

Table 1 shows the typical species found in an optical emission spectrum of CO_2 plasma [13]. The species presented in the Table 1 have been reported in low pressure DC plasma in a 1.6% Ar-2.7%, N_2-95.3%, and CO_2 mixture. The plasma was generated at very low pressure 0.5–8.7 Torr (0.00067–0.0116 bar), 6.3 W (430 V and 14.72 mA) of power and 12 L/min of flow rate. It is very important to point out the conditions under which these species have been observed.

Corona discharges, with typical wire and tube arrangement, are reported to be the reasonable method of reaction processes which could produce high concentration of radicals. However, corona discharges are limited by the power at which they could be operated at. Since the electrodes are “naked”, an increase in power input beyond a certain level leads to arc discharge transition and putting low power could be insufficient to excite some processes [15,23,11]. The power of corona discharges could be increased by raising the voltage by covering one or both electrodes by a dielectric layer [11]. A dielectric barrier discharge (DBD) is a type of non-thermal plasma. It has been found to be an efficient method for inducing reactions, especially of organic chemicals due to the non-equilibrium character but requires high enough power to break the dielectric barrier [20,8,9]. The discharge current between electrodes is limited by the dielectric material. Arcing could be avoided, and a homogenous discharge can be generated. However, advantages of highly non-equilibrium conditions in a streamer present in corona discharges yet avoiding arcing at higher power, a feature of DBD could be achieved by covering single or both electrodes by dielectric layer [11]. The DBD-corona reactor is explored for the first time for CO_2 plasma excitation with the intention of seeking the best kinetics and low power consumption operation. The important design features for any plug flow (tubular) chemical reactor, including the subclass of plasma chemical reactors, are the residence time and volume of the reactor, which are combined into the factor “space-time”. If this factor is known from tubular reactor at any scale, scale up is a straight forward application of chemical reactor engineering principles [10].

Table 1
Summary of emission spectra observed in CO_2 discharge within the wavelength of 200–1100 nm [13].

Species	λ (nm)
CO_2^+	413.76
CO^+	484.00
O_2	400.53
	406.52
CO_2	391.20
CO	452.00
	520.43
C^+	657.80
O_2^+	588.28

In this study, the conversion of CO_2 into CO using a DBD-corona hybrid discharge reactor under non-thermal equilibrium plasma conditions has been studied. The effects of different parameters such as pressure and flow rate of CO_2, power and frequency used to ignite plasma and length of plasma chamber has been studied. The objective of the current study is to optimize the parameters for the production of CO from CO_2 under non-thermal equilibrium plasma conditions, which could be utilized to produce chemicals like methanol or formic acid. The overall economics of this process depend strongly on the existence of “waste” electricity, i.e. electricity generated from solar, wind and hydroelectric power plants that is in excess of demand. Storing that energy as CO as a fuel intermediate is a sensible alternative to many current storage technologies, although the development of new, more storage efficient batteries is the major competitor to storage as a chemical fuel.

The article has been divided into five sections. In the first section, an introduction to the current study is discussed. The second Section deals with the modelling of CO under non-thermal plasma conditions. Materials used and methods applied are studied in third section. A detailed discussion is done on experimental results in Section 4. Conclusions of the study are given in Section 5.

2. Kinetic modelling

The kinetics of CO_2 plasma has been modelled in a similar DBD configuration by Aerts et al. [2]. In one pulse and a long afterglow, 94% of the CO_2 is dissociated in ground state and rest of the 6% decomposes in a vibrationally excited state. At very high frequencies (short interpulse time period), vibrationally excited molecules were found to be more significant. It has been reported that the neutrals and radicals do not play a significant role in dissociation of CO_2. Atomic Oxygen (O) was found to play the key role in the formation of molecular oxygen (O_2) and ozone (O_3). Electron impact dissociation reactions were found to dominate the kinetics of dissociation of CO_2, which was also found to be the major channel of dissociation. Ionization was also found to effect the kinetics. However, a major fraction of the ions thus produced recombines to form CO_2.

The objective of the current study is to predict the kinetics of CO_2 plasmolysis in order to estimate the residence time/reaction time to design and optimize the plasma microreactor. The kinetics of CO_2 is shown in Table 2.

In this study, a kinetic model for CO_2 plasmolysis has been proposed. The model has been implemented using COMSOL Multiphysics™4.2a-Reaction Engineering Laboratory (REL) [34].Table 2 gives the enthalpies ΔH, activation energies E_a, pre-exponential factors $A\left(\frac{cm^3}{s}\right)$ is the unit of the second order reactions, $\frac{cm^6}{s}$ is the unit of the third order reactions), and efficiencies α of vibrational excitation (relation between different units for activation energy: 1 eV/mol = 23 kcal/mol) of the reactions. This package provides an automatic sensing of stiff systems and an adaptive time stepping algorithm with relative tolerance set to 10^{-6}. It was assumed that CO_2 plasmolysis occurs in a hypothetical plasma microreactor where the inlet concentration of the CO_2 was calculated using ideal gas law such that CO_2 is flowing at atmospheric pressure and inlet concentration electrons was calculated using equilibrium number density range of electrons as described in previous study [24]. If the reactor is supposed to be well-mixed (dominated kinetically), then every reaction in the scheme Table 2 contributes mass action law terms to the kinetics model with rate constants (including Arrhenius temperature dependence), with number densities corresponding to the species incorporated in this study (CO_2, CO, electron, O and O_2). The model does not account for the surface reactions. A rationale for this is discussed in a later part of this section. The rate equations for the reactions given in Table 2 can be