# Non-thermal plasma technology for the conversion of $CO_2$

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**Abstract**

The conversion of carbon dioxide is vital if we are to avoid the catastrophic consequences that will result from further global temperature rise as a result of burning fossil fuels. Current techniques, such as catalytic conversion and biochemical processes, are each associated with their own drawbacks such as catalyst deactivation and high energy input. Plasma processes are gaining increasing interest as they have the potential to reduce a greater amount of atmospheric environmental pollutants at any one time due to an increased throughput, whilst using a smaller reactor with improved energy efficiency and near-zero emissions [1]. Non-thermal plasma can dissociate stable molecules, such as $CO_2$, at temperatures as low as room temperature. It is this key feature which makes plasma conversion such a promising technology in the conversion and utilization of $CO_2$. Furthermore, possible products from plasma processes include fuels and chemicals, such as methanol and syngas, which have a high market value; hence potentially making the process feasible on an industrial scale. This paper discusses recent advances in the use of plasma processes for carbon dioxide conversion, along with the future outlook of this technology and the impact these techniques could have on the chemical and energy industries.

Keywords: Non-thermal plasma; $CO_2$ conversion; Plasma-catalysis;

**Introduction**

The monumental task of abating carbon dioxide, and hence reducing global warming, requires a prodigious solution. In order to fulfil targets set out in the agreement that culminated from COP21 in Paris last year, a switch to renewable energy and a reduction in the release of greenhouse gases into the atmosphere are required, necessitating the design of novel technologies that enable this change whilst allowing society to prosper. The utilisation of carbon dioxide is one area which has the potential to fulfil these requirements, as $CO_2$ from fossil fuel and industrial processes accounts for 65 % of total annual anthropogenic greenhouse gas emissions (49 GtCO₂eq in 2010), as detailed in the IPCC AR5 report [2]. A significant reduction in carbon dioxide emissions can therefore be made by capturing $CO_2$ from waste gas streams and converting it into valuable fuels and chemicals.

The main challenge associated with the utilisation of $CO_2$ is overcoming the high stability of the $CO_2$ molecule, as a high energy input is required to break the OC=O double bond and dissociate the molecule. Historically, high temperatures (1600-2000 K) and/or pressures have

been employed to ensure the dissociation of $CO_2$ is thermodynamically favourable; however this invariably results in low energy efficiency and, if fossil fuels are used as the energy source, can result in a process that is detrimental to the environment.

There are several methods that can be used to convert carbon dioxide, including catalytic conversion, photo-catalytic/photochemical processes, electro-catalytic/electrochemical processes, enzymatic/biochemical processes and plasma processes. Each of these methods result in a slight variation in the product created, with hydrocarbons, hydrogen and oxygenates forming via catalytic conversion whilst carbon monoxide, hydrocarbons, syngas and oxygenates are the main products of plasma processes. Along with the need for high temperatures in thermal-catalytic processes, issues can be encountered with catalyst deactivation due to coking. Electro-catalytic processes show promise for producing methanol, formic acid and a variety of other organic chemicals. However, these processes have low thermodynamic efficiency. The least researched, yet predicted to be the most effective, is the plasma process. In comparison to the other processes, it is simple and fast: plasma has the potential to enable thermodynamically unfavourable chemical reactions (e.g. $CO_2$ dissociation) to occur at ambient conditions. Non-thermal plasma (NTP) can be operated at room temperature and atmospheric pressure whilst still generating highly active species and electrons, with mean electron energy between 1 and 10 eV. This electron energy is the optimum range for exciting molecular and atomic species and breaking chemical bonds. For $CO_2$ dissociation (eq. 1) to occur in plasma only 5.5 eV is required to break the OC=O bond via stepwise vibrational excitation. Non-thermal plasma therefore shows great potential in the production of an efficient $CO_2$ utilisation process, as it can overcome the stability of $CO_2$ without the need for the high temperatures required in thermal catalytic processes. Plasma technology is also advantageous over thermal processes as reaction rates are high and steady state is quickly reached [3]. This facilitates quick start-up and shut-down; a promising feature that enables plasma technology powered by renewable energy to act as an efficient chemical energy storage localised or distributed system at peak grid times [4]. Different routes for $CO_2$ conversion have been explored using NTP (Figure 1).
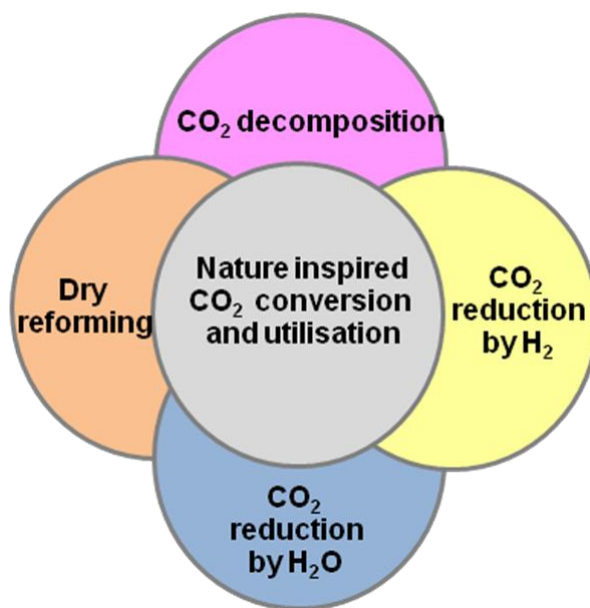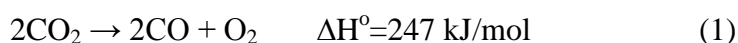
Figure 1: Different routes for $CO_2$ conversion

**$CO_2$ decomposition to CO and $O_2$**

$$2CO_2 \rightarrow 2CO + O_2 \qquad \Delta H^o = 247 \text{ kJ/mol} \qquad (1)$$

Decomposition of $CO_2$ into CO and $O_2$ using NTP has attracted significant interest as this reaction is almost impossible at low temperatures using conventional catalysis, whilst CO is an important chemical feedstock for the further synthesis of fuels and chemicals. Various plasma systems are reported to successfully dissociate $CO_2$ into CO and $O_2$ (eq.1), including: glow discharge, where one study found a $CO_2$ conversion of 30 % is achievable at an input voltage of 7 kV [5]; Radio frequency discharge, which can achieve 90 % $CO_2$ conversion at 1 kW [6]; and microwave discharge, in which a 100 W power input was accompanied by a 90 % conversion [7]. A carrier gas, such as helium or argon, has previously been commonplace in the dissociation of $CO_2$ via plasma systems; however this leads to an additional, undesired cost. Dielectric barrier discharge (DBD) reactors have been shown to successfully dissociate $CO_2$ in the absence of a carrier gas [8], [9], with one study achieving 30 % conversion at a power density of 14.75 $W/cm^3$ [9].

A design of experiments approach using a cylindrical DBD revealed that the main parameter which affects the energy efficiency of this process is the feed flow rate, whilst discharge power has the greatest influence on $CO_2$ conversion [10]. The influence of discharge length has also been studied, with results showing that an increase in both discharge length and discharge power lead to an increased $CO_2$ conversion. This is due to higher discharge power resulting in an increase in the average electron density and number of microdischarges.

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Conversely, a high feed flow rate leads to a lower $CO_2$ conversion but is more energy efficient [10]. A zero dimensional chemical kinetics model has been developed to understand the reaction mechanisms in the plasma $CO_2$ dissociation [11]. Electron impact dissociation has been found dominant in the $CO_2$ decomposition in DBD plasmas, leading to lower energy efficiency compared to microwave plasmas or gliding arc discharges, in which more energy-efficient vibrational excitation of $CO_2$ play a key role in the decomposition of $CO_2$ [12].

**$CO_2$ hydrogenation to value-added fuels and chemicals**

Carbon dioxide can be hydrogenated in plasma via reaction with hydrogen or water at atmospheric pressure, thus avoiding the use of high pressure required by conventional thermal catalytic processes. $CO_2$ methanation (eq. 2) and the reverse water-gas shift reaction (eq. 3) prevail when hydrogen is reacted with $CO_2$ in the plasma process [13]; however it is theoretically possible to produce a variety of different chemicals.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (2)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (3)$$
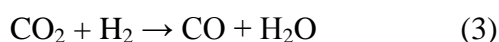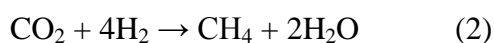
In this process, a higher $H_2$ content in the feed is desirable as this increases the conversion of $CO_2$. A 4:1 ratio ($H_2/CO_2$) is optimal for enhancing $CO_2$ conversion and $CH_4$ selectivity [13], [14]; however, if products other than $CH_4$ are required, the $H_2/CO_2$ ratio can be varied as different products reach their maximum selectivities at different reagent ratios [13]. For DBD plasmas, the use of an alumina reactor instead of quartz is beneficial on reaction performance due to the enhanced relative dielectric permittivity coefficient of alumina [14]. Addition of a magnetic field can also enhance $CO_2$ conversion, increasing the $CH_4$ selectivity by over 10 % at a discharge power of 30 W, whilst also tripling the energy efficiency of the process [15]. Water can also be used for the methanation of $CO_2$, as detailed by Hoeben et al [16], and for the production of syngas [17]. The former, renewable, process uses a pulsed corona to first dissociate $H_2O$ and $CO_2$, followed by hydrogenation of CO. However, conversion efficiencies of $CO_2$ are low, with one study finding the addition of water can cause a significant decrease in $CO_2$ conversion [18]; hence further improvement is required in this area.

**Dry reforming of $CO_2$ with methane**

Dry reforming of methane using $CO_2$ (eq. 4) has the benefit of utilising two greenhouse gases in a single process. This process produces syngas, a mixture of hydrogen and carbon monoxide, alongside other valuable chemicals. Syngas is a vital chemical intermediate that

can be used to produce a variety of chemicals and fuels, including via the Fischer-Tropsch process. The dry reforming process is especially suited to producing oxygenated chemicals due to the low $H_2/CO$ molar ratio (~1) of the product gas [3]. Co-generation of hydrogen and carbon nanomaterials in a gliding arc reactor has been reported, which potentially reduces the cost of the plasma reforming process [3]. The use of NTP allows the process parameters to be tuned in order to minimise energy and material consumption as NTP initiates chemical reactions at much lower temperature than the thermal process, thus minimising energy cost [19].

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \quad \Delta H^o = 247 \text{ kJ/mol} \qquad (4)$$
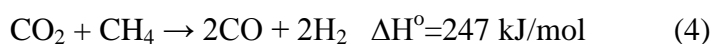
The influence of a wide range of operating parameters on the energy efficiency and conversions of reactants has been investigated using different plasma systems. An experimental approach carried out in a DBD reactor found that the reactant conversion and the $H_2/CO$ ratio, along with the product yields and selectivities, are affected by the ratio of $CO_2/CH_4$ in the feed; however, it was not found possible to manipulate the selectivity to syngas or the $H_2/CO$ ratio by altering the total feed flow rate [20]. One important factor that determines reaction performance is the number of micro-discharge filaments that come into contact with the gas molecules in the DBD. Pulsed plasma has been shown to effectively enhance the performance of this process. Optical emission spectroscopic diagnostics has been used to understand the formation of a wide range of reactive species generated in the reforming process, whilst plasma chemical kinetic modelling has been used to understand the underlying plasma chemistry and reaction pathways of the dry reforming process [21]. The latter model demonstrates how selectivity towards different products can be achieved through manipulation of the residence time due to the spatially averaged densities of some molecules continually increasing with residence time, whilst others peak at a certain value [21].

**Increasing reaction performance and feasibility**
In the plasma systems discussed here, a trade-off exists between $CO_2$ conversion and energy efficiency [6], [22]. In order to solve this problem and hence create a feasible industrial process, further modification of the plasma system is required. One such modification is the addition of a catalyst into the plasma discharge, as research shows the hybrid plasma-catalytic process can result in higher $CO_2$ conversion whilst maintaining low energy consumption [23], [24]. The combination of plasma and catalyst allows the beneficial aspects of each to be realised, along with the effect resulting from their interaction [25], [26]. This can lead to

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synergy in relation to conversion and efficiency; thus creating a more feasible process for the utilisation of $CO_2$ on an industrial scale. The simplest method of combining plasma and catalyst in a one-stage setup is to do so in a DBD reactor (Figure 2), as the catalyst can be placed directly into the discharge without the need for any adjustments in reactor geometry. One study on $CO_2$ hydrogenation found that the addition of various alumina supported copper and manganese catalysts into a DBD increases the $CO_2$ conversion between 6.7 and 36 % and the energy efficiency of CO production by up to 116 % [13]. Catalysts have also been shown to enhance the reactant conversions (by up to 30 %) and energy efficiency (by 22 %) of the dry reforming reaction when combined with an AC gliding arc discharge [27].
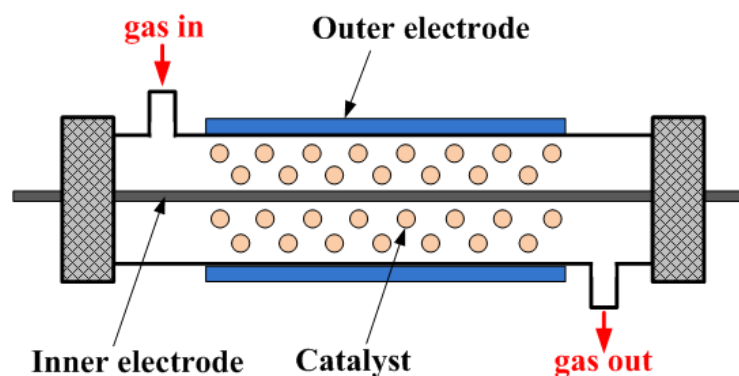


Figure 2: Single-stage setup in a plasma-catalytic dielectric discharge reactor

Catalysts can be incorporated into DBD reactors in a fully- or partially-packed bed configuration, with the former being most beneficial on reaction performance [28]. However, catalysts can be expensive, thus adding to the cost of the process. To solve this issue, an inexpensive packing material, such as barium titanate or quartz wool, can be employed. By mixing the catalyst and packing material before placing in the reactor, a packed bed effect can be realised without the need for high volumes of costly catalyst. This setup also results in a quasi-homogeneous dispersion of the catalyst, which benefits the reaction performance as a greater number of $CO_2$ molecules will come into contact with the catalyst.

As with the catalyst, the packing material will also interact with the plasma. Barium titanate has been shown to beneficially modify the discharge mode for the $CO_2$ decomposition reaction when used as a packing material, resulting in an increase in the average electric field and mean electron energy due to the formation of surface discharges alongside the typical

filamentary discharges formed in the absence of a packed bed [29]. Furthermore, the decrease in electron density caused by the use of a dielectric material promotes oxygen radical recombination which in turn impedes the recombination of CO and O to form $CO_2$ [30]. The reaction performance ($CO_2$ conversion and energy efficiency) is also enhanced due to physical changes resulting from the presence of the packing material [29]. Dry reforming of methane shows an enhanced $CH_4$ conversion and $H_2$ yield when using quartz wool as the packing material in comparison to the reaction performance obtained for the process without any packing; however, both zeolite 3A and $Al_2O_3$ decrease $CH_4$ and $CO_2$ conversions due to a decrease in void fraction in comparison to quartz wool, as this is accompanied by a reduction in the formation of strong filamentary discharges [31].

The size and form of the packing material or catalyst can also affect the reaction performance [32], [22]. One study reported an increase in the size of $BaTiO_3$ balls used in the dry reforming reaction resulted in enhanced $CO_2$ and $CH_4$ conversions due to each individual micro-discharge dissipating a greater amount of energy on average [32]. The interactions between the packing material or catalyst and the plasma, both chemical and physical, are highly complex but greatly influence reaction performance. Further understanding of these interactions is therefore vital for future plasma-catalytic technologies.

**Future prospects and outlook**

Plasma-based technologies for the conversion of $CO_2$ into value added fuels and chemicals show great potential due to the ability of non-thermal plasma to break bonds in the highly stable $CO_2$ molecule whilst operating at room temperature and pressure. Plasma systems therefore have an advantage over thermal processes, which require high temperature inputs; hence plasma conversion of $CO_2$ could prove much more feasible on an industrial scale. However, a trade-off between energy efficiency and $CO_2$ conversion currently exists in the plasma process as conversion increases when energy input is raised, which also causes a decrease in energy efficiency. Initial research has shown that this problem can be overcome by modifying the plasma system, such as by combining the plasma discharge with a catalyst; however, further research is required to promote the simultaneous increase of energy efficiency and conversion. Once plasma processes can concurrently operate at high conversion and energy efficiency, they will become a front runner in green technologies for the conversion of carbon dioxide.

Plasma chemistry is highly complex and although much research is being conducted into plasma modelling, the models being used are greatly simplified versions of the reactions taking place [11], [17], [33]. Newer models can also leave their predecessors redundant; therefore further study is required to produce comprehensive models for a variety of plasma processes [34]. When it comes to plasma-catalysis, the chemistry becomes even more complex due to the interactions occurring between the plasma and catalyst. The number of different catalysts that can be employed in plasma processes, along with variations in catalyst preparation method, loading amount, pre-treatment etc., make it tricky to use a 'one model fits all' approach. If a greater understanding of plasma reactions and the interactions between plasma and catalyst can be realised through modelling, this could drastically reduce the time required to optimise a process and lead to selection of the optimum catalyst without the need for numerous laborious experiments.

The potential exists to produce more complex carbon-based liquid products using plasma. A variety of liquids can currently be produced in small quantities, such as formaldehyde and methanol, as well as ethylene and $C_4$ hydrocarbons [35], [36]. However, the selectivity to many of these products remains too low for the process to be viable. The selection of an appropriate catalyst that can increase the selectivity to the required product is therefore required for progress to be made in this area.

Thermal catalytic techniques are currently used to produce liquid hydrocarbons such as dimethyl ether (DME) from carbon dioxide and hydrogen. For the production of DME, high temperatures (240-270 °C) and pressures (3 MPa), are required [37]–[39]. If NTP processes can be used instead, the energy input can be drastically reduced as non-thermal plasma is operated at room temperature and pressure. In order to produce hydrocarbons directly from $CO_2$, hybrid catalysts are required [40]. Novel catalysts and new reactor setups may help offset the need for high pressures in a plasma reactor. Much more research is needed to create plasma processes that produce liquid hydrocarbons currently only produced by other (non-plasma) techniques, but if successful these processes could transform the chemical and energy industries.

The scope and potential of plasma processes are therefore vast. These processes reduce the concentration of $CO_2$ in our atmosphere and allow the chemical storage of energy which can be transferred to the system from renewable energy sources at peak times. As well as producing fuels, valuable chemicals can also be formed. A greater understanding of the

plasma chemistry, both through modelling of plasma and coupling with other techniques such as catalysis, as well as further insight into synthesising a catalyst which will create synergy when combined with plasma [41], will allow this field to expand. Alongside this, further research into the conversion of $CO_2$ in feed gases mixed with other gases from industrial waste streams could also be beneficial for creating large scale plasma processes [42].

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Short comments
These annotated papers show the recent progress in the plasma conversion of $CO_2$ with and without a catalyst from both experimental and modeling perspectives.