Fakultät Versorgungstechnik

PLASMA-PHOTOCATALYTIC REDUCTION OF CO$_2$ BY HYBRID-DBD REACTOR

BACHELOR OF ENGINEERING

Bio und Umwelttechnik

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Glossary

CCS   Carbon Capture and Sequestration

CCU   Carbon Capture and Utilization

CB   Conduction Band

DBD   Dielectric-barrier discharge

EE   Energy Efficiency (η)

Eg   Band Gap

IPC   In-Plasma Catalysis

MFC   Mass Flow Controller

NTP   Non-thermal Plasma

PPC   Post-Plasma Catalysis

SIE   Specific Input Energy

sLm   Standard liter per minute

STP   Standard Temperature and Pressure

VB   Valence Band

VOC   Volatile Organic Compounds

1.   Introduction

Excess of CO_2 leads to global warming phenomenon and, as a consequence, to constantly increasing planetary temperature. Global warming has drastic effects on nature leading to extreme weather events and interference in important biogeochemical cycles. Ever since industrial revolution took place, massive fossil fuel energy consumption and consequent air pollution has caused number of negative environmental effects. Nowadays, concentration of CO_2 in atmosphere is 350-450 ppm, which indicates high moderate fraction of carbon dioxide in atmosphere [1].

In order to reduce atmospheric CO_2 following approaches shall be considered: 1) use of renewable energy sources and reduction of carbon-based fuels consumption, 2) carbon capture and sequestration (CCS) 3) carbon capture and utilization (CCU). CCU processes are directed to further utilize captured CO_2 in a way that value-added new chemical blocks are built, whereas CCS refers to approaches that capture waste carbon from pollution point sources such as power plants operating on combustion of fossil and depositing it in permanent geological storage [2].

Main target of carbon utilization in terms of new chemicals production is high energy efficiency of the process. At industrial level, when it comes to obtaining CO_2 from exhaust gaseous streams, and recycling of CO_2 into valuable chemicals variety of electrochemical and photocatalytic methods are employed [3].

Conventional catalytic routes for gas conversion are challenged with thermodynamics of CO_2 molecule. Since CO_2 is inert and stable molecule, activation of CO_2 occurs as endothermic process and requires considerable energy input. In this regard, non-thermal plasma (NTP) provides an attractive alternative due to its non-equilibrium properties, low power requirement and unique capacity to induce both physical and chemical reactions at low temperatures. Among diversity of CO_2 reduction approaches NTPs state of the art provides significantly higher and more efficient reduction rates of treated process gases containing CO_2 [4]. However, there are also associated challenges with NTP treatment reliability and economic competitiveness, since the process is associated with significant electrical power input. In this regard, development of synergetic plasma-photocatalytic method is a promising way to improve energy efficiency of plasma process [4].

In order to obtain a solid knowledge of the non-thermal plasma assisted photocatalytic CO_2 conversion significant attention shall be paid to the effects of certain external and internal factors. In this regard, thorough outlook on synergistic NTP-catalytic process mechanisms is obtained by means of assessment of both catalytic and NTP characteristics from both practical engineering and theoretical science points of view.

Importance of greenhouse gas decomposition and emissions control is vital in terms of preventing air pollution and consequent risks to human health and environment. Invention and design of technologies directed to utilize atmosheric CO_2 and produce value-added chemical closely refers to sustainability concepts and climate change mitigation solutions and also represent huge potenitial for development.

2.   Aims

The main target of current thesis is to compare performance of CO_2 non-thermal plasma conversion in two DBD configurations: conventional Bare reactor and coated with TiO_2 catalytic particles hybrid reactor. It was also important to determine critical geometry parameters for both Bare and Hybrid reactors and construct two final configurations in order to conduct experimental procedure. Construction of both reactor types was performed several times until final configurations, which were able to sustain defined experemental conditions, were obtained. Moreover, preparation of measurement set-up by arrangement of required technical elements to carry out the experimental trials in regard with availability of laboratory equipment was another objective of work. Variable process influencing parameters such as different discharge power application, variation of total flow and CO_2 concentration range in order to conduct comparative measurement were determined. Interest was drawn to investigation of synergistic effect of Hybrid configuration compared to reference Bare reactor. Description and interpretation of obtained results based on theoretical knowledge of plasma assisted catalytic CO_2 reduction is a main outcome of the work.

3.   CO₂ emission control

Utilization of CO_2 makes a significant contribution to both designing mitigation greenhouse gas methods and production of value-added bulk chemicals from captured carbon dioxide. The main challenge in production of chemical blocks from CO_2 molecule is to overcome its thermodynamic properties such as low chemical activity and stable molecular structure [5].

3.1.   CO₂ chemistry

CO_2 is used in chemical synthesis and considerable number of carbon utilization metods have been designed in last years in order to conduct conversion of CO_2 into value-added chemicals:
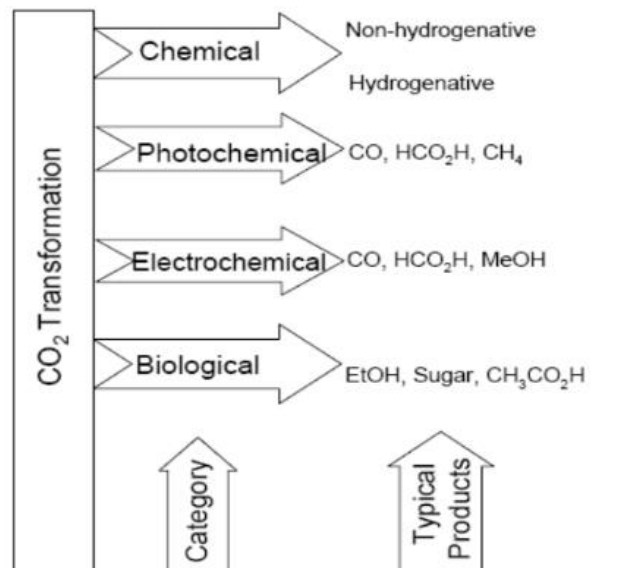
Figure 3-1. Transformation of Carbon Dioxide to Value-Added Products in different technological pathways (Source: [5])

Use of carbon dioxide as feedstock or co-reactant is a challenging opportunity which is stimulating new approaches in the industrial chemistry to develop new processes of CO_2 transformation. Using carbon dioxide as a building block in organic synthesis can follow two major pathways: Carboxylation and Reduction reactions. [7]. First type comprises chemical reactions in which the whole fraction of CO_2 is incorporated into molecular or polymeric compounds containing carboxylic acid groups such as –COOR, ROCOOR (carbonates), N-COOR (carbamates) , NCO (ureas). As a result of carboxylation products containing higher C/H ratio are formed. During reduction reaction CO_2 is reduced to Cn molecule. Carbon dioxide is a fully oxidized and thermodynamically stable compound. Conversion of CO_2

molecule requires high free energy content substances (such as NH_3, amine, etc.) or an external energy supply (thermal, electrical, or photochemical) [5-6]. Application of an appropriate catalyst system promotes reaction rates, directs the selectivity pathway and minimizes the energy of the reaction. Therefore, chemical (catalytic) CO_2 transformation presented in Figure 3-1 was successfully applied in chemical synthesis to convert CO_2 into chemical bulks.

For instance CO_2 dissociation reaction might be conducted either in electrochemical or photochemical process [9]:

$$CO_2 \rightarrow CO + 1/2\ O_2 \qquad\qquad \Delta H298\ K\ ° = 283.3\ kJ\ mol^{-1}$$

Current reaction provides high concentration of CO, which further is utilized in synthesis of oxygenated chemicals and hydrocarbons [7]. One of conditions for direct CO_2 splitting is high enthalpy ΔH, which indicates significant energy input is required in order that chemical conversion takes place. Another reaction of interest in chemical synthesi, is methane (CH_4) formation:

$$CO_2 + CH_4 \rightarrow 2\ CO + 2\ H_2 \qquad\qquad \Delta H298\ K\ ° = 247\ kJ\ mol^{-1}$$

Two main products of CO_2 reforming of CH_4 are CO and H_2 which are main building blocks in chemical synthesis. Moreover, hydrogenation of CO_2 with H_2 is chemical reaction which is characterized by high energy efficiency and moderate operating conditions:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad\qquad \Delta H298\ K\ ° = 41.2\ kJ\ mol^{-1}$$

$$CO_2 + H_2 \rightarrow HCO_2H \qquad\qquad \Delta H298\ K\ ° = -31.5\ kJ\ mol^{-1}$$

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \qquad\qquad \Delta H298\ K\ ° = -49.5\ kJ\ mol^{-1}$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \qquad\qquad \Delta H298\ K\ ° = -164.8\ kJ\ mol^{-1}$$

When it comes to thermodynamic equilibrium of CO_2 molecule and its further decomposition to CO and O_2, it shall be noted that activation of the reaction requires significant energy input of 5.5 eV/molecule is required to break the chemical bond of C=O. Significant energy input is required for activation and upgrading of carbon dioxide molecule. [6,8]. Different artificial approaches have been tested in order to turn mechanism of CO_2 deposition and achieve better energy efficiency. Optimization of selected electrochemical methods in terms of energy efficiency and product formation are one of the most important targets of bulk chemicals production from CO_2. In terms of variation of outcome product, it shall be noted that selected processes results in various reaction products, for instance, production of oxygenates and higher hydrocarbons takes place in catalytic processes, whereas plasma methods assist production of lower hydrocarbons [7,8].

In order to determine efficiency of conversion into further chemical blocks, following parameters are employed [9]:

$$\text{Specific input energy,} \left(\frac{kJ}{L}\right) \text{SIE} = \frac{\text{Discharge power (kW)}}{\text{Totalgas flow rate (L } s^{-1})} \tag{1}$$

SIE is critical in terms of assessment of energy input impact on total flow. It is defined as ratio between applied plasma power and total flow rate. It can be expressed in J cm^{-3} or kJ L^{-1}). Another significant process parameter is Conversion Efficiency of CO_2:

$$\text{Conversion of } CO_2 \text{ , (\%)} = \frac{nCO_2 \ in(mol \ s^{-1}) - nCO_2 \ out(mol \ s^{-1})}{nCO_2 in(mol \ s^{-1})} \tag{2}$$

Where n_{in} represents molar flow rate (mol s^{-1}) of CO_2 entering the system and at output after plasma treatment point n_{out}.

In order to evaluate energy efficiency compared to the standard reaction enthalpy current formula shall be used:

$$\text{Energy efficiency,} \eta \ (\%) = \frac{\Delta H° \ 298(\text{kJ mol}^{-1}) \times Conversion \ of \ CO_2(\%)}{SIE(\text{kJ mol}^{-1}) \times 22.4(\text{L mol}^{-1})} \tag{3}$$

Energy Efficiency (%) calculation is based on SEI (kJ mol^{-1}) and CO_2 Conversion described above. Further parameters in formula are indicated as enthalpy ΔH = 298 kJ mol^{-1} for CO_2 splitting and 22.4 L / mol as volume occupied by one mole of ideal conditions at STP.

3.2. Photocatalysis

Photocatalytic CO_2 reduction is conducted resulting into solar fuels and chemicals appears to be quite promising technique to overcome environmental challenges of CO_2 recycling. One of the main advantages of current method is the fact that during photocatalytic conversion besides removal of effluent gases, useful compounds such as formaldehydes or methane are formed as a product. Moreover, reduction reaction occurs in presence of sunlight, which is less energy consuming in comparison to conventional methods. Artificial photo catalysis is performed on various semiconductor photo catalysts. The research and development of novel photo catalysts which possess higher photocatalytic activity is highly promoted nowadays as well as studying the process enhancement mechanism. The main parameters determining the efficiency of performance include temperature pressure, intensity of the light source and type of reductant [10].

3.2.1. Heterogeneous TiO$_2$ Photocatalysis

Titanium oxide exists in several modifications such as rutile, anatase, and brookite. Rutile is not sufficiently stable to be undergone as photocatalyst and that is why bulk forms of anatase, and brookite are employed. Moreover, anatase shows higher photocatalytic activity. The main principle of heterogeneous catalysis over the semiconductor surface is generation of hole-electron pairs and its reverse process. [10]. Semiconductors are used in the process due to the fact that exhibit a small enough gap between the valence and conduction bands where excitations of electrons takes place, whereas in conductors the valence band (VB) overlaps the conduction band (CB), and in insulators void energy region between (VB) filled with electrons and vacant conduction band (CB) is too large. Band-gap energies of semiconductors used for photocatalytic processes vary and higher energies provide better conversion. Consequently, efficiency of TiO$_2$ in rutile and anatase forms of semiconductors, which have band-gap energies 3.02 and 3.23 eV respectively, was proved to be higher than alternatives [11].

The photocatalytic method may be described as process of acceleration of photoreaction in presence of photo catalyst. The process starts with excitation of electrons by a photon absorption, which has energy higher or equal than semiconductor band gap energy, and production of electron-hole (e$^-$/h$^+$) pairs. Basically, photocatalytic degradation on TiO$_2$ surface of organic/inorganic compounds can be demonstrated by following formula [10,12]:

$$TiO_2 \xrightarrow{hv \geq E_G} TiO_2(e_{CB}^- + h_{VB}^+)$$
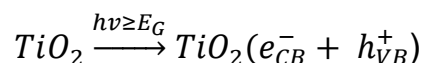
Where:

h is Planck's constant (h= 6.626176 x 10^{-34}Js^{-1}) and relates to energy in a photon of electromagnetic radiation and v is its frequency;

E_G– band gap e_{cb}^- is a conduction band electron and h_{vb}^+ is a hole in the valence band,
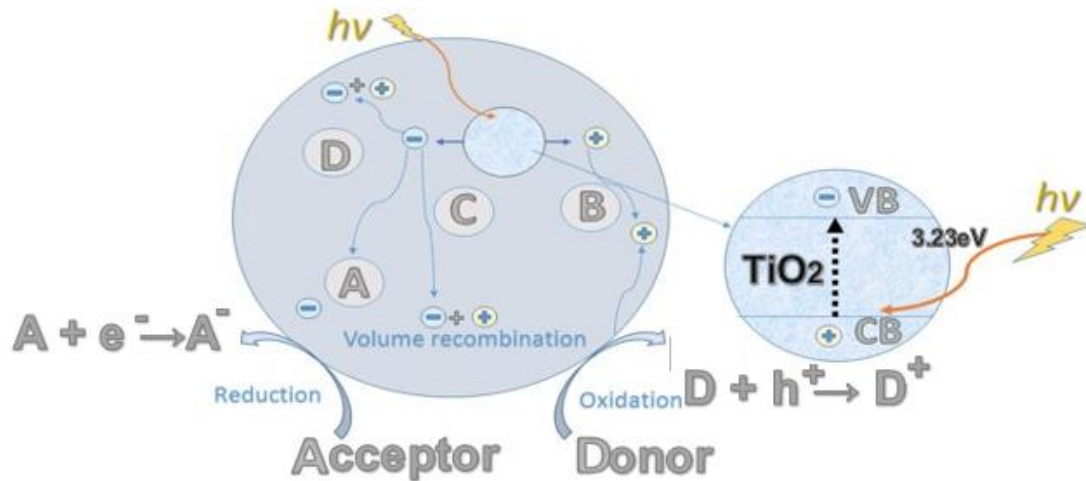
Figure 3-2. Schematic representation of photoexcitation and de-excitation events over semiconductor solid surface

As it can be observed from Figure 3-2 the excitation of an electron from the valence band to the conduction band initiated by light absorption and several pathways may occur further. Due to the acquisition of sufficient amount of irradiance, catalyst particle that absorbed organic/inorganic specie acts either as an electron donor or acceptor. Absorbed species can accept electrons from semiconductor (electron donors) as it is illustrated in pathway A. Moreover, oxidation of donor species (pathway B) is taking place when holes migrate to the surface, where they can combine with electrons from donor species. The charge recombination excludes the electron and hole migration to the surface, thus impeding their reaction with the adsorbed molecules. Recombination can occur in the volume and at the surface of the semiconductor particle (pathways C and D, respectively) Recombination of the separated electron and hole can occur in the volume of the semiconductor particle or on the surface with the release of heat [10].

3.3. Non-thermal Plasma technology for CO_2 conversion

As a state of the matter plasma was defined as special fourth state besides common gas, liquid and solid. Plasma is a quasi-neutral electrified gas, which includes diversity of excited species such as positive and negative ions, electrons, gas atoms and molecules, free radical moving freely in a chemically energetic reactive environment. Consequently, charge carriers are formed due to the supplement of needed energy for plasma generation [13,14].

There are three major groups to classify plasma: equilibrium (thermal), quasi-equilibrium (low temperature) plasma and non-equilibrium (non-thermal plasma). Those types are different in number of temperature characteristic occurring in plasma volume such as electron temperature, ion temperature, temperature of undergone gas and variant vibrational and density number [18].

Plasma technology has undergone significant developments for decades. Non-thermal plasma (NTP) treatment is used in order to improve surfaces morphology, in material processes and as emissions abatement technique. [20,21,22].When it comes to application of NTP in CO_2 conversion, advantages such as its non-equilibrium state, low temperature and power requirement to activate chemical and physical reactions represent massive potential for further development.

Atmospheric NTPs may be obtained from a variety of electrical discharges including corona discharge, amphoteric unifor1`m glow, dielectric barrier (DBD), gliding arc, plasma needle or micro hollow cathode discharge [17, 18].

### 3.3.1. Dielectric Barrier Discharge

The main condition to sustain plasma is application of sufficient voltage range that shall exceed the breakdown voltage of gas utilized in system. When current voltage level is accomplished, system gases do not possess dielectric properties and become conductors [16,18]. Variety of reactor configurations have been employed to proceed experimental trials with non-thermal plasma. DBD (Figure 3-4) is constituted of two electrodes that are separated by a gas gap spacing with at least one dielectric material in the gap. Dielectric-barrier discharge is one of the frequently used type of discharge that can operate under atmospheric pressure and was proved to be an effective tool to measure sustainability of atmospheric plasmas basing electrical breakdown of selected gases. DBD reactors are employed for plasma-catalytic CO_2 conversion into value-added chemical at low pressure and temperature conditions. Electrodes arrangements may vary in regard with design of DBD reactor [16]. In order to build configurations alike, glass, quartz, materials containing titanium dioxide and further dielectric materials are used.

The main types of reaction in volume of plasma include heterogeneous and homogeneous reactions. Performance of homogeneous reactions defined by inelastic collision between electrons in the gaseous phase. In these reactions transfer of ions, electrons or other charged particles get into excitation state and save thermodynamic equilibrium due to unique characteristics of NTP. Homogeneous reactions comprise following: excitation of atoms or molecules, de-excitation, ionization, dissociation, volume recombination, electron-ion and other gas phase reactions [17].

Heterogeneous reactions occur in dielectric-barrier discharge volume in a way that in surfaces such as semiconductors and plasma species maintain the contact. Heterogeneous reactions include: etching, adsorption, deposition, recombination, sputtering and polymerization reactions.

Permittivity of dielectric barrier is a crucial factor in providing efficient and stable charge distribution across reactor surface. In this regard, implementation of materials with higher permittivity may improve conversion of CO_2 [17].

As a result of electron collisions in volume of gas mixture (CO_2, N_2) new excited bulk gas molecules occur. These species lose part of energy by emitting photons and heat. Moreover, due to dissociative electron attachment process results in production of free radicals and ions [18].
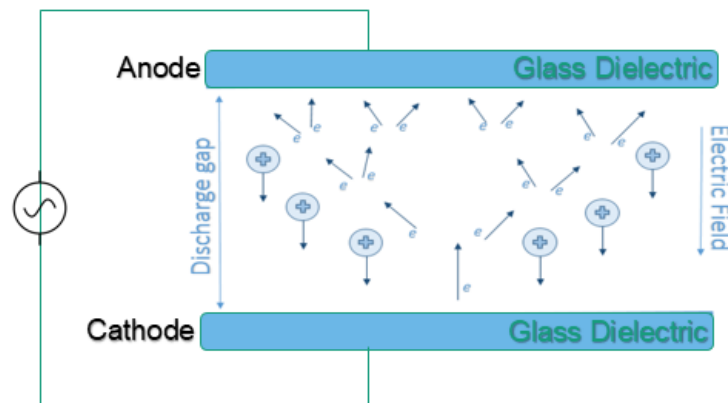
Figure 3-4. Scheme of electric breakdown in volume of NTP

Electric field at both points of DBD reactor occurs when voltage is applied between higher electrode and ground electrode causing also a polarization effect. Moreover, electric field is defined as ratio between voltage and discharge gap. As it might be observed from the picture, electrons drift from cathode to anode zone. In practice this drift electrons generate sparks due to the ionization of neutral gas molecules is taking place. When electrodes covered with insulating material they compose dielectric barrier in volume of which stable discharge is carried [18].

When it comes to consideration of gap distance between dielectric components, it was reported that shorter distance results in higher conversion and energy efficiency in case with CO_2 conversion [18].

3.3.2. Hybrid DBD Set-Up

Synergistic methods of plasma catalytic gas conversion in DBD reactor was developed and further investigated. Mutual positive impact and overall process efficiency was reported. In CO_2 plasma catalytic deposition the role of the catalyst is to absorb excited during plasma ignition CO_2 species and desorb the product molecules. Catalyst enhances electric field in DBD due to its high conductivity. Formation of ultra-fine species with higher specific surface and as result physical changes in plasma morphology and enhanced catalytic activity takes place. It was also reported that adsorption of pollutants is enhanced in hybrid configurations due to active sites of catalyst [19].

The role of plasma on catalytic reaction has also been explored, in a way it was reported that physicochemical properties of the catalyst such as reduction potential, surface area as well as morphology are enhanced in plasma assisted processes. Overall reaction efficiency is improved due to increment of active sites on the catalyst surface [20]. Moreover, impact of thermal activation of catalyst was observed during non-thermal plasma operation. The effect is explained by the fact that more electrons-collisions initiated by plasma application cause increment of temperature of the gas in system. Temperatures inside the reactor depend on gas commotion itself as well as residence time in volume of reactor. It has been proven that higher temperatures of catalyst improve removal rates in experiments with VOCs [20]. Moreover, plasma emission of light triggers heterogeneous catalysis, especially when it comes to semiconductors with higher photo-stability such as TiO_2. UV waves which plasma discharge possess triggers kinetics of reaction in a way that more electron-hole pairs reformed on the surface of catalyst. However, it shall be noticed that current positive effects a certain limitation, in regards with particular reactor geometry and discharge type application of higher powers may lead to demolition of catalyst pores and as result formation of empty spaces on the catalytic surfaces [21].

The coupling between catalyst and plasma mechanisms can be done in two different ways (Figure 3-4): Two stage post-plasma catalysis when catalyst is positioned downstream of power discharge zone and one stage in-plasma catalysis when the catalytic element is placed in the discharge zone [22].
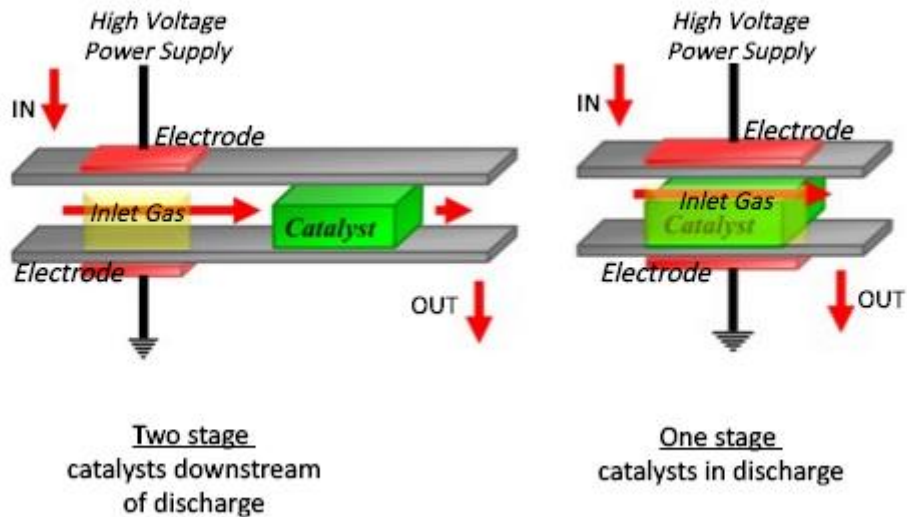
Figure 3-4. Configurations of NTP catalytic process

In the first case only the long-lived species can reach the catalyst surface and react, while short-lived radicals, ions and excited species decay in the first part of the reactor. In a two-stage set-up, the main role of the plasma is to alter the gas composition fed to the catalytic reactor. In in-plasma catalysis system, synergistic effects are greater since short-lived excited species are formed near the catalyst surface the way the catalyst is inserted in reactor influence the overall performance [19,20].

Moreover, introduction of the catalyst into between electrodes zone of discharge as in case with IPC leads to better homogeneity, stronger electric fields and as a results higher threshold of energy during process.In order to achieve high conversion efficiency in PPC higher energy densities, in terms of amount of energy within reactor volume than IPC. However, there is significant potential to explore further processes where current configuration would represent remarkable outcomes [20,24].

4.   Methods

CO₂ reduction diluted in N₂ gas flow was investigated by means of plasma-photocatalytic process. Conversion of CO_2 was conducted in atmospheric pressure DBD glass reactor by optimizing process parameters of plasma such as electrical properties of applied discharge and manipulating the residence time and CO_2 concentration of inlet gas. Based on assumption that synergistic method of plasma-photocatalysis gas deposition would demonstrate higher performance than conventional bare configuration, two reactor types were tested: bare glass reactor and hybrid reactor with TiO_2 coated surface parts. The effects of discharge power, gas flow rate and CO_2 concentration in inlet gas on CO_2 conversion and energy efficiency of the process were further studied and analyzed.

## 4.1.   Reactor Preparation

Reduction of concentration of carbon dioxide was conducted using a non-thermal dielectric barrier discharge (DBD) plasma reactor at ambient conditions. While considering the reactor design, the literature reviews were considered [18] as well as opportunity and applicability of reactor operation in existing laboratory conditions. Finally, it was decided to arrange planar DBD electrode configuration:
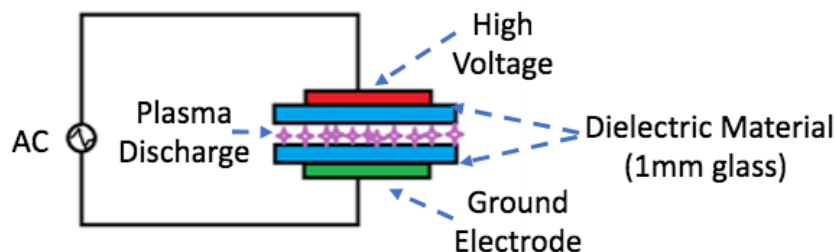
Picture 4-1. Planar DBD configuration used in experiment

For current experiment two reactor systems were built: bare DBD glass reactor and TiO_2 coated DBD glass reactor. Geometry of the DBD glass reactor was adjusted in regard with estimated proportions and corresponding parts were cut from glass. Gap distance of 1 mm was assumed for both systems. Since hybrid configuration required coating, which was completed by tapping the side corners of surface part in order to achieve fine TiO_2 particles distribution, it was decided to elongate the surface width (B parts) for 4 mm as it is represented on Figure 4-1.
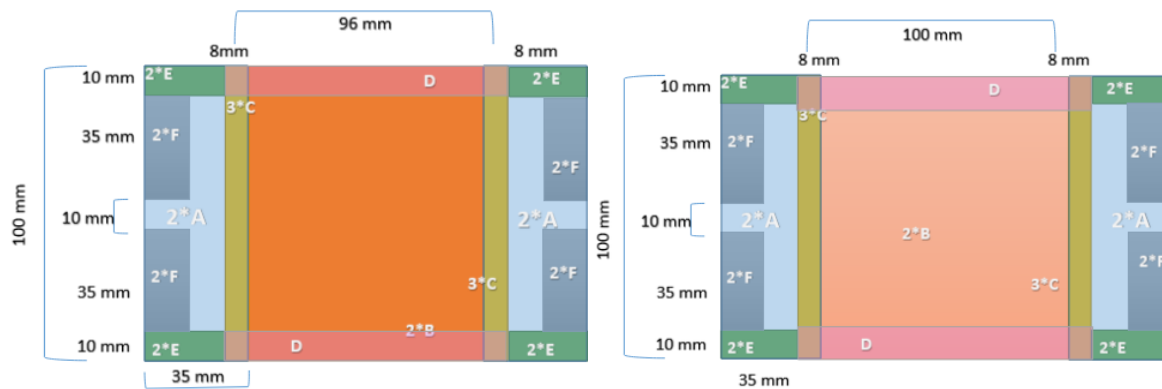
Figure 4-1. Top side view of bare (left) and hybrid (right) reactor configurations with corresponding sizes of constitutional parts

Parts of both Bare and Hybrid configurations were cut by hand with glass cutting pencil cutter from clear glass sheets of a different thickness in order to fulfil the requirements of design template. In a way parts E and F were cut from 3 mm standard glass, whereas the rest parts A, B, C, D were made from 1 mm glass. As it may be noted from Figure 4-2, the dielectric barriers were built with 1 mm thick glass with 1mm distance between each other.. Selection of thicker parts was rational since only supporting blocks were constructed with this glass type.
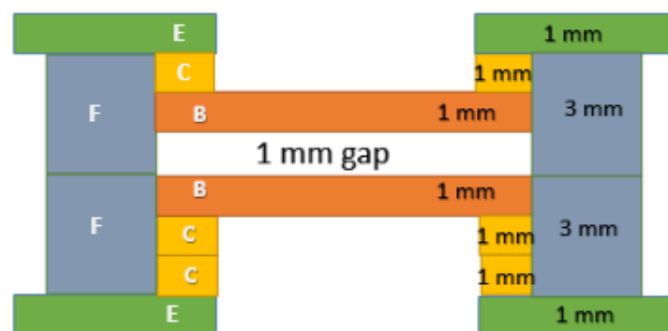

Figure 4-2. Profile side view of bare reactor configuration with corresponding sizes of constitutional parts

DELO-ML DB135 anaerobic and light curing high-strength glue was used in order to attach parts. In order to proceed correctly it was important to control that bonded surfaces were dry and free of any kind of contamination. Individual plastic pipettes were employed to spread glue across the bonding surfaces. Curing (drying) of glued parts was performed with UV light (UV COB LED 395 nm) in wavelength range of 320-420 nm.

After glass parts of reactors were glued, the pipe for inlet and outlet of the gas was also attached by gluing. It was important to secure gas tightness of the glass configuration. For current purpose, bare reactor system was washed with isopropanol in order to observe possible leakages. Afterwards, bare reactor was left to dry in oven for 2 h at 80 °C. Based on

experience of where possible leakages might occur, Hybrid reactor was glued more carefully, as due to the fact that inner surfaces of DBD were covered with TiO_2 powder it was not possible to flush it with isopropanol, otherwise coating would have been washed.

Moreover, electrode zone made from aluminum foil tape of a round shape was attached on the outer surface of both sides for each of two reactors. It is worth being noted that round electrode shape is better than any angled one due to the fact that plasma load is uniformly distributed across required defined surface. Conduction part was cut from cupper tape and attached with adhesive electrical insulating tape (polyimide film, amber, 33 mm x 9 mm) to the electrode part.
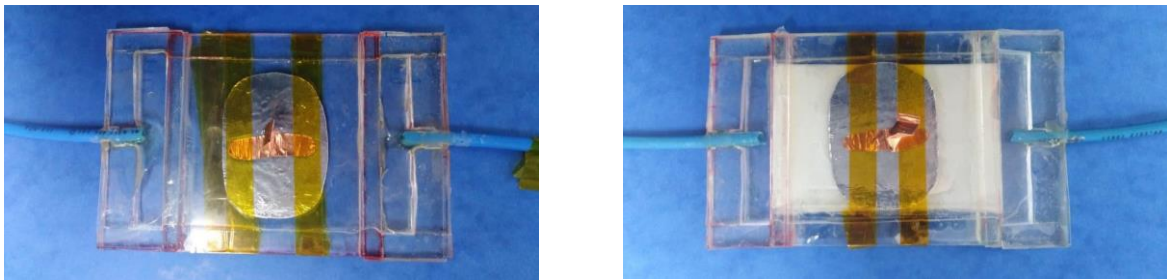

Picture 4-3. Complete Bare (left side) and Hybrid (right side) DBD reactor configurations

With hybrid configuration the reactor construction procedure was different due to layering of catalyst on surface of DBD. Coating was conducted by mixing TiO_2 powder KRONOClean 7050 (a photocatalyst designed for use in conjunction with UV radiation) and isopropanol (C_3H_8O) in following proportion: 5 g of TiO_2 to 50 mL of isopropanol. Current suspension was mixed manually with stir rod for 5 minutes. Afterwards, mixture was delivered on desired region of surface by careful spilling over a glass surface. Then coated parts were paced in oven for 20 h at 80 °C and after surface parts were glued with the rest blocks of reactor.

4.2. Measurement Set-Up

CO_2 plasma-catalytic conversion was conducted in DBD planar reactor, which was the main component of the system shown on Figure 4-3. The DBD reactor was supplied with AC high power from high voltage pulse generator at initial frequency of 93.5 kHz and pulse time 10 µs. However, due to malfunction of main pulse part of pulse generator and consequent replacement of high voltage cable, parameters of frequency and pulse time were changed to 84.3 kHz and 15 µs correspondingly. Current parameter changes were made in order to build resonant circuit which would operate with the same power supply as was previously established.
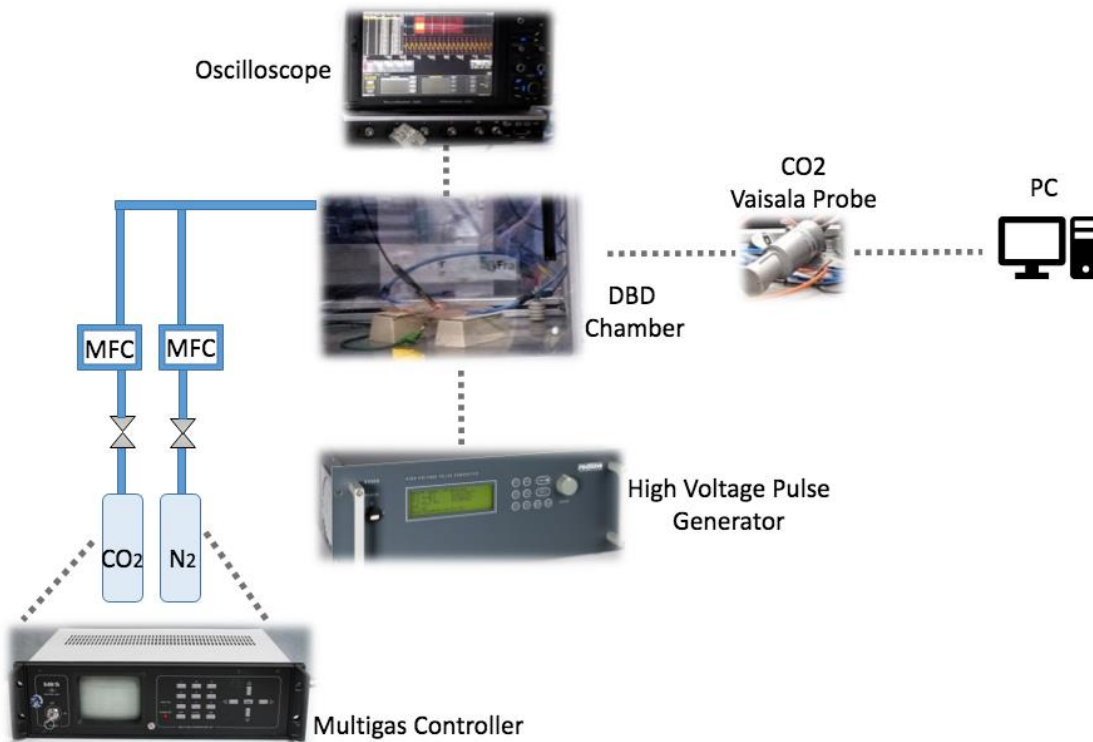
**Figure 4-3. Schematic diagram of experimental set-up**

Introduction of oscilloscope (Teledyne LeCroy HD04104A-MS) in measurement set-up was made in order to observe behavior of wave shapes and detect significant variation of plasma discharge in case of interference or malfunction.

In order to perform experiment the DBD configuration was placed inside experimental chamber Figure 4-4 and connected to gas inlet and outlet with tubes. Feed gas was composed of two gases N_2 and CO_2 and total flows were changed by replacing the mass flow controllers calibrated to current gases in regards wit defined experiment conditions. MFCs were calibrated to N_2 200 sccm, N_2 1 sLm and N_2 2 sLm and replaced manually in regard with requirement of experimental trials. Value for gas flows were regulated using multigas controller. As it was decided to have a gas mixture in total flow of N_2 and CO_2 multi gas controller was manually adjusted in order to sustain required fraction of CO_2.

The DBD chamber was organized in such a way that there were inlet pipe connected to the gasses source supplying constant mass flow in reactor. Outlet tubes were connected to Vaisala CO_2 probe in order to monitor values of volumetric concentration of carbon dioxide and record this data on PC with Putty terminal application. Vaisala CO_2 probe main component is IR (infrared radiation) sensor which detects CO_2 at its wavelength of in range of 4000-4500 nm [25].
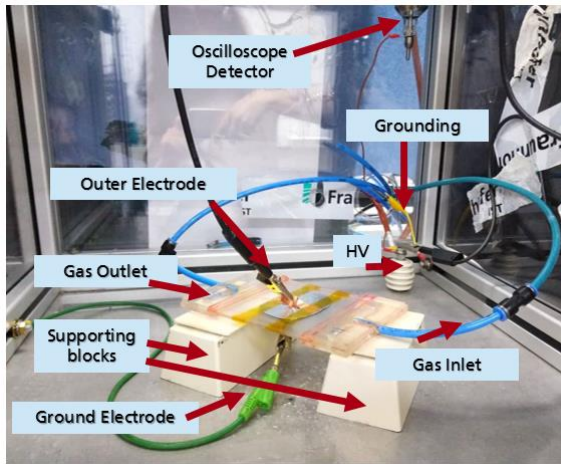
Figure 4-4. Inside of DBD chamber
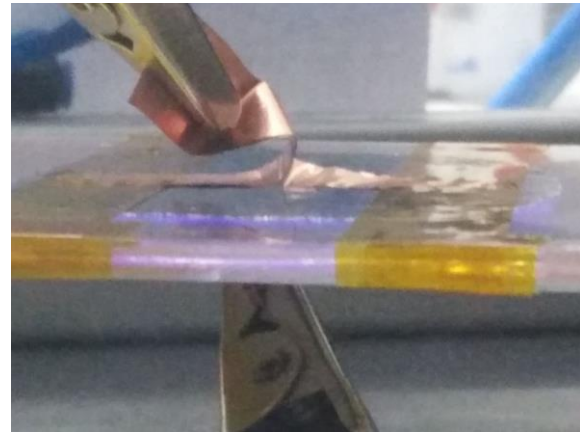
Figure 4-5. DBD reactor during plasma ignition

Probe read was conducted every 10 sec and afterwards based on the data, plots of the process in terms of CO_2 concentration reduction during plasma ignition (Figure 4-5) were modeled.

Moreover, DBD chamber was closed with grounding insured door and in case door was opened, the pulse generator would be immediately shout down automatically. This safety precaution was set in order to avoid accidents. However, this foresight limited introduction of thermometer to the system, which was suggested in order to measure and compare surface temperature of Hybrid and Bare modes; as in case of application the door would not have been able to close due to wire component of thermometer. It was further suggested to use IR thermometer and measure the temperature straight after the plasma ignition phase, unfortunately, the results were not reliable and in this regard were not taken in consideration.

4.3. Experimental Part

The very first experimental trials were run with main objective to test mechanical properties of Bare reactor configuration in terms of maximum power input and total applicability of current reactor to existing laboratory equipment. As Bare reactor was the reference point, all experiments on determination of process parameters by empirical examination were conducted only in this mode. When the experiment conditions were defined, both Hybrid and Bare configuration were undergone same set of experiment trial.

Testing capacities of reactor configurations

The very first experiments helped forward to realize that some adjustment in the reactor design shall be made. For instance, by gluing the parts of first reactor, it become clear that glue material may have pores and that is the reason why absences of any whole and gas tightness had to be insured by running a test. For current test definite amount of isopropanol was washed through the system and the leakages were defined as well insignificant glue amounts were washed out of system. Moreover, this procedure helped forward to detected potential spots of leakages which was quite useful when it came to Hybrid reactor construction, as system was not being able to be flashed due to presence of TiO_2 coating. However, in order to make sure air tightness of current configuration was achieved, system was flashed with indefinite amount of N_2 gas.

Mechanical extent of utilized for reactors construction glass was tested in further experiments with plasma application.

Optimization of concentration range within variable residence time

Variation of CO_2 concentration with three major peaks of 1000 ppm, 1500 ppm and 2000 ppm was assumed as an experimental condition to observe impact of CO_2 fraction in total gas mixture on final CO_2 conversion and energy efficiency. Another suggested test condition was variation of residence time of gas in reactor, by increasing total flow rates; three major total flows were tested: 0.2 sLm, 1 sLm and 2 sLm. In order to adjust desired CO_2 concentration range to each of selected total flows, CO_2 flow was manually manipulated with multigas controller and based on Vaisala CO_2 probe read it was further modified until corresponding concentration in each of the total flow was equalized (Table 4-1):

Table 4-1. Gas controller parameters for each of the total flow streams in regard to corresponding CO_2 concentration

CO_2 concentration:	1000 ppm	1500 ppm	2000 ppm
N_2 total flow (sLm)	CO_2 flow (sLm)	CO_2 flow (sLm)	CO_2 flow (sLm)
2	0.0017(5-7)	0.0026(5-6)	0.002(8-9)
1	0.0009(1-2)	0.0013(6-8)	0.0019(2-4)
0.2	0.00018	0.0002(8-9)	0.00049

Optimization of DBD plasma parameters

Discharge power is one of major factors contributing to CO_2 decomposition rate, for this reason variation of applied discharge power was appointed to be one of the test conditions. In order to select lower threshold, it was decide to operate on the lowest discharge causing voltage and corresponding power, which for give high voltage pulse generator (Figure 4-3) was appointed to be 8 W. For upper discharge power application limit, 15 W, 20 W and 24 W were tested at different ignition times. In case with 1 h trial with 15 W no mechanical breakdowns or process malfunction were detected. Application of 20 W power for 15 and 30 minutes went successful in terms of reactor operability, however, in case of 1 hour ignition time, crack on the glass surface close to conduction zone was observed. In trials with 24 W discharge power application, glass surface of DBD was fractured after 7 minutes of plasma ignition. Based on obtained experience it was decided to establish upper threshold to 16 W and appoint middle peak to 12 W.

Frequency, pulse time and density of plasma was appointed with help of laboratory assistance based on experience and in regards with their recommendation. Plasma ignition phases were also decided, basing assumption on optimum ignition time on observed behavior of CO_2 concentration.

Final Experimental trials and Data analysis

Finally, total 54 experimental trials were performed based on defined previously conditions: Selected reactor type (Hybrid/Bare) was placed in DBD chamber (Figure 4-4) on plastic supporting and checked for proper connection with high voltage upper and lower electrodes and on tight connection with gas inlet and outlet. Series of experiments (27 trials for Hybrid and 27 trials for Bare configuration) with plasma ignition time: 15 min off/20 min on/ 15 min off were performed according to the plan (Table 4-2)

Table 4-2. Measurement plan for individual configuration type

Total flow (sLm)	CO_2 Target (ppm)	Power (W)	Total flow (sLm)	CO_2 Target (ppm)	Power (W)	Total flow (sLm)	CO_2 Target (ppm)	Power (W)
	1000	8		1000	8		1000	8
		12			12			12
		16			16			16

Total flow (sLm)	CO₂ Target (ppm)	Power (W)	Total flow (sLm)	CO₂ Target (ppm)	Power (W)	Total flow (sLm)	CO₂ Target (ppm)	Power (W)
2	1500	8	1	1500	8	0.2	1500	8
		12			12			12
		16			16			16
	2000	8		2000	8		2000	8
		12			12			12
		16			16			16

In order to summarize the results of experimental trials certain calculations were undertaken. For determination of energy efficiency, specific input energy and CO_2 conversion formulas from Chapter 3.1 and corresponding graphs were plotted with OriginLab program. Collected with Putty Terminal Application data on CO_2 concentration behavior in regard with plasma Ignition was also further analyzed.

5.   Results and Discussion

Adjusting of process parameters, determination of operational thresholds and limits of particular laboratory set-up was accomplished by empirical examination. At the very first stage experiments with application of high power, it was experienced that application of discharge power higher than 20 W would lead to instant fracture of 1 mm glass surface of DBD reactor. Moreover, lowest applicable voltage of 123 V and outcome power of 8 W can cause plasma ignition in current set-up. For this reasons, following trials were appointed to three major peaks of power discharge application: 8 W, 12 W and 16 W. Constant monitoring of data was conducted at all stages of experiment proceeding.

Observation of the reactor operation was carried out through comparison inlet and outlet concentrations of CO_2 with Vaisala CO_2 probe. In order to assess performance of both Hybrid and Bare reactors, energy efficiency of reduction and percentage of conversion of CO_2, firstly, they were calculated and further plotted in regard with interdependent factors such as applied power and specific input energy.

5.1.   Influence of DBD ignition time

Plasma ignition time interval definition and stabilization of constant reduction conditions were performed at first stage. In order to define an interval with stable flow and optimize plasma ignition number experiments were conducted. Variation of time of ignition was performed at a different phase times starting with 5 min ignition and up two 1 h trials.

Graph 5-1 represents trials in Bare reactor system conducted at the first stage of experiment with lightning sign indicating plasma ignition. Two CO_2 concentrations points were tested based on assumption that higher concentration might have an impact on stability of operation. The hypothesis was incorrect, as it might be observed for both concentrations equalization was not observed. It was assumed that there would not be difference in overall behavior of gas mixture under plasma ignition for both Hybrid and Bare system since gas composition of N_2 and CO_2 would remain the same without dilution of other gases in all of performed trials and for this reason only one reactor system was tested.
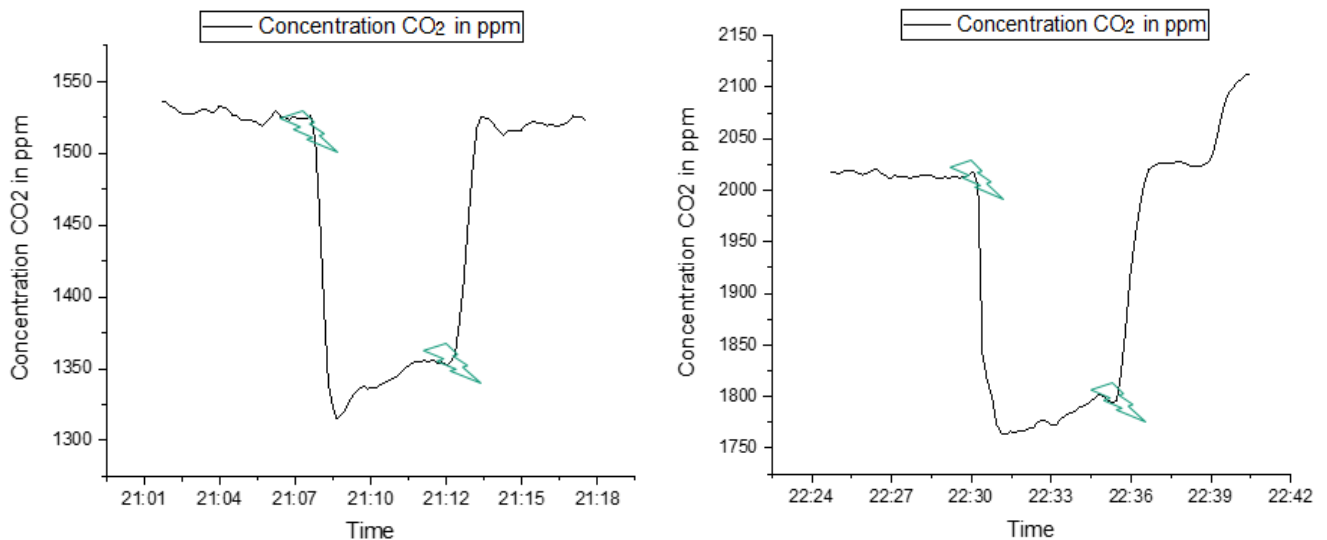
Graph 5-1. Ignition phase: 5min off/5min on/5min off with 12 W applied power for 1500 ppm and 2000 ppm CO₂ concentrations

Current measurements were taken at total flow 0.2 sLm N_2 and CO_2 0.0028 sLm for CO_2 concentration 1500 ppm; for CO_2 concentration 2000 ppm total flow was 0.2 sLm N_2 and CO_2 0.0049 sLm. Measurements were taken several times for each of individual concentration, nevertheless, difference in behavior of same trials was not observed. As it indicates on Graph 5-1 relative equalization of gas flow was established at the beginning 5 min of plasma off phase, however, the variation of behavior through all plasma on time is quite intense and stabilization was not achieved for such a short ignition time period. This can be explained by the fact stable plasma operation and discharge distribution requires longer times to be established.

Further experiments on definition of reliable plasma ignition phase were conducted operating several trials with same concentration CO_2 of 1500 ppm (total flow 0.2 sLm N_2 and CO_2 0.0028 sLm). Ignition time of 10, 15, 20, 40 and 60 min were tested at 12 W applied discharge power. During 60 min trial one sample of reactor was fractured due to thermal impact. It was observed that longer plasma ignition time results in better stabilization of CO_2 reduced concentration.
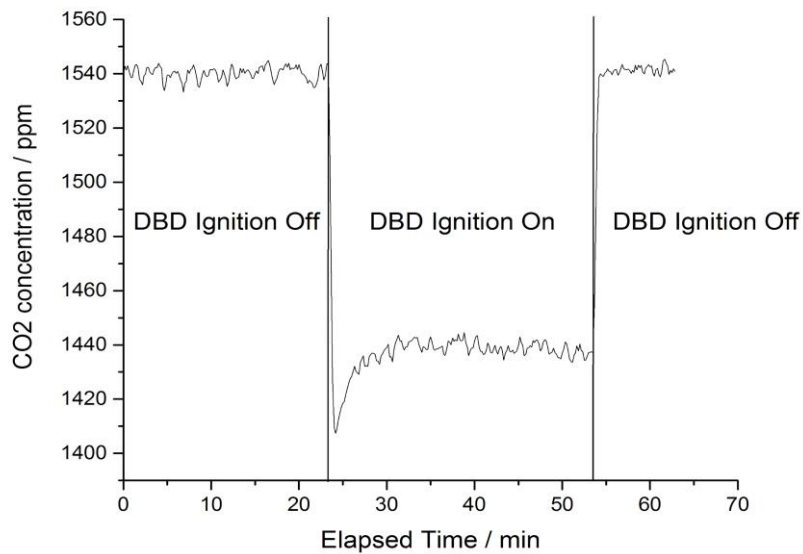
Graph 5-2. Ignition phase: 15min off/30min on/5min off with 12 W applied power for 1500 ppm CO₂ concentration

In this case scenario total flow was set to 1 sLm N_2 and to 0.00137 sLm CO_2. Beginning of the curve represents interval of non-ignition time, which was let longer than in previous experiments, in order to achieve relatively stable gas fluctuation through reactor and to adjust Vaisala CO_2 probe read. It can be noted from Graph 5-2 that in current experiment the variations of concentration even at DBD ignition off time is insignificant and (less than 10 ppm). Moreover, gas behavior is stabilized flow after 10 min of discharge power application. Further experiments (20, 40 min ignition periods) indicated same trend it was observed from Graph 5-2. Finally, it was decided to conduct further examination of CO_2 concentration reduction remaining at following plasma ignition phase: 15 min plasma off/ 20 min plasma on/15 min plasma off.

5.2.   Flow Variation

Manipulation of residence time of gas in reactor was conducted in order to observe effect of dilution on of CO_2 conversion and energy efficiency of the process. Both Bare and Hybrid configuration undergone same set of experimental trials with variable of CO_2 concentration and power application (Table 4-2).

Total Flow 2sLm

In particular total flow, it was assumed that with applied voltage range (8 W, 12 W, and 16 W) it would be possible to observe different impact on reduction of CO_2 concentration and overall energy efficiency of the process. The results indicate following trends:
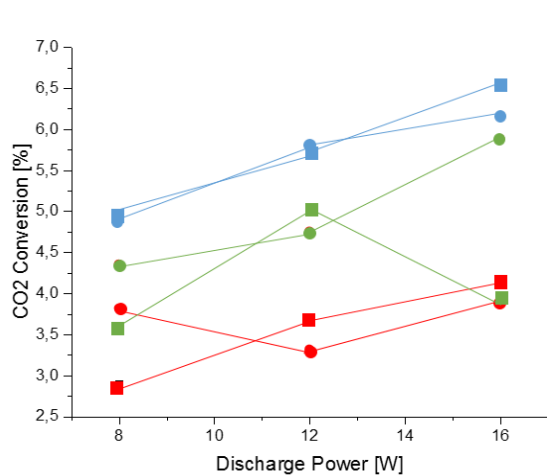
Graph 5-3. Comparative plot of Hybrid and Bare reactor performance of CO_2 reduction in regard to applied discharge power

Graph 5-4. Energy Efficiency performance of both Bare and Hybrid reactor types in regard to applied discharge power
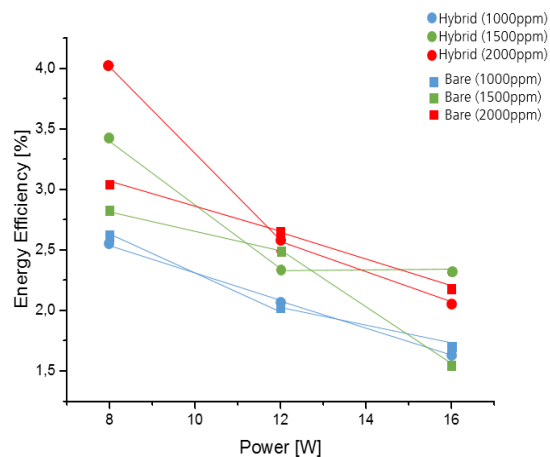
As it may be observed from Graph 5-3, the results appear to be rather controversial in terms of justifying superior performance on CO_2 conversion in Hybrid reactor configuration. For instance, in case with concentration 2000 ppm with higher power application Bare type achieves higher percentage of conversion and demonstrates better performance than Hybrid configuration. Even though the difference is not significant, it shall not be neglected. Furthermore, the trial case of Bare at concentration CO_2 1500 ppm, higher CO_2 conversion was achieved at 12 W and not at 16 W, 5.0 % to 3.9 % correspondingly. Possible reason for this phenomena might be the fact in current residence time, moderate CO_2 dilution and was preferable for current DBD power application. This assumption may also be justified by the fact that for trial of Bare at concentration CO_2 1000 ppm there was no significant difference observed between 12 W and 16 W application trials and overall percentage of CO_2 conversion was at highest level even in comparison with Hybrid configuration.

When it comes to interpretation of energy efficiency performance Graph 5-4, for Hybrid configuration the best outcome was obtained at CO_2 2000 ppm concentration trials where maximum energy efficiency was appointed to 3.2 %. However, in comparison to Hybrid, Bare

mode represent absolute best result in current total flow rate with EE sustained at 4.1 % in case with CO_2 2000 ppm concentration and at 8 W applied discharge power.

It might be also noted further noted from Graph 5-4 that behavior in between concentration range of Hybrid DBD in terms of energy efficiency remains sustained in contrast with Bare reactor. Hybrid configuration in case with CO_2 2000 ppm and 1000 ppm maintains relatively insignificant change difference of EE percentage.

Other observation worth being noted from Graph 5-4 is the fact that higher energy efficiency was obtained with less discharge power application for both Hybrid and Bare reactor configurations. On the other hand, Graph 5-5 represents opposite trend indicating increment of CO_2 conversion percentage in regard with higher magnitudes of power. Current remark suggests that higher conversion efficiency does not result in higher energy efficiency.

Total Flow 1sLm

Performance of Hybrid reactor in comparison to Bare one in terms of reduction of CO_2 concertation at different peak concentration points conducted in total flow of 1 sLm can be observed from Figure 5-5. Results suggest that reduction of CO_2 at 1 sLm total gas flow was more efficient in Hybrid reactor occurs particularly in case with 1000 ppm tested CO_2 concentration. At current CO_2 concentration range and in dependence with different discharge power application, reduction percentage achieved in Hybrid mode was more than 12 %, whereas in Bare reactor it was percentage below 9 % in cases with 8 W and 12 W more than 11 % for 16 W power applications. The highest CO_2 reduction rate 12 % was observed in Hybrid reactor configuration at 1000 ppm CO_2 in gas concentration. Trials of Hybrid reactor in current total gas flow result in all cases higher conversion rates in comparison to Bare reactor. At a 2000 ppm concentration in Hybrid mode, unexpectedly lower conversion was detected at 16 W power application than in 12 W, which might be explained by the permittivity of catalytic layer and possible side-effect.
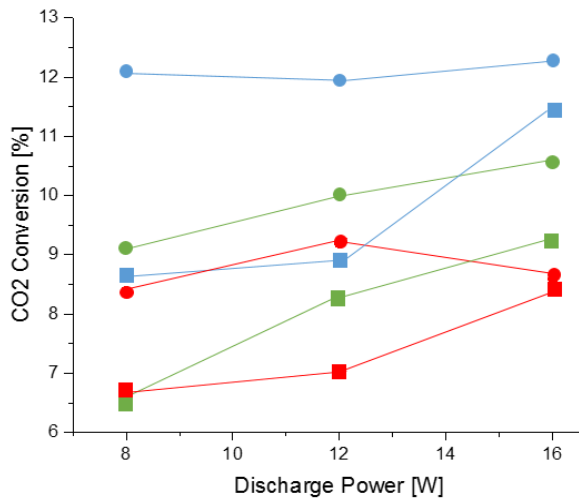
Graph 5-5. Comparative plot of Hybrid and Bare reactor performance of CO₂ reduction in regard to applied discharge power
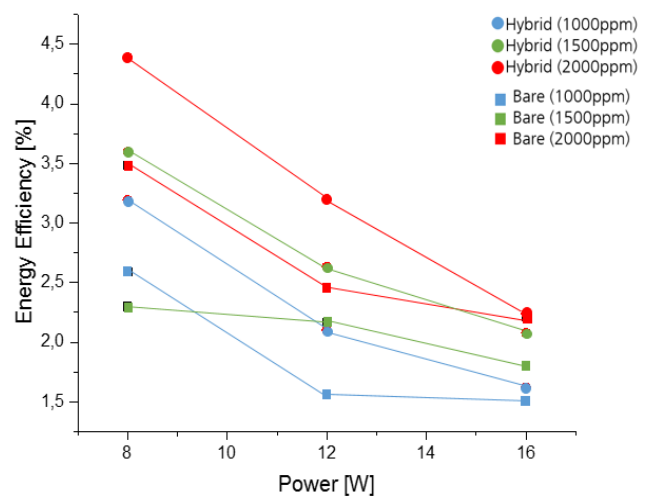
Graph 5-6. Energy Efficiency performance of both Bare and Hybrid reactor types in regard to applied discharge power

While correlating current results of higher percentage of CO_2 conversion with overall process EE from Figure 5-6, it might be noted that opposite trend of lowest, under 3.5 % was indicated in case with Hybrid reactor. Observing, current plot in general one can notice that feasible difference between configurations can be detected at 8 W power application in both of 1500 ppm and 2000 ppm CO_2 concentration, which means that for particular total flow CO_2 reduction is preferably being proceed at higher CO_2 concentration and at lower plasma ignition powers. As it can also be indicated from Graph 5-6, there is an apparent dominant performance in terms of energy efficiency up to 4.5 % at CO_2 concentration of 2000 ppm comparably to others trial concentration range. For Hybrid reactor in the same concentration even CO_2 conversion efficiency was resultative > 8 % of CO_2 conversion percent.

Total Flow 0.2sLm

In hybrid reactor mode, energy efficiency is significantly higher than in Bare mode and at every tested concentration it is accounted to be higher than 3% which represents better performance even with 2000 ppm trials (high efficiency was obtained) of Bare reactor.

Graph 5-7. Comparative plot of Hybrid and Bare reactor performance of CO₂ reduction in regard to applied discharge power

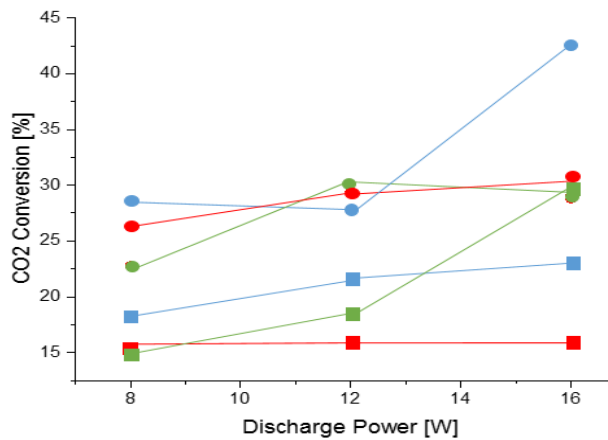**Graph 5-8. Energy Efficiency performance of both Bare and Hybrid reactor types in regard to applied discharge power**
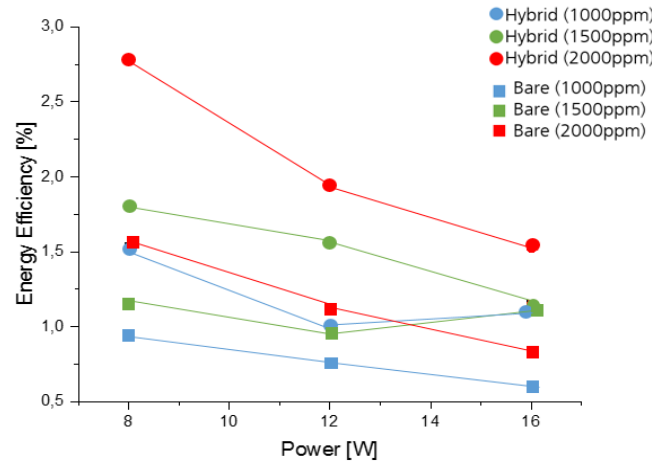
Controversial behavior in regard with applied power was observed and plotted on the graph above, in a way that increment of power in most of the cases did not cause significant energy conversion. Only in case of Hybrid reactor with running CO_2 concentration of 1000ppm absolute conversion maximum of 44.8 % was detected. In regard, to Bare reactor mode, CO_2 conversion remained lower at all concentration points than the conversion percentage of Hybrid reactor. Moreover, in Bare reactor, it was noted that increment of concentration of CO_2 results in lower conversion rates. For instance, in case with 12 W plasma discharge application it was noted that conversion dropped from 20 % to 15 % throughout concentration change in gas input from 1000 ppm to 2000 ppm accordingly.

Current cases represent outstanding conversion rates up to 40 % of CO_2 reduction in Hybrid reactor configuration. In terms of Energy efficiency of the operation, Hybrid mode shows higher potential. Higher energy efficiencies were obtained at lower applied power ranges.

Most importantly, in comparison to 2 sLm total flow, higher conversion rates were indicated even at low discharge power applications.

In addition, for selected CO_2 concentration of 2000 ppm in current total flow of 0.2 sLm CO_2 conversion in variation with applied power range did not significantly vary, especially in case with Bare reactor when the CO_2 conversion remained 15.0 ± 0.5 % for each of three trials. In hybrid reactor, increment of 1-2 % (21-22 %CO_2 conversion) was indicated.

The impact of total flow rate change on CO_2 reduction process can be explained in a way that concentration of CO_2 inflow to total case in case with total flow of 0.2 sLm is 0.001 sLm

and for total flow of 1 which that smaller mass fraction in mixture with N_2 is reduced more efficiently due to appropriate proportion. sLm it is 1.26 sLm (Table 4-1)

5.3.   Reactor Comparison

Results indicate that higher energy efficiencies are attributed to lower power application for both Bare and Hybrid DBD configurations. This relation is better justified with ratio between power (W) and total flow (L/s) indicated by SEI.

Graph 5-9 and Graph 5-10 represent comparative energy efficiency performance in regard to SEI between Hybrid and Bare configurations correspondingly. As it might be noted from the plots, Hybrid reactor for most of the trials on CO_2 reduction is more preferable configuration due to the fact that highest energy efficiency percentages of 4.5 and 4.0 % were discovered. CO_2 concentration of 2000 ppm is of particular interest as both Graph 5-9 and Graph 5-10 demonstrate higher energy efficiency with concentration increment.
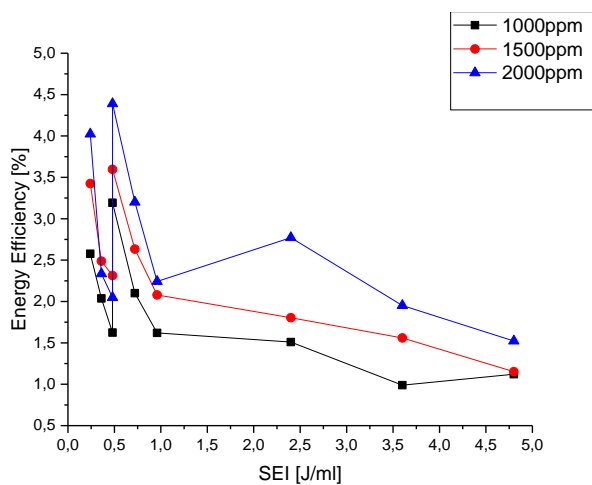
Graph 5-9. Hybrid reactor energy efficiency performance plotted VS SEI
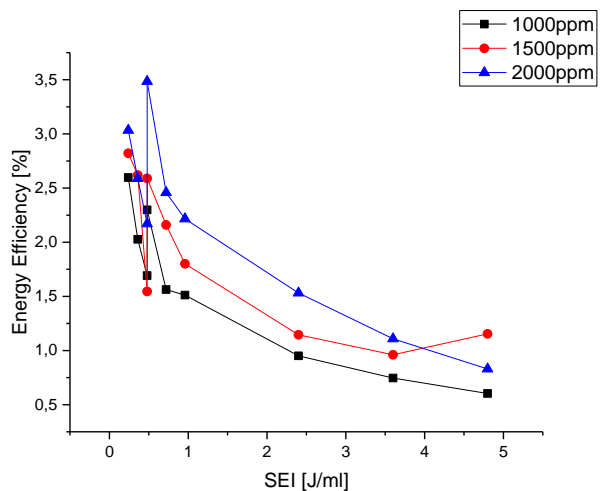
Graph 5-10. Bare reactor energy efficiency performance plotted VS SEI

As in majority of cases it was also observed that lower SEI positively influencing energy EE. Taking into consideration, that most of the trials were performed within SEI less than 1 J/ml) indicating either higher total flow or lower discharge power application, overall performance with lower SEI results in most of the cases in higher EE percentages. Current result can be explained by the fact that certain optimum conditions were obtained at higher residence time

or lower plasma power applications, after which the process was undergone under less favorable conditions.

End of the curve for each of presented lines corresponds with decrement of the residence time. In other words, for higher flows less specific energy input is required. In this regard, most of the dots, representing each individual trial are located in range ≤ 1J/ml. Current zone may be defined as an optimum zone where better outcomes are expected. It shall also be noted that in comparison to other concentrations, CO_2 concentration 2000 ppm is positions higher on a graph and comprises points indicating the highest performance, which suggest that operation on current or higher concentration level is preferable in order to obtain higher energy efficiency rates. Moreover, an obvious trend between all of the three lines shall be emphasized, in a way that increment of CO_2 concentration is related to overall increment of energy efficiency. However, it shall also be taken into consideration that there is a certain upper limit for observation of current effect.

As it can be observed Hybrid reactor performance prevails significantly. Particularly, when it comes to performance in CO_2 concentration range 2000 ppm, result indicate most energy efficiency (4.5%). It shall be also noted that Bare reactor mode trials conducted at 1000 ppm and 1500 ppm concentration does not represent significant variations in energy efficiency percentage.

In terms of CO_2 conversion, result indicate drastic positive impact of catalyst only in trials with 1000 ppm concentration. Questionably, at CO_2 1500 ppm concentration conversion in Bare configuration does not majorly differ from Hybrid mode. This effect can be explained by the fact that for some total flow (in current case 0.2 sLm) adjust rather well and in regards with gas composition (N_2) the dilution is preferable.

In order to further quantitatively analyze the results of experimental trials, Specific Energy Input (J/ml) to Energy Efficiency of each individual CO_2 conversion process was plotted.
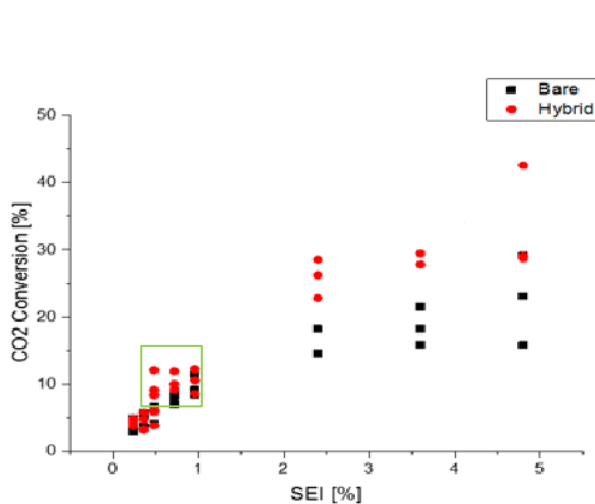
Graph 5-11. Specific Energy Input VS CO_2 conversion for all experimental trials
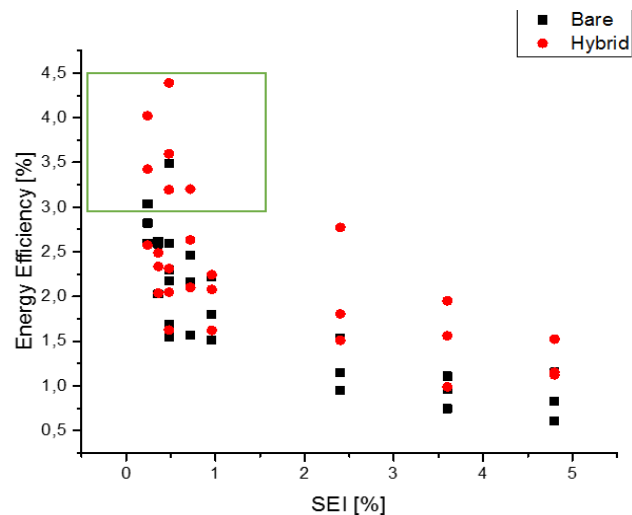
Graph 5-12. Specific Energy Input VS Energy Efficiency for all experimental trials

As it may be observed from the Graph 5-11 indicating performance of Hybrid and Bare reactor in terms of CO_2 conversion, higher conversion efficiency in certain cases (particularly in case with Hybrid reactor) increases with higher specific energy input. Whereas, Graph 5-12 represents opposite effect and illustrates also that for Hybrid configuration operating in lower SEI, process energy efficiency in comparison to other trials of Bare reactor was the highest. What both graphs indicate is the fact that there is proven effect of Hybrid configuration effectiveness. In order to correlate graphs between each other, it is possible to suggest a process window at which both EE and CO_2 conversion would retain at high level, operation of further processes with Hybrid reactor with SEI ≤1 would make much sence.

As it was mentioned higher SEI is attributed to both lower total flows and applied power discharge. A clear trend is observed, in a way that CO_2 conversion increases with increment of discharge power at a given flow rate. Current result can be explained by the fact that at higher discharge power and, consequently, higher voltages, more reactive chemical species are formed due to number of collisions inn excited electronic or vibrational states causing higher conversion of CO_2 reduction.

Main goal of current experimental work was comparison of Hybrid mode to Bare one and determining best case scenarios by determination of their conditoons. Current task can be clearly represented from Histogram 5-1
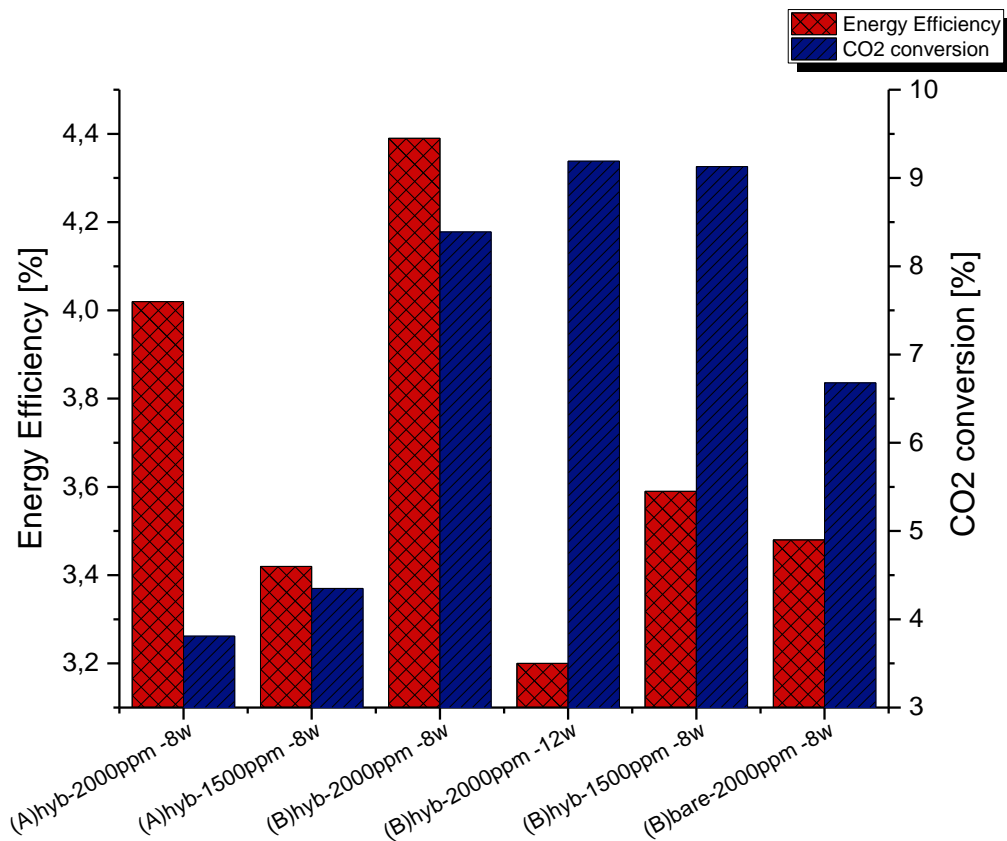
Histogram 5-1.Demonstration of synergistic effect on trials with highest Energy Efficiency %: (A)- attributed to 2 sLm total flow, (B) – regards to 1sLm

Trials operated in lowest total flow (0.2 sLm) were not characterized with higher energy efficiency of CO_2 reduction, process, even though rather significant conversion rates were indicated before (up to 40%).

As it has been represented, there is a significant impact of residence time variation and final results on conversion and energy efficiency Manipulation of flow rates indicated at different discharge powers showed that higher process energy efficiency is attributed to higher total flows and lower power inputs. Moreover, it could also be observes that higher performance of conversion process is atributed to higher concentration of CO2 in inlet cooncentration, as following is implied, at concenteation CO_2 2000 ppm level, highest energy efficicnies were obtained.

Taking all the points above into consideration it is suggested for further trials to use low discharge power of applied power, operate with higher CO_2 concentrations and maintain lower residebce time of gas in reactor by upgrading the total flows.

6.   Conclusion and Outlook

Reduction of CO_2 concentration in a self-cooling DBD reactor coated with TiO_2 and in regular bare reactor system has been carried out at ambient temperature and pressure. It has been proven that Hybrid system with a catalyst layer demonstrated superior conversion and energy efficiency performance in comparison with reference Bare configuration.

Variation of the concentrations at each individual mass flow (0.02 sLm, 1 sLm , 2 sLm) was performed in order to observe impact of gas dilution and residence time on process. discover optimum range at which the efficiency of both energy and conversion would be at a highest point. Operating at a lower CO_2 mass flows appears not to be rational in terms of energy efficiency, even though rather significant conversion rates were indicated before (up to 40%). Moreover, due to higher conversion efficiency and considerable specific energy input NTP dielectric barrier discharge systems has a great potential for up-scaling and similar applications with emission treatments. It shall also be noted that for current set of experiments the gas mixture of N_2 and CO_2 and not the pure CO_2 gas was tested, which means that positive results might also be contributed to the fact of assisting gas suitability for current process. Positive results of energy efficiency of CO_2 reduction can be also attributed to preferable dilution of CO_2 by N_2 and formation other products, which could have been investigated with corresponding equipment. Represented positive results on CO_2 conversion can be attributed to dilution with N_2 in gas composition entering volume of DBD reactor

As an improvement suggestion in order to gain detailed understanding of gas decomposition process occurring in volume of NTP advanced gas analysis can be employed such as gas chromatography. As it was indicated in result section, Hybrid confingration with coated surface part obtain higher performance within experiment trials. In this regard, application of advanced catalytic materials such as nano-catalysts with modified active sites with enhanced physic-chemical properties shall be considered in order to increase efficiency of the process and improve the conversion in hybrid modes. Another practical solution in order to improve specific surface area of a catalyst is spray application of catalytic coat on a surface or beads (for instance glass). In addition, further discoveries can be made in exploring unknown mechanism of plasma-catalysis which eventually would lead to better process optimization..

Current experimental work helped forward deeper understanding of plasma-photocatalytic process, in a way that certain trends such as higher CO_2 conversion corelation does not results in same higher energy efficiency were observed, analyzed and understood.

Observation of possitve results and proving higher performance of Hybrid reactor was only possible because of thorough preparation of experiment set up. Construction of reactors was conducted with careful consideration of their geometry. In order to approximate and forecast

suitable dimensions and overall applicability of reactor size to the existing set-up a massive effort was made. for contributes massively to success in last experimental trials.

However, in order to improve existing laboratory set- up further additions are wellcome. Gas Chromatograher connected to the outlet of the reactor in order to further analyze products of CO_2 reduction. One of desirable and useful for better understanding of cross-effect of plasma-catalysis would have been temperature measurement. Advanced laboratory equipment (UV-Vis diffuse) can be employed in order to monitor and analyze photon-induced electronic transitions of the catalyst phases and temperature of reduction process.

Reference List

[1] NASA. Global climate change. Vital Signs of the planet. https://climate.nasa.gov/

[2] D. Leung, G. Caramannab, M. Maroto-Valerb, An overview of current status of carbon dioxide capture and storage technologies, Renewable and Sustainable Energy Reviews, Vol. 39, p.426-443 (2014)

[3] Aresta, M. In Greenhouse gases: Mitigation and utilization, CHEMRAWN-XVII and ICCDU-IX, (2007)

[4] Y. Bai, J. Chen, X. Li, and C. Zhang, "Non-thermal plasmas chemistry as a tool for environmental pollutants abatement," Rev. Environ. Contam. Toxicol (2009)

[5] B.,Reddy, & T, Gode, Carbon dioxide-based technologies: Converting greenhouse gas to value-added products. Chem Ind Dig. 22. 61-67.. (2009).

[6] M. Aresta. Carbon Dioxide Utilization: Chemical, Biological and Technological Applications (2014)

[7] D. Marxer, P. Furler, M. Takacs, A. Steinfeld, Solar thermochemical splitting of CO2 into separate streams of CO and O2 with high selectivity, stability, conversion, and efficiency, Energy Environ. Sci., 10 (2017)

[8] R. Snoeckx, A. Baogaerts, Plasma technology – a novel solution for CO2 conversion? , Chapter 4. Chem. Soc. Rev. (2017)

[9] G. Chen, L. Wang, T. Godfroid, R. Snyders, Progress in Plasma-Assisted Catalysis for Carbon Dioxide Reduction. Pl. Chem. G. Conv. (2018)

[10] A. L. Linsebigler, G. Lu, J. T. Yates, Photocatalysis on TiO2 surfaces: Principles, Mechanisms, and selected results, J. Chem. Revs., 95 (1995)

[11] A. Wypych at al., Dielectric properties and characterization of titanium dioxide obtained by a different chemistry methods, Jouurnal of nanomaterials Hindawi (2014)

[12] X. Chen, S. S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications and applications, Chemical Reviews, vol. 107, (2007)

[13] Fridman, A. and Kennedy, L. (2004). Plasma physics and engineering. New York: Taylor & Francis.

[14] V. Nehra, A. Kumar, H. Dwivedi, Atmospheric non-thermal plasma sources, Int J Eng, (2008)

[15] B. Ashford, X. Tu, Non-thermal plasma technology for the conversion of CO2, Current Opinion in Green and Sustainable Chemistry, 3 (2017)

[16] X. Tu, J.C. Whitehead, Plasma-catalytic dry reforming of methane in an atmospheric dielectric barrier discharge: Understanding the synergistic effect at low temperature, Appl. Catal., B., 125 (2012)

[17] R.Aerts. W. Somers, A.Bogaerts, Carbon dioxide dissociation in a dielectric barrier discharge plasma: a combined experimental a computational study, ChemSusChem 8. (2015)

[18] A. Fridman, Plasma chemistry, Cambridge University Press,(2008).

[19] J. Amorous, S. Cavadias, A.Doubla, Carbon Reduction by non-equilibrium electrocatalysis plasma reactor. Materials Science and Engineering 19 (2011)

[20] F. Thevenet, L. Sivachandiran, O. Guaitella, C. Barakat, A. Rousseau, Plasma–catalyst coupling for volatile organic compound removal and indoor air treatment: a review, J. Phys. D: Appl. Phys., 47 (2014)

[21] T. Oda, "Non-thermal plasma processing for environmental proection: Decomposition of dilute VOCs in air," Journal of Electrostatics, vol. 57, no. 3-4, (2003)

[22] H. L. Chen, H. M. Lee, S. H. Chen, M. B. Chang, S. J. Yu, and S. N. Li, "Removal of volatile organic compounds by single-stage and two-stage plasma catalysis systems: A review of the performance enhancement mechanisms, current status, and suitable applications," Environmental Science and Technology (2009)

[23] Neyts EC, Ostrikov K, Sunkara MK, Bogaerts A. Plasma catalysis: Synergistic effects at the nanoscale. Chemical Reviews. 2015;115:13408-13446

[24] D.H. Mei, J.D. Yan, X. Tu, Plasma-photocatalytic conversion of carbon dioxide into value-added chemicals, Materials of 22nd International Symposium on Plasma Chemistry (2015)

[25] Vaisala CARBOCAP. Carbon Dioxide Probe GMP343 User's Guide. https://www.vaisala.com/sites/default/files/documents/GMP343%20User%27s%20Guide%20in%20English%20M210514EN.pdf