Packing effect of SiO₂, ZrO₂ and Al₂O₃ beads on CO₂ conversion in a packed-bed DBD reactor

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Abstract: In this work we investigate the effect of three different packing materials on the splitting of CO₂ in a packed-bed DBD reactor. The three different packings are made of SiO₂, ZrO₂ and Al₂O₃. The experiments include tests at different gas flow rates and powers.

Keywords: packing effect, DBD, CO₂ splitting, conversion, energy efficiency

1. Introduction

The interest in the conversion of greenhouse gases into new fuels or value-added chemicals has been growing over the past years, since it has both an economical and an ecological advantage. It reduces our dependence on fossil fuels, and it provides a more environmental friendly solution, where the value-added chemicals can be used as building blocks for the chemical industry [1-3]. The classic bottleneck in this procedure is the large amount of energy that is required for this conversion, as the greenhouse gases are very inert, and the conversion reactions are strongly endothermic [4-5]. The activation of the inert molecules can be achieved by the collision with energetic electrons. This will result in dissociation, ionization and/or vibrational and/or electronic excitation of the inert molecules. The conditions for these processes are best achieved in a non-thermal plasma, which contains energetic electrons, while the gas itself can remain at room temperature [6-9]. Moreover, non-thermal plasmas allow storing the surplus of electricity generated from fluctuating renewable energy sources in chemical energy, since they can be quickly switched on and off [6].

We present research conducted on the splitting of CO₂ into CO and O₂, were CO is indeed a valuable feedstock gas for the chemical industry. The conversion, by means of a packed-bed dielectric barrier discharge (DBD), is carried out in experiments, performed with different packing materials/sizes, gas flow rates and powers. Both the conversion and energy-efficiency are measured and presented here.

2. Description of the experiments

The reactor is depicted in Fig. 1. It is a cylindrical DBD reactor, consisting of an inner electrode and a coaxial alumina tube, covered by a stainless steel mesh electrode. The outer electrode is connected to an AC high voltage power supply (AFS) and the inner electrode is grounded via an external capacitor (10 nF). The discharge gap is fixed at 3.25 mm, resulting in a discharge volume of 12.2 cm³. CO₂ is used as feed gas and both the feed and product gases (CO₂, CO and O₂) are analysed by a three-channel compact-gas chromatograph (Interscience), equipped with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). The gas flow rate is varied at 20, 50 and 100 ml min⁻¹, while the power is set at 60, 80 or 100 W. The frequency is fixed at 23.5 kHz. The applied voltage is measured by a high voltage probe (Tek P6015A), while the total current is recorded by a Rogowski-type current monitor (Pearson 4100). The voltage on the external capacitor is measured to obtain the charge generated in the discharge and all the electrical signals are sampled by a four-channel digital oscilloscope (Picotech PicoScope). A control system is used for the measurement of the discharge power by the area calculation of the Lissajous figures.

Fig. 1. Schematic diagram of the experimental setup.
The conversion, $X$, of CO$_2$ is defined as:

$$X = \frac{CO_{2 \text{,in}} - CO_{2 \text{,out}}}{CO_{2 \text{,in}}} \times 100\%$$

The conversion is used to calculate the energy efficiency of the process. The following formulas are applied for this purpose:

$$\eta(\%) = \frac{\Delta H_R \left( \frac{kJ}{mol} \right) \times X_{CO_2}(\%)}{SEI \left( \frac{kJ}{mol} \right)}$$

where $\Delta H_R$ is the reaction enthalpy of CO$_2$ splitting (i.e., 279.8 kJ/mol), $X_{CO_2}$ is the amount of CO$_2$ converted, and SEI is the specific energy input in the plasma, defined as:

$$SEI \left( \frac{kJ}{mol} \right) = \frac{\text{Plasma Power} \left( kW \right) \times 60 \left( \frac{s}{min} \right)}{\text{Flow rate} \left( \frac{L}{min} \right) \times 22.4 \left( \frac{mol}{L} \right)}$$

3. Results and discussion

To improve the conversion and energy efficiency of CO$_2$ splitting in a DBD reactor, a packing was inserted in the reactor. For each series of experiments, a different packing was used, with the beads either varying from the previous one in chemical composition, or in size of the beads. For every packing, the gas flow rate was set at 20, 50 and 100 ml min$^{-1}$, and the power was raised from 60 to 80 to 100 W. The packings were made of Al$_2$O$_3$, ZrO$_2$, and SiO$_2$ and had the following bead sizes: 600 - 800 µm, 800 - 900 µm, 900 - 1000 µm, 1000 - 1180 µm, 1250 - 1400 µm, 1600 - 1800 µm and 2000 - 2240 µm.

An experiment without packing was also performed, to function as a benchmark.

The general observation is that there definitely is an influence of the packing on both the conversion and the energy efficiency. Only a selection of the results will be discussed in this abstract, which include the trends in conversion for the zirconia packings, and the most interesting values and trends for all packings.

Fig. 2 depicts the conversion (%) as a function of the bead size (mm), measured with ZrO$_2$ beads at 80 W, for 3 different flow rates. The first point on the x-axis, at 0 mm, indicates the benchmark-experiment, which was performed without packing.

As can be seen, a higher flow rate results in a lower conversion, which is logical, because of the shorter residence time in the reactor, resulting in a shorter period of time for molecules to get converted. Fewer collisions can occur in a shorter time, which gives rise to a lower conversion.

A second conclusion is that the conversion increases with the bead size, with the two smallest packings (0.6 - 0.8 mm and 0.9 - 1.0 mm) performing worse than the empty reactor, whereas all the other packings have a higher conversion than the empty reactor. This could be attributed to the changing void space between the beads, changes in surface enhanced electric fields and surface discharges, for a different bead size, resulting in a lower residence time for the smaller bead sizes and more gas-surface interactions. This could explain the lower conversion for smaller beads.

The conversion is higher for a packed bed reactor (starting from 1 mm beads), because the beads act as a dielectric barrier, creating a stronger, local electric field, which accelerates the electrons more, giving rise to more effective collisions and thus to a higher conversion.

When comparing the experiments at different powers, a rise in conversion is observed at rising power, which is logical, although this is not always the case for larger bead sizes.

When comparing the different packing materials, the results indicate a lower conversion and energy-efficiency for SiO$_2$ (for the same bead size), and an increase when using alumina. This cannot only be explained by the difference in dielectric constant of the beads, because the dielectric constant of alumina is 9.1, for silica it is 3.9 and for zirconia it is 10 - 23. The reason is probably that there is also a difference in chemical composition (e.g., the acidity) between these materials.

Looking at all the results, we can identify three very interesting cases.

First, when using a ZrO$_2$ packing, a bead size of 1.6 - 1.8 mm, a flow rate of 20 ml min$^{-1}$ and a power of 60 W, the highest rise in conversion was obtained. Indeed, the conversion increases in this case with a factor of 1.85, while the energy-efficiency increases with a factor of 1.93, compared to the empty reactor.

Second, when using a ZrO$_2$ packing with a bead size of 0.6 - 0.8 mm, a flow rate of 20 ml min$^{-1}$ and a power of 100 W, the most pronounced rise in energy efficiency was observed. Indeed, energy-efficiency increases with a factor of 3.91, but the conversion decreases with a factor of 0.67.
Finally, when using alumina beads of 0.6 - 0.8 mm, a flow rate of 20 ml min$^{-1}$ and a power of 100 W, both the conversion and energy efficiency were significantly increased, with a factor 1.42 and 3.53, respectively. This last result is very important, as it is our goal to optimise both the conversion and the energy-efficiency through a packed-bed DBD reactor.

4. Conclusion
As can be seen from the results from the different experiments, all packings have an influence on the conversion and energy-efficiency. This change is caused by the difference between the packings in chemical composition and bead size. The bead size has an influence on the void space and thus on the residence time, and the chemical composition has an influence on the gas-surface interactions. Additionally, the dielectric constant has an effect on the electric field and thus on the conversion and energy-efficiency as well. To better optimise both the energy-efficiency and the conversion simultaneously, further research will be conducted.

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6. References