

Dissociation of CO₂ by means of a microwave plasma process for solar fuels production

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Abstract: Due to the ambition to cover more and more energy consumption by renewable energy some challenges are arising. Here, the storage of surplus electrical energy, the production of synthetic fuels or of platform chemicals can be named. The dissociation of CO₂ into CO and oxygen by a microwave plasma process could provide a promising solution. The CO₂ dissociation plasma process itself and first results will be presented.

Keywords: CO₂-dissociation, microwave plasma, solar fuels, chemical energy storage

1. Introduction

If a secure, clean, efficient and CO₂-neutral energy supply shall be realized by renewable energy some challenges have to be faced. For example surplus electrical energy from wind and photovoltaic has to be stored for times when no renewable energy is available. Further on, for the transport sector petrochemical-free fuels have to be provided and also platform chemicals for the chemical industry. An approach to convert surplus electrical energy from renewable energies into chemical energy is the dissociation of CO₂ into CO and oxygen. The CO can together with hydrogen (syngas) directly be stored to a certain extent in the already existing gas grid and used for example for heating purposes. Alternatively, the CO represents a platform chemical for the chemical industry or it can be further processed for example to methane or other gaseous or liquid fuels.

Microwave plasma processes provide a promising approach for the dissociation of CO₂ to CO and oxygen since energy efficiencies of approx. 90 % were already reported by Azizov *et al.* and Fridman [1, 2].

The present publication will provide an overview of the used microwave plasma process and first experimental results of the characterisation of the plasma by means of optical emission spectroscopy and estimates of the conversion and energy efficiency.

2. Experimental Setup

The used microwave plasma source is based on a resonator system. A cylindrical resonator is combined with a coaxial one. The coaxial resonator provides the ignition of the plasma without any additional igniters whereas the cylindrical resonator guarantees a stable and continuous plasma operation. The microwave of a frequency of 915 MHz is guided via rectangular waveguides to the microwave plasma torch. The gas can be supplied via the coaxial resonator, either axially through the inner conductor of the coaxial resonator or

tangentially. The plasma is confined in a microwave transparent tube. A schematic of the microwave plasma torch is depicted in Fig. 1.

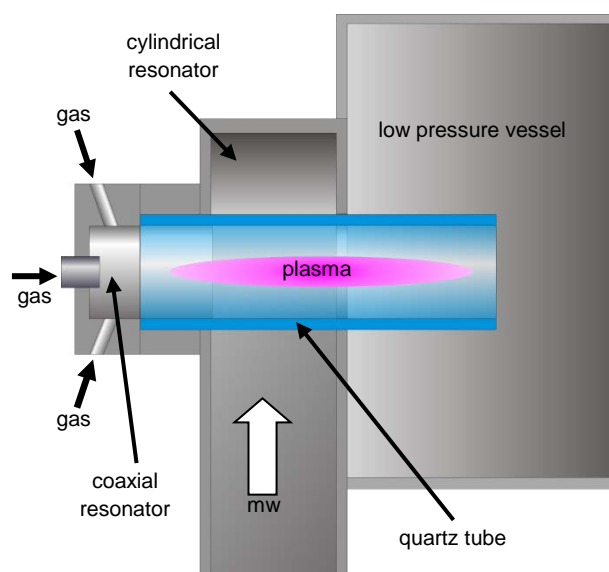


Fig. 1. Experimental set up.

For the presented experiments differently shaped quartz tubes were used and the discharge pressure was varied. Therefore, the plasma was expanded into a low pressure vessel.

3. Experimental Results

First experiments were conducted with a constricted quartz tube. The inner diameter *D* of the quartz tube was 26 mm and at the constriction only 10 mm. The constriction – also called nozzle in the following – was placed to the left inside of the cylindrical resonator. The pressure in the low pressure vessel was kept constant at

0.8 mbar so that the pressure in the discharge tube adapted in dependence of the supplied gas flow and microwave power.

In dependence of the supplied microwave power and the gas flow the discharge switches between two regimes: at low gas flows and low supplied microwave power the discharge has a subsonic character while at higher gas flows and microwave power the discharge behaves supersonic. Photos of the CO₂ discharge for both regimes are shown in Fig. 2.

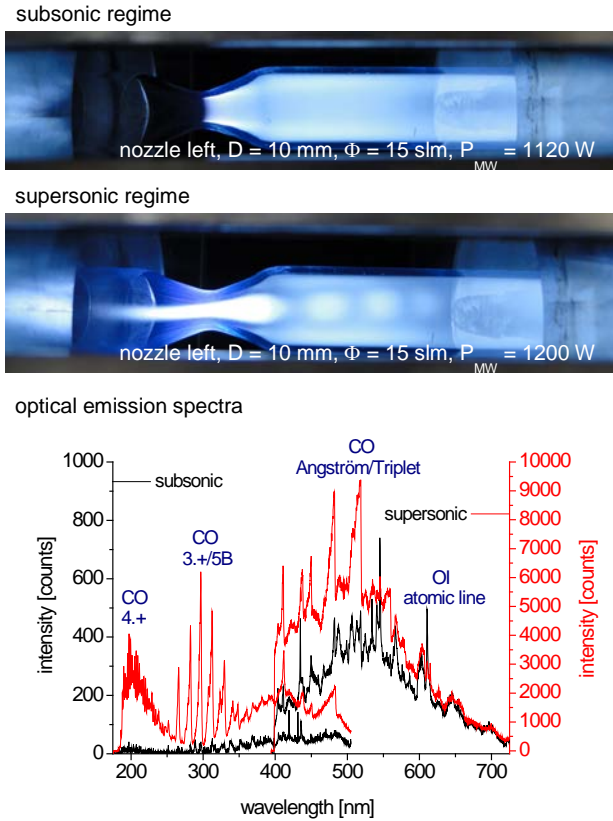


Fig. 2. Sub- and supersonic regime and their optical emission spectra.

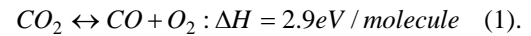
The upper photo shows a subsonic CO₂ discharge. The gas flow is 15 slm and the supplied microwave power 1120 W. The plasma burns only after the constriction of the quartz tube and bluish diffusively. When the microwave power is increased by 80 W to 1200 W the plasma switches to the supersonic regime. The plasma shrinks and becomes brighter, the discharge starts already before the constriction and darker blobs appear after the nozzle which could be indicated as Mach cones.

The plasmas were characterised by means of optical emission spectroscopy. The spectra for both regimes are depicted in the lower part of Fig. 2. Both spectra exhibited CO bands from the UV up to 700 nm. The CO bands belong to the fourth positive and the third positive/5B transition in the UV range and to the Angström and Triplet system in the visible region.

Furthermore, atomic oxygen lines could be identified in the visible region.

What can be observed first is that the intensity of the emission of the supersonic discharge has increased by approximately a factor of 10 compared to the emission of the subsonic discharge. Furthermore, the intensity of the fourth positive and third positive/5B bands in the UV have increased even more dramatically.

Besides the characterisation of the plasma by optical emission spectroscopy the conversion and energy efficiency was estimated by means of mass spectrometry of the out coming gas mixture. After the cracking and the relative sensitivity of the mass spectrometer had been determined the energy and conversion efficiencies were calculated by using the following reaction:



Conversion efficiency X:

$$X = \text{CO}^{\text{out}} / \text{CO}^{\text{in}} \approx \frac{\text{CO}}{\text{CO} + \text{CO}_2} \quad (2)$$

Energy efficiency η :

$$\eta = \Delta H / E_{\text{used}} = 0.208 \frac{\text{kW}}{\text{sl / min}} \cdot \frac{\Phi_{\text{CO}_2}(\text{sl / min})}{P(\text{kW})} \cdot X \quad (3)$$

Since the energy and the conversion efficiency of the sub- as well as of the supersonic discharge were very low – around or even below 10% – the setup was modified: the nozzle was reduced to an inner diameter of 5 mm and placed between the cylindrical resonator structure and the low pressure vessel.

The conversion and energy efficiencies for this configuration for different CO₂ gas flows are depicted in Fig. 3.

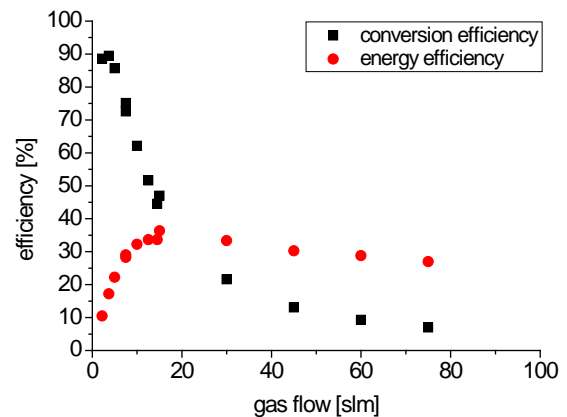


Fig. 3. Conversion and energy efficiency in dependence of the supplied CO₂ gas flow.

It can be seen that the conversion efficiency decrease with the increase of the gas flow. The highest conversion efficiency of almost 90% is reached at a gas flow of 2.2 slm CO₂ and drops to only 7% at 75 slm CO₂. The energy efficiency behaves differently: the energy efficiency start around 10% at very low gas flows, increase up to almost 40% at 15 slm and then decrease slighted when the gas flow is increased more.

Some further experiments with different nozzles, different nozzle positions and variations of the gas flow and microwave power lead to energy efficiencies of up to 50% and 76% of conversion efficiency [3, 4].

4. Conclusions

The presented work on the dissociation of CO₂ to CO and oxygen with a microwave plasm torch revealed that two different regimes can be obtained: a sub- and a supersonic discharge. The emissions of the two different discharges differ a lot from each other in terms of intensity especially in the UV region. However, only very low energy and conversion efficiencies can be obtained with this setup.

Higher energy and conversion efficiencies can be reached with setups where the nozzle is placed between the microwave plasma torch and the low pressure vessel.

To increase the energy efficiency further the experimental setup and the parameter range will be investigated and optimised further.

5. References

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