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Developments in CO_2 dissociation using non-equilibrium microwave plasma activation for solar fuels

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Abstract: Vortex stabilized microwave plasma conversion of CO_2 is considered as promising route for energy efficient dissociation towards CO production. Energy and conversion efficiencies are investigated in scans of reactor pressure, gas flow rate and specific power. Deterioration of efficiencies from 39% to 25% are observed at forward vortex plasmas at increasing pressures which is mitigated in reverse vortex configuration.

Keywords: microwave plasma, CO_2 dissociation, non-equilibrium

1. Outline

Sustainable energy will form a significant part of the energy mix in 2025. The intermittency and regional spread of renewable energy sources requires efficient large scale storage and transport of energy in form of synthetic chemical fuels, compatible to the present infrastructure. Plasma technology, as studied in this paper, can play a prominent role in this great challenge without the use of rare materials. This study addresses the reduction of CO_2 into CO and ½ O_2 (enthalpy 2.9 eV / molecule or 278 kJ/mol). After this dissociation, conventional chemical conversion of CO towards fuels is possible (by Water-Gas-Shift, Fischer-Tropsch or Sabatier, etc.). The CO_2 dissociation has been studied experimentally, initially in a collaboration between DIFFER and the IGVP [1] at Stuttgart and subsequently with newly installed plasma reactors at DIFFER. The focus was thereby on optimization of the energy efficiency of the process using non-thermal (non-equilibrium) microwave plasmas [2] to stimulate vibrational dissociation of the CO_2 molecule (see also [3, 4] for recent results of other groups and [5] for plasma reformation of the CH_4).

2. First CO_2 dissociation experiments

The plasma at IGPV [6] was generated in a 915 MHz TM_{010} cylinder mode cavity into which a quartz tube was inserted. CO_2 was injected tangentially. Up to 10 kW of microwave power was deposited in the reactor. The product formation was measured in a vessel downstream the plasma with a calibrated mass spectrometer (MS). Optical emission spectroscopy (OES) was applied to the active plasma. Several configurations of discharges were investigated [1]: *Type I* in which a nozzle expanded the plasma super-sonically into the cavity (low pressure, order 1 mbar), and *Type II* in which the nozzle was placed after the cavity and plasma (i.e., at the exhaust) such that the output gas expanded supersonically (medium plasma pressure, order 200 mbar). This configuration was intended to prevent vibrational-translational (VT) relaxation losses. Figs. 1 and 2 resent photographs of the running plasma reactors in both configurations. *Type I* experiments resulted in maximum energy efficiency of 15% constant at power accompanied with a linearly increasing conversion with power. The reason for this marginal efficiency was a too low plasma pressure (1 mbar) concerning [2].

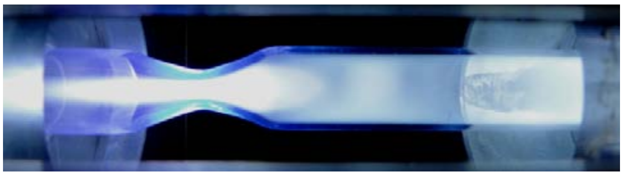

Fig. 1. Photograph of the plasma configuration, *Type I*, inside the cavity the plasma is expanded from left to right supersonically, shockwaves can be observed at the low pressure part of plasma. The energy efficiency was 15%**.**

We will focus on *Type II* experiments in this contribution as efficiencies were much favourable in this configuration.

Type II experiments were performed in the power range of 3.1 to 8.1 kW, first at low input gas flow of 11 slm. High conversion efficiencies (47% till 83%) were observed along with energy efficiencies between 35% and 24%). In *Type II* plasma, the energy efficiency increased with decreasing power input. The plasma could not be sustained below 3 kW input power. Concerning [2] the energy efficiency would increase if the energy per CO_2 molecule is reduced. To accomplish this, the CO_2 input gas flow was increased to 75 slm, see Fig. 3.

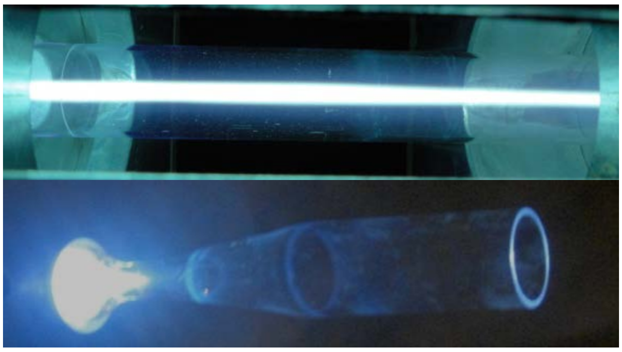

Fig. 2. Top: Photograph of the plasma configuration, Type II, inside the cavity at low input gas flow of 11 slm. Bottom: The plasma is quenched by the nozzle just after the cavity in the vacuum vessel.

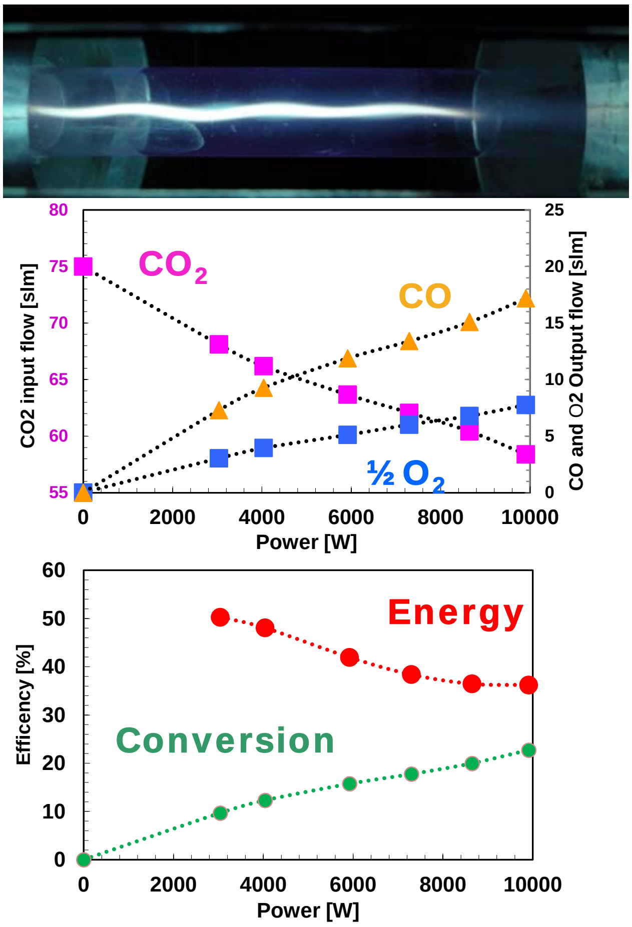

Fig. 3. Plasma configuration, Type II, as Fig. 2, but at high input gas flow of 75 slm. Top: Photo. Middle: MS results: with increasing power CO_2 is converted to CO and $1/2O_2$. Bottom: The corresponding efficiencies.

These experiments led to significant higher energy efficiencies (between 36% and 50%) at the expense of reduced conversion (11% to 23%). Fig. 6 shows a comparison of the results obtained in a microwave plasma with *Type II* nozzle and the results of [2].

3. Recent CO_2 dissociation experiments

First results at DIFFER were obtained with a 2.45 GHz 1 kW plasma source (InitSF). This source consists of a quartz tube placed inside a circular TEM mode coaxial cavity coupled to a TE_{10} rectangular waveguide mode cavity. The source is equipped with a tangential gas injection system from the top and the exhaust is at the bottom, see Fig. 4. At an input of 7 slm of CO_2 energy efficiencies up to 39% were obtained at pressure of 130 mbar even without using a nozzle after the plasma. The efficiencies increase at lower pressure, see Fig. 5. At higher pressures a reduction of the active plasma volume is observed. This could explain the decrease of efficiency.

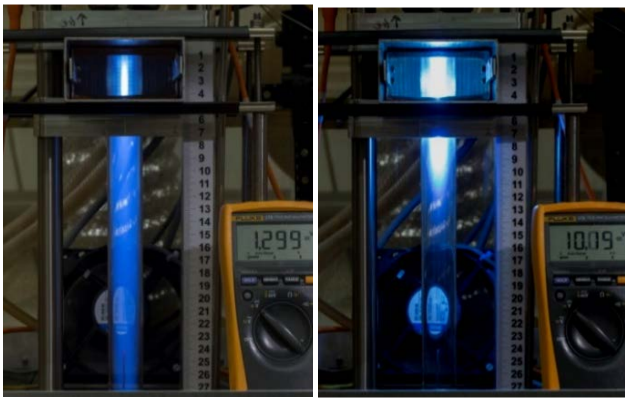

Fig. 4. Photograph of the InitSF plasma source. Stable plasmas in pressure range from a few mbar up to 1000 mbar can be generated. Plasmas of 130 mbar (left) and 1020 mbar (right) are shown (10V is 1 Bar). The forward vortex (FV) generated by the gas flow separates the visible plasma part from quartz tube.

The InitSF plasma source could also be reconfigured to form a reverse vortex (RV)system, with the bottom exhaust closed, to have both the input (tangential) and the output (central) at the top. In this setup the inner conductor of the coaxial cavity was shortened to optimize the heat exchange between outside input and central output gas (partly quenching of output gas to prevent vibrational to translational losses). These reverse vortex experiments were also repeated for lower energies per molecule by a pressure scan. In Fig. 5 a comparison is made between energy and conversion efficiencies over a pressure range of FV and RV configurations. The RV gives higher efficiencies at higher pressures then FV. This could be explained by that the RV causes a radial pressure gradient which keeps exited particles within the plasma volume. Fig. 6 is given for a summary of the results compared to [2].

4. Conclusion

The joined DIFFER-IGVP and the DIFFER measurements were in line with the results reported in [2]. In these experiments, *Type I*, supersonic expansion inside the plasma did not resulted in high energy efficiencies (15%) ascribed to lack of plasma pressure [2]. However with a nozzle placed after the plasma, type II, efficiencies up to 50% were achieved by partly preventing VT relaxation. Furthermore it was shown that the plasma configuration like FV and RV change the efficiency behaviour of the plasma as function of the pressure significant.

In FV we observe at rising pressure a decrease of active plasma volume presumably causing a decrease of energy efficiency while RV mitigates this by causing a radial pressure gradient which keeps the exited particles within the plasma volume such that the energy efficiencies stay more constant at elevated pressures above 200 mbar. More diagnostics like optical emission spectroscopy are used to determine e.g., the rotational temperature [7]. The obtained efficiencies are at the thermodynamical limit [8]. So non-equilibrium vibrational excitation must be optimized further in combination with preventing of VT relaxation. The experiments confirm, as given in [2], that combination of high energy and conversion energy is still contradictory and a great challenge, see [9] for possible solution.

Future measurements will concentrate on proper quenching of the plasma to prevent VT relaxation losses and stimulation of the vibrational modes by optimizing the electron energy distribution function. The kinetic energy distribution of the electrons mainly determined by the reduced electric field (E/n) plays thereby an important role at vibrationally stimulated CO_2 dissociation [4]. This may be achieved by means of several novel methods planned to be tested in the future at DIFFER. Among them are tuning the E/n in the microwave cavity or exploiting the relaxation time difference of translational and vibrational modes of CO_2 through control of the microwave field.

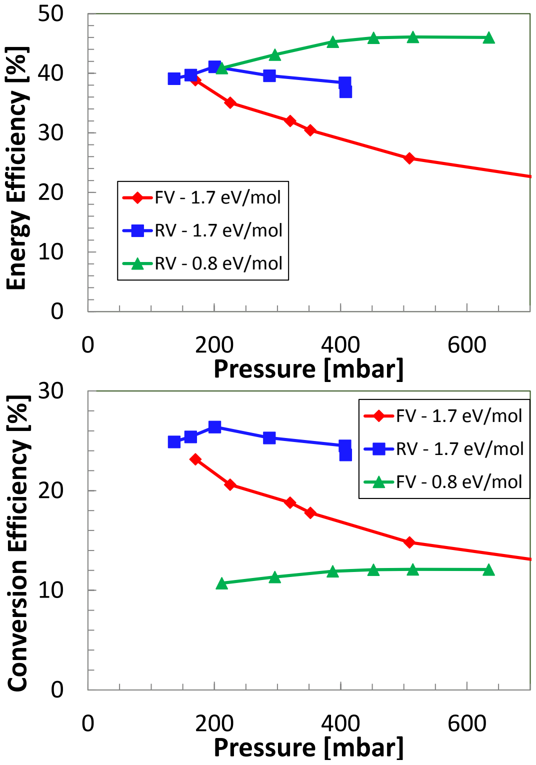

Fig. 5. Results of InitSF plasma source at 0.9 kW for 7 slm (1.7eV/molecule) and 17 slm (0.8eV/molecule) CO_2 gas input for forward vortex (FV) and reverse vortex (RV) operation: optimal energy efficiencies of more than 40% were obtained at elevated pressures with the RV configuration. Depending on the energy pro molecule the optimum shifts between 200 and 400 mbar.

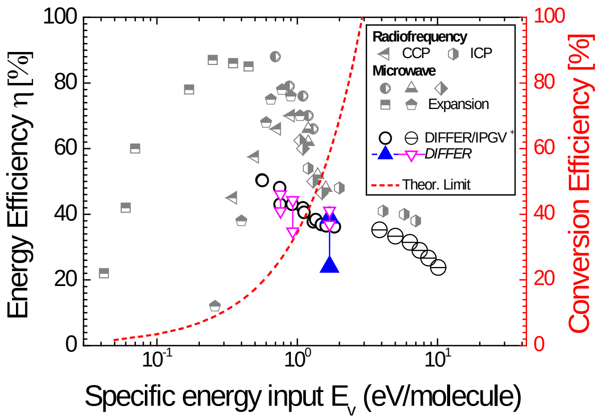

Fig. 6. Graph of [2] showing energy as a function of the energy pro CO_2 molecule including MS results of configuration, *Type II*, at low- and high- input gas flow: of the joined measurements of DIFFER and IGVP. The open and filled triangles show the new measurements at DIFFER at the pressure range of 175 to 500 mbar. The dotted line indicates the conversion efficiency at 100% energy efficiency (2.9 eV is 100%).

5. Acknowledgements

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