Optimizing plasma-assisted CO_2 conversion in pulsed microwave discharges

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Abstract: The plasma-assisted CO_2 conversion efficiency has been significantly enhanced in a pulsed microwave surfaguide discharges working at ~ 10 Torr as a result of the applied power modulation. Among the main physical parameters responsible for the enhancement are the plasma -on and -off time duration, residence time, gas flow, etc., as well as their relation to the e-V and V-T relaxation time in plasma. The effect of plasma catalysis has been also studied showing additional improvements in CO_2 conversion efficiency.

Keywords: Green energy, CO_2 conversion, pulsed microwave plasma, diagnostics.

1. Introduction

Interest to the plasma-assisted greenhouse gas conversion continuously increases nowadays, as a part of the global green energy trends. Among the plasma sources suitable for conversion of CO_2 and the other greenhouse gases, the non-equilibrium (low-temperature) discharges where the electron temperature (~ 1-2 eV) is considerably higher than the gas temperature (< 0.1 eV) represent a special interest. In particular, the flowing gas discharges sustained by microwave (MW) radiation are proven to be suitable for the greenhouse gas conversion due to their high degree of non-equilibrium and, as a result, high plasma selectivity [1,2]. Along with a general effectiveness for molecular gas decomposition, *power modulation* in the MW plasmas represents an additional alternative for enhancing this process [3]. For power modulation, the electromagnetic wave with a 'filling' frequency in the GHz range (sustaining the discharge) is periodically modulated by rectangular pulses with certain repetition rate, typically in the kHz range. Such modulation might be very important when vibrational excitation defines molecular decomposition in plasma, as in the case of CO_2 [1]. Since in the pulsed MW discharges the characteristic time of vibrational-translational (V-T) energy transfer may be comparable to a typical pulse repetition period, the resonance-like effects between the power delivery and the energy transfer may take place. Thus, periodic power delivery to MW plasma potentially represents a promising way for further improvement of CO_2 conversion efficiency.

In spite of the numerous works devoted to plasma-based greenhouse gas conversion, related to MW plasma [4–6], dielectric barrier discharge (DBD) [7–12], gliding arc plasma (GAP) [13–15], radiofrequency (RF) discharges [16] as well as the works involving plasma catalysis [5,17–19], the effects of CO_2 conversion and power modulation are still far from being understood clearly. The number of the research works in this domain is limited by theoretical considerations about the usability of the pulsed plasma regime in MW and DBD cases [20]. The beneficial effect of power modulation for CO_2 decomposition have been shown only in the atmospheric DBD case so far [8–10]. Thus, the domain of the power modulation in the MW low-pressure plasmas, representing one of the most promising non-equilibrium media for selective plasma chemistry, remains mainly unexplored. The present study is targeted for clarification of the power modulation for efficient CO_2 conversion in MW surfaguide discharges. Its beneficial character for the enhancement of both CO_2 conversion efficiency (χ) and energy efficiency (η) is clearly shown.

2. The plasma sources used

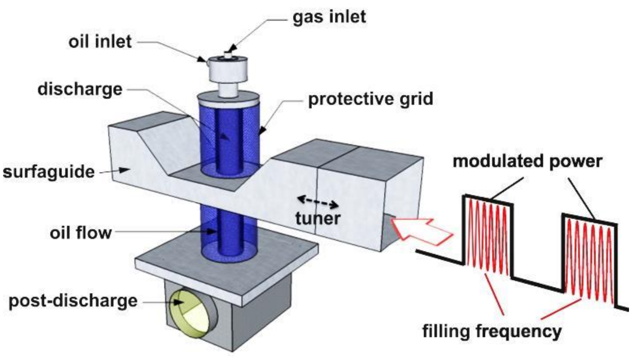

Fig. 1. Schematic representation of the MW plasma source with modulated applied power.

The pulsed microwave (surfaguide-type) plasma sources have been used in this study. In this discharge type plasma is sustained by electromagnetic waves with filling frequency in the GHz range (either 0.915 or 2.45 GHz in our case) coming out of two orifices in the surfaguide [21], as schematically shown in **Fig. 1**. In our case the electromagnetic radiation has been modulated by nearly rectangular pulses with the repetition frequency globally ranging from 0.01 to 33 kHz. The ration between the plasma pulse duration and repetition period was equal to 0.5 in the most cases. The discharges were sustained in the quartz tubes (14 mm in diameter and 31 cm long) in which the gas flow has been regulated by digital mass flow controllers. Each quartz tube has been cooled down additionally by a Si oil flow (approx. 2 l/min) having the temperature of about 5-10 °C depending on the plasma source. The total gas flow rate in the discharge was ranging from about 0.08 to 3 slm (standard liter per minute). Pure CO_2 and CO_2+5% N_2 gas mixtures have been utilized. The time-averaged power applied to the discharge was fixed during the measurements having typical values in the range of 0.4 – 1.0 kW. The reflected electromagnetic radiation has been minimized using three-stub tuning systems. The reflected power was always less than 10% for 2.45 GHz MW systems, and totally negligible (presumably < 1%) in the case of 0.915 GHz system. The main MW discharge parameters are summarized in **Table 1**.

Table 1. The main parameters of the studied MW plasma sources.

Parameter	**Value/Range**		
	MW-1	**MW-2**	**MW-3**
Filling frequency	2.45 GHz	0.915 GHz	2.45 GHz
Modulation frequency range	0.5 – 33 kHz	0.01 – 2.4 kHz	0.5 – 10 kHz
Pulse duty ratio	0.5	0.5	0.5
Gas flow range	0.08 – 2.7 slm	3, 6 slm	0.1 – 2 slm
Mean power	0.4 kW	1 kW	0.8 kW
Tuning type	Automatic	Automatic	Manual
Reflected power	< 10 %	< 1 %	~ 5-10 %
Gas pressure range	1 – 20 Torr	10 – 30 Torr	1.5 – 15 Torr
Diagnostics techniques used	OES, TALIF	OES, GC	OES, TALIF, GC

3. The diagnostic techniques

Optical emission spectroscopy (OES), including emission actinometry and ro-vibrational spectral analysis, has been applied for characterization of the CO_2 conversion efficiency and the gas temperature in the discharge zone, respectively. Gas temperature has also been monitored by a thermocouple at the beginning of the post-discharge (18 cm below the excitation point). The rotational band from the CO Angstrom system corresponding to the B $^1\Sigma^+$(v'=0) – A $^1\Pi$(v"=1) transition has been used for rotational temperature determination. Gas temperature has been assumed equal to the rotational temperature of CO molecules based on the analysis undertaken elsewhere [6,22]. In order to determine the CO_2 conversion efficiency in the discharge area, optical actinometry method based on the addition of a small amount of molecular nitrogen (5% in our case) to the CO_2 gas, has been applied. Using this approach, the CO concentration was determined based on the CO to N_2 emission lines ratio (CO 482 nm rotational sub-band and N_2 Second Positive band were used), as performed by Silva et al. [6]. The relative error of this method is supposed to be < 10%, based on our estimations.

In the MW-1 and MW-3 cases the products of CO_2 dissociation (such as the ground state CO and O) have been detected in the post-discharge area using two photon absorption laser-induced fluorescence (TALIF) technique [23]. This technique is based on the laser excitation of the molecular or atomic species in the discharge or post-discharge by a simultaneous absorption of two laser photons, following by fluorescence corresponding to an optical transition between the upper (excited) state and the intermediate state. The spectral transitions used for TALIF technique are summarized in **Table 2**. A Sirah dye laser working at 10 Hz of repetition rate and having 5 ns of the pulse duration with the Coumarin 450 dye solution has been utilized. During the measurements the laser pulses were *not* synchronized with the plasma pulses, thus giving the time-averaged values of the corresponding ground state densities in the post-discharge. In addition, gas chromatography (GC) technique has been used for ex-situ characterization of the decomposition products. A Bruker 450 - GC gas chromatograph equipped with a sampling system has been used. The GC system has been connected to the post-discharge region and low-pressure gas samples have been diluted with carrier gas (argon) before their injection into the gas chromatograph for the further analysis.

Table 2. The spectral transitions used for TALIF measurements of CO and O ground states.

Specie of interest	**CO**	**O**
Lower state	$X^1\Sigma^+$	$^3P_2$
Upper (laser-excited) state	$B^1\Sigma^+$	^5P
Energy gap	10.78 eV	10.74 eV
Laser excitation wavelength	230.07 nm	225.6 nm
Fluorescence wavelength	483.50 nm	844.68 nm
Bandpass filter used	480 nm	840 nm

4. The main experimental results

The evolution of the CO ground state density in the post-discharge of the MW-1 and MW-2 sources is shown in **Fig. 2**. The effect of power modulation results in this case to a fourfold increase of the CO density (and corresponding CO_2 conversion efficiency) at low plasma pulse frequency. The maxima of CO relative density are observed at about 0.5 kHz (in the MW-1 system) and at about 0.8 kHz (in the MW-2 system). Apart from the different positions of the observed maxima, in the 2.45 GHz case the maximum appears to be much narrower than the one detected in the 0.915 GHz discharge case. At the same time, the O atoms production is strongly suppressed at low pulse frequencies, when the dissociation of CO_2 reaches its maximum.

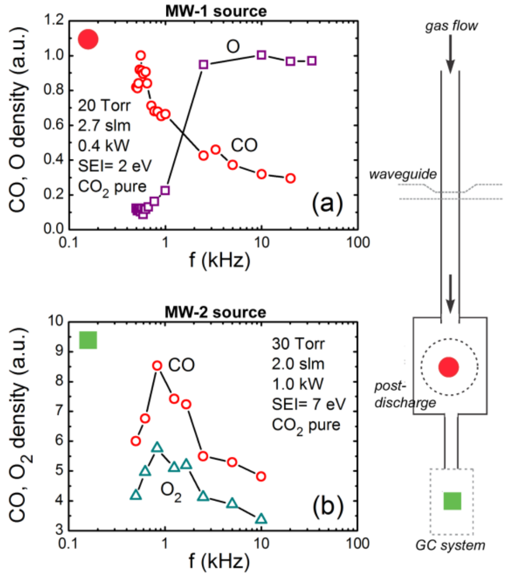

Fig. 2. The relative densities of the ground state O, CO and O_2 measured in the post-discharge by TALIF (a) and GC (b) techniques as a function of the plasma repetition frequency f.

Besides this, the O_2 density has a clear maximum at low frequency, likely pointing out on the efficient O-recombination under these conditions, as shown in Fig. 2(b). Finally, the CO density decay slopes measured in two different plasma sources reveal rather similar behavior.

In order to explain the observed increase in CO_2 conversion at low frequency the gas displacement in the tube should be taken into account. Three cases can be considered: (i) slow gas displacement, when the gas shift in the tube is small between two consecutive plasma pulses, (ii) 'resonant' gas displacement, when the gas shift time in the active zone is almost equal to the plasma pulse duration, and (iii) fast gas displacement, when the gas shift time is shorter comparing to the time between two plasma pulses. Since in our case the gas velocities are comparable in the MW-1 (~ 40 m/s), MW-2 (~ 30 m/s), and MW-3 plasma sources, it can be shown that nearly the resonant case is realized at low plasma pulse frequency (~0.5 kHz) in these systems. This results in a nearly maximum system performance in terms of CO_2 decomposition and corresponding energy efficiency. More pronounced χ-maximum found in the MW-2 (0.915 GHz discharge) case, as well as its position shifted towards higher plasma pulse frequency values may be a result of the differences in system geometry as well as the errors related to gas pressure and gas temperature determination.

We should note that, at the lower pulse frequencies (or higher gas flows) one may expect a significant drop in CO_2 decomposition, as the fast gas displacement limit should be achieved and some portions of the passing gas will remain untreated by plasma. On the other hand, at higher pulse frequencies, as observed in our case, a considerable drop in the CO_2 conversion should be likely explained by a combination of several factors, such as (i) a decrease of the electron-vibrational (e-V) energy transfer contribution at shorter pulse durations, (ii) a decrease of the role of dissociative recombination of CO_2^+ (via the reaction: e + $CO_2^+ \rightarrow$ CO + O, see [20]) in this frequency range, as suggested by Silva et al. [24], (iii) decomposition of CO molecules in the active zone when residence time is too long. The third argument, however, is supposed to play minor role, due to the synchronous CO and O_2 density behavior in the post-discharge (see Fig. 2(b)). Let us also note that both the gas temperature and the vibrational temperature of N_2 molecules behave in similar way significantly increasing at low frequencies. These effects may be related to higher vibrational excitation of CO and CO_2 molecules in this case as a result of more efficient e-V transfer, as well as more efficient gas heating at longer pulse durations, due to both electron-translational (e-T) and V-T channels.

The optimized CO_2 conversion results obtained in this work and the available literature data related to different MW, GAP, DBD and RF discharges are compared in **Fig. 3**. The most competitive results group around the line corresponding to specific energy input (SEI) of 2.9 eV/molec. The typical frequency optimized χ-values obtained in this work without using plasma catalysis are denoted by the green stars. In addition, the effect of plasma catalysis studied by Chen et al. [19] in the MW-2 plasma source results in more than a twofold increase in both χ and η values (a predicted value for our data using plasma catalysis is shown by the dashed arrow).

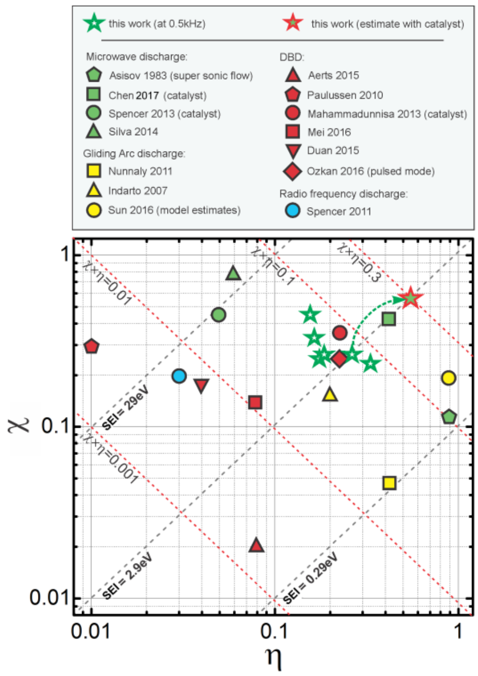

Fig. 3. The CO_2 conversion efficiency (χ) vs. energy efficiency (η) diagram comparing the results obtained in this work with the available literature data.

Considering the other discharge types, the most promising results on the CO_2 conversion have been obtained so far in an atmospheric DBD with power modulation, one more time underlining the significance of this effect for better CO_2 conversion. Somewhat lower conversion efficiency has been achieved in atmospheric gliding arc discharge, as studied by Indarto et al. [14]. Finally, the examples related to the low-to-moderate pressure microwave discharges, one representing high conversion efficiency, but rather low energy efficiency attained as a result of applying high SEI [6] (open up-triangle), and the other representing the well-known work of Asisov et al. [4] where a supersonic gas flow enabled high energy efficiency. The plasma catalysis generally show a clear advantage over the catalyst-free cases, e.g. in the case studied by Mahammadunnisa et al. [18]. Based on this comparison, a combination of the frequency-optimized MW plasma with plasma catalysis [5] may represent the most efficient solution for the low-pressure plasma -based CO_2 conversion (red star in Fig. 3).

5. Summary

The work demonstrates importance of the applied power modulation for enhancement of the plasma-assisted CO_2 conversion and energy efficiencies in MW discharges. Roughly a fourfold improvement in the CO_2 conversion efficiency has been achieved solely based on the power tuning in the MW plasma at 20 Torr in our case. Based on the estimations of the characteristic time of the relevant energy transfer processes it was concluded, that the e-V as well as V-T energy transfer mechanisms, along with the gas shift in the tube may be mainly responsible for the optimization of CO_2 conversion in a flowing gas MW discharge. The maximum efficiency found so far corresponds to the frequencies of about 0.5-0.8 kHz depending on the studied plasma source.

The gas temperature in the discharge zone (near the excitation point) is supposed to be strongly influenced by the V-T and e-T energy transfer, as well as by the intense O atoms recombination at low repetition frequencies. Numerous processes involving O atom kinetics, however, require a separate study involving additional experimental and modeling work in order to be fully understood.

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