Study of CO_2 Conversion in the DC Corona Discharge in Carbon Dioxide – Helium - Nitrogen Gas Mixtures

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Abstract - In the current study, the conversion of CO_2 in a DC corona discharge in the CO_2:He and CO_2:He:N_2 gas mixtures is investigated. The tests are carried out using a compact corona discharge ionizer. The ionizer includes a grounded tube electrode. The corona discharge is generated on the sharp points of star-form high voltage electrodes, installed inside the grounded tube. Tests are carried out at room temperature conditions for variable gas pressure. The Fourier-transform infrared spectrometer is applied for the study of CO_2 conversion efficiency. The test shows, that the negative polarity DC corona discharge allows higher power consumption values than the positive polarity corona, what enhances the CO_2 conversion. At constant applied voltage, after ~1 h of operation, the corona discharge power consumption is considerably lower, than at the beginning of the test, what confirms the change of gas composition inside the corona discharge ionizer.

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I. INTRODUCTION

One of the effective approaches, which assumes the CO_2 disposal or conversion into chemicals, material and fuels, is the use of non-thermal plasma (NTP) technologies [1, 2].

New horizons are expanded by use of corona discharge for gas ionization, by use of electrohydrodynamic phenomena for gas movement, as well as for enhancement of heat transfer processes [3-5].

The design of a compact corona discharge ionizer is an important step in the development of CO_2 conversion technology. The results of the development of such compact ionizer are presented in ref. [5].

The scope of the current work is the study of the CO_2 conversion phenomena in the 2-gas and 3-gas mixtures, namely CO_2:He and CO_2:He:N_2, in a DC corona discharge.

In the focus of the study is the investigation of the influence of gas mixture pressure and applied voltage polarity on the CO_2 conversion.

II. PLASMA PHENOMENA

Plasma is an ionized gas, consisting of molecules, electrons, ions, radicals, excited species and photons [1]. High temperature plasma is fully ionized and the non-thermal plasma (NTP) is partially ionized.

The non-thermal plasma allows the CO_2 splitting to be carried out at atmospheric pressure and near room temperature. In the NTP, the CO_2 conversion is instantaneous upon plasma ignition. The energetic electrons activate CO_2 molecules causing excitation, ionization and dissociation. The NTP activates the gas molecules in an energy-efficient way, as gas does not have to be heated as a whole. In the NTP, the temperature of (light) electrons is much higher than for the other (heavy) species, typically of few eV.

The NTP is characterized with the process versatility: here is possible both the pure CO_2 splitting and the combined CO_2 conversion (with CH_4, H_2 or H_2O in the presence of suitable catalysts). Plasma catalysis might yield direct production of higher hydrocarbons or oxygenates in a one-step process.

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Reactor	Advantage
MW	High energy efficiency for conversion Reduced electric field
GA	Plasmatron instead of „classical“ design Enhanced concersion (plasmotron) Operates at atmospheric pressure
DBD	Operates at atmospheric pressure Simple design and easy scaling up Use of pack-bed material + catalyst
CR	Simple design and easy scaling Operation at atmospheric and overpressure

Table 1. Advantages of plasma reactors

Reactor	Disadvantage
MW	High gas temperatures Operation at low pressure (mainly)
GA	High gas temperatures Most of gas passes not through plasma Limited gas conversion High gas flow rates
DBD	Limited energy efficiency for conversion High reduced electric field Residence time/smaller discharge volume Loss of electrons at packing material surface
CR	High reduced electric field Limited/low energy efficiency for conversion

Table 2. Disadvantages of plasma reactors, MW - Microwave Reactor, GA - Glider Arc Discharge Reactor, DBD - Dielectric Barrier Discharge Reactor, CR - Corona Discharge Reactor

The NTP technology has low investment and operating costs. Non-thermal plasma does not make use of rare earth metals [1]. Plasma is a turnkey process: it requires no pre-heating, long stabilization and cool-down times, it can be quickly turned on and off. In comparison with emerging technologies (solar thermochemical, photochemical, biochemical conversion), plasma technology can be operated independent of solar radiation availability.

Plasma reactors can be used in a modular setting and could be useful for local on-demand production processes. The advantages and disadvantages of high-temperature plasma (MW and GA) reactors and non-thermal plasma (DBD and CR) reactors are summarized in the Table 1 and Table 2, correspondingly [1].

III. EXPERIMENTAL FACILITY AND TEST CONDITIONS

The experimental study is carried out, using a high pressure casing, in which a DC corona discharge ionizer (see Fig. 1) is installed. The detail description of the ionizer is presented in the ref. [5]. The following gas mixtures are investigated: CO_2:He (69,7 Vol.%:30,3 Vol.%) and CO_2:He:N_2 (68,7 Vol% : 16,42 Vol.% : 14,88 Vol.%). The test are carried out at room temperature conditions at variable pressure of the gas mixtures.

The DC high voltage (HV) power supply units are used for generation of negative and positive polarity corona discharge inside the ionizer (see Fig. 2). The corona discharge current-voltage characteristic are measured at the beginning and at the end of every test. The so called “direct” (with increase of applied voltage) and “indirect” (with decrease of applied voltage) CVCs are measured. The long-term operation of the corona discharge is carried out predominantly at constant value of applied voltage, which is defined by the spark-over voltage level, which depends on gas composition and pressure inside the casing.

The temperature of the gas, as well as the temperature of the ionizer grounded electrode and the temperature of the high-pressure casing, are measured during the tests.

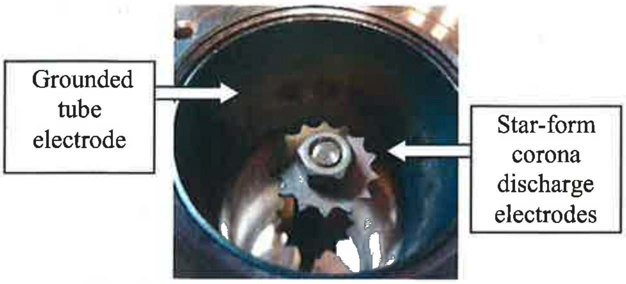
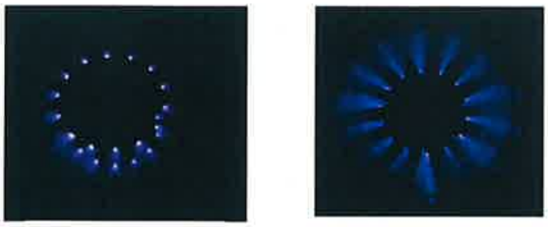


Fig. 1. Electrode system of the corona discharge ionizer



Negative corona discharge

Positive corona discharge

Fig. 2. Negative (left) and positive (right) corona discharge

For the analysis of the efficiency of CO_2 conversion, the Fourier-transform infrared spectrometer is applied.

IV. EXPERIMENTAL RESULTS FOR THE TESTS WITH CO_2:He GAS MIXTURE

The results of the study with gas mixture CO_2:He (69,7 Vol.% : 30,3% Vol.%) are presented in Fig. 3 and Fig. 4 for the negative and positive DC corona discharge, respectively. For negative corona discharge, the maximum conversion of CO_2 into CO is k_-~0,18 Vol.%, being measured at gas pressure of p=2,0 bar and corona discharge mean power consumption P_-~30W. Further increase of corona discharge power consumption results predominantly in the heating of gas and less in CO_2 conversion. For positive corona discharge, at gas pressure of p=2,0 bar, the CO concentration is about k_+~0,04 Vol.% at corona discharge mean power consumption P_+~4,5 W. The analysis shows the $P_-/P_+ \approx k_-/k_+$, hence the efficiency of CO_2 conversion depends mostly from corona discharge power consumption.

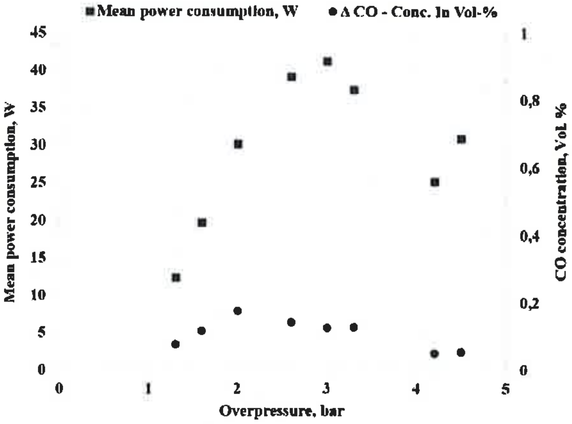


Fig. 3. Corona discharge power consumption and CO Vol.% concentration, negative corona discharge, variable gas pressure

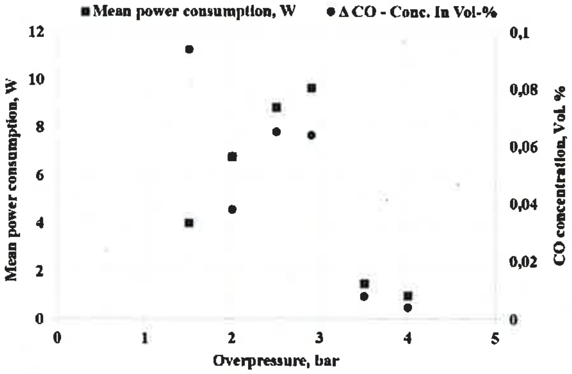


Fig. 4. Corona discharge power consumption and CO Vol.% concentration, positive corona discharge, variable gas pressure

V. EXPERIMENTAL RESULTS FOR THE TESTS WITH CO_2:He:N_2 GAS MIXTURE

The results of the study with gas mixture CO_2:He:N_2 (68,7 Vol.% : 16,42 Vol.% : 14,88 Vol.%) are presented in Fig. 5 and Fig. 6 for negative and positive DC corona discharge, respectively.

The comparison of the data for CO_2:He and CO_2:He:N_2 gas mixtures (Fig. 3 and Fig. 5, CO_2 Vol.% concentration of 69,7 Vol.% and 68,7 Vol.%, respectively), shows that effective conversion of CO_2 for negative corona discharge takes place at gas pressure p=2,0 bar.

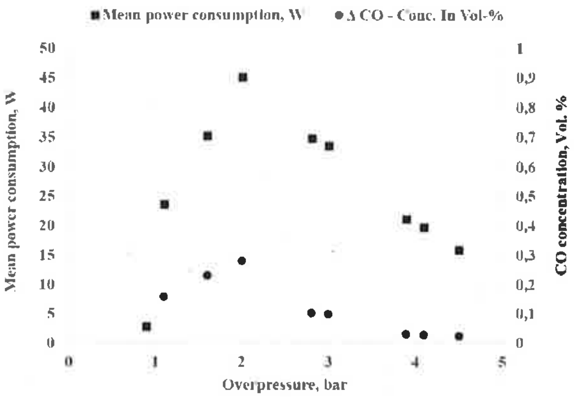


Fig. 5. Corona discharge power consumption and CO Vol.% concentration, negative corona discharge, variable gas pressure

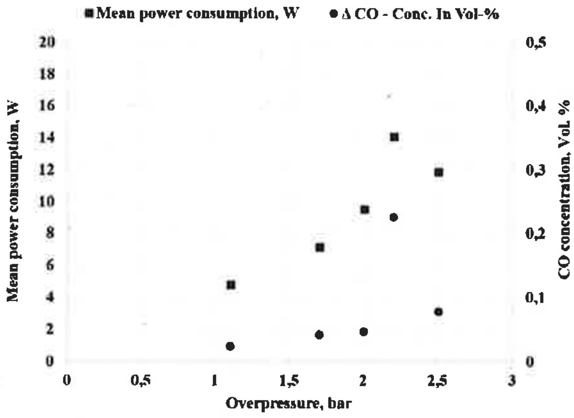


Fig. 6. Corona discharge power consumption and CO Vol.% concentration, positive corona discharge, variable gas pressure

In the 3-gas mixture, the volume of generated CO is about 1,5 times higher, than in the 2-gas mixture (k_{CO}~1,5). The tests show that the corona discharge mean power consumption in the 3-gas mixture for the defined gas pressure is $P_{3\text{-gas}}$~45 W and in the 2-gas mixture it is $P_{2\text{-gas}}$~30 W. Hence $k_P=P_{3\text{-gas}}/P_{2\text{-gas}}$~1,5 and k_{CO}~k_P.

For the positive polarity corona discharge, the maximum CO concentrations are measured at gas pressure p~2.0-2,5 bar. The analysis of the data shows, that at p=2,25 bar, for the 3-gas mixture $P_{3\text{-gas}}$~14 W and CO concentration is ~0,22 Vol.%. For 2-gas mixture, at p=2,5 bar, the value of $P_{2\text{-gas}}$~8 W and CO concentration is ~0,068 Vol.%. Hence, the relation k_{CO}~k_P is also useful.

The experimental data (Fig. 3 and 4 and Fig. 5 and 6) show, that the use of 3-gas mixture allows the generation of corona discharge with higher values of power consumption, what results in enhanced CO_2 conversion in comparison to the 2-gas mixture.

VI. LONG-TERM CORONA DISCHARGE IN CO_2:He:N_2 GAS MIXTURE

The results referring the temporal evolution of the corona discharge power consumption for variable operational time intervals are presented in the Fig. 7. The 1st test, which lasts 10 min, is carried out with the "original" 3-gas mixture. From the beginning, the test is carried out at U_{max}=21,4 kV without any spark-over discharges. After several minutes, at constant applied voltage, the corona discharge current starts to decrease, what results in decrease of corona discharge power consumption. After the 1st test, the applied voltage is switched off. The 2nd test, which lasts 20 min, is carried with the 3-gas mixture, which remained in the casing after the 1st test, hence, the "new gas composition" after the 1st test influences on CVCs characteristics. So, at the beginning of the 2nd test, the stable corona discharge is generated at U=19,4 kV. However, during the test, it is possible to increase the operational voltage up to U_{max}=21,4 kV after ~8 min of corona discharge operation. Further, the corona current starts once again to decrease and the power consumption of corona discharge decreases.

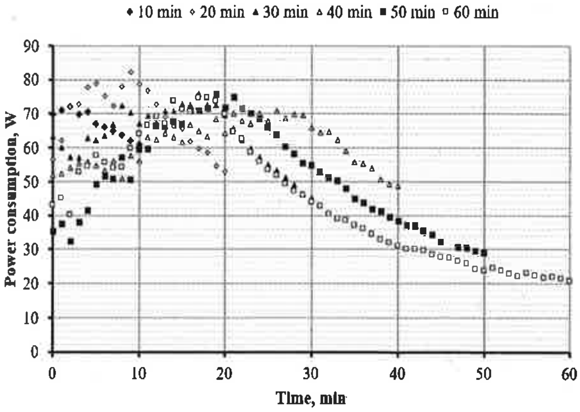


Fig. 7. Temporal evolution of corona discharge power consumption for variable operational time intervals

The test similar to the tests with 10 min and 20 min, are carried out at t=30 min, 40 min, 50 min and 60 min, correspondingly. With increase of the operational time, the power consumption of corona discharge at the beginning of the tests decreases.

It is possible during the test to increase the operational voltage up to HV power supply maximum output voltage. After this, with increase of the operational time, the corona discharge power consumption continuously decreases, what assumes that in the casing continuously takes place the change of gas composition.

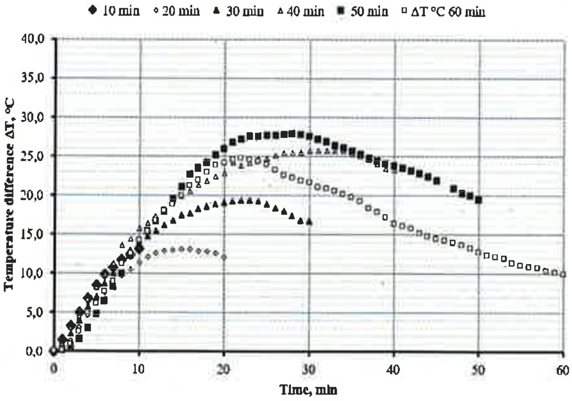


Fig. 8. Temporal evolution of ionizer grounded electrode temperature for variable corona discharge operational time intervals

The results of the study of the temperature evolution of the ionizer grounded electrode for variable corona discharge operational time (see Fig. 8) confirm the assumption. The Fig. 8 presents the evolution of the electrode temperature, e.g. the increase of the electrode temperature in comparison with the beginning of the tests. This increase of the temperature is rather small and not enough to ensure any significant change in the gas composition, e.g. to ensure the thermic conversion of the CO_2 inside the closed casing.

VII. CO_2 CONVERSION

The joint results referring to the CO_2 conversion in the DC corona discharge compact ionizer in the 2-gas and 3 gas mixtures for the negative and positive corona discharge are presented in the Fig. 9 and Fig. 10, correspondingly. The analysis of the results of the study shows that the conversion of CO_2 into CO takes place in the ionizer during the whole time of the corona discharge operation. There is practically a cumulative increase of the CO concentration in the casing.

In the 2-gas mixture, negative corona discharge (see Fig. 9), the temporal evolution of the CO can be linearly approximated. As for the 3-gas mixture, an exponential growing of the CO with time can be observed.

The curves for the 2-gas and 3-gas mixtures, positive corona discharge (see Fig. 10), well coincide one to another and can be approximated with a liniar dependences.

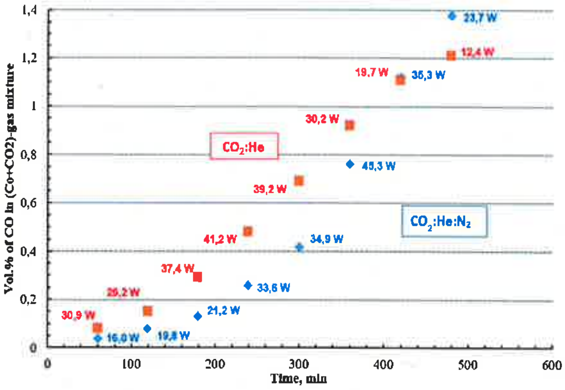


Fig. 9. Conversion of CO_2 into CO in negative corona discharge for varibale time of ionizer operation

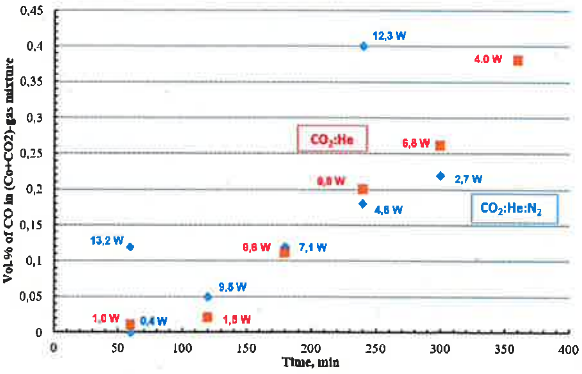


Fig. 10. Conversion of CO_2 into CO in positive corona discharge for varibale time of ionizer operation

For the reactor operation time up to 60 min, the relation $k_{CO} \sim k_P$ is rather useful. However, with increase of the time of operation, it is observed that $k_p > k_{co}$ for both of gas mixtures. Hence, from the point of view of power consumption for the conversion of the same value of CO_2 into CO, at long-term operation conditions, the positive corona discharge is more attractive than the negative one. For example, for the 3-gas mixture, operational time 300 min, the positive corona discharge with mean power consumption of $P_+ = 2{,}7$ W allows the reach CO Vol.% of about 0,22%. The negative corona discharge reach the value of CO Vol.% of about 0,42% at $P_- = 34{,}9$ W, what is ~ 13 times higher than for positive corona, however with only 2-times increase of CO concentration.

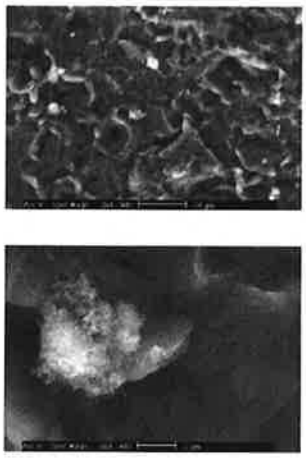


Fig. 11. Photos of the loading of grounded electrode of corona disharge ionizer

The review of the state of corona discharge ionizer shows that the inner surface of the ionizer grounded electrode is covered with a layer of black solid material, e.g. carbon particles (see Fig. 11).

To "clean" the ionizer, the grounded electrode is heated at temperature of 650°C in the synthetic air atmosphere inside the closed test facility casing. After the "cleaning", the casing is flashed with the test gas mixture and the experiments with 2-gas mixture are continued, showing slight change in the corona discharge CVCs in direction of the growing of corona current and in direction of increase of CO_2 conversion efficiency.

VIII. CONCLUSIONS

The results of the study show that the corona discharge power consumption and the polarity of applied voltage are key parameters for CO_2 conversion. Corona discharge power consumption defines gas conversion efficiency. The polarity of applied voltage defines stability of corona discharge. With increase of time of reactor operation, to ensure constant corona current, the operational voltage needs to be continuously increased, what demands the smart control of HV unit parameters.

The developed corona discharge ionizer has a compact design and ensures CO_2 conversion at room temperature conditions, as well as in different gas mixtures and at variable gas pressure. The effective gas conversion takes place at gas pressure p=2-3 bar, where the CVCs hysteresis phenomenon is observed. The designed corona discharge reactor shows the ability for CO_2 conversion at low corona discharge power, realizing the advantages of hysteresis phenomenon.

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