

Alumina and quartz as dielectrics in a dielectric barrier discharges DBD system for CO₂ hydrogenation

E Y Mora¹, A Sarmiento¹ and E Vera¹

¹ Universidad Pedagógica y Tecnológica de Colombia (UPTC), Tunja, Colombia.

E-mail: eduin.mora@uptc.edu.co

Abstract. In this work was studied the CO₂ carbon dioxide treatment, which is a pollutant gas and the main cause of global warming. For this aim, plasma was generated, through dielectric barrier discharges DBD, using hydrogen H₂ together with the CO₂ as reaction gases. There were used as dielectrics, alumina and quartz tubes of identical geometry. It was studied the CO₂ conversion in function of mixture composition CO₂+H₂, of the electrical power and the operation frequency, for three different gas flows. In all cases it was achieved better conversion levels with the alumina; this is because the alumina has a relative dielectric permittivity coefficient higher than the quartz. As products of CO₂ conversion in the chemical reactions, water H₂O and methane gas CH₄ were identified. The CO₂ conversion percentage to fixed work conditions was higher with the decrease the quantity of this gas in the mixture, with increase the active electrical power, and with decrease the operation electrical frequency.

1. Introduction

In the manufacture of products at industrial level, emissions of CO₂, SO₂ and NO_x among others are generated; for example, in cement production about 60% of CO₂ emissions come from the heat treatment to which it is subjected limestone, and 40% of emissions come from the fuels used in production [1]. During this process gases SO₂ and NO_x are also generated [1], forcing the industry to find alternative ways to avoid or reduce emissions, mainly CO₂ given its impact on global warming [2]; then appear possible solutions such as exchange from coal to renewable energy sources, improvements in energy efficiency in the combustion of fossil fuel, replacement of raw material for waste materials rich in CaO and the use of combustible waste materials, etc [3]. An alternative is the use of plasma in the conversion of gases such as NO_x, SO_x and CO₂ [3-6]. Thus the implementation of the dielectric barrier discharge DBD, allowed in some studies, the transformation of other hydrocarbons CH₄ [7], the reaction between CO₂ and H₂ to produce CH₄ and CO [8], the NO₂ gas treatment catalytic processes attending, reducing nitrogen oxides [9], the production of H₂ from CH₄ using zinc and chromium oxide as catalysts [10] or from hydrocarbons [11], the use of cold plasma for dissociation of NO₂ into NO radicals, N and O [12] and the removal of SO₂ of the atmosphere [13].

The DBD have advantages over traditional techniques when pollution concentrations are low, typically in the range of 10 to 1000ppm. In the DBD, the energetic electrons are generated in the microdischarges without substantially increasing initial gas flow enthalpy; also have the advantage over conventional techniques when different pollutants are treated simultaneously [14]. The transformations and use of CO₂ have become an important issue. One proposal is to recycle CO₂ as an energy carrier, perhaps combined with hydrogen in the form of liquid fuel or as a feedstock in the chemical industry. New catalysts are being developed for methanol synthesis from CO₂ and H₂ [14]. Eliasson [15] found that methanol may be used as a fuel in an engine of a conventional vehicle, directly or together with a small reformer to generate hydrogen in a fuel cell for an electric motor.

Different researchers work in the laboratory on the CO₂ hydrogenation and partial oxidation of CH₄ in the DBD. Quartz has been used mainly as dielectric material in these investigations. Methanol formation has been observed in CH₄/Oxygen and CH₄/air mixture [15-18]. Zhou [19] and other researchers obtained high rates of change for conversion in mixtures of CO₂/CH₄ become Syngas (H₂+CO), which is a feedstock for many chemical processes including methanol synthesis. Jan Sentek



and others [20] experimentally studied the plasma conversion of methane and CO₂ in DBD, using catalysts of silver-alumina and palladium-alumina.

2. Experimental

In Figure 1 is shown the schematic diagram of the experimental setup. The reactor camera was a tube of quartz (alumina was also used); the inside diameter of 26mm, thickness of 2.0mm and length of 215mm. A thin stainless steel sheet, serving as the outer electrode, adapted to the outer wall of the reactor. The inner electrode was one dipstick of stainless steel located in the center of the reactor of 15.87mm diameter, giving a discharge volume of approximately 36.67mL. For plasma generation was used a high-voltage alternating current (AC) power supply (Didriv10, PWM500) that has maximum voltage of 40kVp-p and frequency varying of 20kHz to 60kHz. The power was measured by a watt-meter digital (Intertek, GS cat II). The frequency was measured in an oscilloscope (Tektronix, TBS 1062) by mean a high voltage probe. The gas flows of CO₂ and H₂ were controlled by flow meters.

To measure the CO₂ percentage in the mixture was used the digital meter (CO₂ meter, CM-0006) which allows readings of 0 to 100% CO₂, using the no-dispersive infrared technology; this instrument was connected in the output of the reactor. Were analyzed two samples in order to identify the species generated in the plasma. To gas chromatography analysis was used the equipment AGILENT 7890 B and for the study of the liquid sample by mean FTIS, was used an equipment SHIMADZU Prestige 21. The amount of CO₂ introduced was measured at the output of the reactor without electric discharge. The amount of CO₂ consumed is calculated by subtracting the measurement taken at the reactor outlet after discharge of the measurement without discharge. CO₂ conversion was studied for three total flows 52, 74 and 96Nml/min, changing the percentage of CO₂ in the CO₂+H₂ mixture from 10 to 100%, the frequency from 20 to 25kHz and the applied power from 50 to 114W.

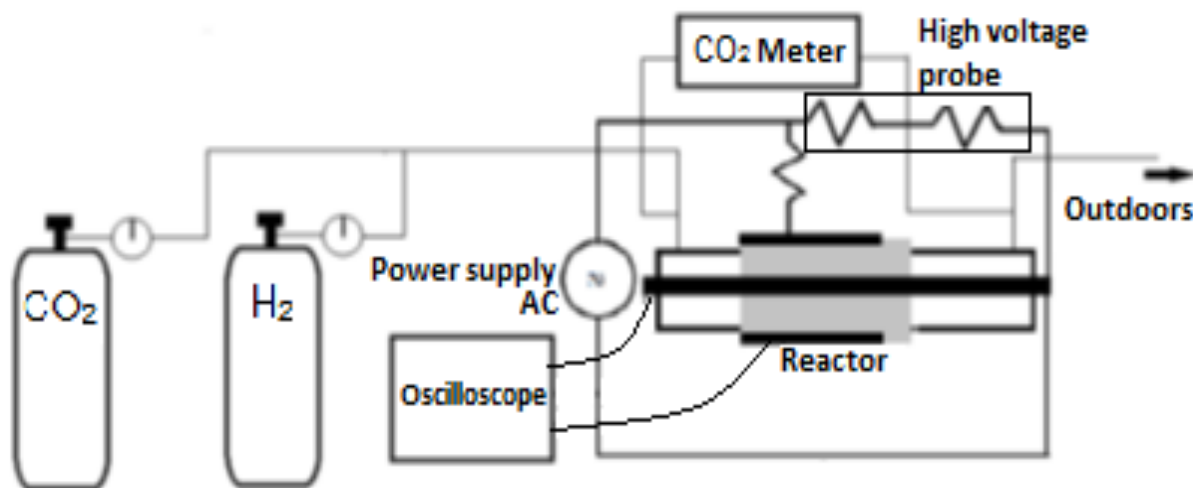


Figure 1. Schematic diagram for experimental set-up.

The CO₂ conversion was calculated as follows:

$$(\%)CO_2 = \frac{\text{amount of } CO_2 \text{ consumed}}{\text{amount of } CO_2 \text{ introduced}} * 100 \quad (\%) \quad (1)$$

3. Results

3.1. Effects of the CO₂+H₂ mixture on the reaction

In this case the conversion of CO₂ was studied varying the percentage of CO₂ in the feed gas mixture of 10 to 100% in flows of 52, 74 and 96Nml/min, for operation frequency and electric power delivered

of 19.72kHz and 105W respectively, using the two dielectric materials. The behaviour can be seen in Figure 2. As shown in the three flows, both the alumina and quartz, with increasing CO₂ content in the mixture, the transformation decreases. The highest conversion is 43.71%; this value was obtained with alumina using the lowest flow, and remains the mixture the possible time highest within the reactor. For all proportions of CO₂ in the mixture, the transformation was higher in alumina than quartz. The reason is due alumina has a coefficient of relative dielectric permittivity higher than that of quartz, 9.8 and 3.75 at 1MHz, respectively. Methane was detected according with chromatography test (see Figure 3(a)) and water according FTIS test due to the vibration bands of 1635 and 3298cm⁻¹ are characteristic of water (see Figure 3(b)). Regardless of the used dielectric, in intermediate ratios in the mixture of CO₂ (30 to 60% approximately), the transformation is favoured due to the increase in the water formation.

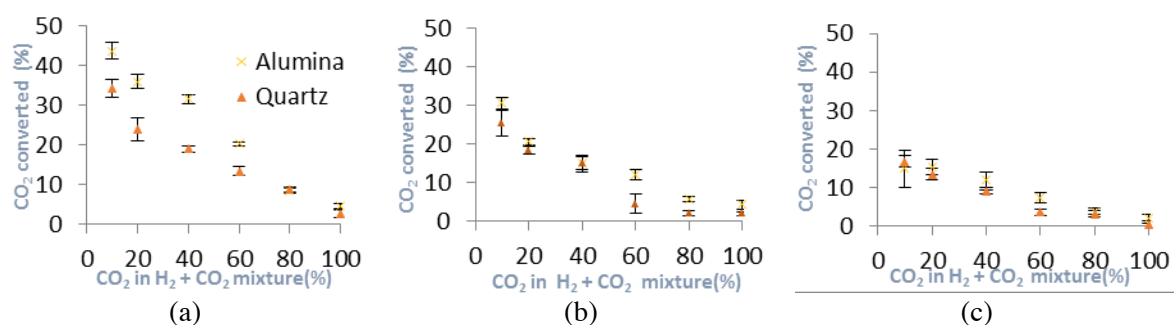


Figure 2. Percentage of CO₂ transformed as a function of the percentage of CO₂ in the H₂+CO₂ mixture at frequency of 19.72kHz and power of 105W for (a) 52Nml/min (b) 74Nml/min (c) 96Nml/min, using alumina and quartz as dielectrics.

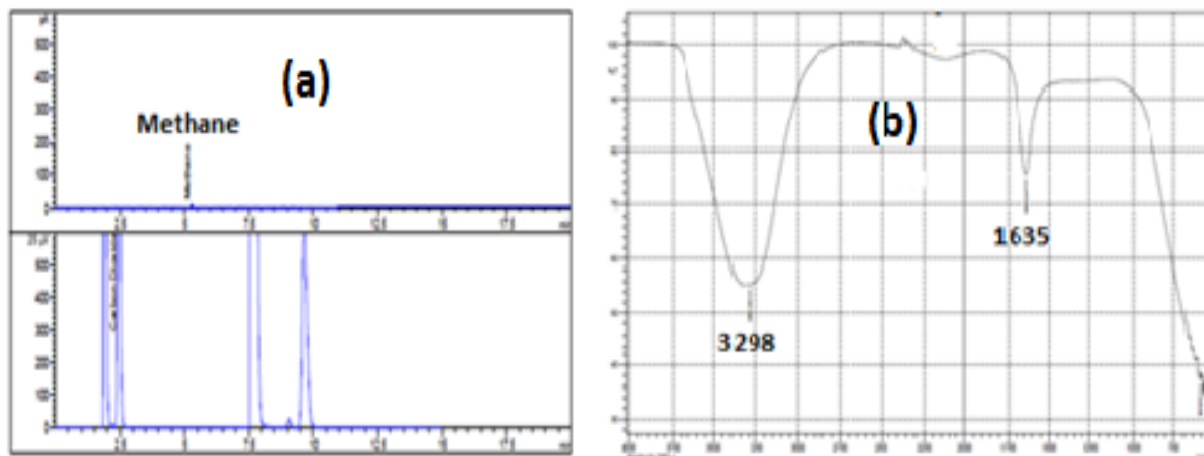


Figure 3. Tests for samples (a) Chromatography, (b) FTIS.

3.2. Effects of delivered power on the reaction

The degree of conversion of CO₂ was studied by varying the power supplied between 50 and 114W, in flows 52, 74 and 96Nml / min, for operating frequency of 19.72kHz and composition of the mixture of 20% CO₂ and 80% H₂. For both alumina as quartz and for the three adjusted flows, the trend is the increase in the transformation of CO₂ when the power supplied to the system is increased, as shown in Figure 4. Again best transformations are confirmed when the flow decreases independently of the dielectric. For the same power applied to the system in the three flows, the conversion is higher in the alumina.

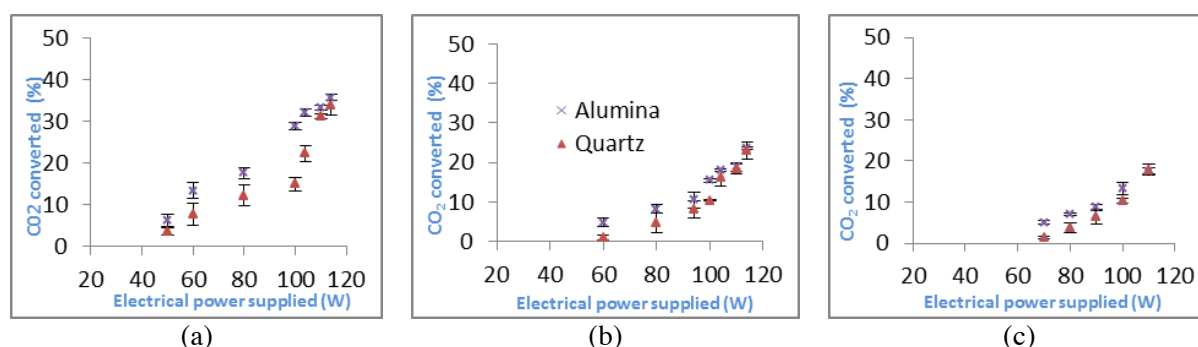


Figure 4. Percentage of CO₂ transformed as a function of the electric power supplied to frequency of 19.72kHz and composition of the mixture of 20% CO₂ and 80% H₂ for (a) 52Nml/min, (b) 74Nml/min, (c) 96Nml/min, using alumina and quartz as dielectrics.

3.3. Effects of the frequency on the reaction

In this case, the degree of conversion of CO₂ was studied by varying the electrical frequency of 20 to 25kHz, in streams of 52, 74 and 96Nml/min to 13.15kV voltage and composition of the mixture of 20% CO₂ and 80% H₂. The behaviour can be seen in Figure 5. For the three flows and the two dielectric materials, the transformation of CO₂ decreases as the operating frequency increases. The highest percentages of transformation are obtained with alumina in the three streams studied, getting as maximum value 31.04%, for flow of 52Nml/min and 20kHz operation frequency. As the frequency is increased, the transformation decreases in spite of small increases in near 22kHz, associated them to system complexity; this behaviour is due to source inductive predominance given for coupling impedance. Furthermore, the minimum frequency fixed in the source is higher than the resonance frequency of the circuit, resulting in lower levels of transformation with increasing frequency.

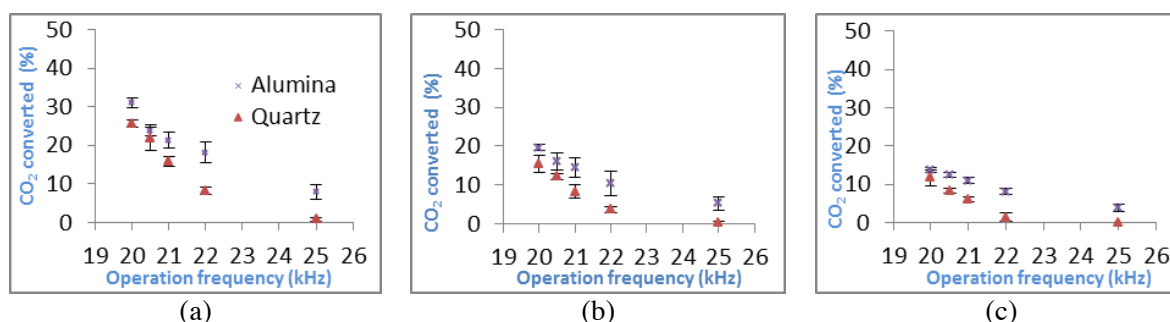


Figure 5. Percentage of CO₂ transformation as a function of electrical frequency in voltage of 13.15kV and composition of the mixture of 20% CO₂ and 80% H₂ for (a) 52 Nml/min, (b) 74 Nml/min, (c) 96Nml /min using alumina and quartz as dielectrics.

4. Conclusions

CO₂ transformation was studied as a function of the mixture composition, of the electrical power and the operation frequency using alumina and quartz as dielectrics in DBD. Reduction in conversion of CO₂ with increasing CO₂ in the mixture regardless of flow and dielectric material used, is associated to CH₄ methane gas formation, which decreases with increasing presence of CO₂ in the mixture; increases in the amount of water to ratios of 30 to 60% of CO₂, increases the conversion. As the power supply increases, so does the conversion, due to the formation of new species such as methane and water into the reactor, is associated directly with the energy supplied. CO₂ conversion decreases with increasing frequency regardless of dielectric material. According to the characteristics of the electrical circuit of the system, occurs inductive predominance due to the source coupling impedance. Higher levels of conversion to alumina were presented in all cases. This is because the alumina has a relative

dielectric permittivity coefficient higher than the quartz. As the capacitance is higher in the alumina, the capacitive reactance is lower, therefore is easier to deliver power to gaseous mixture.

References

- [1] Márquez S 2005 *Estabilización de suelos* (Argentina: Universidad Nacional de la Patagonia San Juan Bosco)
- [2] Francisco Blanco Álvarez 2008 *Materiales de construcción tema 8 cementos* (España: Universidad de Oviedo) (<http://www6.uniovi.es/usr/fblanco/Tema7.CEMENTOS.R.pdf>)
- [3] Hoyos A, Jimenez E, Ortíz M and Montes C 2008 *Revista Ingeniería e Investigación* **28-3** 41
- [4] Leray A, Khacef A and Makerov M 2011 *Diesel oxidation catalyst Ccombined to non-hermal plasma effect on activation catalyst temperature and by-products formation 20th internatinal symposium on plasma chemistry*. (United States: HAL Id: hal-00680790) pp 1-4
- [5] Young Sun M 2006 *Plasma Science & technology* **8-2** 207
- [6] Nunnally T, Gutsol K, Rabinovich A and Fridman V 2009 *Inter Journal of Hydrogen Energy* **34-18** 7618
- [7] Sazal K, Eric M and Kennedy V 2011 *Chemical Engineering Journal* **180** 178
- [8] Kyung T and Won K 2012 *Journal of Industrial and Engineering Chemistry* **18** 1710
- [9] Hoon D and Taegyu K 2009 *IPCS Proceedings International Plasma Chemistry* (<http://www.ispc-conference.org/ispcproc/ispc20/488.pdf>)
- [10] Indarto A 2012 *Journal of the Chinese Institute of Chemical Engineers* **39** 23
- [11] Sarmiento B and Brey J 2007 *Journal of Power Sources* **169** 140
- [12] Welzel S, Ponduri S and Brehmer 2009 *IPCS Proceedings International Plasma Chemistry* (<http://www.ispc-conference.org/ispcproc/ispc20/243.pdf>)
- [13] S Yanzhou, Q Yuchang, Y Fashan and Y Xingcheng 2004 *Plasma Science and Technology* **6-6** 2589
- [14] Hippler R, Kersten H and Schmidt M 2008 *Low temperature plasmas* (Berlin: Wiley-vch)
- [15] Jan Paul and Claire-Marie Pradier 1994 *Carbon dioxide chemistry environmental issues* (England: Royal Society of Chemistry)
- [16] Okazaki K and Nozaki T 1995 *12th Simposy on Plasma Chemistry Proceedings* (Minneapolis: University of Minnesota)
- [17] Kogelschatz U and Eliasson B 1996 *Phys Blatter* **52** 360
- [18] Eliasson B, Kogelschatz , Xue B and Li-Ming Zhou 1998 *Ind Eng Chem* **37-8** 3350
- [19] Zhou L, Xue B, Kogelschatz K and Eliasson B 1998 *Energy Fuels* **12-6** 1191
- [20] Sentek J, Krzstof K, Mlotek M, Kalczewska M, Kroker T, Kolb T, Schenk A, Karl-Heinz G and Schmidt-Szałowski K 2010 *Applied Catalysis B Environmental* **94** 19