Atomic Oxygen Assisted CO₂ and N₂ Conversion: a Theoretical Analysis

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Abstract: We propose a new method of CO_2 and N_2 gas conversion, where the key factor is the utilisation of an O_2 plasma. The first step consists of the creation of an O_2 plasma, after which we add the (non-plasma) gas in a second step. The O_2 plasma will deliver atomic oxygen, which is beneficial for CO production through the reaction $CO_2 + O \rightarrow CO + O_2$, and which can help jumpstart the process of NO_X production through the first Zeldovich reaction. We study these reactions by modelling, and our model predicts up to 40% CO_2 conversion and 5% NO_X production in steady state.

Keywords: CO2, N2, Zeldovich, O₂, modelling, plasma, climate change, agriculture

1.General

In 2015, the United Nations (UN) put forward the sustainable development goals (SDG) and formulated 17 objectives for a better future. Objective 13 is directly related to the call for climate action, but many others are closely related, for example SDG 2, which calls for sustainable agriculture.

One way to look at sustainability would be to look into the CO_2 production of the process. In May 2021, the National Oceanic and Atmospheric Administration (NOAA) measured the highest recorded CO_2 concentrations at 419 ppm up to then [1]. This is almost a 50% increase from pre-industrial levels [2]. This brings us closer to the crucial limit of a 1.5°C increase in global temperature, as established by the Paris Agreements.

Agriculture belongs to one of the most polluting industries and accounts for about 13-21% of global anthropogenic greenhouse gas emissions. [3] Fertilizer production alone through the Haber-Bosch process is already responsible for 1.2% of all (anthropogenic) CO_2 emissions. This is due to the usage of fossil-based fuels as an energy source, as well as the use of natural gas for H₂ production. This all translates also into 1–2% of the world's annual energy supply usage, and 3–5% of the worldwide natural gas consumption. [4]

This gives some insight that both tackling the problem directly through CO_2 conversion or indirectly through creating a cleaner pathway for fertilizer production could help bring CO_2 production down. Plasma could offer a solution for both CO_2 and N_2 conversion, since it allows for the use of renewable energy sources.

One of the issues to tackle is the stability of the CO_2 molecule and thus a great amount of energy (5.5 eV) is needed to break the double bonds (R1). [5]

$$CO_2 \rightarrow CO + O$$
 (R1)

The O atom formed in R1 can also react with CO_2 , leading to the dissociation of the latter:

$$CO_2 + O \rightarrow CO + O_2$$
 (R2)

The sum of both reactions gives us:

$$2 \operatorname{CO}_2 \to 2 \operatorname{CO} + \operatorname{O}_2 \tag{R3}$$

The indirect route (R2) offers some insight into possible optimisations of the conversion, because of the lower reaction enthalpy (R1 = 5.5 eV vs. R2 = 0.3 eV).

The same issue can be observed with the N_2 molecule that has a strong triple bond, and therefore a more favourable pathway, the Zeldovich mechanism, is used to fixate nitrogen with oxygen.

$$N_2 + O \rightarrow NO + N$$
 (R4)

$$O_2 + N \rightarrow NO + O$$
 (R5)

For both CO_2 and N_2 , atomic oxygen seems to play a crucial role in aiding the conversion. Thus, a system that would allow for higher fractions of atomic O could, in theory, increase the conversion. Therefore, we propose a system that focuses on an oxygen plasma as a first step, with the addition of the secondary gas in a second step, thus after the plasma. We approach this by means of modelling, where we look into different ratios of $[O]/[O_2]$ in combination with different ratios of the secondary gas.

2. Model

The chemical reactions are described by a 0D chemical kinetics model in the Fortran 90 ZDPlasKin (Zero-Dimensional Plasma Kinetics solver) code. [6] The model calculates density changes for the various species in the model, in a homogeneous volume element over time. It includes gas heating, but neglects physical parameters related to transport. Therefore, only the mass conservation equation for every species and the gas thermal balance equation are solved. The density changes over time can be represented by:

$$\frac{dn_s}{dt} = \sum_{j=1}^{j_{max}} Q_{sj} = \sum_{j=1}^{j_{max}} R_j [a_{sj}^R - a_{sj}^L], \quad (1)$$

$$R_j = k_j \prod_l n_l, \quad (2)$$

where n_s is the density of the species s, Q_{sj} is the source term for reaction j of the species s, a_{sj}^R and a_{sj}^L represent the stoichiometric coefficients on the right and left sides, respectively, of species s for reaction j. R_j is the reaction rate and k_j is the reaction rate coefficient.

The calculations are performed over time, for a gas in a volume element, comparable to a batch reactor. There is no addition of power to the CO_2 or N_2 gas, which is initially at room temperature, thus the changes are purely chemically driven. However, one could argue that the addition of atomic oxygen to the CO_2 or N_2 gas is an indirect way of adding power. Indeed, power is needed to first split O_2 into O atoms. As a result, we can calculate the energy efficiency of for example the CO_2 process through

$$\eta = \frac{x_{CO_2}}{1 - x_{CO_2}} \frac{\chi_{CO_2}}{\chi_{O_2}} \frac{\Delta H_{CO_2}}{\Delta H_{O_2}} \tag{3}$$

where η represents the energy efficiency, x represents the fraction in the gas, χ the conversion and ΔH the dissociation energy.

The model is on purpose kept simple to give more insight into the basic chemical reactions and changes that occur by the mixing of O atoms (or an O/O_2 mixture) with CO_2 or N_2 gas at room temperature and to lay the groundwork for experimental studies. More details on the model for the mixing of O/O_2 with CO_2 can be found in [7].

3. Results

We explored by means of modelling the addition of a partially dissociated O_2 gas (here represented by the ratio of $[O]/[O_2]$) to either CO_2 or N_2 . The results can be found in figure 1.

Figures 1A and 1B represent the addition of O/O2 to CO2 gas, for different O/O2 ratios and CO2 fractions, and they illustrate the steady state and maximum conversion, respectively. For steady state conversion, we obtain a maximum conversion of around 40%. However, when looking at the maximum conversion, a value of almost 100% can be obtained. This is due to the high temperatures of around 3000 K - 3500 K that are obtained for low fractions of CO_2 and a high O/O_2 fraction. These temperatures are a result of the exothermic recombination of two atomic oxygen into O2. The downside is the creation of more O2 and thus an increased recombination with CO, leading to lower steady state conversions. A solution for this could be working at lower temperatures, around 1500 - 2000 K [7], or the use of quenching, to 'freeze' the higher concentrations.



Fig. 1 – The addition of O/O₂ to either (A-B) CO₂ or (C-D) N₂. A) steady state CO₂ conversion and B) maximum CO₂ conversion; C) steady state NO_x fraction and D) maximum NO_x fraction

Similarly, figures 1C and 1D represent the steady state and maximum fraction of NO_x (NO + NO₂) for the addition of O/O₂ to N₂ gas. For steady state conditions, we obtain a maximum of around 5%, while the maximum NO_x fraction is found around 7.5%. The region where we obtain significant conversion corresponds to the regions where we obtain a temperature of more than 2500 K, indicating that for the process to work, a minimum temperature (and thus energy) is needed. The temperature rise is again due to the recombination of two O atoms into O₂.

4. Conclusion

The addition of O/O_2 to CO_2 or N_2 gas at room temperature leads, without the addition of additional energy, to a significant conversion of these neutral gases: 40% CO₂ conversion and 5% NO_x production when accounting for the steady state. The maxima that are obtained show that there is definitely a possibility for improvement through temperature control and quenching.

5. Acknowledgements

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6. References

[1] National Oceanic and Atmospheric Administration. Trends in Atmospheric Carbon Dioxide. https://gml.noaa.gov/ccgg/trends/

[2] Rebecca Lindsey; National Oceanic and Atmospheric Administration. Climate Change: Atmospheric Carbon Dioxide https://www.climate.gov/ news-features/understanding-climate/climate-changeatmospheric-carbon-dioxide

[3] Nabuurs, G-J., R. Mrabet, A. Abu Hatab, M. Bustamante, H. Clark, P. Havlík, J. House, C. Mbow, K.N. Ninan, A. Popp, S. Roe, B. Sohngen, S. Towprayoon, 2022: Agriculture, Forestry and Other Land Uses (AFOLU). In IPCC, 2022: Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change Cambridge University Press, Cambridge, UK and New York, NY, USA.

[4] C. Smith, A.K. Hill, L. Torrente-Murciano, Energy & Environmental Science 13 (2020) 331–344.

[5] Fridman, A. *Plasma Chemistry*, 2nd ed.; Cambridge University Press: Drexel, 2008.

[6] Pancheshnyi, S.; Eismann, B.; Hagelaar, G. J. M.; Pitchford, L. C. Computer Code ZDPlasKin. University of Toulouse, LAPLACE, CNRS-UPS-INP: Toulouse 2008. <u>http://www.zdplaskin.laplace.univ-tlse.fr</u>.

[7] C. Verheyen, K. van 't Veer, R. Snyders, A. Bogaerts, Journal of CO2 Utilization, 67 (2023) 102347