

NITROGEN OXIDES BEHAVIOR UNDER OXY-COMBUSTION CONDITIONS

Astrid Sanchez¹, Eric Eddings², Fanor Mondragon^{1*}

*fmondra@udea.edu.co

¹Chemistry Institute, University of Antioquia, A.A. 1226. Medellín-Colombia

²Dept. of Chemical Engineering, University of Utah. Salt Lake City. Utah-USA

Abstract

Oxy-combustion is one of the promising technologies to achieve CO₂ capture, reducing in this way the emission of this greenhouse gas. In this process the combustion reaction takes place in an oxygen rich environment with CO₂ in place of nitrogen. One of the inherent advantages in this technology consists in the reduction of NO emissions given the low N₂ coming from the air. However, coal in its structure contains nitrogen which is identified as fuel-N that can have different reactivity under high O₂/CO₂ partial pressures, as is the case in oxy-fuel combustion. Particularly, N₂O emission can be highly affected during fluidized bed oxy-combustion reactions.

This study is focused in the evolution of N-complexes to NO, NO₂ and N₂O (N_xO_y) from a char with high nitrogen content (PAN-8), obtained by the pyrolysis of polyacrylonitrile at 800 °C. Evolution of CO₂, CO, and N_xO_y species was determined by means of FTIR with a gas cell; spectra were taken every two seconds giving rise to detailed evolution profiles for species of interest. Combustion experiments were carried out at 800 °C under bubbling fluidized bed conditions.

In general, it was observed that, mainly NO₂ and N₂O are significantly affected by the presence of both O₂ and CO₂ in higher concentrations than in the case of conventional combustion. Increasing in O₂ partial pressures promotes the homogeneous oxidation of NO to NO₂.

Experiments carried out at constant O₂ concentration with increments in CO₂ partial pressures were evaluated, indicating that CO₂ presence affects the net emission of N₂O and NO₂ by the displacement of gaseous phase equilibriums promoting its formation.

Introduction

Combustion process is highly employed to obtain energy from coal, the main products from this process are CO₂ and H₂O; however, coal contains in its structure N and S that can be converted to N_xO_y compounds and SO₂ respectively, promoting some negative environmental effects [1] [2-3]. In order to diminish the emission of these pollutants, several technologies have been proposed demonstrating capability of reducing both N_xO_y and SO_x emissions. Recently, the focus has been put in the reduction of CO₂ emissions due to its effect on the global warming.

The general idea to reduce the emissions of CO₂ consists in its separation from the fuel gases followed by its capture and storage. When coal combustion is carried out employing air as oxidizing gas, CO₂ is produced in about 15% by volume [2-3]. This low concentration makes unfavorable the separation processes; however, if combustion is carried out in higher O₂ concentrations [4], the CO₂ levels can be raised as high as 95% [5]. This change not only affects the CO₂ concentration, it modifies the process increasing the temperature, reducing the total volume of the gases, and hence the heat transfer efficiency. In order to obtain similar

conditions to those offered in conventional combustion, flue gases can be partially recycled to the combustion chamber [4-5], thus, the combustion is carried out in a mixture of O₂ and CO₂.

This modification has different effects in the combustion properties such as burner stability, flame propagation, pollutant emissions [4-6], among others. One of the advantages is the reduction of thermal NO_x given the low N₂ coming from the air; however, it is important to study the behavior of the fuel-N under this new environment and the effect on the gaseous equilibriums of N_xO_y involving high concentrations of O₂ and CO₂.

Experimental

Two different carbonaceous materials were employed to carry out this work. A char with high N content (PAN-8), obtained by the pyrolysis of polyacrylonitrile, was employed for determination of N_xO_y evolution coming from fuel-N. PAN-8 has 16% of N making it easier the monitoring of N-compounds. A thermal coke identified as BC, with low amount of N (2.8%) was employed as the reference.

In all cases, FTIR with a gas cell was employed to follow the evolution of N_xO_y, CO₂ and CO emissions under different oxidizing conditions. A spectrum was taken every two seconds with the aim to obtain a detailed evolution profile.

Reactions were carried out in a fluidization regime, the reactor consists of a stainless steel tube with a 2.6 cm internal diameter and a 76 cm length electrically heated. About 100 g of sand from the Merck Company®, with particle size 0.1-0.21 mm was used as the fluidizing medium. The combustion temperature was controlled at 800 °C using the signal of a K type thermocouple placed directly into the sand bed. Total gas flow rate was 500 mL/min STP.

Results

During combustion reactions spectra of gases produced were taken every two seconds, allowing a detailed evolution profile for different oxidizing conditions. One of the most interesting comparisons can be done when combustion is carried out at a fixed O₂ partial pressure varying the CO₂ concentration in the gas balance. Figure 1 shows an example in the case of BC combustion employing 30O₂/20CO₂/50Ar, that should be read as: 30% O₂, 20% CO₂ and 50 % Ar. Each point in this figure corresponds to the area of the signal for each compound in every spectrum. From this figure it is possible to see that SO₂ emission starts after all other compounds; and that emission of CO₂, NO and NO₂ shows a similar trend, indicating consumption of all elements is highly uniform. It is important to note that area corresponding to CO₂ never reaches the zero value given that it is 20% in the reactant gases.

Figure 2 shows the evolution profile in the case 30O₂/50CO₂/30Ar where it is possible to see that reaction time is very similar given the same O₂ concentration. As expected the CO₂ absorbance is much higher making it hard to determine small increments in concentration produced by the consumption of the char. However, the most important observation in this case is the increasing in NO₂ emission. In the first case (20% CO₂), NO₂ area was very low, while when CO₂ was increased to 50% its area became larger, even higher than the NO area.

It is possible that CO₂ promotes the homogeneous NO oxidation to NO₂ by a third body effect. Figure 3 shows the average area of NO, NO₂ and SO₂ signal during these experiments,

indicating the NO₂ signal is the most affected by CO₂, while NO and SO₂ remain almost constant.

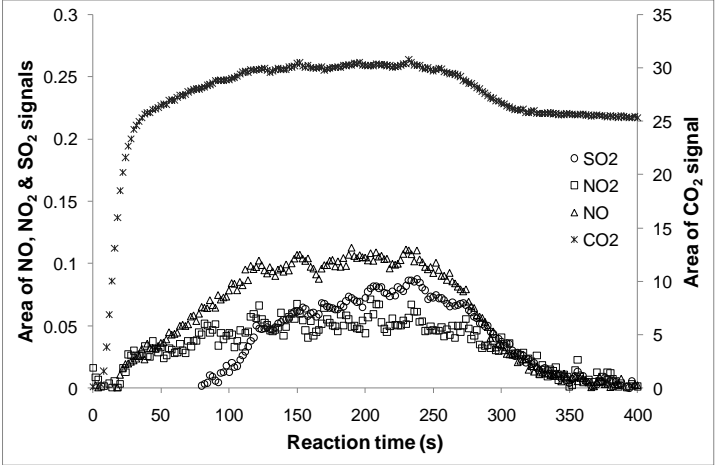


Figure 1. Evolution profile for BC combustion in 30O₂/20CO₂/50Ar

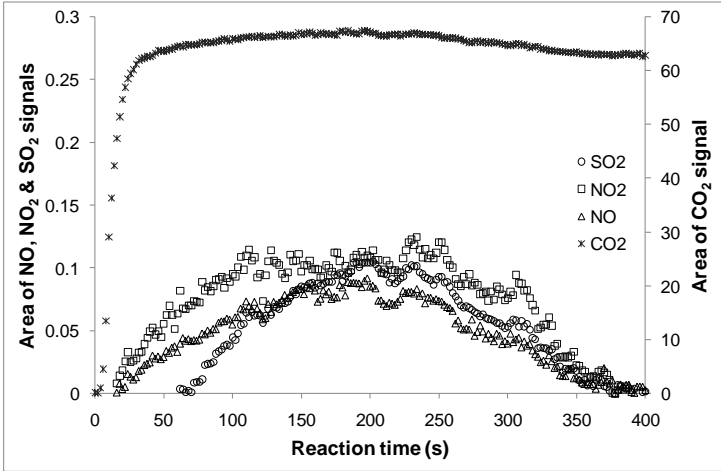


Figure 2. Evolution profile for BC combustion in 30O₂/50CO₂/30Ar

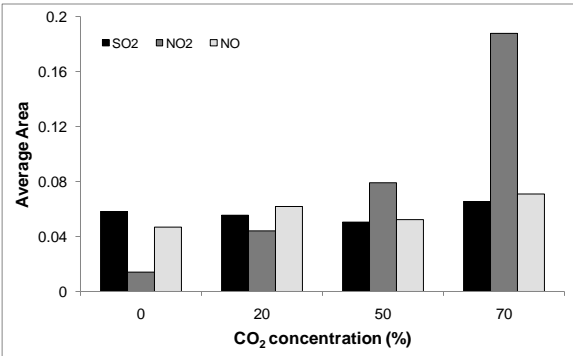


Figure 3. Average area for NO, NO₂ and SO₂ for 30O₂/xCO₂/70-xAr, x: CO₂ concentration

When O₂ concentration is increased, reaction times are shorter and instantaneous concentration of all emitted compounds are higher. Figure 4 and Figure 5 show the combustion profiles in the cases 30O₂/70Ar and 100% O₂.

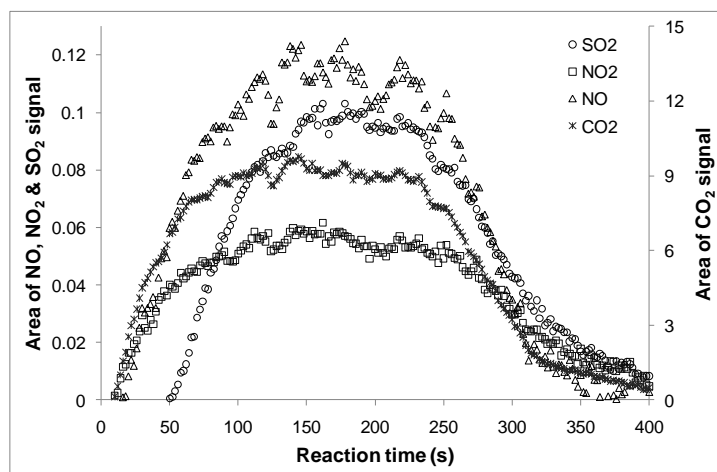


Figure 4. Evolution profile for BC combustion in 30O₂/70Ar

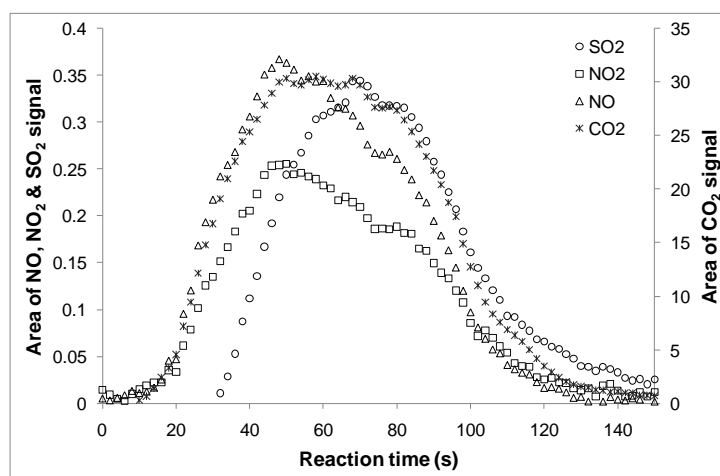


Figure 5. Evolution profile for BC combustion in 100O₂

In the case of PAN-8 combustion similar conclusions can be obtained; however important observations can be done when spectra are evaluated in more detail. Figure 6 shows the spectra corresponding to 75% of conversion for PAN-8 employing several O₂ partial pressures. In this figure is evident that NO₂ becomes larger with the O₂ concentration, although NO area is not significantly affected. Another important observation is regarding CO emission, with the increasing in O₂ concentration CO signal is smaller.

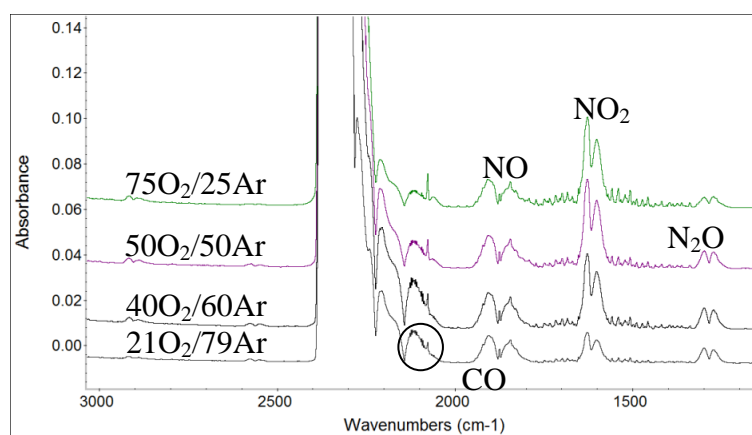


Figure 6. Spectra corresponding to 75% of conversion for combustion of PAN-8 with several O₂ concentrations

N_2O signal has not a clear trend in this case; however, experiments in gas phase indicated that O_2 inhibits the decomposition of N_2O giving rise to a higher N_2O concentration.

With the aim to evaluate in more detail the CO emission, the combustion experiment carried out in 21% O_2 was analyzed for several levels of conversion, and can be seen that CO formation increases with the conversion; implicating that, one of the possible mechanisms of CO oxidation is the heterogeneous oxidation over the char surface. However, from these set of experiments it was noticed that CO_2 has an important effect on the formation of CO, increasing its concentration in a big proportion as can be seen in Figure 8 for the comparison of the CO signal for combustion in 40% O_2 employing Ar and CO_2 as balance gas,

When CO_2 is present, CO signal is higher indicating different possibilities: CO_2 is participating in gasification reactions or CO_2 displaces the equilibrium between CO/ CO_2 , or CO_2 presence inhibits the heterogeneous oxidation of CO over the char surface.

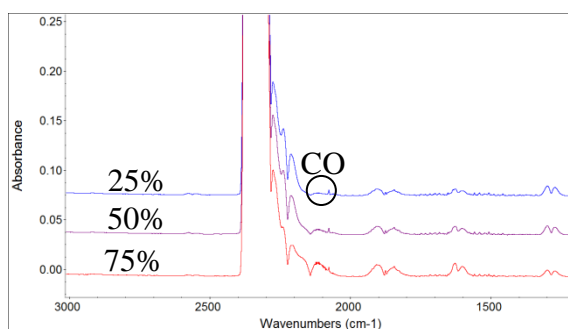


Figure 7. Spectra corresponding to 25%, 50% and 75% of conversion for PAN-8 combustion in 21 O_2 /79Ar

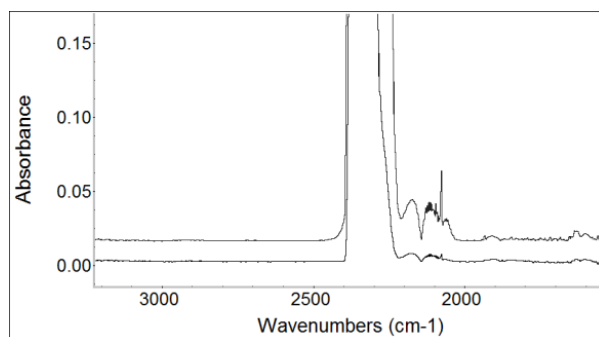


Figure 8. Comparison of CO signal for 40 O_2 /60Ar (bottom) and 40 O_2 / CO_2 (top)

Conclusions

Oxy-fuel combustion involves the increasing in O_2 and CO_2 partial pressures inducing several differences in coal combustion, this work focuses in the emission of both N_xO_y and CO modifying the reactant atmosphere. When O_2 partial pressures increases there is a diminishing in the formation of CO, and the instantaneous concentration of all emitted species increases given the faster consumption of the char.

Increasing in CO_2 concentration raises the formation of CO, probably by different mechanisms, as gasification reactions, or equilibrium displacements; in addition CO_2 enhances the formation of NO_2 that represent a disadvantage of this new technology.

Acknowledgments

The authors gratefully acknowledge support from the “Programa Sostenibilidad 2009-2011” of the “Universidad de Antioquia. A.S. thanks Colciencias and the “Universidad de Antioquia” for her Ph.D. scholarship and the U.S. Department of Energy (DOE) through the Utah Clean and Secure Energy (CASE) Program (FC26-08NT0005015) for her internship.

References

- [1] Ren Q., Zhao C., Wu X., Liang C., Chen X., Shen J., et al. Effect of mineral matter on the formation of NO_x precursors during biomass pyrolysis. *J. Anal. Appl. Pyrolysis* 2008;85:447-53.
- [2] Zhu J., Lu Q., Niu T., Song G., Na Y. NO emission on pulverized coal combustion in high temperature air from circulating fluidized bed – An experimental study. *Fuel Process. Technol.* 2009;90:664-70.
- [3] Thomas K.M. The release of nitrogen oxides during char combustion. *Fuel* 1997;76:457-73.
- [4] Bejarano P.A., Levensis Y.A. Single-coal-particle combustion in O₂/N₂ and O₂/CO₂ environments. *Combust.Flame* 2008;153:270-87.
- [5] Rathnam R.K., Elliott L.K., Wall T.F., Liu Y., Moghtaderi B. Differences in reactivity of pulverised coal in air (O₂/N₂) and oxy-fuel (O₂/CO₂) conditions. *Fuel Process. Technol.* 2009;90:797-802.
- [6] Wall T., Liu Y., Spero C., Elliott L., Khare S., Rathnam R., et al. An overview on oxyfuel coal combustion--State of the art research and technology development. *Chem. Eng. Res. Des.* 2009;87:1003-16.