Oxy-steam combustion: the effect of coal rank and steam concentration on combustion characteristics

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Abstract

This paper addresses the experimental investigation of coal combustion characteristics (ignition, burnout and NO formation) under oxy-steam combustion conditions. Two coals are selected in order to compare the effect of the rank: bituminous and sub-bituminous ones. The experiments have been conducted in an electrically-heated entrained flow reactor for a set of O_2/N_2, O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres, with O_2 concentrations up to 35% and H_2O concentrations up to 40%. Regarding ignition, 10% H_2O reduces ignition temperature (max. 16–19 K) but the trend is reversed when supplying additional steam to 25% and 40%. This behaviour is similar for both coals, with slight larger variations in the case of the low rank coal. Burnout degree of the sub-bituminous coal is barely affected by the steam concentration since all observed conversions are very high. Larger increments (up to 6.1 percentage points) are obtained for the bituminous coal, with a maximum burnout degree for the 25/35% H_2O/O_2 atmosphere. A very different effect of steam on NO formation is found depending on the coal rank. Significant reduction rates are observed for the bituminous coal in comparison to the dry O_2/CO_2 atmospheres, with a maximum diminution of 24% when 40% H_2O replaces CO_2. On the contrary, the higher volatile content in the sub-bituminous coal leads to NO increments up to 9%. For all the combustion characteristics studied, the increase of O_2 concentrations attenuates the effects caused by the steam addition.

Keywords

Oxy-combustion; Steam moderation; Coal rank; Ignition; Burnout; NO formation

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1. Introduction.

A large deployment of renewable energies is currently being required to obtain a significant reduction of CO_2 emissions, as an urgent target to mitigate the effects of global warming. Nevertheless, coal still contributed in 2018 to the 38.5% of the world electricity production [1]. This global frame turns CO_2 capture technologies as essential to match the pathways of the Paris Agreement.

Oxy-fuel combustion is one of the capture technologies suitable for coal-fired power plants. Many results have been obtained in the last years concerning oxy-coal combustion, including lab-, pilot- and demo-scale facilities. A related concept, but significantly new and different, is the so-called oxy-steam combustion. It consists on the full avoidance of the flue gases recycle, replacing CO_2 by H_2O to dilute the oxygen. Condensed water from the flue gases is re-boiled and redirected to the furnace, acting as O_2 dilution [2, 3]. The main advantages of this alternative are simplified plant operation, reduction of auxiliary consumptions and lower air in-leakages. Replacement of CO_2 by H_2O in the firing atmosphere may bring several differences in the combustion characteristics of solid fuels, due to their different thermophysical and chemical behaviour. Some coupled phenomena like volatiles oxidation, char reactivity and conversion, gas-particle heat transfer and pollutants formation/depletion, have to be well characterized to determine the consequences of shifting from the O_2/CO_2 atmosphere to the O_2/H_2O one.

Few studies are available so far addressing oxy-steam combustion of pulverized coal, most of them focused on the ignition behaviour of single/few particles, under different steam concentrations. A summary of experiences, conditions and findings is shown in Table 1. There is not a common outcome from these works, since the effect of steam on ignition depends on several factors like the coal rank, the coal supply conditions (particle size and flow rates), the O_2 concentration and the H_2O concentration [4].

Besides ignition and conversion, steam can also play a role in NO_x formation/depletion mechanisms. Many studies are available, for a wide range of scales, assessing NO_x behaviour for O_2/CO_2 atmospheres [11–14]. However, the effect of the steam on NO_x under oxy-combustion conditions has been scarcely investigated, and with limited steam rates. Moron and Rybak [15] investigated NO_x formation for hard and brown coals in an oxy-fired EFR, with steam addition up to 10%. Steam lowered the NO_x levels detected. Small influences were reported by Álvarez et al. [16], who conducted oxy-combustion

experiments for a high-volatile bituminous coal with steam concentrations in the range 5–20%. Yupeng et al. [17] studied the char-nitrogen conversion for a bituminous coal, under 20% H_2O content. They found that steam addition promoted nitrogen release at low oxygen concentration, but it was inhibited at higher oxygen concentrations. To our knowledge, only the work by Zhijun et al. [18] surpassed 20% H_2O, conducting tests up to 40% H_2O for anthracite and bituminous coals in an oxy-fired DTF. These authors reported steam rates minimizing NO emissions, with a competitive effect between CO_2 and H_2O concentrations in the atmosphere.

Reference	**Coal type**	**Facility**	**Atmosphere**	**% H_2O**	**Main outcomes**
Kops et al., 2019 [5]	Sub-bituminous	DTF + high speed camera	$O_2/N_2/H_2O$ $O_2/CO_2/H_2O$	0–10%	Shortening of ignition delay time due to steam addition
Riaza et al., 2011 [6]	Anthracite Bituminous	EFR	$O_2/N_2/H_2O$ $O_2/CO_2/H_2O$	0–20%	Increase of ignition temperature when replacing CO_2 by H_2O
Prationo and Zhang, 2016 [4]	Bituminous Sub-bituminous	EFR + high speed camera	$O_2/N_2/H_2O$ $O_2/CO_2/H_2O$	0–26%	The lower the rank of the coal, the higher the effect of the steam Negligible steam effect for O_2 enriched atmospheres
Cai et al., 2016 [7]	Bituminous	DTF + high speed camera	$O_2/CO_2/H_2O$	0–30%	Negligible effect for steam up to 20% Significant ignition overtake for 30%
Escudero et al., 2020 [8]	Anthracite	EFR	$O_2/CO_2/H_2O$	0–40%	Decrease of ignition temperature for low steam rates, increase for the higher ones
Zou et al., 2015 [9]	Bituminous	DTF + high speed camera	O_2/H_2O	50–79%	Shortening of ignition delay time due to steam addition
Hao et al., 2019 [10]	Bituminous	SPR + high speed camera	O_2/H_2O	50–79%	Shortening of ignition delay time due to steam addition

Table 1.- Summary of experimental works related to oxy-coal ignition under steam-containing atmospheres. DTF = drop tube furnace. EFR = entrained flow reactor. SPR = single particle reactor.

Our study aims to widen the limited knowledge about coal oxy-combustion with large steam additions as CO_2 replacement. In particular, scarce results are reported for low-rank coals. This paper presents a detailed, comprehensive characterization of the oxy-steam combustion characteristics (ignition, burnout and NO_x formation) for a pair of coals: one sub-bituminous and one bituminous, also seeking the effect of the coal rank on

81 the results. The experiments are not focused on single/few particles, but on a steady
82 flowrate in an entrained flow reactor, operated under atmospheres containing up to 40%
83 H_2O and up to 35% O_2.

84 ## 2. Experiments.

85 ### 2.1. Coals.

86 Two different coals were tested to comparatively study their oxy-steam combustion
87 characteristics: 1) South-African hard coal (SA onwards), 2) blend of imported hard coals
88 and domestic Spanish lignite, as fired in Teruel power station (CB onwards). According
89 to ASTM D388-97 standard, the former is a medium-volatile bituminous coal and the
90 latter and a B-type sub-bituminous one. The proximate analysis, ultimate analysis and
91 low heating value (LHV) of these coals are listed in Table 2. Prior to tests, each sample
92 was grounded and sieved to the size range of 75–150 μm.

93

Coal	SA	CB
ASTM D388-97	Medium-volatile bituminous	B-type sub-bituminous
Proximate analysis (% wt.)		
Moisture (as fired)	3.6	7.7
Ash (as fired)	13.1	23.4
Volatile matter (dry ash free)	30.9	46.4
Fixed carbon (dry ash free)	69.1	53.6
Ultimate analysis (% wt., dry ash free)		
Carbon	82.2	65.9
Hydrogen	4.2	3.8
Nitrogen	2.0	0.9
Sulphur	0.5	10.0
Heating value		
LHV (kJ/kg, as fired)	25 866	16 680

94 **Table 2.-** Coal analysis and heating value.

95 The moisture, volatile and ash contents of the coal samples were determined
96 according to the standards ISO 5068-2:2007, ISO 562:2010 and ISO 1171:2010,
97 respectively. The elemental analyses were performed using an elemental analyzer

Thermo Flash 1112. The lower heating values of the samples were determined according to the standard ISO 1928:2009. These results were provided by a certified laboratory, belonging to the Instituto de Carboquímica (Spanish National Research Council).

2.2. Experimental facility.

The tests were carried out in a lab-scale entrained flow reactor (EFR), with continuous fuel and gas feeding systems. Figure 1 displays a diagram of the plant. The reactor is made of a Kanthal alloy, with an inner diameter of 38 mm. The height can be varied by a bottom-movable sampling probe, in the range 0.8–1.6 m. The reactor is electrically heated by means of four independent furnaces. Maximum set-point temperature for the furnaces is 1150 ºC. The pulverized fuel is supplied by a mechanical screw, driven by a variable-frequency motor. Several mass flow controllers provide the gases from bottles, while a Coriolis flow meter is used to control water flowrate.

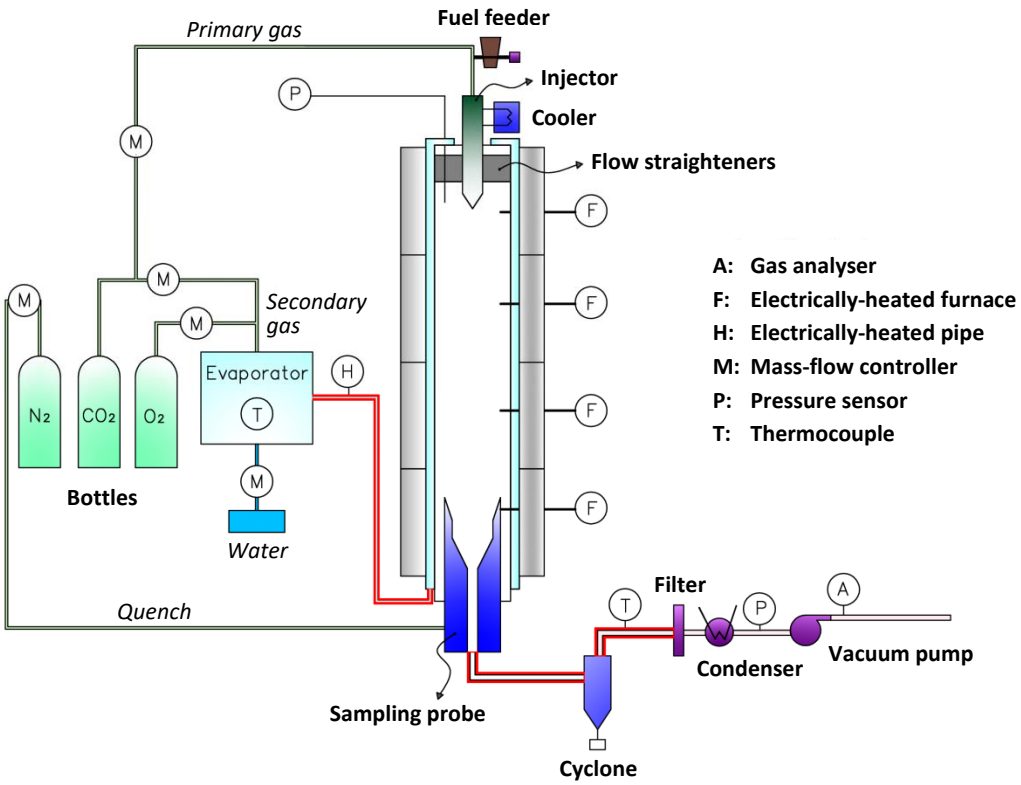


Figure 1.- Diagram of the lab-scale entrained flow reactor.

Downstream the reactor, a cyclone and a filter retains the fly solids from the gas stream, and then a condenser is placed to remove most of the moisture in the flue gases.

Finally, a continuous emission monitoring system provides the flue gas composition at the cold-end section: non-dispersive infrared sensors for CO_2, CO SO_2, NO, and paramagnetic sensor for O_2. A more detailed description of the facility can be found elsewhere [8]. Table 3 summarizes the accuracy of the instruments used for measurements during the tests.

Measurement	**Accuracy**
Feeding gases flow rate (O_2, CO_2, N_2)	± 0.5%
Feeding water flow rate	± 0.2%
Temperature	± 2º C
Pressure	± 3 mbar
Flue gases composition (CO_2, SO_2, CO, NO)	± 1%
Flue gases composition (O_2)	± 1.5%

Table 3.- Accuracy of the on-line measurements.

2.3. Experimental procedure.

2.3.1. *Ignition tests.*

The effect of oxygen concentration (21 and 35% O_2) and steam addition (0, 10, 25 and 40%) over the ignition temperature has been experimentally assessed for the two selected coals (SA bituminous and CB sub-bituminous). Thus, sixteen oxy-fired trials were conducted in the entrained flow reactor (eight for each coal). Besides, two additional tests were run under conventional combustion (21/79% O_2/N_2). The reactor was heated from room temperature to 1000 ºC, at a fixed heating rate of 15 ºC/min. O_2 and CO_2 concentrations in flue gases were recorded to determine the ignition point. In this way, three zones are identified: 1) pre-ignition, where changes in CO_2 and O_2 concentrations can be neglected, 2) ignition and conversion of particles, where CO_2 concentration begins to quickly grow at the same time that O_2 concentration decreases, and 3) steady-evolution when burnout is reached, and concentrations remain constant. This indirect method has been previously used by other researchers [19, 20]. In our case, ignition temperature T_{ig} is obtained from the following approach:

$$\left|\frac{[X(T_{ig})]-[X(T_p)]}{[X(T_{bo})]-[X(T_p)]}\right| = 0.1 \quad (1)$$

where $[X(T_p)]$ is the O_2 or CO_2 molar concentration during the pre-ignition temperatures range, $[X(T_{bo})]$ is the molar concentration when steady burnout degree is reached and $[X(T_{ig})]$ is the molar concentration at the ignition temperature point. The ignition temperature was obtained by averaging the results obtained from O_2 and CO_2 measurements.

2.3.2. *Oxy-steam combustion tests.*

Combustion experiments were carried out under different atmospheres: 21/79% O_2/N_2, 21/79% O_2/CO_2, 30/70% O_2/CO_2 and 35/65% O_2/CO_2. To assess the effect of steam moderation, it was added to the oxy-firing atmospheres replacing CO_2 at the following percentages: 10%, 25% and 40% for a fixed value of oxygen excess (λ = 1.25). Thus, 13 tests were carried out for each coal. In order to compare the results obtained under the different situations (coal type, % O_2, % H_2O), the experimental conditions were defined to keep the same mean residence time (3 s) for all the tests. The corresponding flow rates are presented in Tables 4 and 5. The initial reactor temperature was kept at 1000 ºC throughout the experimental campaign, while the reaction height was set to 1.5 m. The independent effect of oxygen excess (λ = 1.35, λ = 1.45) was also analysed by means of some additional tests for the dry atmospheres.

Test #	**Atmosphere** (% vol.)	**Coal flow rate** (g/min)	**O_2 flow rate** (g/min)	**CO_2 flow rate** (g/min)	**Water flow rate** (g/min)
1	21/79 O_2/N_2	0.55	1.39	4.59 (N_2)	0
2	21/79 O_2/CO_2	0.55	1.39	7.21	0
3	21/69/10 O_2/CO_2H_2O	0.55	1.39	6.30	0.37
4	21/54/25 O_2/CO_2H_2O	0.55	1.39	4.93	0.93
5	21/39/40 $O_2/CO_2/H_2O$	0.55	1.39	3.56	1.49
6	30/70 O_2/CO_2	0.78	1.96	6.29	0
7	30/60/10 $O_2/CO_2/H_2O$	0.78	1.96	5.39	0.37
8	30/45/25 $O_2/CO_2/H_2O$	0.78	1.96	4.05	0.92
9	30/30/40 $O_2/CO_2/H_2O$	0.78	1.96	2.70	1.47
10	35/65 O_2/CO_2	0.90	2.27	5.79	0
11	35/55/10 $O_2/CO_2/H_2O$	0.90	2.27	4.90	0.36
12	35/40/25 $O_2/CO_2/H_2O$	0.90	2.27	3.57	0.91
13	35/25/40 $O_2/CO_2/H_2O$	0.90	2.27	2.23	1.46

Table 4.- Mass flow rates during the combustion tests of the SA bituminous coal (λ = 1.25).

Test #	Atmosphere (% vol.)	Coal flow rate (g/min)	O_2 flow rate (g/min)	CO_2 flow rate (g/min)	Water flow rate (g/min)
1	21/79 O_2/N_2	0.81	1.36	4.49 (N_2)	0
2	21/79 O_2/CO_2	0.81	1.36	7.06	0
3	21/69/10 O_2/CO_2H_2O	0.81	1.36	6.17	0.37
4	21/54/25 O_2/CO_2H_2O	0.81	1.36	4.83	0.91
5	21/39/40 $O_2/CO_2/H_2O$	0.81	1.36	3.49	1.46
6	30/70 O_2/CO_2	1.12	1.90	6.11	0
7	30/60/10 $O_2/CO_2/H_2O$	1.12	1.90	5.24	0.36
8	30/45/25 $O_2/CO_2/H_2O$	1.12	1.90	3.92	0.89
9	30/30/40 $O_2/CO_2/H_2O$	1.12	1.90	2.62	1.43
10	35/65 O_2/CO_2	1.30	2.19	5.60	0
11	35/55/10 $O_2/CO_2/H_2O$	1.30	2.19	4.74	0.35
12	35/40/25 $O_2/CO_2/H_2O$	1.30	2.19	3.45	0.88
13	35/25/40 $O_2/CO_2/H_2O$	1.30	2.19	2.15	1.41

Table 5.- Mass flow rates during the combustion tests of the CB sub-bituminous coal (λ = 1.25).

All the results related to the combustion tests —sections 3.2, 3.3, 3.4— have been obtained from measurements taken under steady-state operation (mass flow rates, temperatures, pressures and flue gases composition). Once the furnace temperature set-point is achieved, coal feeding starts. After a short transient period, composition of flue gases is stabilized and then operation reaches the steadiness. Data are recorded every 5 seconds, and steady periods can last up to 60 minutes. Flame temperature inside the reactor is higher than the furnace set-points, and only one electrical furnace (the bottommost one) is supplying its full power during the combustion tests.

Solid residues in cyclone were also collected during the steady-state regime. Ash weight fractions in these solid residues were determined according to the standard UNE-32-004-84. Coal burnout degree β was calculated by the ash tracer method:

$$\beta = \frac{\alpha_f - \alpha_i}{\alpha_f(1-\alpha_i)} \quad (2)$$

where α_f is the ash weight fraction (dry basis) of solid residues recovered in the cyclone and α_i is the ash weight fraction (dry basis) of the fired coal.

The closures of elemental carbon balances and heat balances have been done for the combustion tests. The deviations of the mass balances range ±4%, while the deviations of the heat balances are comprised within ±6%. The heat balances can be only closed for the tests with the higher steam concentrations (25% and 40% vol.), since then the bottom

probe is not water-cooled –this prevents the condensing in flue gases prior to the cyclone and filter, and a possible blockage–. Anyway, the low deviations in the available mass and heat balances support the reliability of the results obtained.

3. Results and discussion.

3.1. Ignition.

Figure 2 displays the results for the ignition temperatures of both coals, under air (21/79% O_2/N_2) and several O_2/CO_2 and $O_2/H_2O/CO_2$ conditions. The larger amount of volatile matter in the CB sub-bituminous coal leads to lower values of the ignition temperatures in comparison to the SA bituminous one. But the effect of changing the atmosphere is quite similar for both coals.

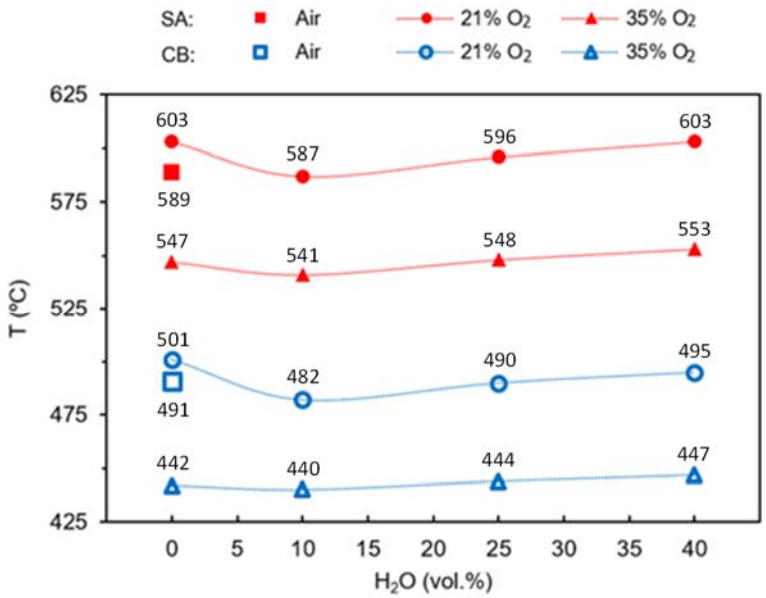


Figure 2.- Ignition temperatures under air and different O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres (steam is added as CO_2 replacement). SA: bituminous coal. CB: sub-bituminous coal.

When 79% N_2 is substituted by 79% CO_2, an increase is observed in the ignition temperatures (14 K for the bituminous and 10 K for the sub-bituminous). Due to the higher specific heat of CO_2 in comparison with N_2, the temperature increase of the CO_2-containing atmosphere around the particle is comparatively lower during the heat release produced by the initial oxidation of volatiles. Besides, O_2 diffusivity in CO_2 is also

196 lower than in N_2. If the O_2 concentration is risen, from 21/79% O_2/CO_2 to 35/65% O_2/CO_2,
197 the ignition temperature decreases (56 K for SA and 59 K for CB) due to the higher
198 oxidation rates caused the by the oxygen partial pressure [4, 6].

199 When 10% H_2O is added as CO_2 replacement in the 21% O_2 cases, there is an
200 advancement of the ignition: a decrease of 16 K for the SA bituminous coal and 19 K for
201 the CB sub-bituminous one. Several phenomena explain this reduction of the ignition
202 temperature: 1) the lower value of the molar specific heat of H_2O in comparison with
203 CO_2, 2) the higher O_2 diffusivity in H_2O in comparison to CO_2, and 3) the increase of H_2
204 concentration due both to the char gasification by steam and to the water-shift reaction
205 in the gas-phase [5, 9, 10]. This influence of the 10% H_2O addition can be also observed
206 for the 35% O_2 atmospheres, but with a more limited extent.

207 However, if the steam concentration is increased from 10% to 25% the trend is
208 reversed and the ignition temperature increases. This behaviour is related, on the one
209 hand, to the increase of radiative absorption by H_2O in comparison to CO_2. According to
210 Cai et al. [6], this effect prevails over the reduction of the specific heat for large steam
211 concentrations. On the other hand, the enhancement of char gasification by steam
212 increases CO concentration in the surroundings of the particle, displacing the oxygen,
213 and reduces the temperature due to its endothermicity. The increase of ignition
214 temperature is also observed when steam is further added up to 40%. For the 21% O_2
215 atmospheres, these increases are of 16 K for the bituminous and 13 K for the sub-
216 bituminous coal, when replacing CO_2 by H_2O from 10% to 40%.

217 The effect of the progressive CO_2 substitution by H_2O results in a "U-shape" evolution,
218 firstly decreasing the ignition temperature and later increasing it. As the steam
219 concentration grows, it can be supposed that the increase of radiative heat absorption
220 and the enhancement of char gasification contribute to a delay of the ignition in
221 comparison to the lower H_2O case, prevailing over the effect caused by a larger O_2
222 diffusivity in the atmosphere.

223 When oxygen concentration is augmented from 21% to 35%, the trend is the same but
224 the evolution is flattened with softer temperature variations. The effect of the steam is
225 attenuated under high O_2 concentrations, which is consistent with previous experiences
226 [4, 8]. In comparison to the dry O_2/CO_2 atmospheres, a 40% CO_2 replacement by H_2O
227 barely affects the ignition temperature, with maximum differences of 6 K.

3.2. Burnout.

Figures 3 and 4 show the burnout degrees obtained under the different atmospheres tested, for SA and CB coals respectively. These conversion rates have been calculated according to the Eq. (2) provided in the section 2.2. Replacement of CO_2 by H_2O should yield larger burnout degrees, due to the higher H_2O reactivity. This is related to the increase of the gas-phase temperature, the higher O_2 diffusivity in H_2O than in CO_2, and the enhancement of char gasification when H_2O concentration is augmented.

Since the tests were defined to keep the same residence time, burnout degrees are consistently higher for the sub-bituminous coal, due to its major reactivity. Indeed, very high conversion rates are obtained for all the conditions during the CB tests –see Figure 4–, with small differences among them. In the case of the SA bituminous coal, supply of 10% H_2O as CO_2 replacement always increases the burnout degree in comparison to the dry O_2/CO_2 situations. For the 21% O_2 atmosphere, a significant increase of nearly 5 percentage points is observed. This steam-induced effect is explained by the increase of both the gas-phase temperature and the O_2 diffusivity. The comparative increases also observed for the 30% O_2 and 35% O_2 atmospheres are not so large; the higher conversion rates and oxidant availability attenuate the rising effect caused by the 10% H_2O addition. When steam is further added from 10% to 25% an additional increase of burnout is obtained, but not proportionally to the steam concentration leap. These differences range within 0.51–1.98 percentage points. Besides the influences on the temperature and the O_2 diffusivity, H_2O also enhances char gasification in comparison to CO_2 [21]. This also contributes to a larger solid-to-gas conversion rates when steam concentration is augmented as CO_2 replacement.

Contrariwise, a different trend is shown when increasing steam addition from 25% to 40%. For the 21% O_2 atmosphere the variation is small, but a decrease of burnout degree is detected for the 30% O_2 and 35% O_2 cases: 1.85 and 1.03 percentage points respectively. The only explanation for this behaviour relies on the reduction of the char specific surface caused by the enriched-H_2O atmosphere in comparison to CO_2 [22], which affects the char conversion rates. To support this conclusion, BET surface areas have been determined for residues samples taken from two of the bituminous coal tests: 35/65% O_2/CO_2 and 35/25/40% $O_2/CO_2/H_2O$. The used technique is N_2 isothermal adsorption at 77 K, determined with a gas sorption analyzer ASAP 2020 (Micromeritics) in a certified laboratory. The samples were previously degassed at 250 ºC during 5 hours.

The BET surface areas obtained are 164.5 m^2/g (35/65% O_2/CO_2) and 107.5 m^2/g (35/25/40% $O_2/CO_2/H_2O$), which means a reduction of 34.6%.

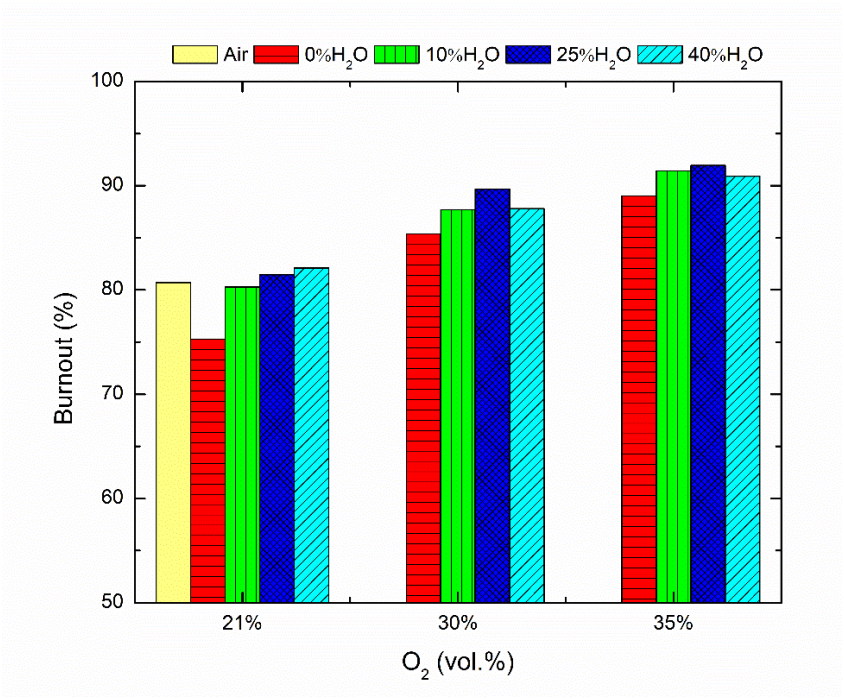


Figure 3.- Burnout degree obtained under air and different O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres (steam is added as CO_2 replacement), for the SA bituminous coal.

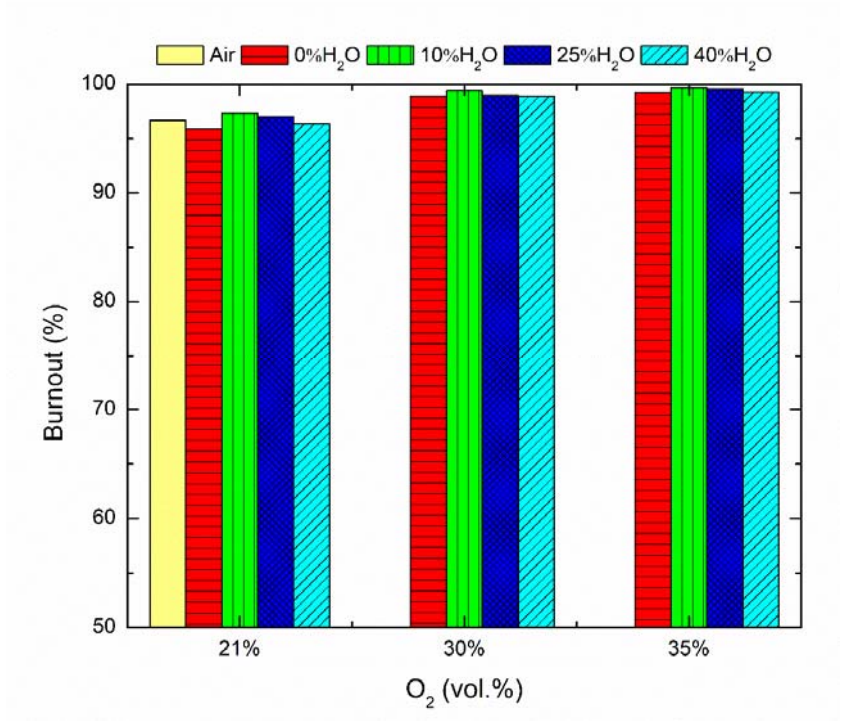


Figure 4.- Burnout degree obtained under air and different O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres (steam is added as CO_2 replacement), for the CB sub-bituminous coal.

The effect of steam on the burnout degree for the CB sub-bituminous coal is partially hindered by the high conversion rates achieved under all the atmospheres, as shown in Figure 4. Anyway, although in a much lower extent, the trend is similar to the discussed for the high-rank coal. Replacement of 10% CO_2 by H_2O yields an increase of burnout degree for all the three O_2 concentrations (0.45–1.45 percentage points), the maximum values are not obtained for the 40% H_2O cases, and the effect of steam on burnout is attenuated when atmospheres are enriched in O_2.

The slight burnout decrease observed when increasing steam concentration from 10% to 25% and to 40% is again explained by the decrease of the char specific surface. According to Feng et al. [23], the lower the rank of the coal, the more the pore development inside the char structure due to a quick precipitation of volatile matter. Pallarés et al. [24] reported a maximum reduction of 43% in BET specific surfaces for a high volatile fuel, when replacing CO_2 by H_2O for activation. These experiences are consistent with the observations in Figures 3 and 4: the maximum burnout degree was detected for the 35/10% O_2/H_2O case when firing the CB sub-bituminous coal, but it was for the 35/25% O_2/H_2O case when firing the SA bituminous one. Notwithstanding, the high reactivity of the sub-bituminous coal brings burnout to be very little sensitive to the firing atmosphere.

The burnout degrees under conventional air combustion are also included in Figures 3 and 4: 80.7% for the SA coal and 96.7% for the CB one. The shift from O_2/N_2 to O_2/CO_2 combustion involves a burnout decrease, due to the reduction of the gas temperature caused by the higher specific heat of CO_2 compared to N_2, and the lower diffusivity of O_2 in CO_2 than in N_2. As explained in the previous paragraphs, steam addition as CO_2 replacement produces the opposite effect, thereby resulting in similar or higher burnout values than the obtained under air combustion.

3.3. CO in flue gases.

Burnout degree accounts for the solid-to-gas conversion, but it does not provide information about the evolution to final products in the gas-phase. This can be indicated by the presence of carbon monoxide in the flue gases leaving the reactor. CO specific concentrations in flue gases are shown in Tables 6 and 7, for the SA and CB coals respectively. It is clearly seen in these tables that CO levels are significantly lowered when the atmosphere is O_2-enriched. Indeed, the concentrations are below the detection limit for some of the experiments with the CB sub-bituminous coal.

	Air	21% O_2	30% O_2	35% O_2
0% H_2O	5.7	7.1	3.2	2.3
25% H_2O	—	6.6	2.2	1.2
40% H_2O	—	16.0	2.8	2.1

Table 6.- CO specific emissions (mg/g_{coal}) obtained under air and different O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres (steam is added as CO_2 replacement), for the SA bituminous coal.

	Air	21% O_2	30% O_2	35% O_2
0% H_2O	2.7	9.6	1.1	0.2
25% H_2O	—	6.0	0.2	0.0
40% H_2O	—	7.7	2.9	0.2

Table 7.- CO specific emissions (mg/g_{coal}) obtained under air and different O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres (steam is added as CO_2 replacement), for the CB sub-bituminous coal.

The CO_2 replacement by H_2O can affect to CO detected at reactor outlet by several, overlapped pathways. On the one hand, steam enhances char gasification in comparison to CO_2 but, on the other hand, O_2 diffusivity is higher in H_2O than in CO_2. Whilst the former promotes CO release, the latter enhances CO oxidation to CO_2. Besides, steam gasification effects are weakened for high O_2 concentrations, according to Hecht et al. [22]. In addition, as discussed in the following section, H_2O also plays a role in the NO formation/depletion mechanisms, and NO can interact with CO evolving towards CO_2 and N_2.

The results shown in Tables 6 and 7 point to a decrease in CO concentrations when CO_2 is replaced in a rate of 25% H_2O: all they are lower than the measured under the dry O_2/CO_2 atmospheres. But the trend is reversed for the 40% H_2O addition, even surpassing in some cases the levels corresponding to the dry atmospheres. The effect is more relevant for the high-rank coal and the poorer O_2 atmosphere (21%). According to these observations, large steam addition significantly enhances char gasification promoting CO release, which cannot be totally compensated by the increase of oxidant diffusivity along the reactor height. Anyway, all the values are very low (below 3.2 mg CO/g coal) for the 30% and 35% O_2 atmospheres, independently of the coal rank or the steam concentration.

Aiming at relating the operating conditions with the carbon behaviour, an index has been defined as the ratio of carbon solid-to-gas conversion divided by the burnout degree

(i.e. a comparison of the carbon conversion with the fuel averaged conversion). This index has been obtained from the carbon content in the coal and the CO and CO_2 concentrations in flue gases. The results have been comprised in the range 0.95–0.98 for the bituminous coal and 0.98–0.99 for the sub-bituminous coal. Differences are very small, and cannot be related to the specifics of every test.

3.4. NO formation.

The extent of NO_x formation and reduction under O_2/CO_2 combustion has already been experimentally characterized for a wide range of fuels and conditions [13, 25–28], but large steam concentrations under oxy-steam combustion can result in very different insights. Steam participates in both homogeneous reactions (involving N-volatiles) and heterogeneous ones (involving N-char), then the fuel rank is also a question that must be accounted.

CO_2 replacement by H_2O leads to an increase of gas temperature and O_2 diffusivity, as commented in previous sections, which increases the oxidation rates of N-fuel to NO. On the contrary, steam can contribute to reduce or inhibit NO formation by different ways. In the gas-phase, steam interacts with HCN over 600 ºC according to the reaction R.1 [16, 29, 30], competing with HCN oxidation and releasing NH_3 that can further reduce NO (R.2). Besides, large steam concentration promotes the presence of an OH+H radical pool in the flame, also competing with HCN oxidation through the reactions R.3 and R.4 [26].

$$HCN + H_2O \rightarrow NH_3 + CO \quad \text{(R.1)}$$

$$NH_3 + NO + \frac{1}{4}\ O_2 \rightarrow N_2 + \frac{3}{2}\ H_2O \quad \text{(R.2)}$$

$$HCN + H \leftrightarrow H_2 + CN \quad \text{(R.3)}$$

$$HCN + OH \leftrightarrow H_2O + CN \quad \text{(R.4)}$$

In comparison to CO_2, steam intensifies char gasification releasing CO that can contribute to reduce NO by the homogeneous reaction (R.5), catalysed by the char surface [31]. This reducing effect can be attenuated by the presence of OH radicals, since they contribute to CO depletion by means of the reaction (R.6). These opposite trends were suggested by Zhijun et al. [18] to explain H_2O/CO_2 ratios minimizing NO formation rates.

$$CO + NO \rightarrow \frac{1}{2} N_2 + CO_2 \quad \text{(R.5)}$$

$$CO + OH \rightarrow CO_2 + H \quad \text{(R.6)}$$

Enhancement of char gasification by steam increases carbon-free sites on the char surface, which can reduce NO by the heterogeneous reaction R.7 [31]. Competitively, char also reacts with H radicals releasing HCN according to reaction R.8 [32]. The fate of HCN in the gas-phase will produce either NO by oxidation or N_2 by reduction mechanisms.

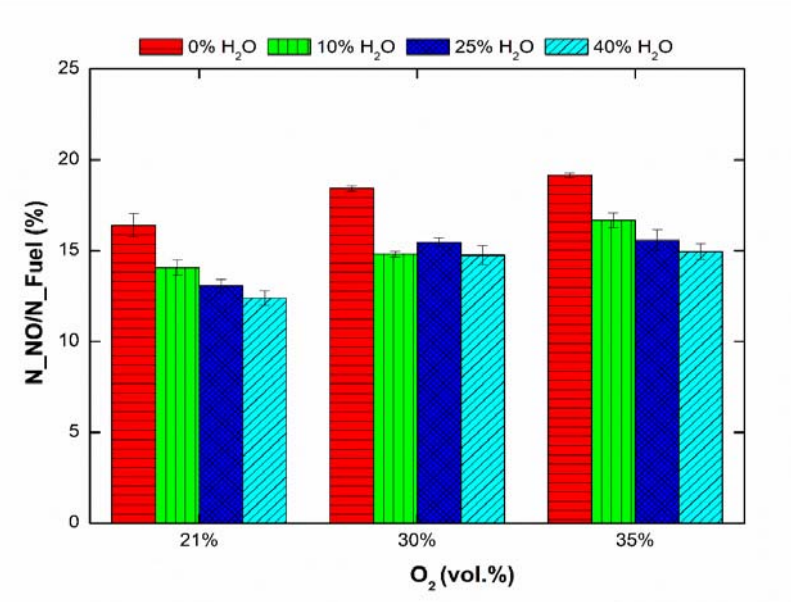
$$C_s + NO \rightarrow \frac{1}{2} N_2 + CO \quad \text{(R.7)}$$

$$C(N)_s + H \rightarrow HCN \quad \text{(R.8)}$$

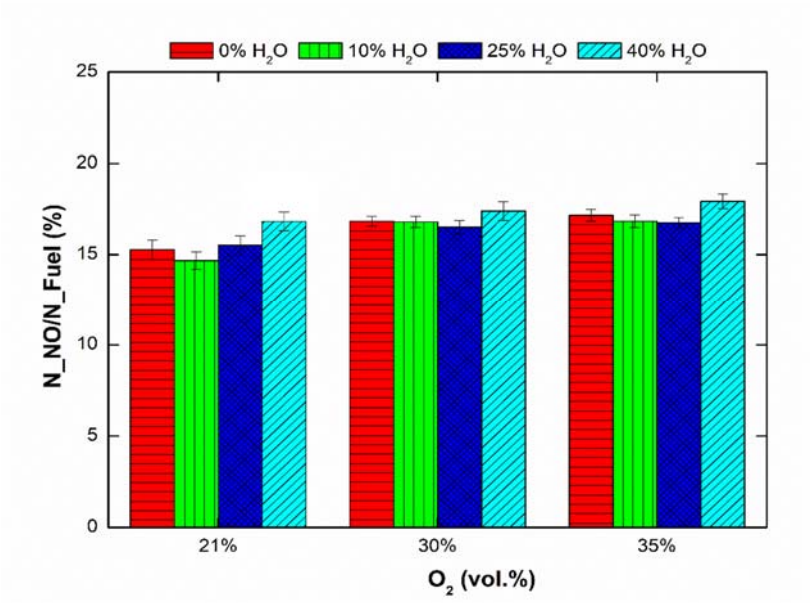
In order to ascertain the role of steam addition on the NO formation for the two coals selected in this work, fuel-N to NO mass conversion rates were calculated for all the $O_2/CO_2/H_2O$ tests previously presented in Tables 4 and 5: three oxygen concentrations (21, 30 and 35%), varying steam fraction in the range 0–40% and oxygen excess λ = 1.25. The mean results and standard deviations are depicted in Figures 5 and 6, for SA and CB coals respectively. The maximum standard deviations of the recorded NO measurements during the steady-state operation were comprised in the range 0.5–3.5% of the mean values.

As concerns the CB sub-bituminous coal, see Figure 6, the effect of the CO_2 replacement by H_2O is small if compared to the SA bituminous coal (Figure 5). For low rank solid fuels, HCN release is attenuated in comparison to NH_3 one, especially under wet conditions [33]. Then, the extent of the HCN–H_2O mechanisms is more limited. No detailed measurements are available in the reactor to discern the role of HCN and NH_3, but the lower variations of the conversions for the CB coal tests are consistent with that limited extent. These limited reductions in the conversion levels are observed in Figure 6 when 10% H_2O is added, with a maximum decrease of 3.5% for the 21% O_2 case. This is reversed in the 40% H_2O tests, even overpassing the conversion rates obtained for the dry O_2/CO_2 atmospheres. Moreover, the effect of steam is smoothed as the atmosphere is enriched in O_2. The trend observed in Figure 6, where an optimum H_2O value is leading to the lower fuel-N to NO conversion rate, may be explained by the opposite, overlapped mechanisms in the gas-phase. Initially, for low steam rates, the reductions given by the

387 set of reactions R.1 to R.4 seem to lead to a diminution in comparison to the dry cases,
388 but for higher steam concentrations the enhancement of the oxidation rates prevails.
389



390
391 **Figure 5.-** Fuel-N to NO conversions obtained under different O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres
392 (steam is added as CO_2 replacement), for the SA bituminous coal.



393

394 **Figure 6.-** Fuel-N to NO conversions obtained under different O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres
395 (steam is added as CO_2 replacement), for the CB sub-bituminous coal.

The results in Figure 5, related to the SA bituminous coal, follow a very different trend to those shown in Figure 6, what points to the effect of the coal rank. Significant decreases in the conversion rates to NO are obtained, for all the O_2 levels, when 10% H_2O replaces CO_2. Further decrements are obtained when 40% H_2O is added to the atmospheres, however not proportional to the increase of the steam percentage. This behaviour is related to the composition of the SA coal, whose fixed carbon/volatiles ratio is 1.9 times higher than the sub-bituminous one (in dry and ash free basis). The observed reduction in the conversions to NO may be mostly related to the intensified gasification caused by H_2O. Heterogeneous reaction R.7 with fixed carbon and homogeneous reaction R.5 with CO (catalysed by char) are influential mechanisms. HCN–H_2O interaction also contribute to the reduction, as well as other intermediate species (CN, NCO, HNCO) reacting with radicals H and OH [26]. The increase in steam concentrations from 10% to 40%, thus rising O_2 diffusivity, does not overturn the decreasing trend for conversion to NO and just attenuates it.

To better see the different effects observed between the fired coals, Figure 7 compares the accumulative variation (%) of fuel-N to NO mass conversion rates when H_2O is replacing CO_2 in the atmosphere. A third coal is also included for comparison purposes: high-rank anthracite, which was tested in the same facility and under the same conditions. Details about those tests and specific results can be found in reference [8]. As seen in the Figure 7, the higher the coal rank, the larger the influence of steam in reducing NO formation rates: maximum reductions of 45% in the case of the anthracite, and 24% in the case of the SA bituminous coal. For the CB sub-bituminous coal, the reduction is very limited and only detected for the lower steam concentrations, and an increase of 2–9% in NO is obtained for the 40% H_2O tests.

High rank coals would demand an increase of oxygen excesses to complete conversion, and it is well-known that this would lead to an increase on NO formation rates from the nitrogen bound in the fuel. For this reason, additional tests were carried out increasing oxygen excess (over stoichiometry) from λ = 1.25 to λ = 1.35 and λ = 1.45 –flow rates defined to keep constant the residence time in the reactor, same as explained in section 2.3.2–. Figure 8 summarizes the results obtained, showing the accumulative variation (%) of fuel-N to NO conversion rates as a function of the oxygen excess. The extent of the increases found for anthracite and bituminous coal is, in all cases, lower that the decreases respectively found for the 40% H_2O atmospheres in Figure 7.

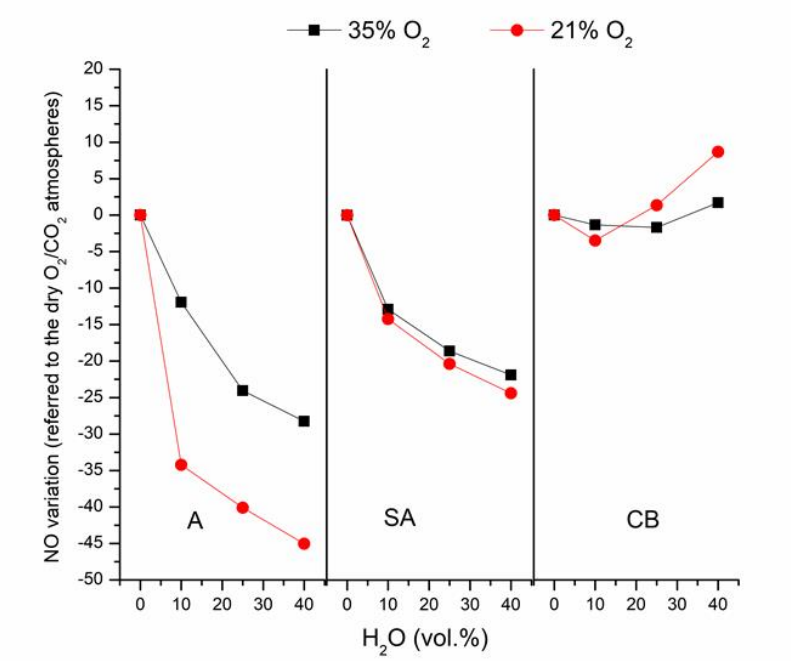


Figure 7.- Comparison of the accumulative variation (%) in fuel-N to NO mass conversion for different H_2O percentages, for anthracite (A), bituminous coal (SA) and sub-bituminous coal (CB). Anthracite results can be consulted in Ref. [8].

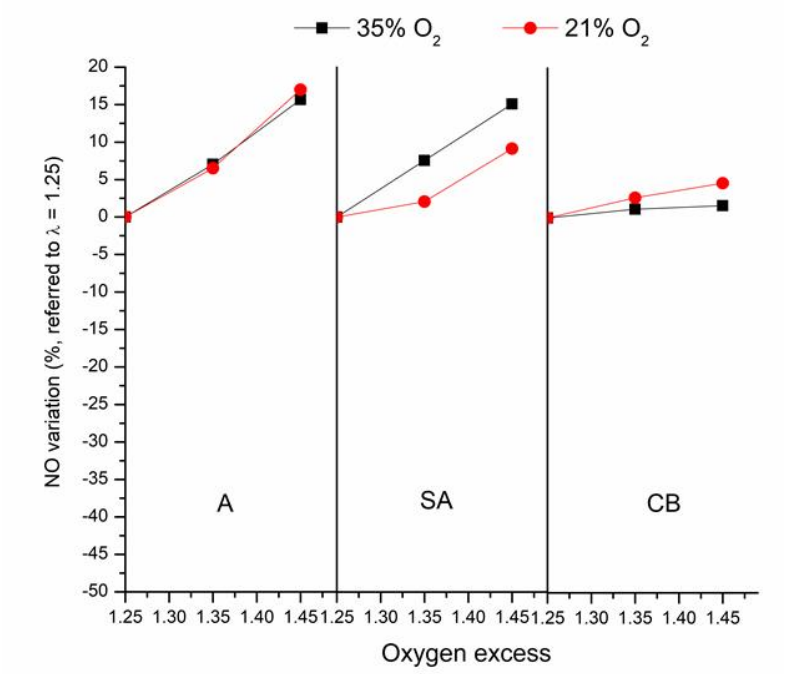


Figure 8.- Comparison of the accumulative variation (%) in fuel-N to NO mass conversion for different oxygen excesses, for anthracite (A), bituminous coal (SA) and sub-bituminous coal (CB). Anthracite results can be consulted in Ref. [8].

To conclude, it is worth mentioning that CO_2 replacement by H_2O is leading to a twofold benefit for the SA bituminous coal, in comparison to the dry situations: an increase of burnout degrees along with a decrease of fuel-N to NO mass conversion rates, for every O_2 concentration. This joint outcome is represented in Figure 9, merging the results previously shown in Figures 3 and 5. A similar representation is given in Figure 10 for the CB sub-bituminous coal: in this case, the CO_2 replacement by H_2O increases the NO formation rates for the 40% H_2O atmospheres in comparison to the dry ones.

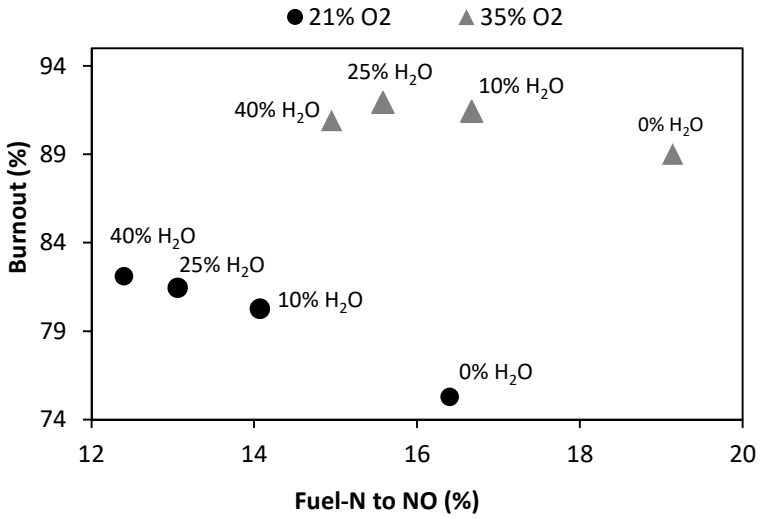


Figure 9.- Fuel-N to NO conversions vs. burnout degrees, for the SA bituminous coal.

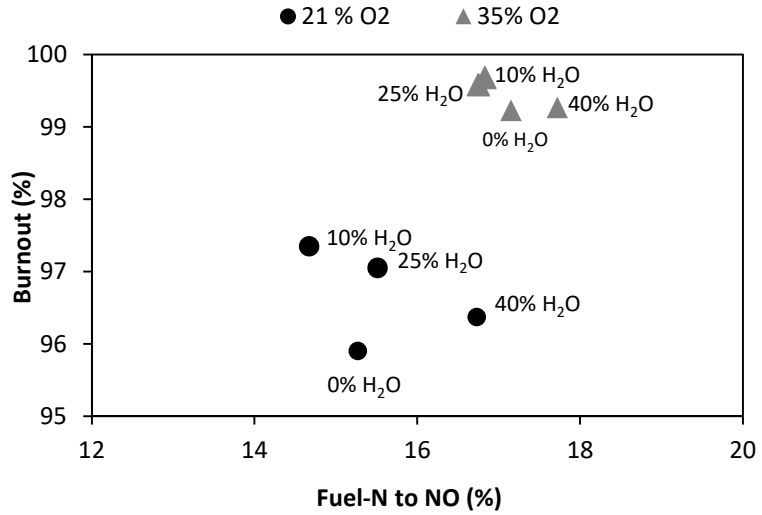


Figure 10.- Fuel-N to NO conversions vs. burnout degrees, for the CB sub-bituminous coal.

Conclusions

The combustion characteristics of two different coals have been experimentally determined in an entrained flow reactor, for a set of O_2/N_2, O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres. Besides the influence of the coal rank, the effect of replacing CO_2 by H_2O on the ignition, burnout and NO formation has been sought. Steam concentration was increased up to 40%, while oxygen concentration up to 35%. The following outcomes have been obtained:

- Regardless the coal type and O_2 concentration, it is observed that: 1) addition of steam in low rates (10%) decreases ignition temperature, 2) the trend is reversed when steam concentration is further incremented to 25% and 40%. The differences in ignition temperatures are minimally higher for the sub-bituminous coal. Replacement of 40% CO_2 by H_2O yields a small variation of the ignition temperature in comparison to the dry atmospheres.

- The burnout degree of the bituminous coal is increased when CO_2 is replaced by H_2O in the firing atmosphere, but the largest conversions are not detected for the maximum steam concentrations. The extent of the steam influence on the burnout degree is attenuated when the atmosphere is enriched in O_2. As concerns the sub-bituminous coal, its reactivity produces very high conversion rates for all the atmospheres tested and the effect of CO_2 replacement by H_2O is similar but much more narrowed.

- The influence of steam on NO formation is very different depending on the coal rank. A significant decrease in fuel-N to NO conversion rate is observed for the bituminous coal when replacing 40% CO_2, but an increase is observed for the sub-bituminous one. Their different volatiles/char ratio determines the extent of homogeneous and heterogeneous mechanisms in which steam is involved. The effect of oxygen excess on NO formation has been proved to be less influential than the effect of the steam concentration.

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