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Ignition and NO emissions of coal and biomass blends under different oxy-fuel atmospheres

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Abstract

The effect of co-firing coal and biomass on the ignition behaviour and NO emissions was evaluated under both air and O₂/CO₂ (21-35% O₂) atmospheres. The results showed a worsening of the ignition properties in the 21%O₂/79%CO₂ atmosphere in comparison with air. Furthermore, in order to obtain similar or better ignition properties, the oxygen concentration in the O₂/CO₂ mixture must be 30% or higher. A decrease of the ignition temperature was observed with the addition of biomass in air and oxy-fuel conditions. The results also indicate that NO emissions in the 21%O₂/79%CO₂ atmosphere were lower than under air-firing conditions, although they increased in the 30%O₂/70%CO₂ and 35%O₂/65%CO₂ atmospheres. The addition of biomass resulted in lower NO emissions in all cases.

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Keywords: oxy-combustion, coal, biomass, ignition behaviour, NO emissions, entrained flow reactor.

1. Introduction

The use of coal in power plants generates a large amount of CO₂ which is the chief contributor of global climate change. A diverse power portfolio including Carbon Capture and Storage (CCS) technologies and renewable energies is needed to reduce atmospheric CO₂ to below 1990 levels [1]. During oxy-coal combustion, coal is burnt in a mixture of oxygen and recycled flue gas (mainly CO₂ and H₂O), to yield a rich CO₂ stream, which after purification and compression is ready for sequestration [2]. Biomass is a renewable fuel which can be used to reduce CO₂ emissions, as it is considered carbon neutral since biomass consumes CO₂ as it grows. The combination of oxy-coal combustion with biomass co-firing can afford a method of disposal of CO₂. Furthermore, it can also be a method for increasing CO₂ capture efficiency that could reduce cost and efficiency penalties [3].

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The ignition of solid fuel particles is an important preliminary step in the overall combustion process due to its influence on flame stability and pollutant formation. The ignition temperature is not an inherent property of the fuels, as it is dependent on the operating conditions (temperature, heating rate, surrounding atmosphere, etc), and blending fuels of different nature may also affect the ignition properties [4]. In oxy-fuel combustion of pulverised coal, poor ignition quality has been often noted during pilot-scale trials when operating with substantial gas recirculation [5]. During oxy-fuel combustion a significant reduction of NO can be achieved in relation to air-firing, partly due to the suppression of thermal NO formation and, also, because recycled NO is reduced to N₂ after being introduced into the flame zone [4]. Co-firing coal and biomass in air-firing conditions was found to enhance ignition properties and NO emissions reduction [6]. The objective of this work has been to evaluate the effect of biomass blending with coals of different rank on their ignition behavior and NO formation under oxy-firing conditions.

2. Experimental

2.1. Materials

Two coals of different rank were used in this work: a semianthracite from Spain (HVN) and a South African high-volatile bituminous coal (SAB). A biomass, olive residue (OW), was also employed. This biomass is the wet solid residue that remains after the process of pressing and extraction of the olive oil. The coal and biomass were ground and sieved to obtain a particle size fraction of 75-150 µm. The proximate and ultimate analyses together with the high heating values of the samples are given in Table 1.

Table 1. Proximate and ultimate analyses and high heating values of the fuel samples

Sample	Proximate analysis (wt.%, db)			Ultimate analysis (wt.%, daf)					High heating value (MJ kg ⁻¹ , db)
	Ash	V.M.	F.C.	C	H	N	S	O	
HVN	10.7	9.2	80.1	91.7	3.5	1.9	1.6	1.3	31.8
SAB	15.0	29.9	55.1	81.5	5.0	2.1	0.9	10.5	27.8
OW	7.6	71.9	20.5	54.3	6.6	1.9	0.2	37.0	19.9

2.2. Experimental device

An entrained flow reactor (EFR), which has been described in detail elsewhere [7], was employed to carry out the ignition and combustion experiments. Briefly, the reactor has a reaction zone 140 cm length and an internal diameter of 40 mm; the reactor is electrically heated and is capable of reaching a maximum temperature of 1100 °C. The gases are preheated to the oven temperature before being introduced into the reactor through flow straighteners. Fuel particles were introduced through a cooled injector before entering the EFR reaction zone. Reaction products were quenched by aspiration into a stream of nitrogen using a water-cooled probe. This probe was inserted into the reaction chamber from below. Particles were removed by means of a cyclone and a filter. The concentration of the exhaust gases was measured using a battery of analysers (O₂, CO, CO₂, SO₂ and NO).

Two types of experiments were carried out: ignition and combustion tests. For both types of experiments, air (21%O₂/79%N₂) was taken as a reference and three binary mixtures of O₂/CO₂ were compared (21%O₂/79%CO₂, 30%O₂/70%CO₂ and 35%O₂/65%CO₂). During the ignition experiments, the reactor was heated at 15 °C min⁻¹ from 400 to 800 °C, the oxygen excess was set at a value of 25%. The criterion for determining the ignition temperature was based on the first derivative curves of the gases composition. The ignition temperature was taken as the temperature where the first derivative curve, normalised with respect to the maximum derivative value, reached a value of 10 % [7, 8]. The combustion experiments were carried out at a reaction temperature of 1000 °C employing a particle residence time of 2.5 s and different oxygen excess percentages.

3. Ignition results

3.1. Effect of the oxy-fuel atmosphere

Ignition tests were conducted in both air and oxy-fuel environments. As an example, in Figure 1 it can be seen the variation in the concentration of different gases (CO, CO₂, NO and O₂) during the ignition tests of coal SAB in air and oxy-firing conditions.

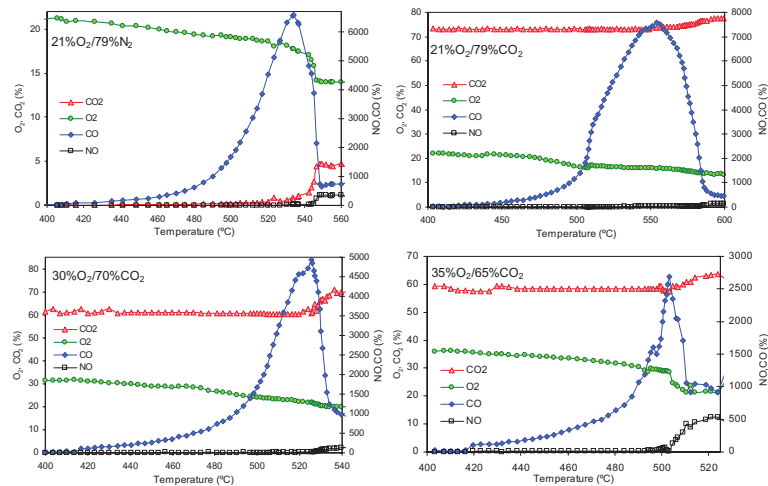


Fig. 1. Derivative curves of the CO₂ concentration during SAB ignition

Faúndez et al. [8] stated that ignition is characterised by a rapid decrease in CO production, a significant O₂ consumption, and an increase in the production of CO₂ and NO. From Figure 1 it can be observed that, for coal SAB, this happened around 530-550 °C in the case of ignition in air, and in the oxy-fuel atmospheres ranged between 500-570 °C depending on the oxygen content. The exact values were derived from their CO₂ and NO derivative curves. As an example in Figure 2, the CO₂ derivative curves of coals HVN and SAB, under air and oxy-firing conditions, are shown.

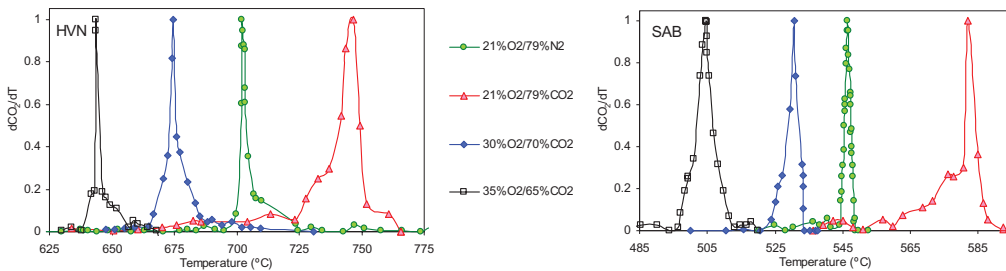


Fig. 2. Derivative curves of the CO₂ concentration during HVN and SAB ignition

Table 2 shows the values of the ignition temperatures for HVN and SAB obtained from their corresponding CO₂ and NO derivative curves.

Table 2. Ignition temperatures (in °C) for coals HVN, SAB and blends HVN-OW and SAB-OW under air and oxy-fuel conditions

Blends	21%O ₂ /79%N ₂	21%O ₂ /79%CO ₂	30%O ₂ /70%CO ₂	35%O ₂ /65%CO ₂
HVN	700	723	669	642
90HVN-10OW	636	662	615	567
80HVN-20OW	574	612	551	503
SAB	543	565	524	498
90SAB-10OW	510	532	491	455
80SAB-20OW	461	478	444	425

As can be observed in Table 2 higher ignition temperatures were required when N₂ (21%O₂/79%N₂) was replaced by CO₂ (21%O₂/79%CO₂), i.e., an ignition delay took place. Also, it can be observed that for oxygen concentrations up to 30%, the ignition temperature was lower than that obtained in air. Other authors [9-14] have also performed ignition experiments for different types of fuel in air and oxy-firing conditions using a wide range of furnaces; their principal findings are summarised in Table 3.

In all cases an ignition delay took place when replacing N₂ by CO₂ for the same oxygen concentration. Khatami et al. [9, 10] have attributed the longer ignition delay partly to the effect of the volumetric heat capacity of the gas mixtures. The temperature rise during ignition is inversely proportional to the heat capacity of the surrounding gases, and since CO₂ capacity is higher than N₂, a reduction in gas temperature will be obtained. However, the heat capacity and the temperature of the surrounding gases are not the only factors that affect ignition; the oxygen concentration, the heating and devolatilisation rates also have a great influence [4]. Shaddix et al. [13] observed that the ignition of the volatiles may be affected since CO₂ decreases the rate of devolatilisation due to the lower mass diffusivity of the volatiles in the CO₂ mixture. Other authors [9-11] have observed that when increasing the oxygen concentration, the ignition delay in O₂/CO₂ atmospheres, in comparison with air, became smaller due to the increase of the oxygen mass flow to the surface of the particle. Similar ignition properties as in air-firing conditions could be achieved in oxy-fuel environments with oxygen concentrations in the range of 27-30%.

Table 3. Ignition of coal and biomass blends in air and different oxy-firing conditions

Authors	Furnace used	Experimental findings
Khatami [9, 10]	Drop tube furnace	Similar ignition temperatures in air and in 27%O ₂ /73%CO ₂ (lignite and bituminous coals) Ignition delay in O ₂ /CO ₂ atmospheres in comparison with O ₂ /N ₂ atmospheres for different oxygen concentrations (20-100% O ₂) for lignite, bituminous and sub-bituminous coals
Arias [11]	Entrained flow reactor	Similar ignition temperatures in air and in 30%O ₂ /70%CO ₂ for a high-volatile bituminous coal and a semianthracite, and for blends of the high-volatile bituminous with biomass
Qiao [12]	Wire mesh	Higher ignition temperatures when replacing N ₂ by CO ₂ for 21% oxygen content. Decrease on ignition temperatures in O ₂ /CO ₂ atmospheres with higher oxygen content. Similar ignition temperatures in 60%O ₂ /40%CO ₂ as in 100% O ₂ . Two coals were employed, a brown coal and a bituminous coal
Shaddix [13]	Entrained flow reactor	Ignition delay in O ₂ /CO ₂ atmospheres in comparison with O ₂ /N ₂ atmospheres for different oxygen concentrations (11-36% O ₂) for a bituminous coal
Liu [14]	Entrained flow reactor	Ignition delay when replacing N ₂ by CO ₂ for 20% oxygen content at different furnace temperatures. Two bituminous coals were employed
This work	Entrained flow reactor	Similar ignition temperatures in air and in 30%O ₂ /70%CO ₂ for a high-volatile bituminous coal and a semianthracite, and for the blends of the two coals with biomass

3.2. Effect of the addition of biomass

The effect of blending coal and biomass on the ignition behaviour was studied under air and oxy-firing conditions. Blends of the two coals considered, the semianthracite HVN and the high-volatile bituminous coal SAB, with 10 and 20 wt% of the olive waste OW were used. The ignition temperatures are shown in Table 2.

It can be observed that the addition of the olive residue, OW, caused a significant reduction in the ignition temperature of both coals in all the atmospheres studied. This decrease was proportional to the amount of biomass in the blends and it was more pronounced for the blends HVN-OW. These results suggest that the effect of addition of biomass is more significant in high rank coals. When two fuels are fired as a blend, the ignition properties may be different to those exhibited when they are ignited individually [11]. Faúndez et al. [8] have observed that, when blending fuels with different volatile content, the ignition of the higher volatile component of the blend enhances the ignition of the lower component. However, when both fuels have similar volatile content, they compete for the oxygen available. As a result, the enhancement of the ignition properties would be lower when blending low rank coal and biomass, than when blending high rank coal and biomass.

4. NO emissions

Coals HVN and SAB and their blends with biomass were burnt at different levels of excess oxygen for each atmosphere studied. The fuel equivalence ratio, defined as the ratio between the fuel mass flow rate and the stoichiometric value, was used to determine the excess oxygen during combustion. As an example, the NO concentrations (in ppm) of blends SAB-OW under the different atmospheres studied are shown in Fig 3. A decrease in NO concentration was observed as the fuel equivalence ratio increased,

since the lower amount of oxygen available would reduce fuel-N conversion to NO. Also, under fuel-rich condition, the presence of large amounts of hydrocarbons from coal pyrolysis, unburnt char and CO favoured the reduction of NO to HCN, NH₃ and molecular nitrogen N₂ [14].

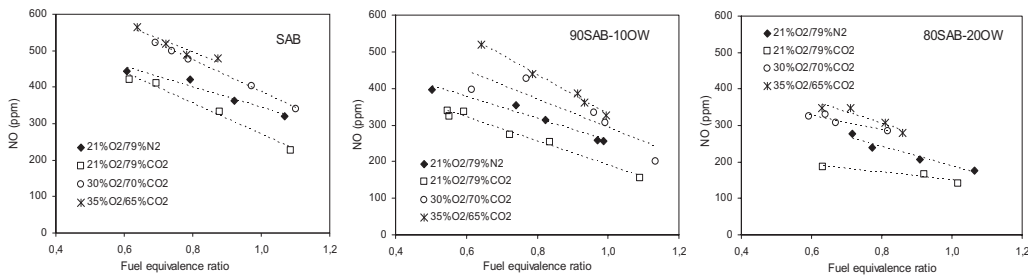


Fig 3. NO concentrations (in ppm) of blends SAB-OW at different fuel equivalence ratio in air and oxy-fuel conditions

In order to facilitate a comparison of the behaviour of these coals and their blends with biomass, under air and oxy-firing conditions, the NO values were interpolated at a fuel equivalence ratio of 0.8 (which corresponds to a 25% oxygen excess) using the curves shown in Fig. 3. These NO emissions (in ppm) for coals HVN and SAB and their blends with olive residue, OW, are shown in Table 4.

Table 4. NO emissions (in ppm) for blends HVN-OW and SAB-OW under air and oxy-fuel conditions

Blends	21%O ₂ /79%N ₂	21%O ₂ /79%CO ₂	30%O ₂ /70%CO ₂	35%O ₂ /65%CO ₂
HVN	384	360	578	613
90HVN-10OW	392	346	547	585
80HVN-20OW	395	339	548	578
SAB	400	359	498	527
90SAB-10OW	333	290	418	422
80SAB-20OW	270	181	270	354

For both blends, HVN-OW and SAB-OW, the NO concentration obtained under the 21%O₂/79%CO₂ atmosphere was lower than that achieved in air combustion. The lower NO concentrations in the oxy-fuel combustion atmospheres than in air are partly explained by the suppression of thermal NO formation. However, at the temperature used in this work (1000 °C), the thermal NO formation could make only a minor contribution to the formation of NO. It would appear, therefore, that the lower NO concentration obtained in the 21%O₂/79%CO₂ atmosphere was probably due to the greater NO reduction to N₂ resulting from the higher CO concentrations in oxy-firing systems [15]. The NO concentrations measured in this work showed a marked increase as the oxygen concentration in the O₂/CO₂ mixture increased to a value of 30 or 35%. This is due to an enhancement of the combustion rate and therefore of fuel-N to NO conversion [16]. Other authors [7, 17] have reported the NO concentrations in terms of NO per unit of energy supplied or NO per unit of fuel burnt, and they have found small differences in NO emissions under oxy-firing conditions for different O₂ concentrations.

For the SAB coal the NO concentration in air and oxy-firing conditions decreased after the addition of biomass, this decrease became greater as the biomass concentration increased. For the HVN semianthracite the same tendency was observed but the decrease in NO concentration values was smaller. Since HVN and the biomass used in the present work have similar nitrogen contents, the lower NO emissions during co-firing experiments cannot be explained by the dilution of N in the mixed fuel. However, in the case of coal SAB the dilution of N might have a greater effect since the nitrogen content of OW is slightly lower than that of SAB. Besides these differences in nitrogen content, most of the biomass is released as volatiles (about 75% at temperatures above 800 °C) and the fuel-N is predominantly liberated as NH₃, which may be oxidised to NO but also act as a reducing agent in further reactions with NO to form N₂ [18]. On the other hand, coals released less volatiles and the fuel-N is mainly evolved as HCN, which has a lower potential to reduce NO to N₂.

5. Conclusions

The goal of this study was to evaluate the effect of blending biomass with coals of different rank on the ignition characteristics and NO emissions in air and oxy-firing conditions. The most important conclusions of this work are as follows:

- (a) A significant ignition delay was observed when N₂ was replaced by CO₂ for an oxygen concentration of 21% for both individual coals and coal and biomass blends, due to differences in the specific molar heats of N₂ and CO₂. However, when the oxygen concentration was increased to 30% in the O₂/CO₂ mixture, the ignition properties were similar to those obtained in air-firing conditions; this is due to an increase in the mass flow of oxygen to the surface of the fuel particles.
- (b) Co-firing coal and biomass resulted in a decrease of the ignition temperature in both air and oxy-firing conditions. However, this improvement was more significant for the case of the semianthracite due to its lower volatiles content in comparison with the biomass. The ignition properties of the high-volatile bituminous coal seemed to be less affected by the addition of biomass.
- (c) NO emissions were lower in the 21%O₂/79%CO₂ atmosphere in comparison with those obtained in air-firing conditions due to the additional reduction of NO to N₂ by reaction with CO. However, when increasing the oxygen concentration in the oxy-firing atmospheres, the NO emissions also increase due to the higher fuel-N conversion to NO.
- (d) The addition of biomass reduced significantly the NO emissions for both the semianthracite and the high-volatile bituminous coal in air and oxy-firing conditions. This decrease was proportional to the concentration of biomass. However, the reduction of NO emissions was less noticeable in the case of the semianthracite.

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