

GHGT-12

## Oxy-combustion studies into the co –firing of coal and biomass blends: effects on heat transfer, gas and ash compositions

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### Abstract

Oxy-combustion with coal and biomass co-firing is a technology that could revolutionize fossil fuel power generation. It can significantly reduce harmful greenhouse gas emissions and permit the continued use of plentiful coal supplies and thereby secure our future energy needs without the severe environmental impacts expected if fossil fuels are used without CCS.

The work presented here was conducted by means of experimental tests co-firing coal and biomass under oxy-firing conditions at the retrofitted 100kW<sub>th</sub> oxy-combustor facility at Cranfield University. A parametric study was performed with respect to the effect of recycled ratio and fuel variability on gas composition (including SO<sub>3</sub>), temperatures, heat flux, burn-out and ash deposition. Furthermore, the possible compensation in heat transfer resulting from the higher heat capacity and emissivity of the gases in the oxy-combustion process as compared to the air-firing case was explored. This was done by the use of blends of coal and biomass, and we concluded that this compensation is unlikely to be significant due to the marked differences between heat fluxes reached under air and oxy-firing conditions.

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### 1. Background

The rapid increase in emissions of greenhouse gasses has led to new policies being developed to mitigate this problem. Amongst the most important initiatives, are the Kyoto Protocol (1998) and the Intergovernmental Panel on Climate Change (IPCC, 2007).

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As a consequence of new regulations, the use of renewable sources of energy such as hydro power, solar, wind or biomass are being promoted by the governments of developed countries. However, the use of fossil fuel power plants is still necessary to address rising energy demands. The second result of the new policies is changes to fossil fuel-fired power generation technology to satisfy the current regulations regarding reduction of greenhouse gas emissions. As a result, several carbon capture and storage (CCS) technologies are being developed.

Oxy-combustion is one option being considered for the capture of CO<sub>2</sub> from fossil fuel-fired power generation. The generation of a gas stream with a high percentage of CO<sub>2</sub> in the combustor, permitting the use of much more compact flue gas conditioning equipment downstream of the furnace is a major advantage that this technology has over other carbon capture technologies (pre-combustion and post-combustion). However, the main disadvantage of the use of the oxy-fuel combustion technology remains the elevated cost associated with producing high purity O<sub>2</sub> by cryogenic distillation.

Oxy-combustion can be combined with the use of biomass as a fuel to allow a near-zero emission process to produce electricity. The use of biomass to generate power, by itself or by when blended with coal, strongly influences the combustion process, due to its different elemental and mineral composition. A crucial aspect related to the use of biomass, as fuel, is its variability, especially with respect to its volatile fraction, particle size and nitrogen content[1]. The volatile fraction of a fuel is an aspect of this process that has direct effects on its ignition temperature. Generally, biomass has higher volatile content than coal, which makes it easier to use for start-up, since it has a lower ignition temperature. The co-combustion of biomass and coal has also been suggested as an alternative method to vary the recycle flue gas to control heat transfer under oxy-firing conditions[2].

### *1.1. Heat flux characterization*

There are several factors, inherent to the oxy-combustion process, which contribute to the heat transfer generated under these conditions being different from that of the air-firing case. The main causes are: the different composition of the environment inside the furnace, and the effect of the recycle on the flame.

It is well established that the different chemical composition (higher presence of CO<sub>2</sub> and H<sub>2</sub>O, and lower presence of N<sub>2</sub>) inside the oxy-combustor, ensures that this gas has different characteristics: thus there is an increase in the emissivity which will have a direct effect on the heat transfer ([3], [4]). Nonetheless, it has been noted [3] that one must consider the importance of the large contribution of particle radiation in the flame because they emit over a continuous spectrum and one main conclusion of their work is that when using pulverized fuels, the dominant effect of the particles radiation contribution to heat transfer ensures that the difference in specific emissivity that occurs, for the change in the environment from air to oxy-firing conditions, do not provide a decisive effect on the process. In the case of the recycle rate, the adjustment of this parameter has been suggested as a way of controlling the temperature inside the oxy-combustor and therefore as a means to regulate the distribution of heat[3]. Studies on this subject have concluded that the radiation flux peak decreases and slightly moves downstream in the furnace when the recycled flue gas increases[5]. The decrease in this peak is mainly due to the higher mass flow that exists when the percentage of recycled flue gas is increased, which causes a reduction in the flame temperature. The shift of the peak is also related to the higher mass flow, which has a direct effect on the level of oxygen enrichment, which is lower. As a consequence, the flame generated is longer and “lazier”, achieving the maximum effect for the radiative heat flux delayed, in comparison to the cases with lower recycle. According to these Smart et al. [5], similar radiative heat flux to air-firing case can be achieved, when the recycle ratio is set to 72%. Conversely to the situation with the radiative heat transfer, there is an increase in the peak of convection flux when the percentage of recycle flue gas increases. This is a consequence of the higher mass flow and temperature of the flue gas in the convective zone.

### *1.2. SO<sub>3</sub> formation and measurement*

In the oxy-combustion process, it is necessary to recycle part of the flue gas to control the temperature inside the combustor. A direct consequence of this parameter is the accumulation of the chemical species in the recycled gases, which leads to the accumulation of undesirable corrosive species in the boiler: sulfur oxides (SO<sub>2</sub> and SO<sub>3</sub>) which can increase up to 3-4 times in processes using wet recycles[6].

The higher presence of acid species in the flue gas generated in oxy-combustion demands that special attention must be paid to the generation of  $\text{SO}_3$  inside the combustor and the evolution of this species downstream of the furnace ([7], [8], [9], [10]).

The difficulty associated with the measurement of  $\text{SO}_3$  during operation of a combustor has been identified by some authors as a major issue ([11], [12]). The reasons for this are explained as follows:

- Highly reactive nature of the  $\text{SO}_3$  (leading to high probability of negative bias as consequence of the loss of  $\text{SO}_3$  due to reaction with  $\text{H}_2\text{O}$  to generate  $\text{H}_2\text{SO}_4$ , by surface reactions in the sampling line, or reactions in the filter cake with the particles)
- The normal low  $\text{SO}_3$  concentrations in the flue gas
- High  $\text{SO}_2$  concentrations causing interferences.

### 1.3. Fly ash and ash deposits

One important characteristic of the ash generated under oxy-combustion conditions is that it is likely that corrosion problems will appear in the boiler when coals with medium and high content of S, Cl, and F are used, because of the flue gas recycle. This leads to the accumulation of certain undesirable species inside the combustor. This combined with a greater sulfur oxides retention in fly ash when burning blends of coal and biomass due to higher alkali content in biomass ([13], [14], [15], [16]) can be expected to produce more corrosion damage under oxy-firing conditions blends in comparison to air-firing combustion.

The propensity to form ash deposits, as well as slagging and fouling issues related to the use of biomass in thermal applications have been addressed by several authors ([14], [16]). It has been pointed out that the influence of  $\text{Na}_2\text{SO}_4$  in the formation of an adhesive layer on the deposits. However, other authors [17] have highlighted the lack of literature on the behavior of ash, mechanisms of slag layer formation and its interaction with char particles, under oxy-combustion conditions. In consequence, it is clear that more research is needed in this field.

## 2. Methodology

The experimental tests under air and oxy-firing conditions were performed at the pulverized fuel (PF) down-fired combustor with a  $100\text{kW}_{\text{th}}$  thermal capacity located at Cranfield University (see Fig. 1). This combustor is attached to a  $50\text{kW}_{\text{th}}$  fluidized bed (FB), which is located prior to the PF. For the air-firing experiments, the FB module was used as a preheater for the air, with the pulverized fuel fed directly to the burner associated to the PF combustor. However, for the tests performed under oxy-firing conditions the PF combustor was isolated from the FB combustor by a gate valve located in between. In any case, the fuel fed to the burner corresponds to a heat input of  $100\text{kW}_{\text{th}}$ .

The pulverized fuel is fed to the oxy-combustor at a constant rate using a fuel feeder provided by a metering screw, a vibratory tray and a Venturi eductor. Additionally, the feeder has three purge points located: at the main storage hopper, at the feeding hopper, and at the end of the vibratory tray feeder.  $\text{CO}_2$  is injected through these purge points to keep a positive pressure inside the pulverized fuel feeding system so as to avoid air ingress. Once the pulverized fuel reaches the Venturi eductor, it is fluidized and conveyed to the burner by a stream of pure  $\text{CO}_2$  gas coming from  $\text{CO}_2$  cylinders. Prior to this stream being fed to the burner, the primary  $\text{O}_2$ , coming from  $\text{O}_2$  cylinders, is injected into the stream, when using this option for a particular test.

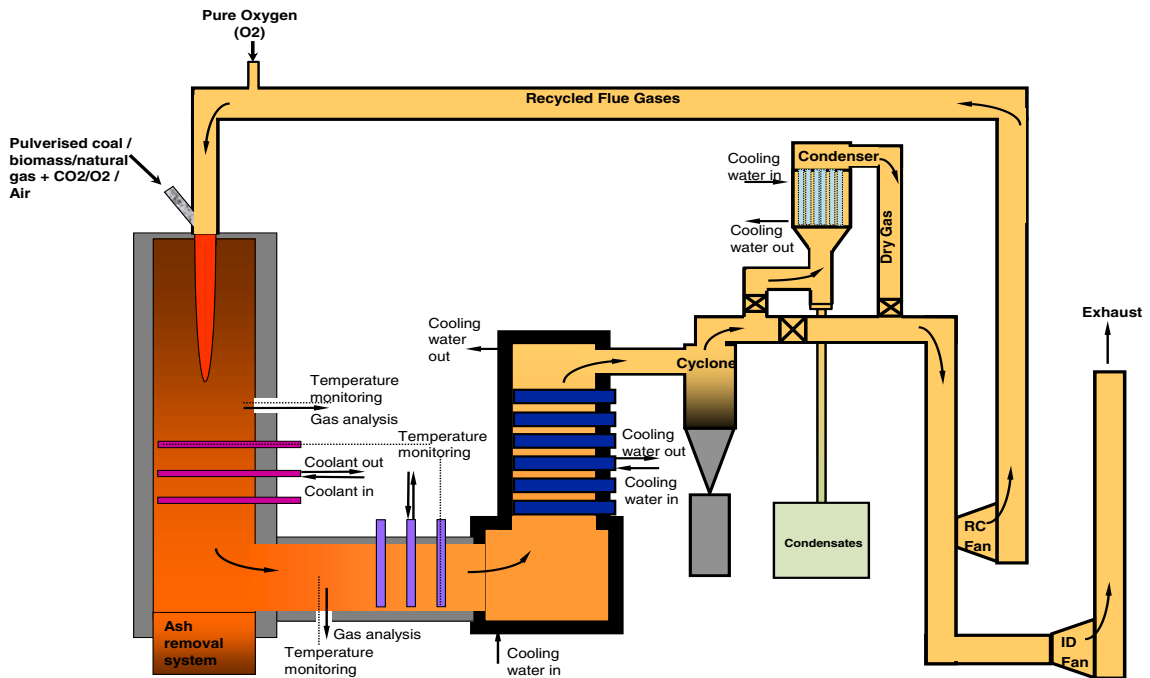


Fig. 1. Schematic diagram of 100kW<sub>th</sub> PF oxy-combustor at Cranfield University.

The combustor is equipped with a down-fired burner, provided with a pilot flame port and a flame detector. The pulverized fuel is combusted in the vertical zone of the combustor (3.7 m height). The combustor has a square cross-section with sides of 650 mm and thermal isolation with thickness 175 mm. The vertical zone has four view ports and ports where sensors are used to measure wall temperatures. The data acquisition system is a Pico Logger Unit-TC-08. More thermocouples are installed along the rig monitoring: inlet and outlet temperature of the water used in the refrigeration system, at the heat exchanger section, temperature after the cyclone, and six more thermocouples to measure the temperature along the recirculation line. These sensors are sampled using the data logger, with 24 sampling ports distributed along the vertical and horizontal sections of the chamber. Three of these ports, located at the bottom part of the vertical section, are used by the deposition probes. To collect the deposits, it was necessary to allow the chamber to cool down for 18 to 24 h, then the ash deposited on the probes was sampled and analyzed using ESEM/EDX and XRD. An on-line high-resolution multi-component Fourier Transform Infra-red (FTIR) was used to analyze CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO, NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, SO<sub>2</sub>, HCl, HF and CH<sub>4</sub>. The rig is provided with two sampling points to allow for the FTIR analysis: one located at the vertical section of the chamber (one of the aforementioned ports), and another at the exit of the condenser.

The exhaust gas goes through two water-cooled heat exchangers, in the horizontal and the vertical section respectively, before exiting the oxy-combustor. After leaving the chamber, the gas enters a cyclone where the suspended particles are removed. From here, depending on the type of recycle flue gas used for the experiment, this stream passes by the condenser (dry RFG) or by-passes it (wet RFG). Then, part of the gas is recirculated to the combustion chamber, through RC fan, and the remainder is sent to the stack, through ID fan. The pipelines that convey the recycled flue gas are thermally isolated with a trace heating system to avoid a temperature drop below the acid dew point of the flue gas. The secondary O<sub>2</sub> is injected into this stream prior to feeding it to the oxy-combustor. A secondary analyzer, an ADC MGA 3000 Multi Gas Analyzer which measures CO<sub>2</sub>, CO, O<sub>2</sub> and SO<sub>2</sub>, samples the gas just before the entrance to the burner to monitor that the percentage of oxygen is in the range specified (27-35% v/v).

## 2.1. Heat flux measurement

Measurements of the radiative and convective flux were scheduled to be performed in the radiative section of the oxy-combustor (vertical section where the flame is located). For the radiative heat flux measurement a Hukseflux water cooled sensor for high temperatures was acquired (see Fig. 2). For the convective heat flux measurement, an in-house air-cooled probe was designed taking into account the guidelines suggested elsewhere [18]. This probe is shown in Fig. 2. The method intended to be used for the calculations of the convective heat flux was also the one suggested by these authors [18]. The main problem found during the experimental campaign, when this in-house probe was used, was the practical impossibility in keeping the temperature of the surface probe at the set temperature (570K) or close enough, even using the maximum amount of cooling air allowed for the rig and since this problem was compounded by the fact that this probe was contaminating by the ash deposits sampled from probes located below it, was decided not to use this convective heat flux probe for subsequent tests.

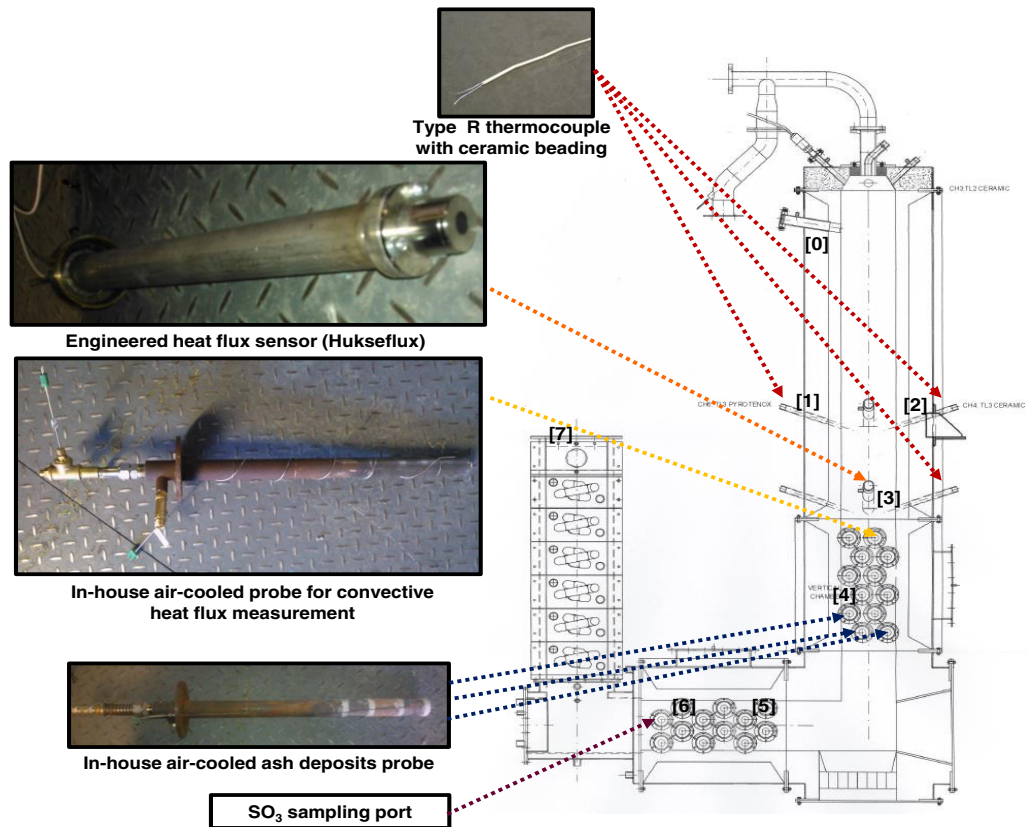


Fig. 2. Location for several measurement systems: R type thermocouples [1-3], K type thermocouples [0-4-5-6-7], heat flux sensors, ash deposits probes and SO<sub>x</sub> sampling port.

## 2.2. SO<sub>3</sub> measurement

The method chosen to measure SO<sub>3</sub> content in the flue gas is the Controlled Condensation Method developed by the Environmental Protection Agency (EPA Method 8A) [19], which scheme is presented in Fig. 3. The standard procedure for sampling, sample recovery and sample analysis is fully described in the reference given for this method. The location selected to install the SO<sub>3</sub> sampling train is the last part of the horizontal section of the oxy-combustor (see Fig. 2), as it is where the optimum window temperature to sample the flue gas is: ~755K [8].

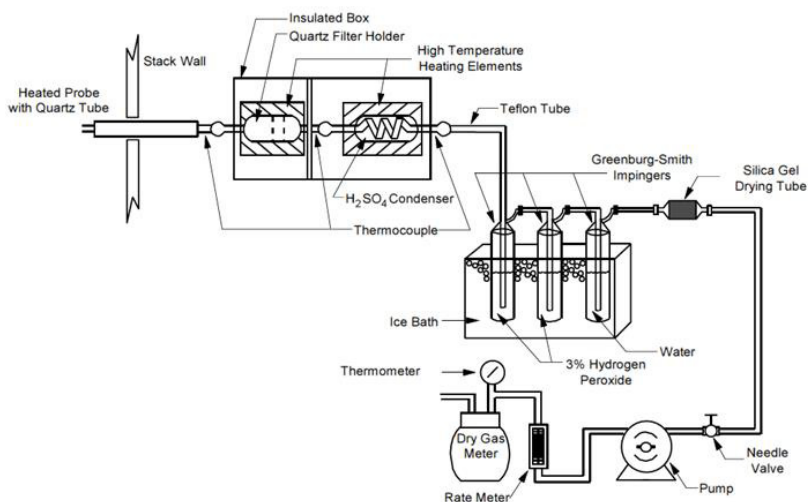


Fig. 3. SO<sub>x</sub> sampling train (EPA Method 8A). Image taken from [19].

## 2.3. Main operational aspects

To study the oxy-combustion process, it is necessary to set a reference case to compare the results generated performing oxy-firing tests. For the experiments carried out at the oxy-combustor facility at Cranfield University, the reference case is the combustion with necessary amount of coal required to generate 100 kW<sub>th</sub>. Additionally, it was considered worthwhile also to carry out tests on air-firing cases using coal-biomass blends for comparison purposes. In this work we have used El Cerrejon coal and cereal co-product (CCP) biomass. Different blends of these fuels were used: 50%-50% and 75%-25% (wt) and the fuels are given in Table 1.

Table 1. Proximate, ultimate and ash analyses of the fuels.

	El Cerrejon coal	CCP
<b>Proximate analysis (% (wt) as received)</b>		
Moisture	5.80	8.10
Volatile matter	34.80	70.80
Ash	8.60	4.20
<b>Calorific value, (MJ/kg)</b>		
Gross calorific value	27.85	17.61
Net calorific value	27.12	16.34
<b>Ultimate analysis (% (wt) as received)</b>		
Carbon	69.2	43.30
Hydrogen	4.40	5.80

Nitrogen	1.42	2.70
Chlorine	0.02	0.17
Sulfur	0.58	0.16
Oxygen	9.98	35.57
<b>Ash analysis (% (wt))</b>		
SiO <sub>2</sub>	60.69	44.36
Al <sub>2</sub> O <sub>3</sub>	22.01	2.79
Fe <sub>2</sub> O <sub>3</sub>	7.43	2.47
TiO <sub>2</sub>	0.92	0.12
CaO	2.27	7.78
MgO	2.90	3.96
Na <sub>2</sub> O	1.06	0.36
K <sub>2</sub> O	2.32	24.72
Mn <sub>3</sub> O <sub>4</sub>	0.06	0.10
P <sub>2</sub> O <sub>5</sub>	0.21	12.04
SO <sub>3</sub>	-	-
BaO	0.11	0.05

The percentage of recycled flue gas was set in the range of 58-65%. The facility had the ability to operate with wet (by-passing the condenser), or dry recycle (using the condenser), depending of the requirements of the case studied. Following the guidelines in the published literature, to ensure safe conditions for the oxygen injection, the oxygen percentage in the primary stream was not permitted to exceed 21% (v/v). During previous campaigns run at the oxy-combustor at Cranfield University, the secondary oxygen was kept under 28% (v/v), because: no literature was found suggesting values above 28% (v/v), and the range of the ADC MGA 3000 Multi Gas Analyzer was between 0 and 30% (v/v). However, for the last campaign a new upper limit of 35% (v/v) was set in consequence of new recommendations established in the literature, plus the fact of the upgrade of the analyzer. With the higher specification for the O<sub>2</sub>, values between 2 and 5% (v/v) of O<sub>2</sub> at the exit of the combustor were reached (this did not happen in previous campaigns), meaning that there was an excess of oxygen in the initial gas mixture fed to the burner, allowing for a complete combustion of the fuel.

The operating pressure selected in the oxy-combustor has a direct effect on the amount of air ingress that occurs into the process. This parameter becomes more important in the cases of retrofitted facilities, as it is the case for our reactor at Cranfield University. Air ingress into the oxy-combustion process in retrofitted plants is a common phenomenon as noted by many researchers ([20], [21]) this causes a drop in the purity of CO<sub>2</sub> seen in the flue gas, which in practice would cause higher costs for the purification of this stream prior to its compression and storage. For previous campaigns of experiments, the operating pressure inside the combustor was set to be below atmospheric for safety and design considerations. However, to minimize the air ingress into the combustion chamber during the test, the pressure was kept as close as possible to atmospheric. For the last campaign and after having checked during the initial tests that the CO levels were low enough, the tests were run in slightly positive pressure, switching it to be negative when the ports associated to the combustor had to be opened momentarily (change of the FTIR sampling probe, and at the start /end of using the SO<sub>x</sub> sampling train).

### 3. Experimental Results and Discussion

#### 3.1. Gas composition

The results for the tests performed under air and oxy-firing conditions varying the composition of the fuel, as regards to the average gas composition, as well as the maximum CO<sub>2</sub> levels reached, identifying the percentage of RFG used for each test, are reported in Table 2. The values presented for RFG percentage were obtained measuring

the flowrates for recycled gas and total flue gas at the exit of the oxy-combustor, and calculating the average percentage of RFG for each test. One of the main operational modifications used during this experimental campaign was the installation of the condenser, in the recirculation line, providing us with the possibility of studying the effects of using dry recycled flue gas. Another important difference in the operation conditions, during this last campaign, was the fact that the slightly positive pressure over the atmospheric ( $\Delta P=0.002$  bar) in the oxy-combustor reduced air ingress into the process. This operational modification made the air ingress drop from 10% (defined as the relative fraction compared to total of the gas supplied to the oxy-combustor) to 5%. This values are in the same range as the data established in the literature ([10], [20]).

Table 2. Gas composition and RFG for air and oxy-combustion tests.

[EC: El Cerrejon coal; CC: Cereal co—product; B1: Blend EC50/CC50; B2: Blend EC75/CC25; A: Air-firing; O: Oxy-firing]

Test	CO <sub>2</sub> max %(v/v) [db]	CO <sub>2</sub> max %(v/v) [wb]	CO <sub>2</sub> %(v/v) [wb]	H <sub>2</sub> O %(v/v) [wb]	O <sub>2</sub> %(v/v) [wb]	NO <sub>x</sub> ppmv [wb]	CO ppmv [wb]	SO <sub>2</sub> ppmv [wb]	HCl ppmv [wb]	CH <sub>4</sub> ppmv [wb]	RFG %, type
EC.A		11.79	11.12	7.40	4.98	634	37	305	8	0	-
B1.A		12.74	12.33	9.39	2.27	404	99	274	37	2	-
CC.A		12.65	12.44	12.19	2.71	391	668	88	39	57	-
EC.O.(a)	70.73	52.38	47.51	26.38	2.23	560	1393	771	6	89	60, wet
EC.O.(b)	67.45	52.89	49.31	24.13	5.46	753	29	689	6	1	58, dry
EC.O.(c)	81.22	66.08	62.13	19.80	3.56	1077	356	820	20	8	70, dry
B2.O	77.19	61.22	60.56	21.59	4.70	594	226	654	31	13	67, dry
B1.O.(a)	74.60	55.29	48.89	29.15	4.16	508	1352	516	56	78	48, dry
B1.O.(b)	77.47	61.85	58.06	20.81	6.38	997	23	442	29	0	60, dry
CC.O	80.36	65.21	57.05	25.35	6.55	612	21	108	100	1	54, dry

The results indicate that the maximum CO<sub>2</sub> level reached, on a wet basis, occurs in the case of 100% coal [EC.O.(c)], as expected given the fuel. Interestingly, similar values for the CO<sub>2</sub> levels on a dry basis were achieved when using both parent fuels, in tests [EC.O.(c)] and [CC.O]. For the H<sub>2</sub>O content, the results obtained are higher than expected after the installation of the condenser, even though its effect can be seen in the last repeat of the tests with each fuel ([EC.O.(c)], [B2.O], [B1.O.(b)], [CC.O]), where the average value is around 20-25%(v/v), being the maximum for the case when using 100% CCP. The O<sub>2</sub> in excess was improved during this last campaign, and was between 3.5 and 6.5 %(v/v), in most cases. The CO levels reached are much lower in comparison with previous campaigns, as a consequence of a better combustion of the fuels. With regards to the NO<sub>x</sub> concentrations, the data shows that [EC.O.(c)] and [B1.O.(b)] reached around 1000ppms, and did not follow the trend set by the rest of oxy-firing tests (550-750ppmv); The high NO<sub>x</sub> concentration reached in the case using pure coal [EC.O.(c)] may be explained by the NO<sub>x</sub> thermal generation being promoted due to the high temperatures reached in this test, maximum over all the last campaign. On the other hand, some authors ([22], [23]) have speculated that increasing the excess of oxygen supplied to the burner, lead to an enhancement of NO production from the N-fuel. This could explain the results obtained for the test using 50%-50% blend [B1.O.(b)], which presented an excess in oxygen, after the oxy-combustion of 6.4%. The data reported regarding the SO<sub>2</sub> levels agrees with the expectation considering the fuels analysis, higher range (680-820ppmv) in the tests using 100% coal, medium range (440-650ppmv) for those tests using coal-biomass blends, and the lowest concentration (around 100ppmv) for the case using only biomass. Likewise, the levels measured inside the combustor for HCl, also follow the trend set by the ultimate analysis of the fuels: increasing with the share of biomass. The concentrations reported for the CH<sub>4</sub> are very low, which supports



the belief that we have achieved effectively complete combustion for the tests from this final campaign, and as consequence, concentration levels are very low for intermediate combustion products such as CO and CH<sub>4</sub>.

From the data presented in Table 2, the average gas composition obtained under air and oxy-firing conditions can be compared. For the main species (CO<sub>2</sub>, H<sub>2</sub>O) and some minor species (SO<sub>2</sub>, HCl) the effect of recycling flue gas is noticeable, causing the levels to increase twice to three times their value in comparison to the air-firing case using the same fuel, however, the NO<sub>x</sub> levels remain similar for most cases. This means an actual decrease of NO<sub>x</sub> emissions per unit of energy produced [6]. Note that the higher concentrations in SO<sub>2</sub> levels inside the oxy-combustor, aforementioned, do not consider the normalization per unit of energy released from the fuel, as this also follows the decreasing trends when using oxy-combustion mode in comparison to air-firing.

### 3.2. Measured SO<sub>2</sub> and SO<sub>3</sub>

The results for SO<sub>2</sub> and SO<sub>3</sub> analysis applying the Controlled Condensation Method (CCM)[19] to evaluate the levels of these species under air and oxy-firing conditions for different fuels are presented in Table 3. Additionally, the concentrations resulted from the CCM technique are presented in ppmv and in mg/m<sup>3</sup> to simplify the comparison of these values with data published in the literature referenced.

Table 3. SO<sub>x</sub> Results.

[EC: El Cerrejon coal; CC: Cereal co—product; B1: Blend EC50/CC50; B2: Blend EC75/CC25; A: Air-firing; O: Oxy-firing]

	SO <sub>2</sub> _FTIR	SO <sub>2</sub> _CCM		SO <sub>3</sub> _CCM		SO <sub>3</sub> /SO <sub>2</sub>
	(ppmv)	(ppmv)	(mg/m <sup>3</sup> )	(ppmv)	(mg/m <sup>3</sup> )	(%)
EC.A	305.20	83.04	217.37	3.65	11.93	5.5
B1.A	274.33	244.35	639.61	20.15	65.94	10.3
CC.A	87.59	98.31	257.32	25.35	82.93	32.2
EC.O.(c)	819.58	563.40	1474.76	20.60	67.41	4.6
B2.O	654.27	521.99	1366.35	16.75	54.81	4.0
B1.O.(b)	442.19	230.01	602.08	35.89	117.42	19.5

From the table above, it can be seen that similar SO<sub>3</sub> levels were obtained for tests carried out under air and oxy-firing conditions, although there is a slightly rising trend as the percentage of biomass increases, in contrast to what occurs with the SO<sub>2</sub> levels, which increase with the share of coal. The higher SO<sub>2</sub> concentrations reached for the oxy-firing cases compared to the ones resulted under air-firing conditions has been explained previously to be a consequence of the use of the recycled gas.

The ratio SO<sub>3</sub>/SO<sub>2</sub> seems to be highly dependent on the fuel used, increasing with the share of biomass. This fact could be explained by assuming that the conversion from SO<sub>2</sub> to SO<sub>3</sub> may be promoted by the alkalis contained in the fly ashes, as these species (K and Na) have been used by several authors ([24], [25]) as catalysts, together with V<sub>2</sub>O<sub>5</sub> to enhance the conversion from SO<sub>2</sub> to SO<sub>3</sub>. This, combined with the fact that the K content is noticeably higher for biomass than for coal, as noted in the section dedicated to ash deposits characterization, suggests given this assumption that this is the most likely explanation for the high SO<sub>3</sub>/SO<sub>2</sub> ratios obtained.

The case of air-firing pure coal where the SO<sub>3</sub> and SO<sub>2</sub> contents detected, using CCM, are much lower than for the rest of the cases evaluated, this is assumed to be due to an error during the sampling process. It seems that part of the sample was missed, most likely during the rinsing of the sampling train. The complexity of this method and its low reproducibility has already been noted by other authors ([26], [12]).

The inaccuracy observed, based on the comparison between the SO<sub>2</sub> levels acquired by the FTIR and the concentration obtained using the CCM, is between 10 and 50%, without considering the test[EC.A].

### 3.3. Temperatures and heat fluxes

The experimental data for the maximum temperatures as well as maximum and average heat fluxes reached during the last experimental campaign at the oxy-combustor facility at Cranfield University are presented in Table 4, and the locations where the measurements were taken are displayed in Fig. 2. Additionally, the RFG percentage and the thermal power expected, considering the fuel flowrate supplied, are included in this table to allow for a better analysis of the results.

Table 4. Maximum temperatures and heat fluxes reached inside the oxy-combustor at Cranfield University.

[EC: El Cerrejon coal; CC: Cereal co—product; B1: Blend EC50/CC50; B2: Blend EC75/CC25; A: Air-firing; O: Oxy-firing]

	[0] Top vert (K)	[1] Flame1 (K)	[2] Flame2 (K)	[3] Flame3 (K)	[4] Bottom vert (K)	Heat flux <sub>Max</sub> (kW/m <sup>2</sup> )	Heat flux <sub>Av</sub> (kW/m <sup>2</sup> )	RFG (%)	Power (kW)
EC.A	803	1345	1346	1230	1135	42.9	35.8	-	108
B1.A	797	1384	1381	1226	1126	33.7	29.2	-	108
CC.A	819	1377	1374	1224	1110	85.5	31.4	-	101
EC.O.(a)	847	1437	1430	1339	1158	191.7	153.8	60	119
EC.O.(b)	819	1401	1393	1307	1204	-	-	58	101
EC.O.(c)	-	1508	1501	1373	1238	188.5	149.9	70	125
B2.O	799	1379	1377	1251	1139	38.8	33.6	67	105
B1.O.(a)	860	1418	1422	1305	1195	-	-	48	114
B1.O.(b)		1384	1380	1255	1161	82.7	63.8	60	105
CC.O	873	1378	1382	1247	1174	150.6	109.9	54	118

The maximum temperature reached was 1508K when oxy-firing El Cerrejon coal in the test labelled [EC.O.(c)]. The noticeable difference between the temperatures obtained in this test compared to the rest, 70K in the best case, is assumed to be a consequence of the higher flowrate of coal supplied during this test. Analyzing the effects of changing the type of combustion, it can be observed that the temperature reached for the case where oxy-firing 100% El Cerrejon coal [EC.O.(b)] was 55K higher than in the corresponding case [EC.A] under air-firing conditions, considering tests with similar thermal power expected. However, for those tests using coal-biomass blends and pure biomass, the thermal levels reached under air and oxy-firing conditions were equivalent. Comparing the temperatures reported when using different coal-biomass shares under oxy-firing conditions, the cases with 100% El Cerrejon coal were the ones with maximum thermal profiles, and these were 20K higher than the cases using blends and 100% biomass. Interestingly, using air-fired combustion; the temperatures reached are higher for those cases using coal- biomass blends and pure biomass.

Previously to the analysis of the data reported with regards to heat fluxes, it is necessary to bear in mind that some problems were observed in the performance of the heat flux sensor. The readings obtained were exceptionally low for some of the tests ([EC.A], [B1.A], [B2.O], [B1.O.(b)]). It is believed that for a few of these tests ([EC.A], [B2.O], [B1.O.(b)]) the cause of the low measurements was ash deposition on the sensor lens. However, test [B1.A] shows no evidence of this possible cause for the malfunctioning, as the sensor was cleaned before the test and re-calibrated after finishing the third experimental campaign to double check that no drift had occurred.

The comparison of the results for heat fluxes were based on the average value measured, and extrapolated to achieve the same thermal power expected for those cases where it was necessary. The effect of changing the type of

combustion can be analyzed considering the tests using 100% biomass [CC.A] and [CC.O], to avoid using results from the tests where the measurements of the sensor were less reliable. The averaged values reported for heat fluxes in Table 4, show that the heat flux for oxy-firing conditions is three times higher compared to air-firing. The reported data also shows that changing the type of fuel, from 100% biomass [CC.O] to 100% El Cerrejon coal [EC.O.(a)], increases the heat flux by 1.4 times. It is interesting also that for El Cerrejon coal and CCP, used individually, the heat flux is higher than with their blends, fact that can be observed under air and oxy-firing conditions. It is further observed that the maximum heat flux value for oxy-firing is double the air-firing case. When changing the type of fuel from biomass to coal under oxy-firing conditions, the maximum heat flux increases by 1.25 times.

### 3.4. Ash deposits and fly ash

Fig. 4 illustrates the deposit probes during the ash sampling for six of the tests accomplished in the last campaign. Images from a) to c) correspond to air-firing tests and d) to f) correspond to oxy-firing cases, varying the type of fuel: 100% El Cerrejon coal, 50% El Cerrejon coal-50% CCP and 100% CCP.

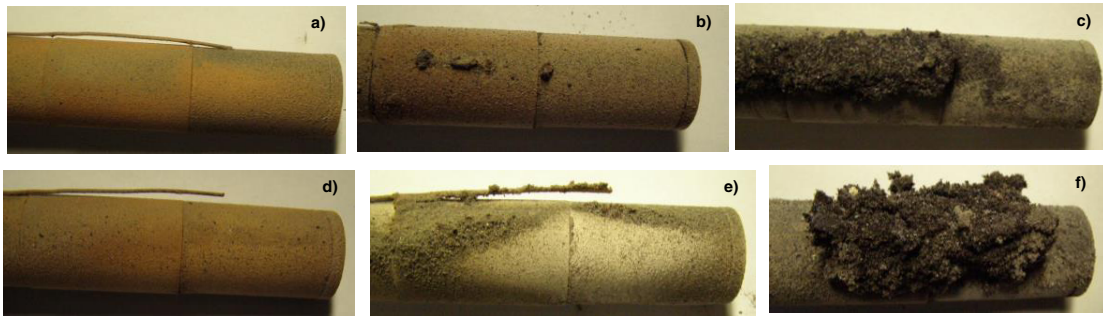


Fig. 4. Ash deposit probes for tests: a) [EC.A] b) [B1.A] c) [TCC.A] d) [EC.O.(e)] e) [B1.O.(b)] f) [CC.O].

From these images, it is noteworthy that when using 100% CCP the structure of the deposit is more fibrous and porous than when oxy-firing 100% El Cerrejon coal or the coal-biomass blend. No significant difference in the aspect of the deposits can be observed comparing the cases under oxy and air-firing conditions.

From the results obtained for the ESEM/EDX analyses, similar trends have been found at high (1023K) and medium (923K) sampling temperatures, where most of the elements followed the trend demonstrated by the previous analyses of the ashes under air-firing conditions. The main exception found to these trends has been the sulfur levels observed. The similar S levels reached in all cases, even though El Cerrejon coal has 3.5 times more S than CCP, is explained by the fact that the higher K levels contained in the biomass would lead to much larger formation of  $K_2SO_4$ .

The analyses carried out for the carbon in ash have shown that for the ashes sampled in the locations nearby the flame, the unburnt C was zero for all the cases. However, high percentages of carbon in ash were found for ashes sampled from the horizontal section of the oxy-combustor and the cyclone. Elevated levels for unburnt C were observed for air-firing cases compared to oxy-firing, where the combustion process is assumed to be enhanced by the higher  $O_2$  concentrations and higher temperatures reached. However, no clear trend was found by varying the type of fuel.

## 4. Conclusions

The main operational difference between air and oxy-firing combustion is the use of recycled flue gas. A direct consequence of this parameter is the accumulation of the chemical species in the recycled gases, a fact that is positive from the perspective of generating a stream with high  $CO_2$  concentration. However, it also leads to the accumulation of undesirable corrosive species in the boiler.

From the results presented it can be observed that the levels of CO<sub>2</sub> obtained under oxy-combustion are five times the concentrations reached in the air-firing cases. The same is true for the H<sub>2</sub>O content, although these are at lower level, with the concentrations up to three times higher than in conventional combustion. The main difference between air and oxy-combustion results with regards to the minor species are increases in the SO<sub>2</sub> concentrations, which are up to 2.6 times higher when using coal in oxy-combustion compared to the same case under air-firing conditions (without considering normalization per unit of energy released from the fuel).

The optimum range for percentage of RFG, for which higher CO<sub>2</sub> levels were achieved, was found to be between 65 and 70%. The type of recycle that contributed to these higher concentrations was using dry RFG.

Comparing the results obtained using coal instead of biomass, it has been highlighted that although the maximum CO<sub>2</sub> levels in wet basis are achieved for those cases oxy-firing coal, considering dry basis the maximum CO<sub>2</sub> values using 100% coal or 100% biomass are similar and over 80%(v/v). This is a significant finding, as one might have expected that due to the lower carbon content in the elemental analysis of biomass, this would affect the CO<sub>2</sub> concentration of the flue gas generated. However, it is clear that while the flue gas generated using biomass before any flue gas treatment will have higher H<sub>2</sub>O content, as a consequence of the higher H<sub>2</sub> and O<sub>2</sub> concentrations of the biomass, so precautions should be taken to avoid reaching the acid dew point temperature. With regards to the minor species, the main differences when increasing the share of biomass in the fuel are that the SO<sub>2</sub> levels decrease and the HCl levels increase, as expected given the ultimate analysis of the parent fuels. The results obtained using the CCM to analyze SO<sub>3</sub> contents in the tests co-firing coal and biomass under air and oxy-combustion conditions have been observed to be between 16 and 36 ppm, independent from the combustion mode or the fuel fired. Noticeable increase in the SO<sub>3</sub>/SO<sub>2</sub> ratio has been identified when increasing the share of biomass.

Comparing the temperatures obtained under air and oxy-firing conditions for the last experimental campaign, the main outcome is that higher thermal profiles are achieved in the oxy-combustion process reaching temperatures around 50K higher, on average, than in conventional combustion with air, allowing for similar thermal power expected. The results obtained for heat fluxes show that the values reached under oxy-firing conditions are up to three times the heat fluxes generated in air-firing, looking at the averaged values, and doubles the air-firing case for the maximum heat flux reached. The noticeable differences, comparing air to oxy-firing mode, observed for the heat fluxes reached make it improbable that one can compensate for this factor through the use of coal-biomass blends.

Characterization of ash deposits generated under oxy-fuel combustion has showed similar trends at 1023 and 923K. Sulfur contents are similar to all oxy-firing cases even when changing from pure coal to pure biomass, possibly as consequence of K<sub>2</sub>SO<sub>4</sub> generation. Regarding the fly ash, it has been verified that lower levels of carbon in ash are present under oxy-fuel combustion.

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