



Full Length Article

Oxy-fuel combustion study of biomass fuels in a 20 kW_{th} fluidized bed combustor



Farooq Sher, Miguel A. Pans, Chenggong Sun, Colin Snape, Hao Liu*

Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

ARTICLE INFO

Keywords:

Biomass combustion
Fluidized bed combustion
Oxy-fuel combustion
Carbon capture
NOx and CO emissions

ABSTRACT

Oxy-fuel combustion is one of the promising carbon capture technologies considered to be suitable for future commercial applications with stationary combustion plants. Although more and more biomass and waste are now being burned in stationary combustion plants, research on oxy-fuel combustion of biomass has received much less attention in comparison to oxy-fuel combustion of coal. In this work, a series of tests was carried out in a 20 kW_{th} fluidized bed combustor under oxy-fuel conditions firing two non-woody fuels (miscanthus and straw pellets) and one woody fuel (domestic wood pellet). The effects of the combustion atmosphere (air and oxy-fuel) and oxygen concentration in the oxidant of the oxy-fuel combustion on gas emissions and temperature profiles were systematically studied with the overall excess oxygen coefficient in the combustor being maintained roughly constant throughout the tests. The experimental results showed that replacing the air with an oxy-fuel oxidant of 21 vol% O₂ and 79 vol% CO₂ resulted in a significant decrease in combustion temperature and ultimately led to the extinction of the biomass flame due to the larger specific heat of CO₂ compared to N₂. To keep a similar temperature profile to that achieved under the air combustion conditions, the oxygen concentration in the oxidant of O₂/CO₂ mixture had to be increased to 30 vol%. A drastic decrease in CO emissions was observed for all three biomass fuels (up to 80% reduction when firing straw) under oxy-fuel combustion conditions providing that the oxygen concentration in the oxidant of O₂/CO₂ mixture was above 25 vol%. NOx emissions were found to decrease with the oxygen concentration in the oxy-fuel oxidant, due to i) the increase of bed temperature, which implies more volatile-N released and converted in the dense bed zone and ii) the less dilution of the gases inside the dense bed zone, which leads to a higher CO concentration in this region enhancing the reduction of NOx. Similar NOx emissions to those obtained with air combustion were found when the oxygen concentration in the oxy-fuel oxidant was kept at 30 vol%. Further analysis of the experimental results showed that the gas emissions when firing the non-woody fuels were controlled mainly by the freeboard temperature instead of the dense bed region temperature due to the characteristically high volatile matter content and fines of this kind of biomass fuels.

1. Introduction

Growing concerns on the greenhouse gas emissions and their potential impact on climate change demand not only the application of CO₂ capture and storage (CCS) technologies to large point anthropogenic CO₂ emission sources such as coal and natural gas fired power plants but also the implementation of CO₂ negative combustion technologies such as Bio-energy with Carbon Capture and Storage (BECCS) within the next decades. Although removing CO₂ from the atmosphere, i.e. direct capture of CO₂ from air, may be necessary in the longer term, direct CO₂ capture is more technically challenging and more expensive than CCS and BECCS applied to large scale combustion plants [1–3]. Biomass is considered as a renewable fuel, a carbon-neutral energy

source and hence its combustion integrated with CCS can lead to negative CO₂ emissions. Biomass has already captured worldwide attention in the context of greenhouse gas control even though fossil fuels are expected to retain their dominant role in the world energy supply in the coming decades [4].

Oxy-fuel combustion is one of the most developed CCS technologies and considered as technically feasible and economically competitive for future commercial applications [5–7]. Oxy-fuel combustion refers to fuel being burned in a mixture of oxygen and recycled flue gas (RFG). Unlike conventional air combustion plants that use air as the oxidant, an oxy-fired plant employs an Air Separation Unit (ASU) to produce an almost pure oxygen stream. The oxygen stream is then combined with RFG to produce an oxygen enriched gas as the oxidant. The flue gas

* Corresponding author.

E-mail address: Liu.Hao@nottingham.ac.uk (H. Liu).

recycle is necessary to moderate the otherwise excessively high flame temperature that would result from fuel combustion in pure oxygen. After the removal of water and other impurities from the flue gas exhaust stream, high-purity CO₂ (up to 95%) is produced and almost ready for sequestration [8,9]. As mentioned above, the combination of oxy-fuel combustion with biomass could effectively provide a method which would not only avoid further CO₂ emissions but also helps reduce the atmospheric CO₂. Furthermore, the oxy-fuel process also offers other advantages such as improving the ignition and burnout performance.

Among all the available combustion technologies, fluidized bed combustion (FBC) is often considered as the best choice for the combustion and/or co-combustion of biomass, waste and other low quality solid fuels due to its fuel flexibility, long residence times, and uniform combustion temperatures. The characteristics of FBC also offers several advantages for its application in oxy-fuel systems [10]. Firstly, the difficulty of flue gas recirculation for temperature control in pulverized fuel (PF) applications could be reduced in circulating fluidized bed (CFB) by means of the bed material recirculation, since the specific heat of the solids is much higher than that of the recycled flue gas. Secondly, lower NO_x emissions and better sulphur removal are possible. Finally, it is easier to retrofit a fluidized bed boiler from air to oxy-fuel combustion as there will be no need for a new burner.

The effects of oxy-fuel atmosphere and O₂ concentration in the oxy-fuel oxidant gas on pollutant emissions (NO_x and CO) in fluidized bed systems firing different kinds of coal have been thoroughly investigated during the past years by a number of researchers. In general, the experimental results showed that NO_x emissions in oxy-fuel combustion with low O₂ concentrations are lower than those obtained under air-firing atmosphere, because of the lower temperatures as well as higher char and CO concentrations in the dense bed [10,11]. Furthermore, NO_x emissions were found to increase with the increasing O₂ concentrations in the oxy-fuel oxidant, which is as a result of i) the increase of the temperature in the furnace which elevates the concentrations of O and OH radicals and enhances NO formation and ii) the lower gas velocity in the riser and longer residence time of fuel particles in the combustor, which may promote the fuel-N conversion into NO_x precursors [10–14]. In some studies an opposite trend was found, i.e. an decrease of NO_x with the increasing O₂ concentration in the oxy-fuel oxidant, as in the work of de las Obras-Loscertales et al. [15]. The authors explained this trend by means of the different operational procedure used, comparing with other investigations: in their work [15], an increase in the oxygen concentration was compensated with an increase of the coal flow rate fed to the reactor, keeping constant the total gas flow rate and excess oxygen coefficient in all tests. As a result, more unconverted char was present in the bed, favouring the NO reduction on the char surface.

Regarding CO emissions, Duan et al. [16] observed a much lower CO emission in air than those in an oxy-fuel atmosphere with the same O₂ concentration when firing two kind of coal in a 50 kW_{th} CFB facility, due to the higher temperature achieved under the air combustion conditions. They also reported a decrease in CO emissions when the O₂ concentration in the oxy-fuel oxidant gas increased; as the oxidation of carbon was more complete and therefore less CO was formed. On the other hand, Hofbauer et al. [14] observed similar CO emissions for air combustion and two oxy-fuel cases investigated (with 26 vol% and 36 vol% of O₂ in the oxidant, respectively), firing bituminous coal in a 150 kW_{th} CFB reactor. Jia et al. [17] performed a series of oxy-fuel tests with flue gas recycle in a 100 kW_{th} CFB combustor firing bituminous coal. The CO emissions of oxy-fuel combustion were found to be equal or slightly lower than those of air firing, mainly due to the higher cyclone temperature achieved with oxy-fuel combustion.

Biomass properties differ from those of coal in many important ways which results in different combustion behaviours [18]. For example, biomass generally has less carbon, more oxygen, higher hydrogen content and lower heating value. There are huge differences in volatile

matter contents between biomass and coal: biomass can lose up to 90% of their masses (as volatiles) in its first stage of combustion, much higher than any ranks of coal (from less than 10% for anthracite to ca. 40% for high-volatile bituminous coals) [19,20]. The effects of oxy-fuel combustion conditions on the combustion performance and emissions of biomass fuels are expected to be differing from those of coal as a result of the differences in properties between biomass and coal. So far, few have investigated oxy-fuel combustion in fluidized bed reactors firing 100% biomass fuels and therefore further research is still needed. Duan et al. [21] conducted a series of experiments firing three kinds of Chinese biomass fuels, i.e. rice husk, wood chips and dry wood flour, under air and oxy-fuel atmosphere in a 10 kW_{th} CFB combustor. The main objective of their study was to investigate the pollutant emissions of the co-firing of biomass with coal under oxy-fuel combustion conditions although experiments firing only the biomass fuels were also carried out for comparison purposes. They observed lower NO emissions in the oxy-fuel atmosphere compared with those with air combustion. This behaviour was explained as the result of the reduced yield of NO_x precursors like NH₃ during the devolatilization process and the enhanced NO reductions via char/NO/CO reactions under the oxy-fuel combustion conditions. They also concluded that the NO emission increased with the bed temperature, overall oxygen concentration and the primary oxidant fraction when co-firing biomass and coal with a mixing ratio of 0.2 in oxy-fuel combustion. However, the effects of the oxygen concentration in the oxy-fuel oxidant gas on the gas emissions and temperature profiles firing 100% biomass fuels were not investigated in this study.

The objective of the present work is to continue delving into the barely-studied oxy-fuel combustion of biomass fuels firing three kind of biomass fuels, two non-woody (miscanthus and straw) and one woody (wood), in a 20 kW_{th} bubbling fluidized bed (BFB) combustor, studying the effects of the combustion atmosphere (air and oxy-fuel) and the oxygen concentration in the oxy-fuel oxidant on the gas emissions and temperature profiles.

2. Experimental

2.1. Experimental setup

The experimental system, shown in Fig. 1, mainly includes a BFB combustor (20 kW_{th}) and the auxiliary systems for air supply, biomass feeding, and gas analysis. The stainless steel combustor consists of a bed zone of 102 mm i.d. and 800 mm height, a freeboard of 154 mm i.d. and 1100 mm height, and a plenum of 102 mm i.d. and 300 mm height. A water cooled heat extraction probe located inside the combustor allows the bed temperature to be controlled by means of the extraction of heat from the combustor. This probe can be moved vertically along the combustor to change the contact surface inside the combustor to prevent the bed from reaching very high temperature values and thus avoid agglomeration and defluidisation of the bed particles. Furthermore, the cooling water flow rate of the probe can be adjusted to control the heat extraction and hence the combustion temperature inside the combustor.

As the real flue gas recirculation is not included with the experimental system, a premixed flow of CO₂ and O₂ which are supplied from gas cylinders and monitored by rota meters (calibrated for O₂ and CO₂ respectively) is used as the main oxidant for the oxy-fuel combustion and is also used as the fluidizing gas of the BFB combustor. For the conventional air combustion tests, compressed air is used as the main oxidant and fluidizing gas. The air flow rate is monitored by a rotameter that is calibrated for air. For both oxy and air combustion tests, a small flow of compressed air is also fed through the biomass feeder hopper to prevent backfire and to stop the sand particles coming into the feeding pipe. The oxidant gas is mainly fed into the combustor through the plenum and a porous stainless gas distribution plate with 100 μm pore size and 12 mm thickness. An electric air pre-heater before the plenum

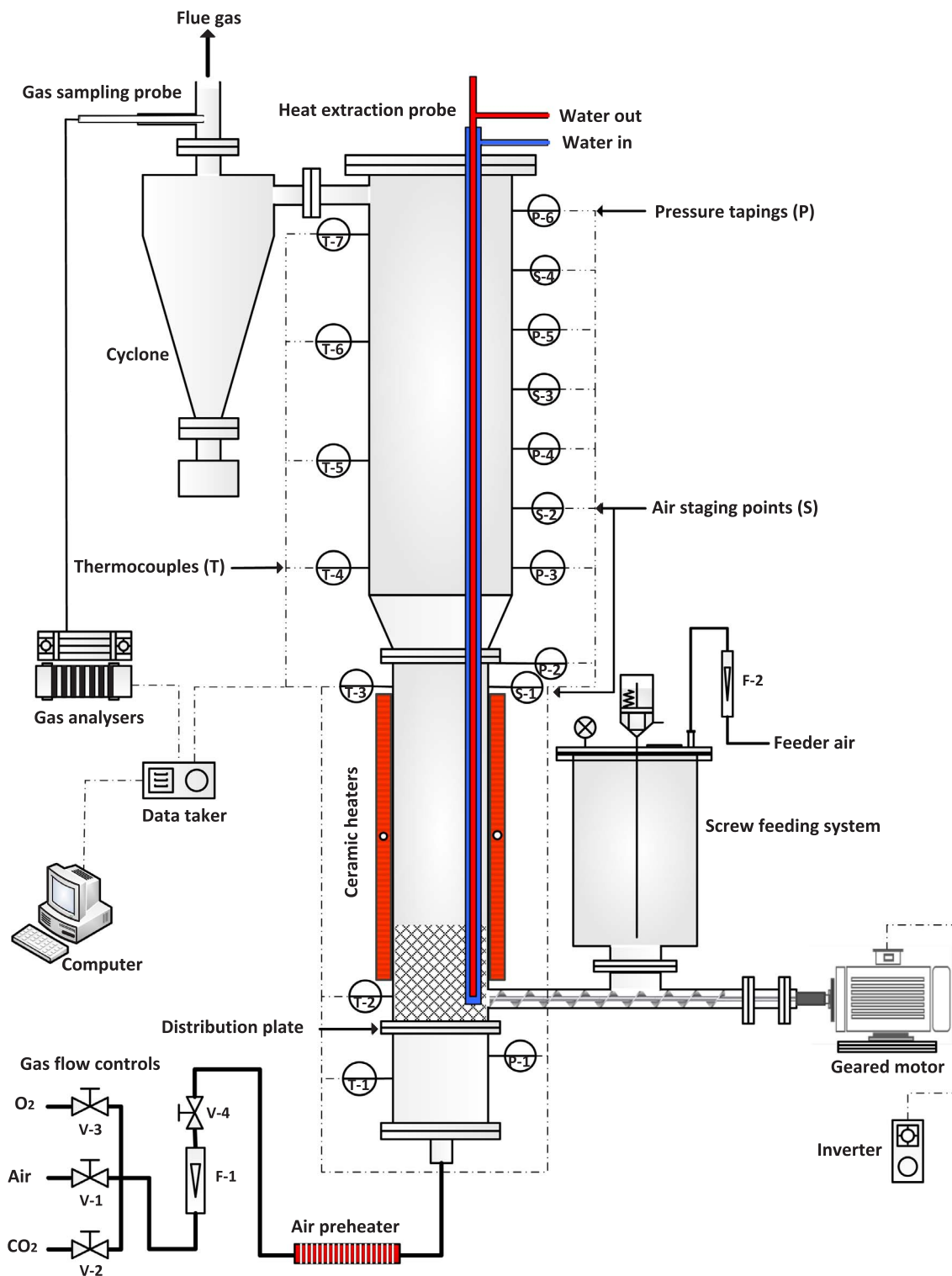


Fig. 1. Schematic representation of 20 kW_{th} BFB combustor experimental setup.

and two electric half-cylindrical ceramic radiant heaters surrounding the main bed area are used to preheat the combustion/fluidization air during the start-up of the combustor. The biomass pellets are fed to the combustor at the location just above the distributor plate by means of a screw feeder. To ensure the fuel feed rate controllable and repeatable, the feeder motor frequency is controlled by an inverter. The flue gas stream leaving the combustor passes through a high efficiency cyclone to recover the elutriated solids and ash and then is exhausted through the ventilation system. The gas composition at the exit of the combustor

is continuously analyzed by on-line gas analyzers after going through the water-cooled sampling probe placed inside the gas exit pipe of the cyclone, water condensation traps and particle filters. O₂, CO₂ and CO concentrations are measured by an ABB Easyline continuous gas analyzer (ABB, EL3020), while the NO_x concentration is measured by a chemiluminescent NO_x analyzer (Horiba VA-3000). In order to minimize instrumental errors and drifts, gas analyzers are regularly calibrated with BOC/Linde Group calibration gases during each test campaign. The combustor is equipped with pressure tapings and K-type

thermocouples at different heights. Both the pressure differential across the dense bed and the temperatures along the combustor are closely monitored during each test so that the signs of agglomeration, defluidisation or extremely high temperature can be spotted at the earliest opportunity. A data taker and computer system are used to continuously record all of the measured process data (pressure differentials, temperatures, gas composition, etc.).

2.2. Biomass fuels

Three different types of biomass fuels, two non-woody (miscanthus and wheat straw) and one woody (domestic wood), were tested with the 20 kW_{th} BFB combustor under both conventional air combustion and oxy-fuel combustion conditions. All fuels were purchased from the UK suppliers, Brites, in the case of the wood, and Agripellets Ltd, in the case of miscanthus and straw, and used in pellet form. Miscanthus pellets have an average diameter of 6.30 mm and an average length of 18.70 mm, with a bulk density of 603 kg/m³. Straw pellets have an average diameter of 6.15 mm and an average length of 15.60 mm, with a bulk density of 628 kg/m³. Wood pellets have an average diameter of 6.00 mm and an average length of 23.10 mm, with a bulk density of 677 kg/m³. The proximate and ultimate analyses of the fuels are shown in Table 1.

2.3. Procedure and operating conditions

The operating conditions for all of the runs and the average flue gas compositions at steady state at every condition are summarized in Table 2. Garside 14/25 sand with a Sauter mean diameter (d_{32}) of 0.78 mm and a density of 2655 kg/m³ was used as the inert bed material [23]. The sand was added to the reactor from the top flange up to a height of 25 cm (3.2 kg). The excess oxygen coefficient levels were maintained roughly constant in all experiments (30%). To investigate the effect of the O₂ concentration in the oxy-fuel oxidant gas on temperature profiles and gas emissions, a mixture of O₂ and CO₂ gases with various O₂/CO₂ ratios was produced and used as the main oxidant of each oxy-fuel combustion test. As the overall excess oxygen coefficient must remain constant, variations in the O₂ concentration in the oxy-fuel oxidant were hence achieved through variations in the CO₂ flow rate and at the same time keeping the O₂ flow rate and fuel feeding rate constant in all the experiments (Table 2). The names given to the different oxy-fuel conditions (oxy-21, oxy-25 and oxy-30, as shown in Table 2) are related with the O₂ concentration in the oxy-fuel oxidant fed to the combustor under each oxy-fuel combustion test condition (i.e. 21, 25 and 30 vol%, respectively, as indicated in the 3rd row at Table 2). However, it is worth mentioning that the overall oxygen concentration for the total amount of oxidants fed to the combustor was somewhat

Table 1
Ultimate analysis, proximate analysis and calorific values of biomass fuels.*

	Miscanthus	Straw	Wood
<i>Proximate (wt%, dry basis, except moisture)</i>			
Moisture (wt%, as received)	3.34	5.22	3.94
Ash	1.80	6.23	0.70
Volatile matter	82.85	76.31	85.11
Fixed carbon	15.37	17.54	14.19
<i>Ultimate (wt%, dry basis)</i>			
Carbon	45.87	43.80	47.18
Hydrogen	6.74	6.78	6.84
Nitrogen	0.38	0.55	0.17
Sulphur	0.19	0.58	0.17
Oxygen (by difference)	46.82	48.29	45.65
Calorific value HHV, MJ/kg [22]	19.10	18.21	19.81

* Fuels are characterised according to the UK/European solid biofuels' standards. In particular, volatile matter is determined at 900 °C.

different from the indicated O₂ concentration in the oxy-fuel oxidant as a small amount of air was always fed to the fuel hopper in order to avoid backfiring. The use of air as the feeder gas instead of an oxy-fuel mixture was resulted from safety concerns, i.e. the failure of the interlock between CO₂ flow and O₂ flow could lead to pure O₂ being fed to the fuel hopper. The 4th row of Table 2 indicates the average O₂/N₂/CO₂ concentration of the all gases fed to the combustor for every condition studied. To investigate the effect of the combustion atmosphere, conventional air combustion experiments were also carried out with all of the investigated biomass fuels. In addition, at least three runs were performed with each biomass fuel for each condition studied, in order to verify the results achieved.

Fig. 2 shows the temperature profiles and the gas product distribution at the outlet of the combustor in a typical experiment (in this case firing miscanthus). Each series of tests was always started with conventional biomass air combustion. After stabilisation, which took about 2 h, the combustion environment was changed from air to oxy-fuel with continuous biomass feeding. After finishing the oxy-fuel tests, the combustion oxidant was switched back to air with continuous biomass feeding operation, minimizing any errors resulted from biomass feeding rate fluctuations between the two combustion environments.

3. Results and discussion

3.1. Effect of combustion atmosphere on fuel combustion and temperature profiles

Fig. 3 shows the temperature profiles along with the height of the combustor under different combustion atmospheres for all fuels. As it can be seen, when using air as oxidant the temperature profile for the non-woody fuels shows a clear maximum located in the splash zone/beginning of the freeboard (T4), above the dense bed, when burned in air. This behaviour happens as a result of the characteristically high volatile matter content of biomass and its release and combustion mostly in the splash zone and freeboard, instead of inside the dense bed as being observed in the case of coal combustion [24]. Other authors reported similar results [25]. The maximum is not that clear in the case of wood as T2 and T4 are quite similar. As the volatile matter contents are similar for all of the studied fuels (Table 1) the differences in the temperature profiles between the woody and the non-woody fuels could be partly due to the difference in the content of fines in the fuels. The fines content of each biomass fuel used in this work was determined by sieving and assuming fines were the particles passing through the sieve with apertures of 3.18 mm. The results obtained showed that wood has significantly less fines content than the non-woody fuels (ca. 4 wt% for wood pellets and ca. 8.5–9.5 wt% for the non-woody biomass pellets), and this implies that a significantly larger fraction of the woody biomass fuel is expected to be burned in the dense bed of the combustor and hence lead to a higher temperatures in that region in comparison to the non-woody biomass fuels. On the other hand, it can also be seen that usually after the temperature peak, a remarkable temperature decrease in the freeboard is observed in all three biomass fuels, due to the fact that the heat extracted by the water cooling probe from the upper part of the freeboard is much higher than the heat released from the combustion of any unburned fuels within the freeboard.

As it can be observed from Figs. 2 and 3, replacing the main combustion air with the oxy-fuel mixture with the same oxygen concentration at 21 vol% caused a significant drop of all temperatures along the reactor and freeboard, with no steady temperature being reached even after one hour of continuous feeding under the same conditions (the arrows in Fig. 3 indicate continuous drop of temperatures). Due to this constant drop in temperatures the steady biomass combustion could no longer be sustained within the reactor and CO and O₂ concentrations increased abruptly, meanwhile NO_x concentration showed a sharp decline (Fig. 2). The main reason for the observed

Table 2
Operating conditions for oxy-fuel and air combustion experiments and average flue gas compositions at steady state for the different conditions studied.

	Air	Oxy-21	Oxy-25	Oxy-30
Excess oxygen coefficient (%)	30	30	30	30
O ₂ in Oxy-fuel mixture (vol%)	–	21	25	30
Average O ₂ /N ₂ /CO ₂ concentration of the all gases fed to the combustor (vol.%)	21/79/0	21/22/57	24/25/52	27/28/45
Feeder air (L/min) ¹	95	95	95	95
Primary air (L/min) ¹	250	–	–	–
Total O ₂ flow (L/min) ¹	72.5	72.5	72.5	72.5
CO ₂ flow (L/min) ¹	–	197.5	157.5	122.5
Total gas flow (L/min) ¹	345	345	305	270
Superficial gas velocity (U) (m/s) ¹	2.56	2.56	2.27	2.01
Fluidization number (U/U _{mf}) ²	8.94	8.90	7.90	7.02
Biomass feed rate (kg/h)	3–5	3–5	3–5	3–5
Static height of bed materials (mm)	250	250	250	250
Average diameter of bed materials (mm)	0.78	0.78	0.78	0.78
Cooling water flow rate (L/min)	1.2 ± 0.2	1.2 ± 0.2	1.2 ± 0.2	1.2 ± 0.2
Wood				
	O ₂ (vol.%)	4.72 ± 0.33	NSV ³	5.49 ± 0.37
	CO ₂ (vol.%)	15.65 ± 0.31	NSV	72.20 ± 2.73
	NOx (ppm)	69.4 ± 8.3	NSV	86.9 ± 5.9
	CO (vol.%)	0.47 ± 0.11	NSV	0.52 ± 0.07
Miscanthus				
	O ₂ (vol.%)	4.70 ± 0.34	NSV	5.03 ± 0.31
	CO ₂ (vol.%)	15.74 ± 0.27	NSV	70.23 ± 2.60
	NOx (ppm)	111.3 ± 13.6	NSV	156.3 ± 19.2
	CO (vol.%)	0.57 ± 0.20	NSV	0.31 ± 0.09
Straw				
	O ₂ (vol.%)	5.03 ± 0.30	NSV	4.97 ± 0.21
	CO ₂ (vol.%)	15.35 ± 0.65	NSV	70.61 ± 2.05
	NOx (ppm)	183.7 ± 15.4	NSV	340.1 ± 0.1
	CO (vol.%)	0.45 ± 0.10	NSV	0.17 ± 0.06

¹ Measured at room temperature (ca.20 °C) and 1 atm.

² Both U and U_{mf} calculated at 800 °C.

³ No Stable Value.

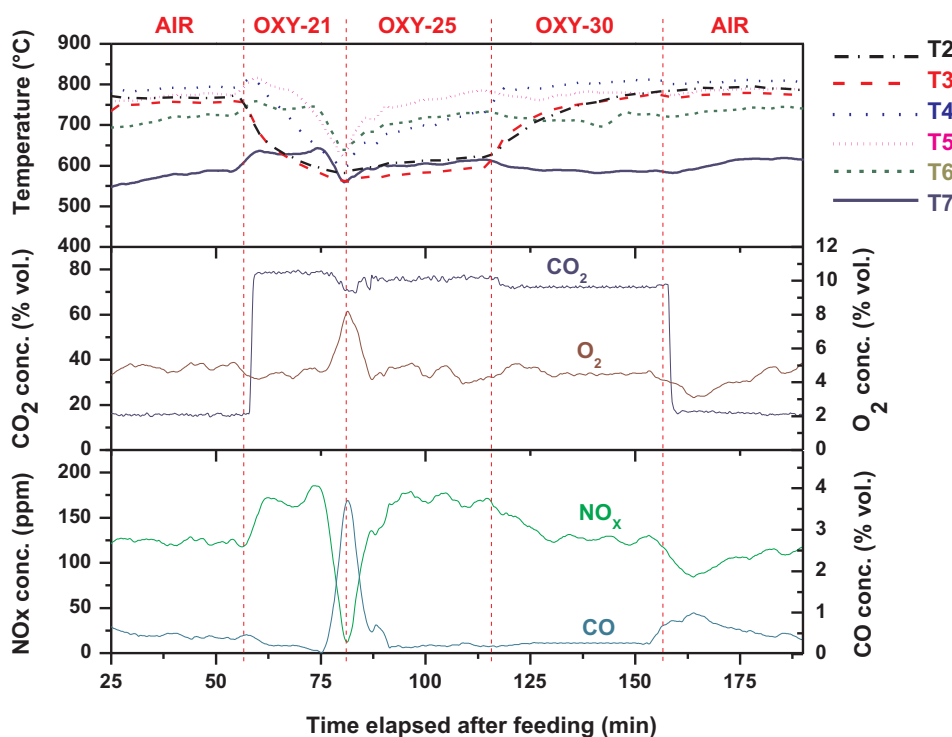


Fig. 2. The temperature profiles, and gas concentrations at the outlet of the combustor during miscanthus pellets combustion under air and oxy-fuel conditions.

temperature decreases is due to the higher specific heat of CO₂ compared with that of nitrogen. It is also mentioned in the literature that CO₂ plays a significant role in reducing the fuel burning rates by limiting the concentration of O and H radicals during oxy-fuel combustion [26]. In order to continue the experiment, the oxygen concentration in the oxy-fuel oxidant gas was increased before the main combustion temperature decreased to about 500–600 °C. By increasing the O₂ concentration from 21 vol% to 25 vol% in the oxy-fuel oxidant gas, a

significant increase in the freeboard temperatures (T5-T7) was noticed for all of the tested fuels, as a consequence of both the increase of the O₂ concentration (which resulted in a higher oxidation rate of the fuel) and the reduction of the CO₂ flow rate, almost matching those temperature values achieved with air combustion and only the temperature values at the beginning of the freeboard (T4) slightly lower than those observed during air combustion (between 30 and 65 °C lower) (Figs. 2 and 3). However, the main bed temperatures (T2 and T3) remained quite low

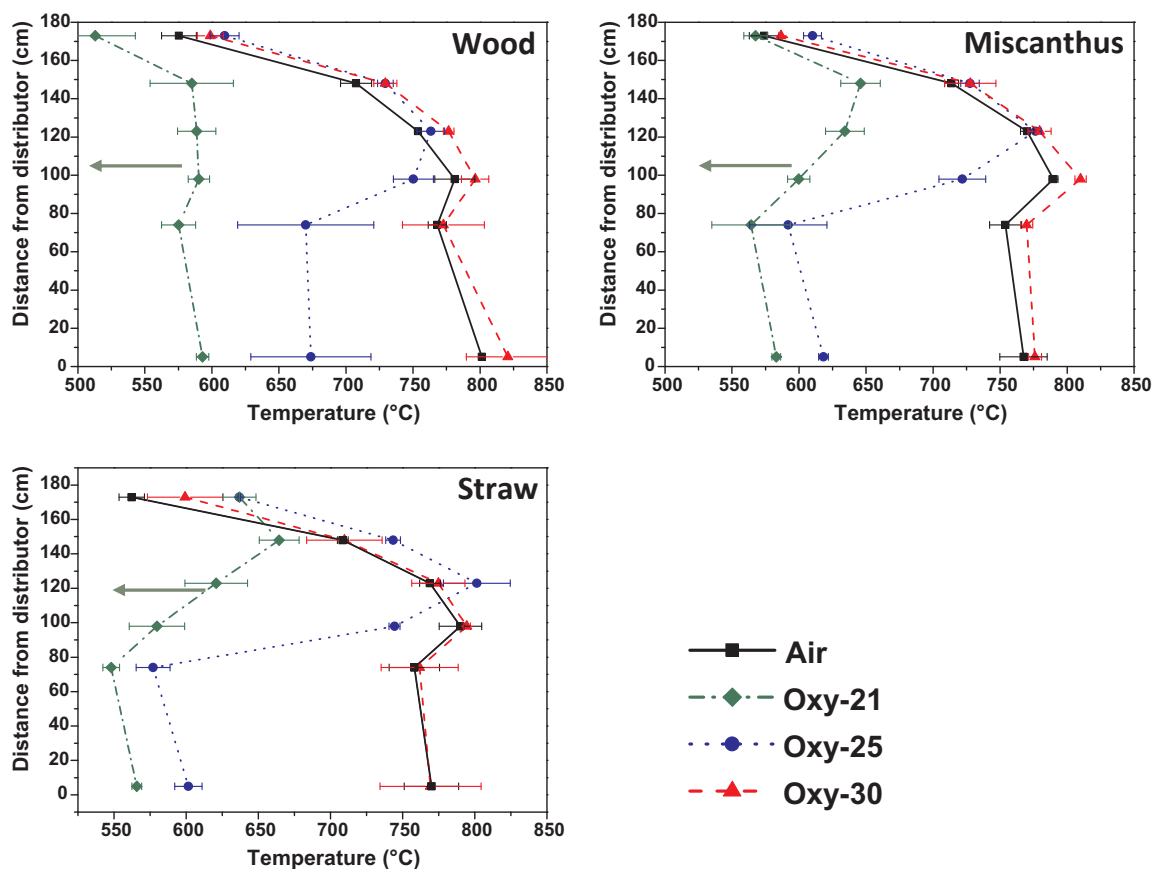


Fig. 3. Temperature profiles for all fuels under air and different oxy-fuel mixtures. The green arrows placed on the left in all graphs indicate continuous drop of temperatures.

and were about 100–200 °C lower than those observed with air combustion. To almost fully match the temperature profile of oxy-fuel combustion to that of air combustion, the oxygen concentration in the oxy-fuel mixture had to be increased to about 30 vol% as it can be seen from Figs. 2 and 3. With 30 vol% O₂ in the oxy-fuel oxidant, the temperatures were seen to be slightly higher than those achieved with air, especially for wood and miscanthus. These results agree with literature which suggest the required O₂ concentration in the oxy-fuel oxidant lies in the range 27–30 vol% [16,27–29].

3.2. Effect of combustion environment on CO emissions

The results of CO emissions from different types of biomass fuels tested under air and oxy-fuel combustion are plotted in Fig. 4. The results are expressed in the amount of emission per energy unit (ng/J). This kind of emission unit is commonly used in oxy-fuel literature as the volumetric flow rate of the flue gas of an oxy-fuel combustion plant with real flue gas recirculation is much lower (up to 80%) than that of conventional air combustion, and thus the conventional emission unit of volumetric concentration (ppm or vol.%) cannot be used for direct comparison of emissions between two combustion environments. As no steady conditions were reached at oxy-21 conditions, CO and NO_x emissions of oxy-21 combustion tests were not going to be compared with those of air combustion and oxy-30 combustion tests both of which had achieved steady-state conditions (Fig. 2). The results of the oxy-25 combustion tests were included for the comparison but it should be noted that these tests were only reached quasi-steady state conditions (Fig. 2). Fig. 4 shows that the switch from air to oxy-25 led a decrease in the CO emission for all the fuels but the reductions in CO emissions were more pronounced with the non-woody biomass fuels. As commented in Section 2.3, the increase of the oxygen concentration from 21 vol% to 25 vol% in the oxy-fuel atmosphere was achieved through

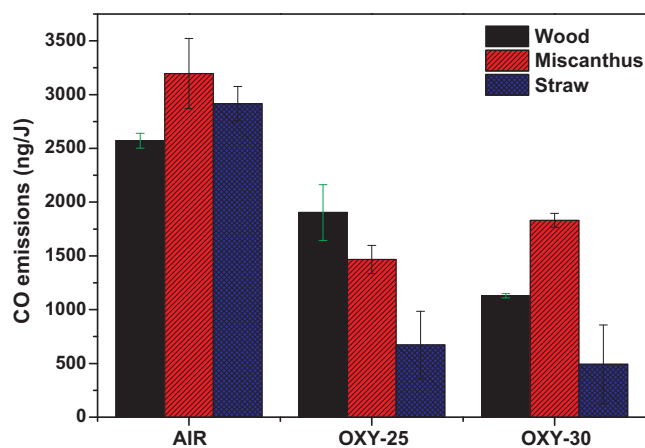


Fig. 4. CO emissions from different types of biomass fuels under air and different oxy-fuel combustion environments.

reducing the CO₂ flow rate while maintaining the O₂ flow rate constant, and this resulted in a lower overall fluidizing gas flow rate than that used with air combustion and hence a longer residence time of the combustible gas in the reactor, benefiting the oxidation of CO with O₂. However, as it can be seen from Figs. 2 and 3, the main bed temperatures (T₂ and T₃) achieved under the oxy-25 combustion conditions were significantly lower than those obtained under the air combustion conditions (between 100 and 200 °C lower as indicated in Section 3.1), due to the aforementioned higher specific heat of CO₂ compared to N₂. The lower bed temperatures meant more incomplete carbon combustion and as a consequence higher CO emissions in the bed zone, agreeing with the trend observed by Duan et al. [16]. The observation

of lower CO emissions with oxy-25 than those of air combustion shown in Fig. 4 further proves that when firing biomass fuels in a FB reactor the main combustion reaction takes place mainly above the dense bed in the splash region and/or at the beginning of the freeboard, while the main bed zone plays a minor role for the combustion of biomass fuels. As shown in Figs. 2 and 3, for each biomass fuel, the gas temperatures in the freeboard with oxy-25 were slightly higher than those achieved with air combustion and this, together with the longer residence time mentioned above, could have led to the lower CO emissions measured at the exit of the cyclone. The reduction in CO emissions when switching from air to oxy-25 was significant in the case of wood (from 2600 to 1900 ng/J, a 26% decrease) and even more pronounced for the non-woody fuels (from 3250 to 1500 ng/J firing miscanthus, a 54% decrease, and from 2900 to 600 ng/J firing straw, a 80% decrease). The difference observed between the woody biomass and the non-woody fuels could partly be due to the difference in the content of fines in the fuels: as the wood has significantly less fines, an important part of the combustion of this fuel should take place in the low-temperature dense bed zone, and hence resulting in higher CO concentrations in the dense bed zone and an overall less reduction in CO emissions when oxy-25 replaces the air combustion.

As it can also be seen from Fig. 4, increasing the O₂ concentration from 25 to 30 vol% resulted in a further decrease in the CO emissions in the case of wood, while CO emissions slightly increased for miscanthus and slightly decreased for straw. When the O₂ concentration in the oxy-fuel oxidant gas reached 30 vol%, the gas temperature profiles in the whole combustor almost completely matched the temperature profiles achieved with air combustion (as seen in Figs. 2 and 3), and hence CO emissions were expected to be lower than those of air combustion and oxy-25 combustion as observed with the oxy-combustion of wood. The trends observed with different fuels could be further complicated by the aforementioned differences in the content of fines in the fuels and by the fact that the oxy-25 combustion tests had only reached quasi-steady state conditions. Wood has a much lower content of fines comparing with the non-woody fuels, which leads to an increase in the importance of the dense bed on the CO chemistry.

3.3. Effect of combustion environment on NO_x emissions

The NO_x emissions from different types of biomass fuels studied under various combustion environments are presented in Fig. 5. Fig. 5 clearly shows that the NO_x emissions' level depends directly on the nitrogen content of the fuel, indicating that NO_x are mainly originated from fuel-N conversions [30]. Prompt-NO_x and thermal-NO_x were not expected to be of importance due to the relatively low combustion temperatures reached at the reactor. It can be seen from Fig. 5 that the

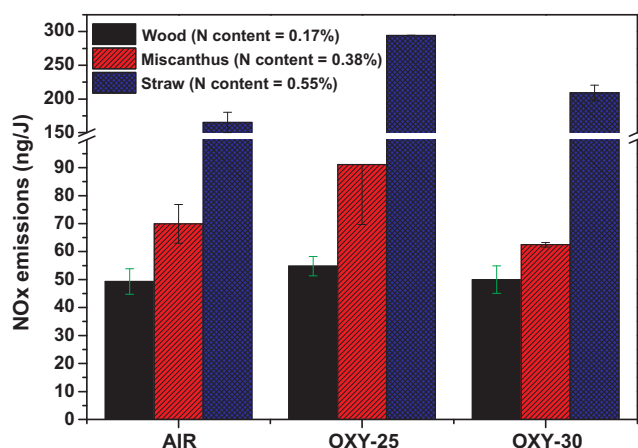
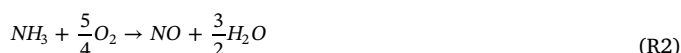


Fig. 5. NO_x emissions from different types of biomass fuels under air and different oxy-fuel combustion environments.

NO_x emissions increased when the combustion environment was switched from air to oxy-25. In order to explain this behaviour it is necessary to briefly review the fuel-NO_x formation mechanism, which can be summarized as follows. As the fuel is fed into the furnace, volatile release takes place. The fuel nitrogen released with the volatiles (volatile-N) further decomposes into NO_x precursors such as cyanide (HCN) and ammonia (NH₃), which are produced mostly from the amino acid containing fuel-N in the pyrolysis process [31]. Furthermore, NH₃ can be regarded as the primary product of fuel-N, directly from pyrolysis or the secondary conversion from HCN through reaction R1 [32–35].



Depending on temperature and oxygen concentration, NH₃ could be partly oxidized to NO (reaction R2) or acts as a reducing agent to reduce NO into N₂ (reaction R3).



In this study, biomass was fed at the bottom of the dense bed zone, right above the distributor plate. Therefore, there were various fuel-rich (or oxygen-depleted) pockets existing in the dense bed zone. Within these fuel-rich pockets, a higher NH₃ concentration would favour NO reduction (reaction R3). At the same time, a large amount of solid fuel particles existed in the dense bed zone, thus enhancing the NO reduction by CO and char via reaction R4 [36]:



As shown in Figs. 2 and 3, the bed temperatures under the oxy-25 combustion conditions were considerably lower than those achieved under the air combustion conditions, whereas the temperatures of the freeboard region, especially the top part of the freeboard, under the oxy-25 combustion conditions were similar to or slightly higher than those under the air combustion conditions. Therefore, more volatiles were combusted in the oxygen-rich freeboard zone under the oxy-25 combustion conditions than under the air combustion conditions, hence favouring the oxidation of volatile-N such as NH₃ and enhancing the formation of NO_x via reaction R2. This explains the higher NO_x emissions found under the oxy-25 combustion conditions. The results obtained here with the biomass fuels disagree with the common trend found in the literature firing coal. NO_x emissions in oxy-coal combustion with low O₂ concentrations (between 21–25 vol%) in the oxidant have been found to be usually lower than those observed with air-firing atmospheres, mainly because of the lower temperatures achieved in the bed region at the oxy-coal conditions [11,37–39]. In the present work, the main bed temperature reached when burning the biomass fuels under the oxy-25 conditions was also lower than that obtained under the air combustion conditions. However, the biomass fuels tested in the present study contain much higher amounts of volatiles (76–85 wt%) than the coals investigated with the previous studies of oxy-coal combustion (5 and 36 wt%) [11,37–39]. The much higher volatile matter contents with the biomass fuels would mean a larger part of each biomass fuel being burned in the high-temperature freeboard zone in comparison to coal, and accentuates again the decrease in the importance of the dense bed on pollutant emissions when firing biomass fuels.

As shown in Fig. 5, the increase in NO_x emissions is more pronounced for fuels with higher fuel-N contents. The increase was seen to be largest for the wheat straw pellet, almost doubling the NO_x emissions value obtained under the air combustion conditions (from 160 ng/J to 300 ng/J approx.). On the other hand, when firing wood the NO_x emissions remained at almost the same value when switching from air to oxy-25. This is not unexpected as the wood pellet fuel contains a very low level of fuel-N which means other NO_x formation routes such as

thermal-NO_x and prompt NO_x can also contribute to the observed NO_x emissions. In addition, the wood pellet fuel has a lower fines content and therefore more fuel combustion and NO_x formation happen in the dense bed region, weakening the difference in NO_x emissions between air combustion and oxy-25 combustion seen with the non-woody biomass fuels.

Switching from oxy-25 to oxy-30 resulted in a significant decrease of the NO_x emissions for the non-woody fuels, leading to similar NO_x emission levels in comparison to the air-fired tests. As it was seen in Section 3.1, switching from oxy-25 to oxy-30 led to an increase of the dense bed zone temperature, matching that achieved under the air combustion conditions. As a result, more volatile-N was released and converted in the dense bed zone which contains many fuel-rich pockets that favour the reduction of NO to N₂ via reaction R3. Furthermore, as explained in Section 2.3, a higher O₂ concentration in the oxidant implies a lower CO₂ flow rate, in order to keep constant overall excess oxygen coefficient to the combustor. The lower CO₂ amount fed to the combustor meant less total oxidant flow to the combustor and therefore less dilution of the gases inside the combustor. Due to this, higher concentrations of NO_x reducing species, especially CO, were expected in the dense bed zone which now has similar temperatures to those of air combustion (Figs. 2 and 3), promoting the heterogeneous reduction of NO_x on the char surfaces, according to reaction R2. Higher O₂ concentrations in the bed zone with oxy-30 could also promote the oxidation of volatile-N to NO_x, hence offsetting the reductions of NO_x by CO, char and other NO_x reducing species. This may partly explain why the NO_x emissions of straw combustion under the oxy-30 condition were found to be slightly higher than those under the air combustion conditions, whereas the opposite trend (i.e. slightly lower) was observed for the miscanthus combustion. A significant portion of the formed CO in the dense bed is burned afterwards in the high-temperature freeboard, leading to lower CO emissions at the outlet of the combustor under the oxy-30 combustion conditions than under the air combustion conditions (Fig. 4). Liu et al. [40] found that the conversion of fuel-N to NO_x for coal combustion in 30 vol% O₂/70 vol% CO₂ was smaller than that for coal combustion in air. They explained this trend in terms of the lower dilution of the gases accomplished when working under the oxy-fuel condition, which increase the concentration of reducing species inside the combustor. Andersson et al. [41] found that the formation of NO from fuel-N in oxy-fuel combustion was the same, or slightly higher, than that under air-firing conditions, whereas the reduction of NO could be up to 50% greater under oxy-combustion conditions. Lupiañez et al. [42] found similar NO_x emissions in both air and oxy-fuel conditions (with O₂/CO₂ ratios of 25/75 and 40/60) in the combustion of lignite in a 90 kW fluidized bed combustor. Díez et al. [43] observed a strong diminution in NO_x emissions when the O₂ concentration in the oxy-fuel oxidant of O₂/CO₂ mixture was increased from 23 vol% to 40 vol% and 60 vol% when firing anthracite in a 90 kW fluidized bed combustor. The authors explained this behaviour in terms of the heterogeneous (char, CaCO₃, CaO) and homogeneous (CO) interactions of the NO_x formed, which can significantly contribute to NO_x reduction in the dense bed zone.

4. Conclusions

Three biomass fuels, one woody and two non-woody, have been tested in a 20 kW_{th} fluidized bed combustor. The effect of combustion atmosphere (air or oxy-fuel) and oxygen concentration in the oxidant under the oxy-fuel combustion conditions on temperature profiles and gas emissions (NO_x and CO) were systematically investigated. The following conclusions can be drawn from the obtained experimental results:

- (1) Replacing the air with an oxy-fuel oxidant comprised of 21 vol% O₂ and 79 vol% CO₂ results in a significant decrease in gas temperatures and ultimately leads to the extinction of the biomass flame

due to the larger specific heat of CO₂ compared to N₂. To keep a similar temperature profile to that achieved under the air combustion conditions, the oxygen concentration in the oxy-fuel oxidant of O₂/CO₂ mixture has to be increased to ca. 30 vol%.

- (2) A drastic decrease in CO emissions can be achieved for all three biomass fuels (up to 80% reduction when firing straw) under oxy-fuel conditions when the oxygen concentration in the oxy-fuel oxidant is 25 vol% or more as a result of the higher residence time of the gas inside the combustor and the freeboard/reactor temperature profile matching that of air combustion.
- (3) NO_x emissions decrease with the oxygen concentration in the oxy-fuel oxidant due to i) the increase of bed temperature, which implies more volatile-N released and converted in the dense bed zone that contains many fuel-rich pockets and ii) the less dilution of the gases inside the dense bed zone, which leads to a higher CO concentration in this region enhancing the reduction of NO_x. Similar NO_x emissions to those obtained with air combustion were found when the biomass fuels were burned in the oxy-fuel oxidant gas containing 30 vol% oxygen.
- (4) The freeboard temperature is the dominant variable influencing both CO and NO_x emissions compared with the influence of bed temperature, especially when firing the non-woody fuels.

Acknowledgment

This work was supported by the UK Engineering and Physical Sciences Research Council [Grant Number EP/M01536X/1].

References

- [1] Zhang WB, Liu H, Sun CG, Drage TC, Snape CE. Capturing CO₂ from ambient air using a polyethyleneimine-silica adsorbent in fluidized beds. *Chem Eng Sci* 2014;116:306–16.
- [2] Lackner KS, Grimes P, Ziock HJ. Carbon dioxide extraction from air: is it an option? Washington, DC (US), NM (US): Coal and Slurry Technology Association, Los Alamos National Lab; 1999.
- [3] Lackner KS, Brennan S, Matter JM, Park AHA, Wright A, van der Zwaan B. The urgency of the development of CO₂ capture from ambient air. *PNAS* 2012;109(33):13156–62.
- [4] IEA. *World Energy Outlook 2016*; 2016.
- [5] Toftegaard MB, Brix J, Jensen PA, Carlborg P, Jensen AD. Oxy-fuel combustion of solid fuels. *Prog Energy Combust Sci* 2010;36(5):581–625.
- [6] Scheffknecht G, Al-Makhdem L, Schnell U, Maier J. Oxy-fuel coal combustion – a review of the current state-of-the-art. *Int J Greenhouse Gas Control* 2011;5:S16–35.
- [7] Wall T, Liu Y, Spero C, Elliott L, Khare S, Rathnam R, et al. An overview on oxyfuel coal combustion—State of the art research and technology development. *Chem Eng Res Des* 2009;87(8):1003–16.
- [8] Croiset E, Thambimuthu K, Palmer A. Coal combustion in O₂/CO₂ mixtures compared with air. *Can J Chem Eng* 2000;78(2):402–7.
- [9] Croiset E, Thambimuthu KV. NO_x and SO₂ emissions from O₂/CO₂ recycle coal combustion. *Fuel* 2001;80(14):2117–21.
- [10] Matheka HI, Oboirien BO, North BC. A review of oxy-fuel combustion in fluidized bed reactors. *Int J Energy Res* 2016;40(7):878–902.
- [11] Duan L, Zhao C, Zhou W, Qu C, Chen X. Effects of operation parameters on NO emission in an oxy-fired CFB combustor. *Fuel Process Technol* 2011;92(3):379–84.
- [12] Singh RI, Kumar R. Current status and experimental investigation of oxy-fired fluidized bed. *Renewable Sustainable Energy Rev* 2016;61:398–420.
- [13] Roy B, Chen LG, Bhattacharya S. Nitrogen oxides, sulfur trioxide, and mercury emissions during oxyfuel fluidized bed combustion of Victorian brown coal. *Environ Sci Technol* 2014;48(24):14844–50.
- [14] Hofbauer G, Beisheim T, Dieter H, Scheffknecht G. Experiences from oxy-fuel combustion of bituminous coal in a 150 kW_{th} circulating fluidized bed pilot facility. In: Rokke NA, Svendsen H, editors. 7th Trondheim Conference on CO₂ capture, transport and storage. Amsterdam: Elsevier Science Bv; 2014. p. 24–30.
- [15] de las Obras-Loscertales M, Mendiara T, Rufas A, de Diego LF, García-Labiano F, Gayán P, et al. NO and N₂O emissions in oxy-fuel combustion of coal in a bubbling fluidized bed combustor. *Fuel* 2015;150:146–53.
- [16] Duan LB, Zhao CS, Zhou W, Qu CR, Chen XP. O₂/CO₂ coal combustion characteristics in a 50 kW_{th} circulating fluidized bed. *Int J Greenhouse Gas Control* 2011;5(4):770–6.
- [17] Jia L, Tan Y, Anthony EJ. Emissions of SO₂ and NO_x during oxy-fuel CFB combustion tests in a mini-circulating fluidized bed combustion reactor. *Energy Fuels* 2010;24:910–5.
- [18] Saidur R, Abdelaziz EA, Demirbas A, Hossain MS, Mekhilef S. A review on biomass as a fuel for boilers. *Renewable Sustainable Energy Rev* 2011;15(5):2262–89.
- [19] Jenkins BM, Baxter LL, Miles TR, Miles TR. Combustion properties of biomass. *Fuel*

- Process Technol 1998;54(1–3):17–46.
- [20] Niu YQ, Tan HZ, Hui SE. Ash-related issues during biomass combustion: alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. *Prog Energy Combust Sci* 2016;52:1–61.
- [21] Duan LB, Duan YQ, Zhao CS, Anthony EJ. NO emission during co-firing coal and biomass in an oxy-fuel circulating fluidized bed combustor. *Fuel* 2015;150:8–13.
- [22] Channiwala S, Parikh P. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 2002;81(8):1051–63.
- [23] <http://www.aggregate.com/documents/tds/dried-silica-sand-filler-14-25-tds.pdf>.
- [24] Tarelho LAC, Matos MAA, Pereira F. Axial and radial CO concentration profiles in an atmospheric bubbling FB combustor. *Fuel* 2005;84(9):1128–35.
- [25] Kumar R, Singh RI. An investigation in 20 kW_{th} oxygen-enriched bubbling fluidized bed combustor using coal and biomass. *Fuel Process Technol* 2016;148:256–68.
- [26] Molina A, Shaddix CR. Ignition and devolatilization of pulverized bituminous coal particles during oxygen/carbon dioxide coal combustion. *Proc Combust Inst* 2007;31(2):1905–12.
- [27] Pickard SC, Daood SS, Pourkashanian M, Nimmo W. Co-firing coal with biomass in oxygen- and carbon dioxide-enriched atmospheres for CCS applications. *Fuel* 2014;137:185–92.
- [28] Liu H, Zailani R, Gibbs BM. Comparisons of pulverized coal combustion in air and in mixtures of O₂/CO₂. *Fuel* 2005;84(7):833–40.
- [29] Tan Y, Croiset E, Douglas MA, Thambimuthu KV. Combustion characteristics of coal in a mixture of oxygen and recycled flue gas. *Fuel* 2006;85(4):507–12.
- [30] Winter F. Formation and reduction of pollutants in cfbc: from heavy metals, particulates, alkali, NOx, N₂O, SOx, HCl. In: Yue G, Zhang H, Zhao C, Luo Z, editors. *Proceedings of the 20th international conference on fluidized bed combustion*. Berlin, Heidelberg: Springer, Berlin Heidelberg; 2010, p. 43–8.
- [31] Ren QQ, Zhao CS, Chen XP, Duan LB, Li YJ, Ma CY. NOx and N₂O precursors (NH₃ and HCN) from biomass pyrolysis: Co-pyrolysis of amino acids and cellulose, hemicellulose and lignin. *Proc Combust Inst* 2011;33:1715–22.
- [32] Liu H, Gibbs BM. Modelling of NO and N₂O emissions from biomass-fired circulating fluidized bed combustors. *Fuel* 2002;81(3):271–80.
- [33] Shimizu T, Toyono M, Ohsawa H. Emissions of NOx and N₂O during co-combustion of dried sewage sludge with coal in a bubbling fluidized bed combustor. *Fuel* 2007;86(7–8):957–64.
- [34] Kouprianov VI, Permchart W. Emissions from a conical FBC fired with a biomass fuel. *Appl Energy* 2003;74(3):383–92.
- [35] Glarborg P, Jensen AD, Johnsson JE. Fuel nitrogen conversion in solid fuel fired systems. *Prog Energy Combust Sci* 2003;29(2):89–113.
- [36] Aarna I, Suuberg EM. The role of carbon monoxide in the NO-carbon reaction. *Energy Fuels* 1999;13(6):1145–53.
- [37] Jia L, Tan Y, McCalden D, Wu Y, He I, Symonds R, et al. Commissioning of a 0.8 MW_{th} CFBC for oxy-fuel combustion. *Int J Greenhouse Gas Control* 2012;7:240–3.
- [38] Czakiert T, Bis Z, Muskala W, Nowak W. Fuel conversion from oxy-fuel combustion in a circulating fluidized bed. *Fuel Process Technol* 2006;87(6):531–8.
- [39] Duan LB, Sun HC, Zhao CS, Zhou W, Chen XP. Coal combustion characteristics on an oxy-fuel circulating fluidized bed combustor with warm flue gas recycle. *Fuel* 2014;127:47–51.
- [40] Liu H, Zailani R, Gibbs BM. Comparisons of pulverized coal combustion in air and in mixtures of O₂/CO₂. *Fuel* 2005;84(7–8):833–40.
- [41] Andersson K, Normann F, Johnsson F, Leckner B. NO emission during oxy-fuel combustion of lignite. *Ind Eng Chem Res* 2008;47(6):1835–45.
- [42] Lupianez C, Guedea I, Bolea I, Díez LI, Romeo LM. Experimental study of SO₂ and NOx emissions in fluidized bed oxy-fuel combustion. *Fuel Process Technol* 2013;106:587–94.
- [43] Díez LI, Lupiáñez C, Guedea I, Bolea I, Romeo LM. Anthracite oxy-combustion characteristics in a 90 kW_{th} fluidized bed reactor. *Fuel Process Technol* 2015;139:196–203.