



## Co-combustion of cereal co-product (CCP) with a UK coal (Daw Mill): Combustion gas composition and deposition



T. Hussain\*, A.H.M. Khodier, N.J. Simms

Centre for Energy & Resource Technology, Cranfield University, Bedfordshire MK43 0AL, UK

### HIGHLIGHTS

- ▶ Pilot scale co-firing experiments were performed using CCP with Daw Mill Coal at levels of 0, 20, 40, 60, 80 and 100 wt.%.
- ▶ Increasing the share of CCP in the fuel mixes resulted in a reduction of SO<sub>x</sub> and HCl but no significant change in NO<sub>x</sub>.
- ▶ Increasing the levels of CCP in the fuel mixes showed a decreasing trend in deposition fluxes.
- ▶ With increasing levels of CCP co-firing the levels of K, S, P increased and Al, Fe, Ti decreased in the deposits.
- ▶ Alkali chlorides were only found (on all three probes) when the CCP was fired without any coal addition.

### ARTICLE INFO

#### Article history:

Received 30 September 2012

Received in revised form 12 December 2012

Accepted 2 January 2013

Available online 25 January 2013

#### Keywords:

Biomass  
Co-firing  
Emissions  
Superheater  
Deposition  
CCP

### ABSTRACT

This paper presents an investigation into combustion gas composition and deposit formation obtained by co-firing mixtures of cereal co-product (CCP) with a UK coal (Daw Mill) in a 100 kW<sub>th</sub> pilot-scale pulverised fuel (PF) combustion test rig operating at a feed rate of ~7.5–11.2 kg/h. The biomass additions to the coal were at 0, 20, 40, 60, 80 and 100 wt.%. A high resolution multi-component Fourier Transform Infra-Red (FTIR) gas analyser was used to monitor the combustion gas stream for CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, CO, NO, NO<sub>2</sub>, N<sub>2</sub>O and HCl. It was observed that increasing the share of CCP in the fuel mixtures resulted in a reduction of SO<sub>x</sub> and HCl, due to the lower sulphur and chlorine contents of the biomass. Deposit formation in co-firing conditions was also studied on air-cooled probes (with surface temperatures of ~500, 600 and 700 °C) to simulate the superheater/reheater surface conditions in a conventional pulverised fuel boiler. The deposition flux on the upstream, sidestream and downstream of the probes were measured. The deposition flux on the upstream surfaces showed a decrease with an increasing biomass content in the fuel. Environmental scanning electron microscopy (ESEM) with energy dispersive X-ray (EDX) analysis and X-ray diffraction (XRD) were used to characterise the deposits. Chlorine was found in all three probes when the CCP was fired without any coal addition, suggesting formation of alkali chlorides through condensation on cooler surfaces (also confirmed by XRD analysis). The study highlights the complex relationship between the fuel mixtures and compositions of the combustion gas streams, as well as deposition fluxes and deposit compositions.

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### 1. Introduction

CO<sub>2</sub> emissions from conventional fossil fuel power stations contribute to around one third of the total CO<sub>2</sub> emissions from the UK and the CO<sub>2</sub> emissions account for 85% of the UK greenhouse gas (GHG) emissions [1]. The UK government has an ambitious target of reducing CO<sub>2</sub> emissions to 80% of their 1990 levels by 2050 [1]. To meet this target renewable fuels such as biomass and carbon capture and storage (CCS) technologies will play significant roles. Co-firing biomass with coal is a near term option to reduce

CO<sub>2</sub> emissions from the utility boilers and to increase the energy output from renewable sources [2,3]. Biomass is a major contributor to renewable energy, currently accounting for approximately 70% of worldwide renewable energy production [4,5]. Biomass is classed as carbon neutral when used as a fuel (alone or co-fired with coal) [1]. Co-firing reduces the net CO<sub>2</sub> emissions when the biomass is used in a sustainable fashion. Co-firing biomass with coal is still amongst the cheaper alternatives that electricity utilities have for reducing net CO<sub>2</sub> emissions [6,7].

Biomass, such as wood, has low levels of volatile inorganic elements, such as K, Cl and S, but it is costly to use as a fuel [8]. Herbaceous biomass (e.g., straw, grassy energy crops) has higher levels of elements, such as K and Cl, but much less S compared

\* Corresponding author. Tel.: +44 1234750111.

E-mail address: [t.hussain@cranfield.ac.uk](mailto:t.hussain@cranfield.ac.uk) (T. Hussain).

to most coals [9–12]. Co-firing of coal with biomass has the potential to create deposition problems because of the differences in the inorganic composition (high alkali levels) and mode of occurrence of inorganic species (mostly mobile forms) in biomass compared to coals [2,13,14]. The future of co-firing or even dedicated biomass firing for electricity production depends, in part, on the deposition characteristic. Depositions on heat exchangers surfaces (superheaters/reheaters) can have significant impact on boiler operations, overall efficiencies and corrosion of heat exchanger materials. A vast literature exists on deposition characteristics of coal; however limited data are available on the deposition characteristics of biomass fuels [2]. The gaseous emissions are also of concerns to the power generation industry due to strict environmental legislations. Major polluting species in the emissions, such as SO<sub>x</sub>, are directly related to the S content in the fuels, but NO<sub>x</sub> emissions depend on combustion environments as well as the fuel compositions [15]. It is difficult to predict the levels of gaseous emissions from co-firing of biomass with coal.

Co-firing low levels of biomass (5–10%) in conventional pulverised coal-fired power plants has proved to be a successful way to introduce carbon neutral biomass fuels into the electricity generation market to meet national and EU legislation. However, there is pressure to use more biomass for power generation, either through significantly increasing the levels in co-firing or by using pure biomass firing. Lower levels of biomass co-firing have been achieved with relatively minor modifications to the existing plants; however, higher levels of co-firing are more difficult to adopt due to operational issues, e.g.: control of feeding two different fuels, stability of combustion, changes to ash chemistry, changes to deposition (fouling/slagging) and reduced reliability of key high temperature components [16]. As many old pulverised coal fired power plants in the EU are due to close in the near future (by 2015) after being opted out of the Large Combustion Plant Directive (LCPD), there is an intense interest in the EU in converting existing facilities to fire biomass. Research programmes sponsored by the UK government and the power generating companies are actively investigating the possibility of firing, as much as 100%, biomass in the existing pulverised fuel boilers. Co-firing a range of fuel blends in pilot scale experiments can provide a useful way to study the potential fuel mixtures for industrial scale operations.

This paper reports the results of the pilot scale (100 kW<sub>th</sub>) co-firing experiments of cereal co-product (CCP) with the Daw Mill Coal at levels of 0, 20, 40, 60, 80 and 100 wt.%. Emissions from the combustion of these blends of pulverised fuels were measured using a Fourier Transform Infra-Red (FTIR) gas analyser. Air-cooled probes were inserted into the combustion rig and maintained at surface temperatures of ~500, 600 and 700 °C (to simulate superheater/reheater surfaces) to study the deposition behaviour of the fuel blends. The deposition fluxes on the upstream, sidestream and downstream of the probes were measured and the deposits were characterised in an ESEM with EDX analysis. Thermodynamic equilibrium modelling was also performed to predict the species in the deposits and in the combustion environment.

## 2. Experimental procedure

### 2.1. Fuel characteristics

The Daw Mill Coal and cereal co-product (CCP) used in this study were supplied by E.ON New Build and Technology Ltd. (Power Technology Centre, Ratcliffe-on-Soar, Nottingham, UK). Daw Mill is a common UK power station fuel and around 6% of the UK power generation (energy basis) is produced from it. CCP was chosen based on the current interest from the UK power stations and its availability as a world traded biomass product. Both

the Daw Mill Coal and the CCP were sourced in a pulverised form for these tests. CCP samples were sieved to <2 mm size, with an average size of 0.5 mm, to remove any lumps before blending in a mixer with the coal samples. A consistent fuel feeding rate was applied for the duration of each run. Constant fuel feed rates of ~7.4, 8.1, 8.9, 9.9, 11.2 and 9.2 kg/h were fed through the pulverised fuel combustor with CCP addition of 0, 20, 40, 60, 80 and 100 wt.% respectively. Table 1 shows the proximate, ultimate and ashed analyses of both CCP and Daw Mill Coal. CCP contains more moisture and volatile matter than Daw Mill Coal and has a lower calorific value. Ultimate analyses of the fuels show that CCP contains less carbon but more oxygen compared to Daw Mill Coal. Also, CCP has a lower amount of sulphur than Daw Mill Coal but similar chlorine content.

### 2.2. Pilot scale experimental setup

The experiments were conducted in a pilot-scale combustion rig (located in the Centre for Energy and Resource Technology, Cranfield University) with a capacity of 100 kW<sub>th</sub>. The pilot-scale rig contains a downward firing pulverised fuel burner. A schematic diagram of the pulverised fuel combustion rig is shown in Fig. 1. The rig has a number of ports for temperature measurements, gas analysis, fly ash sampling and collection of deposits on air-cooled probes. Air-cooled deposition probes were located in the path of the combustion gases in the vertical section of the combustor. The temperature around the deposition probes were measured using R type thermocouples (housed in ceramic sheaths). The combustion gas temperatures around the deposition probes were ~820–900 °C and typical gas velocity in the combustion chamber, which has a dimension of 300 × 300 mm, was ~1.6 m/s (at fuel feed rate of ~7.5 kg/h and air flow rate of 1730 L/min). The pulverised fuel combustor operates in the fuel feed rate of 7–15 kg/h. The fuel feeding system consisted of a fuel hopper attached to a speed controlled shaker device and a pneumatic delivery system operating at a constant nitrogen flow rate of 30 L/min. The shaker unit

**Table 1**  
Characterisation of elements (wt.%) on as received basis of CCP and Daw Mill Coal.

	CCP	Daw Mill Coal
<i>Proximate analysis (wt.%, AR)</i>		
Moisture	8.10	4.60
Ash	4.20	4.20
Volatile matter	70.80	31.30
<i>Calorific value (kJ/kg)</i>		
Gross calorific value	17,610	25,260
Net calorific value	16,340	24,107
<i>Ultimate analysis (wt.%, AR)</i>		
Carbon	43.30	74.15
Hydrogen	5.80	4.38
Nitrogen	2.70	1.17
Oxygen	35.57	10.49
Sulphur	0.16	1.28
Chlorine	0.17	0.20
<i>Ash composition (wt.%, of total ash)</i>		
SiO <sub>2</sub>	44.36	36.80
Al <sub>2</sub> O <sub>3</sub>	2.79	23.90
Fe <sub>2</sub> O <sub>3</sub>	2.47	11.20
TiO <sub>2</sub>	0.12	1.10
CaO	7.78	12.00
MgO	3.96	2.50
Na <sub>2</sub> O	0.36	1.50
K <sub>2</sub> O	24.72	0.50
Mn <sub>3</sub> O <sub>4</sub>	0.10	0.40
P <sub>2</sub> O <sub>5</sub>	12.04	–
SO <sub>3</sub>	–	–
BaO	0.05	–

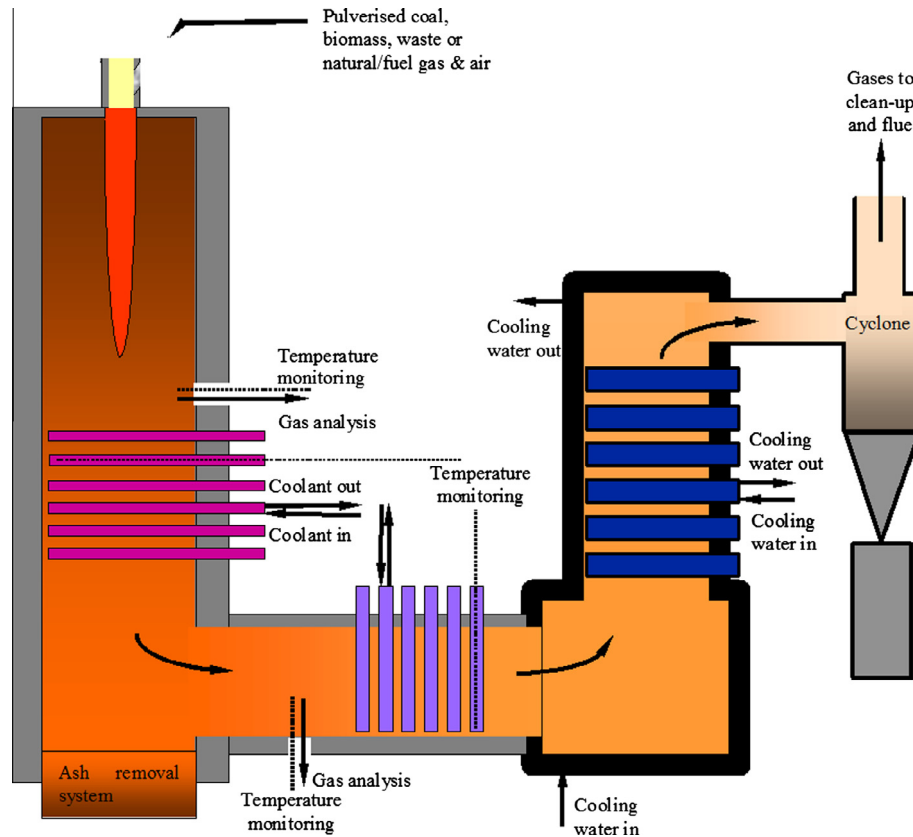


Fig. 1. A schematic diagram of the pilot-scale (100 kW<sub>th</sub>) pulverised fuel combustion rig facility at Cranfield University.

agitates the fuels to prevent slumping, bridging and agglomeration of materials.

The combustor uses a multi-fuel excess air burner to ensure complete combustion. Air is preheated before introducing to the combustion chamber. The test rig was heated up using natural gas firing before switching to the pulverised fuels. The flue gases pass through a water-cooled heat exchanger assembly before entering a cyclone for any particle removal. Then the flue gases pass through a fan and go to the stack. The rig was run at negative pressure to prevent any combustion gases escaping into the combustion hall. A more detailed description have been provided by Khodier et al. [15,17]. Online monitoring of temperatures at various sections of the rigs were performed using a number of thermocouples and infra-red pyrometers.

### 2.3. Flue gas and deposit analysis

Online measurements of CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, CO, NO, NO<sub>2</sub>, N<sub>2</sub>O and HCl in the combustion gas stream were conducted using a high resolution multi-component Fourier Transform Infra-Red (FTIR) device (Protea-Protir 240M Mobile FTIR Analyser, Protea Ltd., Cheshire, UK). The analyser was fitted with an integral sampling control system and linked to a sampling port located on the side of the rig by a trace heated sampling line. The FTIR has pre-loaded calibration methods for 28 gas species and contains an on-board electrochemical (integrated zirconia or Lambda sensor) oxygen sensor which allowed the monitoring of oxygen levels in parallel with the main combustion gas results and provide a system with the ability to correct for oxygen content.

Deposits were collected using ceramic sections in air-cooled probes that were inserted horizontally into the side of the rig across the flow of the combustion gas stream. The surface temperatures of the probes were maintained at ~700, 600 and 500 °C

(to simulate the surface temperatures of superheaters/reheaters in co-fired boilers) using a flow of compressed air through the centre of the probes. The surface temperatures of the probes were monitored using thermocouples. The compressed air supply was adjusted throughout the tests to maintain constant surface temperatures. A more detailed description of the probe geometry and functions can be found in the Ref. [17]. To examine the deposits collected on the ceramic sections, the surfaces of these sections were divided into three areas. These areas represented the upstream, sidestream and downstream surfaces of the probes; referred to as top, side and underside deposits. At the end of the test runs the deposits were weighed and deposition fluxes calculated by dividing the deposit weight by the surface area and the time of exposure. The compositions of the deposits were examined using Environmental Scanning Electron Microscope (ESEM) equipped with Energy Dispersive X-ray (EDX) analysis, and X-ray Diffraction (XRD) analysis.

### 2.4. Mathematical modelling

Thermodynamic modelling was carried out using MTDATA (National Physical Laboratory, Teddington, London, UK) in its “multi-phase” module with SGTE (Scientific Group Thermodynamic Europe) database. A detailed description of the method has been published previously [17,18]. MTDATA [19] was used to model the fate of the trace elements present in the fuel mixtures in terms of their partitioning between the gas phase species and condensed species as the combustion gas stream is cooled (i.e., the vapour condensation route for heat exchanger deposit formation). During the modelling 15 elements (C, H, N, O, S, Cl, Fe, Ca, Mg, K, Na, Ti, Ba, Mn and P) were considered. Al and Si were omitted from the calculations as it was previously suggested that they are present in fuels in forms which are largely un-reacted in the combustion environment due to kinetic factors [20]. Thermody-

dynamic modelling was performed for each fuel mixtures described in the experimental section to complement the experimental results.

### 3. Results and discussion

#### 3.1. Effect of co-firing on gaseous emissions

Fig. 2a shows emission profiles of major gaseous species and Fig. 2b shows emission profiles of minor gaseous species from combustion of a mixture of CCP: Daw Mill Coal (40:60) wt.% for ~3 h. The oxygen content of the combustion gas stream was targeted to be at ~4 vol.% with the air/fuel ratio adjusted accordingly. The moisture content of the combustion gas stream was relatively stable but the CO<sub>2</sub> content varied in line with the change in O<sub>2</sub> content (i.e. a spike in oxygen corresponds to a drop in CO<sub>2</sub> levels and indicates a disruption in the fuel feeding). Emission profiles of the minor gaseous species also show stable values over test duration of ~3 h with occasional variations.

##### 3.1.1. Major gaseous species

The mean values of the major gaseous species (CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub>), with the standard deviations as error bars, produced by the

combustion co-firing CCP at 0, 20, 40, 60, 80 and 100 wt.% are shown in Fig. 3a. All the emission levels have been normalised to 6 vol.% oxygen for ease of comparison (also in line with EU standards on emissions from utility sector). The CO<sub>2</sub> emissions showed a decreasing trend with increasing quantity of CCP in the fuel mix. Ultimate analysis of the fuels showed that CCP has ~43 wt.% carbon and Daw Mill Coal has ~74 wt.% carbon, i.e. Daw Mill Coal is richer in carbon than CCP. Therefore, as the quantity of biomass increased in the fuel mix the CO<sub>2</sub> emissions decreased. The H<sub>2</sub>O content in the combustion gas stream also increased as the amount of CCP increased in the fuel mixes. Table 1 shows that the moisture content of the as received CCP was approximately twice the amount of moisture in the Daw Mill Coal and H/C ratio is higher for CCP than the Daw Mill Coal. Therefore, increasing the percentages of CCP co-firing will result in an increase in H<sub>2</sub>O content in the combustion gas stream.

##### 3.1.2. Minor gaseous species

Fig. 3b shows the mean values of minor gaseous species (CO, NO, NO<sub>2</sub>, N<sub>2</sub>O, SO<sub>2</sub> and HCl) which were adjusted to 6 vol.% oxygen in the combustion gas stream, with standard deviation as error bars, produced by the combustion of co-firing CCP at 0, 20, 40, 60, 80 and 100 wt.%. Under the test conditions, low levels of CO were measured in the flue gases indicating relatively high combus-

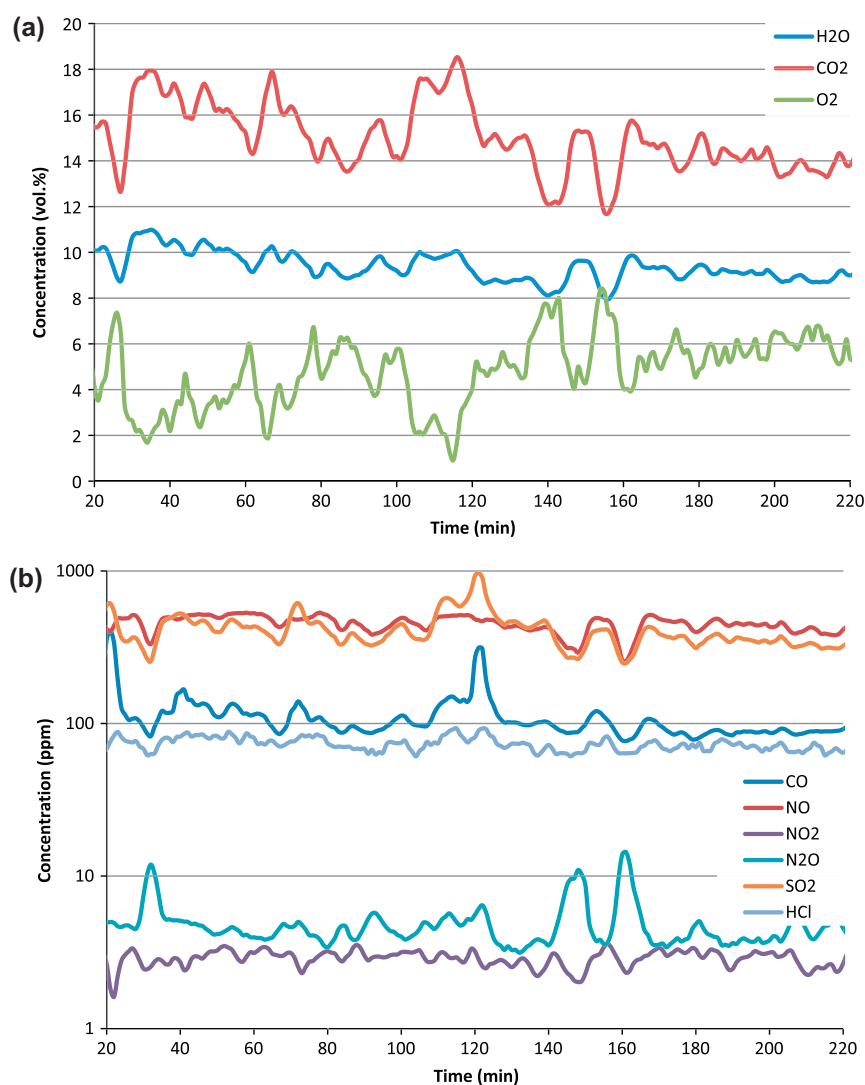


Fig. 2. Online FTIR measurements of (a) major gaseous species and (b) minor gaseous species from combustion of CCP: Daw Mill Coal (40:60) wt.%.

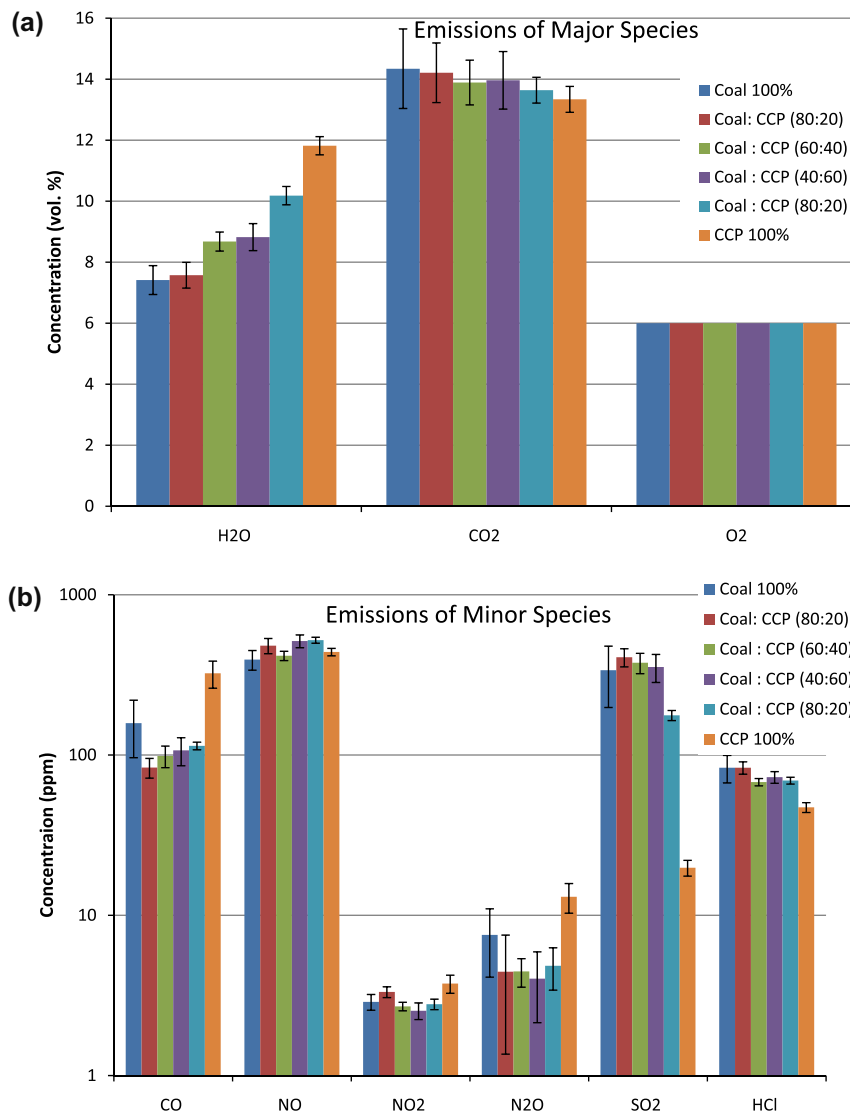


Fig. 3. (a) Major gaseous species and (b) minor gaseous species emissions from combustion of various levels of CCP with Daw Mill Coal (adjusted to 6 vol.% O<sub>2</sub>).

tion efficiency, in other words most of the carbon in the fuels was converted to CO<sub>2</sub>. CO emissions from the combustion of 100% CCP was the highest of all the fuel mixes and the CO levels arising from co-firing in all cases were lower than the pure fuels. A similar trend is also seen in the emissions of N<sub>2</sub>O. NO<sub>x</sub> emissions (NO and NO<sub>2</sub>) from increasing percentages of CCP in the fuel mixes did not show any significant changes. However, in a previous study using Daw Mill Coal with miscanthus it was reported that increasing the miscanthus percentages in the fuel mixes resulted in a reduction of NO<sub>x</sub> (miscanthus contains less nitrogen than Daw Mill Coal) [18]. Although, biomass addition to the coal contributes to NO<sub>x</sub> reduction due to its high content of volatile matter [16,21], this is very much fuel dependent. Unlike SO<sub>x</sub> emissions which are directly related to the S content of the fuels, NO<sub>x</sub> emission levels depend on the combustion temperature as well as the fuel compositions [22,23]. It should be noted that CCP contained more nitrogen than the Daw Mill Coal (on as received basis Table 1).

The SO<sub>2</sub> concentration was the highest (taking into consideration the error bars) when 100% Daw Mill Coal was fired and with increasing the percentages of CCP in the fuel mixes the SO<sub>2</sub> concentration decreased. Typically, biomass contains less sulphur than coal and thus co-firing of biomass with coal is expected to produce less SO<sub>2</sub> [24]. The SO<sub>2</sub> levels from the combustion of 100% CCP

were ~15 times less than emissions from the combustion of 100% Daw Mill Coal.

The levels of HCl also decreased with increasing the percentage of CCP in the fuel blends. In all cases, the amount of HCl in the combustion stream was less than 100 ppm. The ultimate analysis of the fuels (Table 1) shows that CCP contains only a little less chlorine than Daw Mill Coal, however this resulted in a detectable change in HCl emissions in the combustion stream.

### 3.2. Effect of co-firing on deposition

#### 3.2.1. Deposit characterisation

Fig. 4 shows images of the deposits collected on the coolest probe, which was maintained at ~500 °C. The deposits were collected for ~3 h of exposure at Daw Mill Coal: CCP co-firing: 0, 20, 40, 60, 80 and 100 wt.%. The amount of deposit collected from the combustion of 100% CCP showed an increase in quantity and reduced contrast (the dark colour of the particles is not due to unburnt carbon; the carbon content of the deposits were very low in EDX analyses). The high alkali content of CCP resulted in stickier particles and softer deposits, which increased the probability that particles hitting the deposits will stick [2]. Alkali species have low melting points when not chemically combined with other



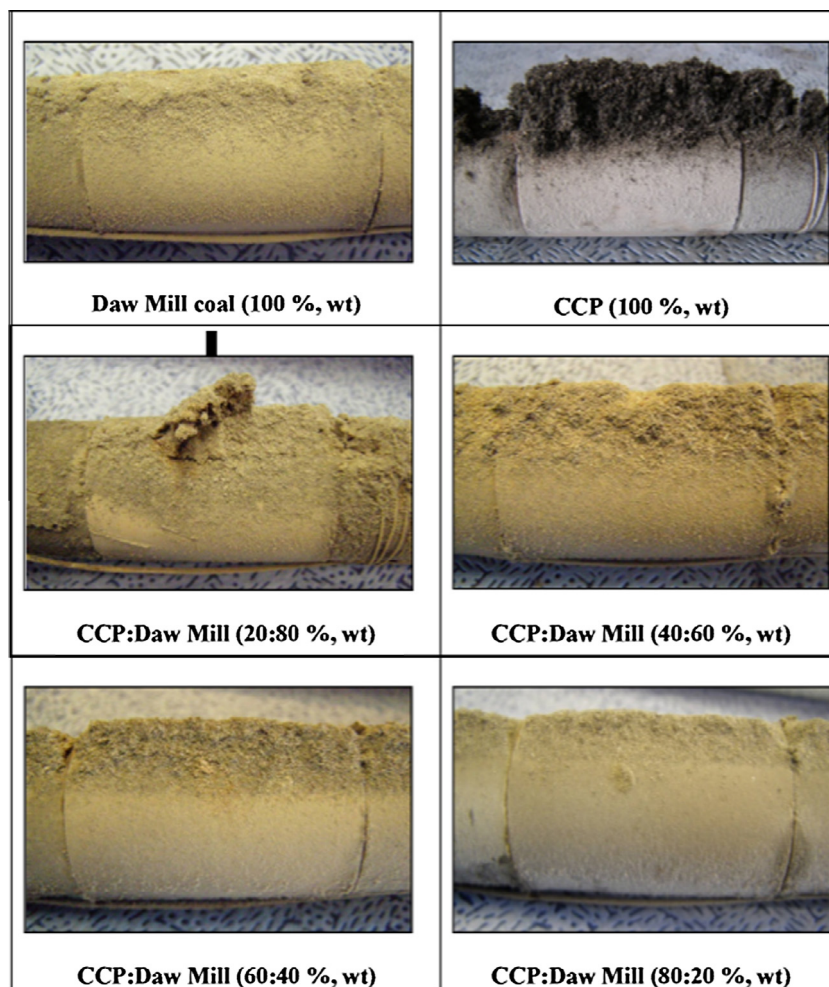


Fig. 4. Images of deposits formed on probe with a surface temperature of 500 °C from co-firing various fuel mixtures.

elements and lower the melting point of silica-based materials. The proximate analysis of the fuels showed that the ashed contents of both the fuels were similar; however, the amount of deposits collected on the probe from 100 wt.% CCP combustion was significantly more.

The deposits were examined in an ESEM and Fig. 5 shows the images of deposits from the upstream surfaces of the coolest probe (at ~500 °C) from co-firing various fuel mixtures. The deposits from unblended fuels show particle sizes in the range of ~200–300 μm. Particles in the deposits had well defined shapes and their shapes were also observed in the deposits from CCP: Daw Mill (20:80). However, with increasing levels of CCP co-firing the distinctive shapes of the particles became less obvious. The deposits from co-firing of CCP at levels of 40, 60 and 80 were finer. Blending CCP with Daw Mill Coal resulted in a deposit with finer ash particles. Larger particles increase the impaction rates because inertial impaction efficiencies on probes depend on the square of the particle diameter (assuming same density) [13]. The formation of deposits on heat exchanger surfaces are a result of physical and chemical processes, and can involve up to five mechanisms: direct inertial impaction, condensation, thermophoresis, eddy impaction and chemical reactions [13]. Deposits formed in the path of the flue gas (upstream surfaces) are dominated by inertial impaction of larger particles (Fig. 5). For comparison, ESEM images of the deposits formed on the downstream (bottom) surfaces are shown in Fig. 6. In general, deposits formed on the downstream surface were finer, especially when CCP co-firing levels were above 20 wt.%. Deposits

on the downstream surfaces are dominated by vapour phase condensation and eddy impaction of smaller particles [25,26].

### 3.2.2. Deposition flux

Deposition flux is a useful parameter for assessing overall fouling potential of a fuel. The rate of deposit build up is defined by the amount of deposit collected per unit surface area of the probe per unit time. Fig. 7 shows the deposition fluxes for all three probes, which were kept at ~500, 600 and 700 °C, along with the location of the deposits (i.e., top, side and underside). At all three temperatures, deposition fluxes on the top surfaces of the probes were much higher than the deposition fluxes on the side and underside surfaces (note the logarithmic axis). The main mechanism for deposition on the top surfaces is inertial impaction which results in higher deposition fluxes compared to other mechanisms (i.e. thermophoresis, condensation, etc.). There was no distinctive difference between the side and underside surfaces of the deposits from deposition flux point (except, at the highest temperature, ~700 °C, in few cases there were no underside deposits). Deposition fluxes on the top surfaces of ~500 and 600 °C probes showed that the amount of deposition from firing 100 wt.% CCP was higher than deposition flux from firing 100% Daw Mill Coal. When the fuels were blended a trend emerged in the deposition fluxes. In all the top surface probes, increasing the levels of CCP co-firing showed a decreasing trend in deposition fluxes. This trend in decreasing deposition rate also corresponds to finer deposits on the top and side surfaces of the probes. The lowest deposition flux

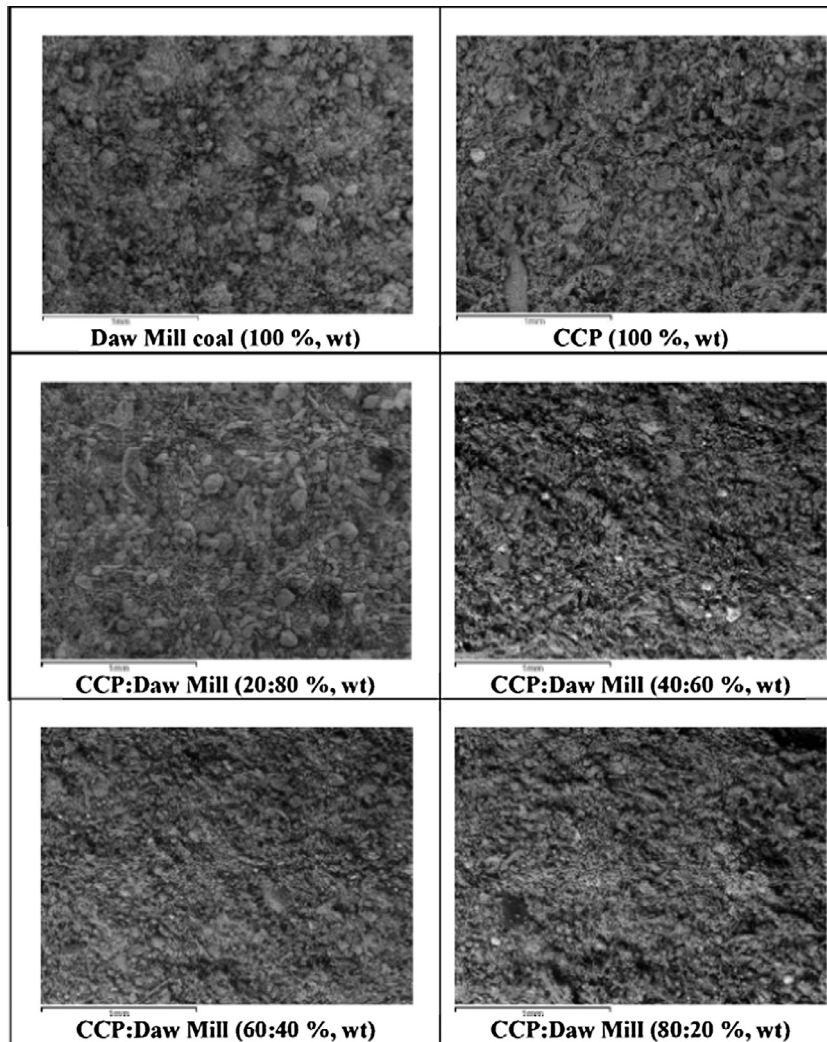


Fig. 5. ESEM images of deposits on the upstream of the probes (surface temperature of  $\sim 500$  °C) from co-firing various fuel mixtures.

was observed when CCP was added at 80 wt.% to the Daw Mill Coal. On all three probe top surfaces there was an increase in deposition flux when 20 wt.% CCP was added to the coal compared to the deposition flux arising from 100 wt.% coal combustion. The alkali released from the CCP reacts with the silicates from the coal, which will increase the sticking of the coal fly ash relative to firing un-blended coal [2]. A complex interaction between fuels occurs in the co-firing conditions. The deposition fluxes in these co-firing conditions (CCP with the Daw Mill Coal) do not behave as if the fuels were combusted in isolation.

### 3.2.3. Elemental characterisation

The elemental compositions of the deposits formed on the probes at three different surface temperatures  $\sim 500$ , 600 and 700 °C were analysed by ESEM/EDX. The compositions (in terms of mole%) of the deposits on upstream surfaces of the probes from six combustion runs are shown in Fig. 8. Al and Fe were found in higher concentration in the deposits from 100% Daw Mill Coal combustion, but with increasing levels of co-firing CCP their concentrations gradually decreased. The levels of Si in the deposits remain unaffected (both the fuels had similar amount of Si in the ashed analysis but they are in different forms). Other non-volatile species, such as Ca, did not show any significant change in concentration with increased levels of co-firing. The amount of P in the deposits increased as the levels of CCP was increased in the fuel

mixes. These elements behaved as if the fuels were combusted in isolation and the deposits were mixed before analysis.

Semi volatile species of elements such as Na and K indicated interaction between the fuels which changed the deposit chemical composition. The levels of Na in the deposits from the co-firing blends were always lower than the deposits from the combustion of pure fuels. With increasing levels of CCP co-firing the levels of K increased. The fate of the alkali species is one key to understanding the coal-biomass interactions.

Volatile species of elements such as S and Cl reveal the major changes in deposits due to co-firing. CCP is a low chlorine fuel and chlorine in the deposits was only found when 100% CCP was used (in all three probes). Chlorine in these deposits was confirmed to be in the form of KCl by XRD and EDX mapping. The large amount of K available in the CCP reacted with the HCl released from the combustion to form condensed KCl. In the all four co-firing conditions, the S content showed an increasing trend with increasing amount of CCP co-fired. Although the total amount of available S in the fuel mix was decreasing  $\text{SO}_2$  was still available in excess so the volatile K species from the combustion of the CCP were being converting into sulphates in the deposits. Sulphur in the coal is primarily in the form of sulphates and pyrites which decompose to form  $\text{SO}_2$ . This gas phase  $\text{SO}_2$  can also react with the alkaline earth material to form sulphates; however, most of the  $\text{SO}_x$  stays in the gas phase from coal combustion [2]. Chlorine in

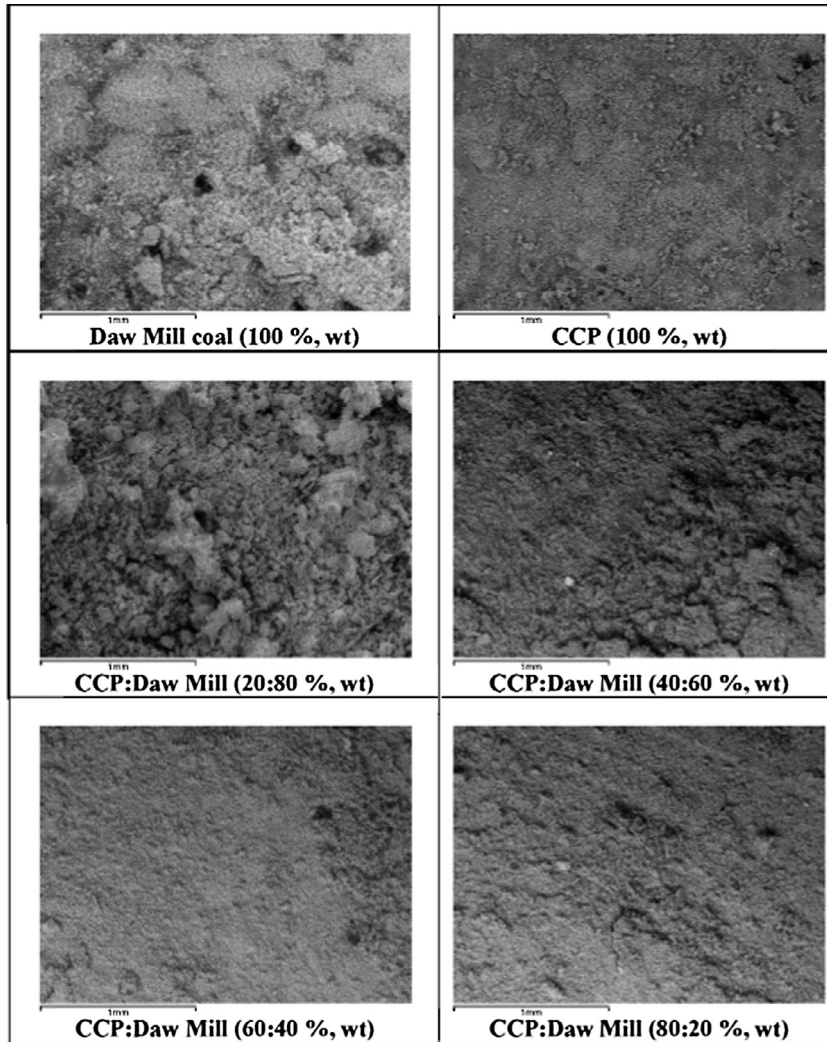


Fig. 6. ESEM images of deposits on the downstream of the probes (surface temperature of ~500 °C) from co-firing various fuel mixtures.

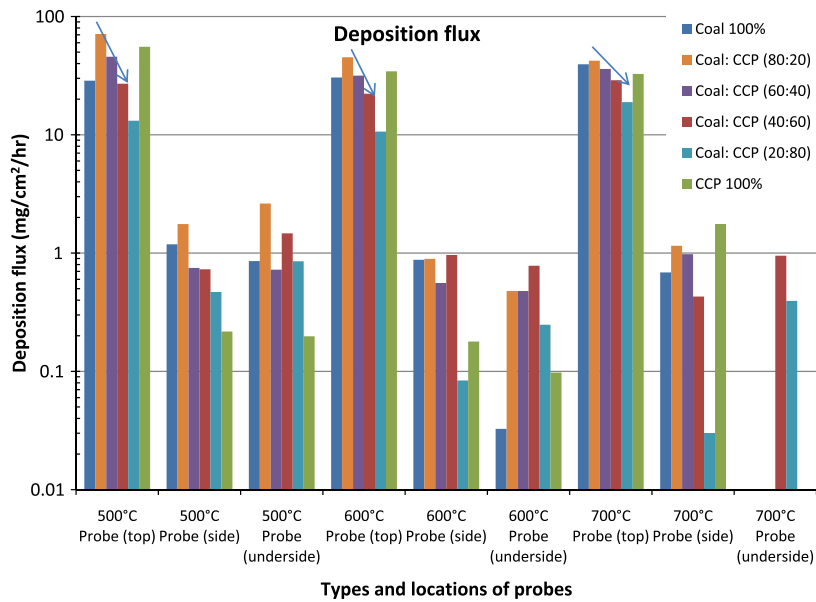


Fig. 7. Deposition flux on probes at ~500, 600 and 700 °C from co-firing various fuel mixtures.



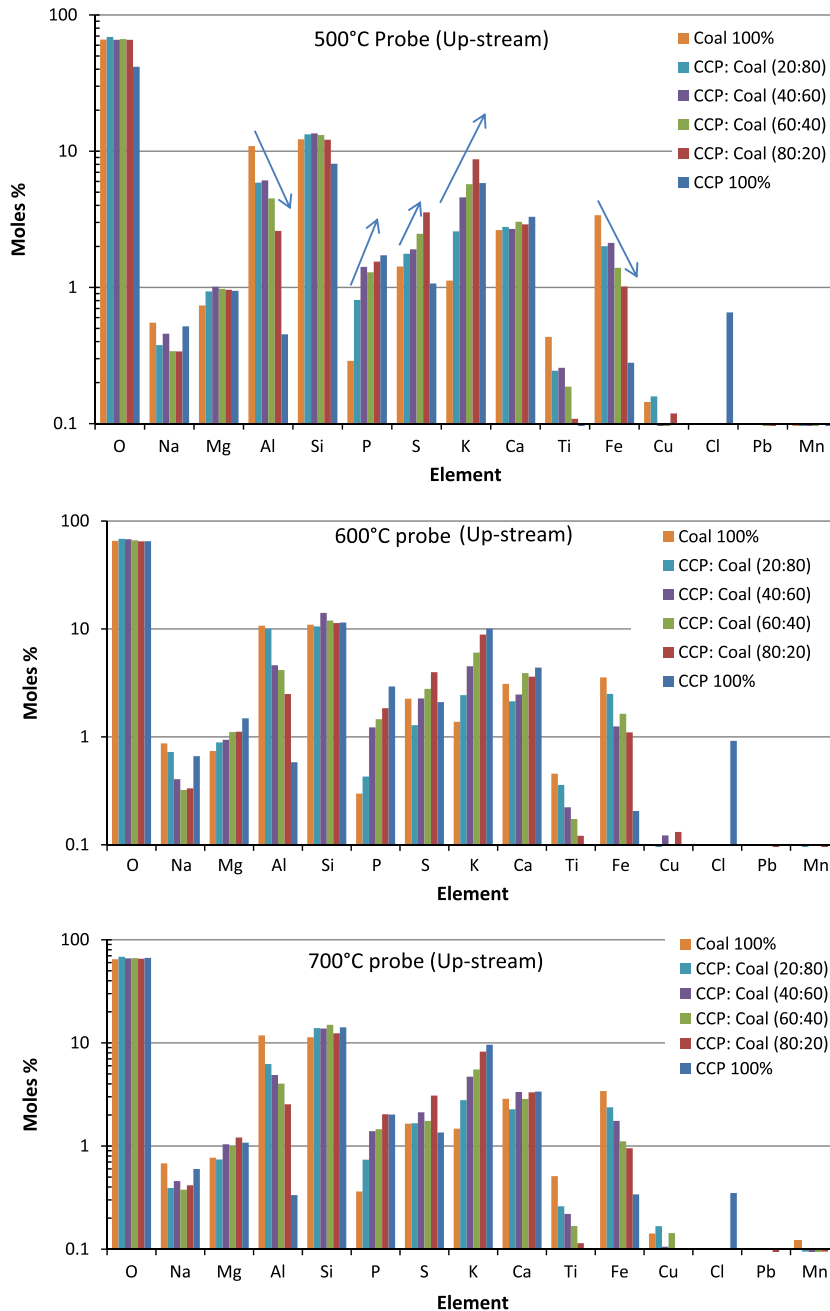


Fig. 8. Elemental concentration of deposits on upstream of the probes (at ~500, 600 and 700 °C) from co-firing various fuel mixtures.

the UK coal occurs in a mobile form which is released fairly early in the combustion process. Sulphates are more thermodynamically stable than chlorides, so if the coal provides sufficient sulphur to react with the alkali, there will be no condensed chlorine. As the amount of S in the deposits increased with CCP percentage in the co-firing mix (Fig. 8), the deposition flux decreased (Fig. 7). Sulphates in the deposits decrease the stickiness of the deposits compared to chlorides. However, when 100% CCP was combusted the amount of S in the deposit decreased sharply and Cl was detected in the deposits. A sticky alkali chloride deposit was formed and resulting in an increase in the deposition flux. If there is insufficient S in the combustion gases the sulphation of the alkali species cannot take place.

Fig. 9 shows the elemental concentration of deposits on the sidestream and downstream surfaces of the coolest probe (kept at ~500 °C). Similar trends in the elemental concentrations to the

upstream surfaces of the probe were observed. However, the amount (mole%) of Na, K, Cl and S detected on the side and downstream surfaces were higher than on the upstream surfaces. Alkali chloride/sulphides in the combustion gas stream are mainly deposited on the heat exchanger surfaces by thermophoresis and condensation mechanisms rather than direct inertial impaction (and the former mechanisms are favoured on the side and downstream surfaces).

#### 3.2.4. Modelling of combustion environment

Thermodynamic modelling using MTDATA software was performed to simulate the thermal stability of gaseous species and condensed species from combustion of pure fuels and various CCP with Daw Mill Coal co-firing conditions. The oxygen content of the combustion gas stream was fixed at 4 vol.% (same as the pilot scale runs) to keep it consistent with the experimental results.

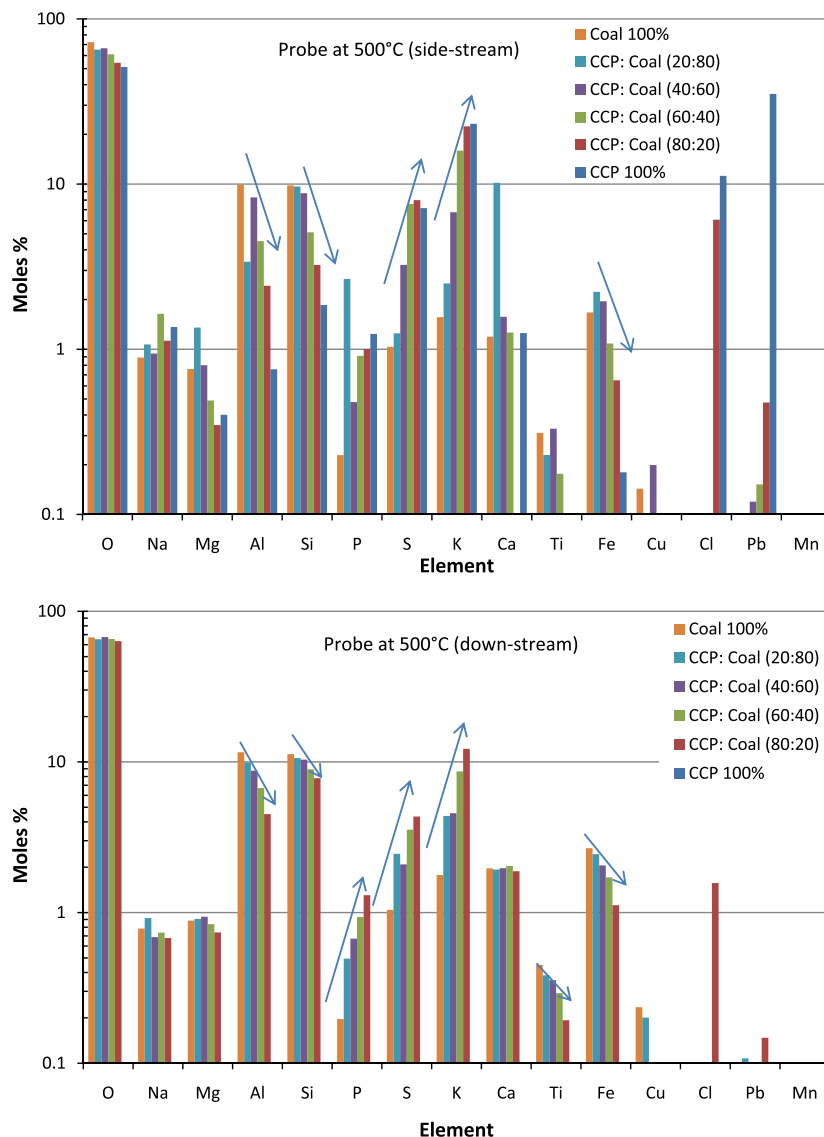


Fig. 9. Elemental concentration of deposits on sidestream and downstream of the probes (at  $\sim 500$  °C) from co-firing various fuel mixtures.

Thermodynamic models showed trends of decreasing  $\text{CO}_2$ ,  $\text{SO}_2$ , HCl and increasing  $\text{H}_2\text{O}$  content with increasing percentage of CCP in the fuel mix, consistent with the pilot scale experiments.

Fig. 10 shows the molar quantities of the gaseous and condensed species in the combustion gases at thermodynamic equilibrium in the temperature range of 200–1200 °C for pure fuels (100% Daw Mill Coal and 100% CCP). Condensed alkali sulphates:  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  were present in the combustion environment from 100% Daw Mill Coal. Other sulphate base deposits ( $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{MnSO}_4$ ,  $\text{CaSO}_4$ ) were also found in condensed form, as well as gaseous chlorine and alkali chloride gases. Alkali chlorides have higher vapour pressure than alkali sulphates, hence alkali sulphates are the first to form [10]. There was no condensed alkali chloride present from 100% Daw Mill Coal at thermodynamic equilibrium. Daw Mill Coal has a S/Cl ratio of  $\sim 6.4$  (wt.%) (ultimate analysis in Table 1) and thermodynamic equilibrium suggests that alkali sulphates are much more stable than alkali chlorides, so if the coal provides sufficient sulphur species to react with the available alkali then there will be no condensed phase chloride [2]. Whereas, condensed phase alkali chloride (KCl) was predicted along with some other condensed sulphate species when 100% CCP was used as a fuel. The S/Cl ratio in the CCP was  $\sim 1$  (wt.%) and due to insufficient

amount of S in the combustion gases alkali chlorides were formed. In a thermodynamic equilibrium KCl was stable up to  $\sim 650$  °C. Chlorine was detected in the deposit using ESEM/EDX on the upstream surfaces of the probes which were at  $\sim 500$ , 600 and 700 °C. XRD analysis was used to identify the chemical compounds present in the deposits. It was confirmed that KCl was present in the deposits from combustion of 100% CCP.

#### 4. Conclusions

Pilot scale co-firing experiments were performed using cereal co-product (CCP) with Daw Mill Coal at levels of 0, 20, 40, 60, 80 and 100 wt.%. Gaseous emissions from the combustion of these blends of pulverised fuels were measured using a Fourier Transform Infra-Red (FTIR) gas analyser with oxygen sensor. To study the deposition behaviour of the fuel blends, air-cooled probes were inserted into the combustion rig and maintained at surface temperatures of  $\sim 500$ , 600 and 700 °C (to simulate superheater/reheater surfaces). Thermodynamic equilibrium modelling was performed to predict the species in the deposits and in the combustion environment.

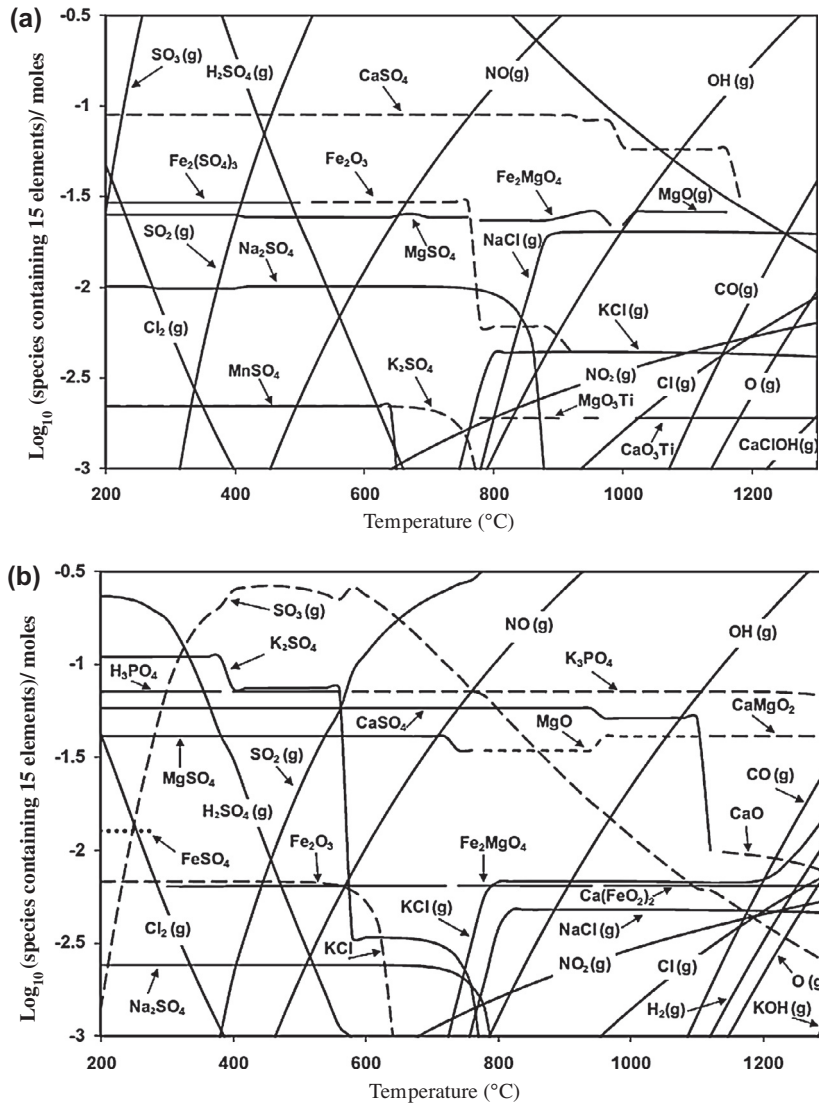


Fig. 10. Calculated gaseous and condensed species using MTDATA from combustion of (a) 100 wt.% Daw Mill Coal and (b) 100 wt.% CCP.

The pilot plant experiments showed no significant operational problems during co-firing of Daw Mill Coal with CCP, though there were occasional hold-up in the fuel feeding system. The addition of CCP to Daw Mill Coal showed a reduction in CO<sub>2</sub> emissions and an increase in H<sub>2</sub>O content in the combustion gases. Low levels of CO were detected in the flue gases which indicate high combustion efficiencies. Measurements of the minor gaseous species showed that SO<sub>x</sub> and HCl emissions decreased as the biomass percentages in the fuel blends increased. No significant change in NO<sub>x</sub> (NO and NO<sub>2</sub>) emissions was detected with changing levels of biomass co-firing.

Deposition flux is a useful parameter to identify the fouling potential of a fuel blend. Deposition fluxes on the upstream surfaces of the probes (at all three temperatures) were higher than side-stream and downstream surfaces. Deposition on the upstream surfaces of the probes is mainly associated with inertial impaction (and condensation) mechanisms. Increasing the levels of CCP in the fuel mixes showed a decreasing trend in deposition fluxes. This reduction is attributed to interactions between the potassium chlorides from the CCP and the S from the coal. This trend in decreasing deposition flux also corresponded to finer particles in the deposits. Therefore, co-firing biomass with S containing coal may result in a

fuel blend with reduced deposition fluxes compared to the un-blended biomass.

Non volatile compounds of Al and Fe decreased in concentration in the deposits as the levels of CCP co-firing increased. The non-volatile compounds behaved as if the fuels were combusted in isolation and the deposits were mixed before analysis. However, the situation was different for semi-volatile species of elements. Sodium showed signs of interaction during co-firing experiments; the levels of Na in the deposits from co-firing fuel mixes (on the upstream surfaces) were always lower than the deposits from the combustion of pure fuels. With increasing levels of CCP co-firing the levels of K (via semi-volatile species) increased in the deposits. Elements that form volatile species, such as Cl was only found in the deposits from 100% CCP combustion. Chlorine in these deposits was confirmed to be in the form of KCl by XRD and EDX mapping. Thermodynamic equilibrium modelling also predicted the presence of KCl in condensed phases from 100% CCP combustion. However, alkali chlorides were not detected in the deposits from co-firing fuel blends, as sulphation of alkali species is the major interaction that occurs within the co-fired deposits, four mixes of CCP and the Daw Mill Coal, as a result of the levels of SO<sub>2</sub> available from the combustion of this coal. Pilot scale experiments of

various fuel mixes can provide valuable information regarding fouling and emissions and should be carried out before large scale trials.

### Acknowledgements

The authors gratefully acknowledge the Engineering and Physical Sciences Research Council (EPSRC) funding via the Sustainable Power Generation and Supply (SUPERGEN) “Bio-energy, Bio-fuels and Energy Crops” consortium.

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