



## Deposit formation and emissions from co-firing miscanthus with Daw Mill coal: Pilot plant experiments

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### ABSTRACT

An investigation has been carried out into the deposits generated on cooled probes and the gas compositions produced from co-firing miscanthus mixed with Daw Mill coal. The biomass additions to the coal were at 0, 20, 40, 60, 80, 100 wt.% in a 100 kW<sub>th</sub> pilot-scale pulverised fuel (PF) combustion test rig operated with a feed rate of ~7–15 kg/h. Online monitoring of the combustion gas stream was carried out 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, HCl and HF using a high resolution multi-component Fourier Transform Infra-Red (FTIR) gas analyser. The deposits were collected from the upstream, side and downstream surfaces of three air-cooled probes that were exposed in the flue gas path and operated at surface temperatures of 500, 600 and 700 °C (to simulate heat exchanger tubes). The compositions of these deposits were determined using a range of analytical techniques including Environmental Scanning Electron Microscopy (ESEM) with Energy Dispersive X-ray (EDX) and X-ray Diffraction (XRD). The composition of the combustion gas streams and deposits changed as a function of the fuel mixtures used in the combustion process. The increasing miscanthus share in combination with the Daw Mill coal resulted in a reduction of SO<sub>x</sub>, NO<sub>x</sub> and HCl levels. The deposition on the upstream surfaces of the probes decreased with increasing biomass percentage, but increased on the downstream surfaces. The concentration of K and S in the deposits increased with increasing miscanthus share in the fuel up to 80 wt.%, particularly on the coolest probe (~500 °C surface temperature). In addition, Cl was detected in the deposit on the two lower temperature probes only when 100% miscanthus was used in the combustion process. Thermodynamic modelling of the combustion/deposition process carried out in parallel also suggested formation of KCl only at the highest levels of biomass co-firing for miscanthus/Daw Mill coal, with K<sub>2</sub>SO<sub>4</sub> being predicted at lower co-firing levels for these specific fuels.

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### 1. Introduction

It is generally acknowledged that CO<sub>2</sub> emissions from the combustion of fossil fuels (coal, petroleum and natural gas) are major contributors to the enhanced greenhouse effect, or global warming [1]. In response to concerns about global CO<sub>2</sub> emissions leading to global warming, regulations have been introduced in the UK power generation industry to encourage the use of renewable energy sources. While these regulations are changing with time, co-firing of coal and biomass is still encouraged on the basis that biomass is a sustainable, carbon neutral fuel. Co-firing biomass with coal is still amongst the cheaper alternatives that electricity utilities have for reducing net CO<sub>2</sub> emissions [2,3]. Co-firing biomass with coal (up to ~10 wt.%) is widely practiced in the UK pulverised fuel power plants. However, as these power plants were originally designed for coal combustion alone, co-firing of coal with a share of

biomass higher than 10% is still challenging and requires careful investigation [4]. As many old coal plants 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 UK and across Europe in converting existing coal fired plants to fire biomass. Alternatives such as firing 100% biomass, or co-firing high percentages of biomass, in old coal boilers are being actively investigated in research programmes and by power generating companies in the UK at the moment.

Issues limiting the extension of co-firing technology include: fuel supply; fuel storage, preparation and feeding; ash disposal; formation of deposits on heat exchanger surfaces, which can cause enhanced corrosion and/or limit the heat transfer between the hot combustion gases and the water/steam system used to generate power. Therefore, the sensitivity of fuel combustion, emissions and deposition need to be studied for a wide range of coal and biomass fuel blends, as well as for coal and biomass fuels alone. Also, the combustion efficiency has to be considered for burning higher percentages of biomass in the fuel blend, as it has been reported

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that at an existing power station, coal co-fired with biomass resulted in a reduction in efficiency of  $\sim 0.5\%$ , when the mixed fuel firing rate was 5%, and  $\sim 0.8\%$  when the mixed fuel firing rate was 10% [5]. Co-firing biomass with coal can lead to either decrease or increase in deposition rates on heat exchanger surfaces compared to pure coal combustion, depending on the specific biomass and coal used. One of the major concerns in co-firing is the behaviour of the inorganic matter present (in different forms and relative abundances) in both the biomass and coal, and the impact of their mixtures on the resultant gases, vapours, fly ashes and deposits.

A wide range of R&D activities in co-firing biomass have been carried out, from laboratory scale up to industrial scale, for a variety of boiler technologies (e.g., pulverised combustion, grate bed combustion, fluidised bed combustion etc.) [6]. Co-firing of coals from various sources: Colombia, UK and Poland were investigated by several researchers in a number of studies [7,4,8–11], and a wide range of biomass e.g., sawdust, sewage sludge, RDF, switchgrass, wood chips and straw were studied by others [4,12,13]. Co-firing on a commercial scale has been trialled in over sixteen countries [14]. For example, up to 10 wt.% of switchgrass with coal has been commercially co-fired in the USA [15], and coal with sewage sludge, straw and wood has been co-fired in Germany [16]. In Netherlands, a higher blend mixtures of fuel, up to 40 wt.% was co-fired with various biomass fuels such as wood, paper sludge, coco-shells, chicken litter, plastics and olive kernels in a 1 MW<sub>th</sub> pilot-scale plant [17]. In the UK, 16 major coal power plants have been co-firing biomass (up to  $\sim 10\%$  on an energy basis) [18].

The objectives of this study were to investigate the formation of deposits on cooled surfaces (simulating heat exchanger tubing) and the flue gas composition produced by the combustion of miscanthus mixed with Daw Mill coal with a high share of biomass in the fuel mix ( $\geq 20$  wt.%) in a 100 kW<sub>th</sub> pilot-scale combustion test rig. The deposits formed on surface temperatures of 500, 600 and 700 °C (to simulate different heat exchanger surface conditions) were examined using SEM/EDX and XRD. To support this activity, a thermodynamic software package (Metallurgical and Thermochemical Databank, MTDATA) was also used to investigate

the relative stability of the wide range of potential gaseous and condensed species that could be formed during the combustion and deposition processes.

## 2. Experimental procedure

### 2.1. Fuels

The Daw Mill coal and miscanthus used in this study were supplied by E.ON Engineering plc (Power Technology Centre, Ratcliffe-on-Soar, Nottingham, UK). The proximate, ultimate and ash composition analyses of both the fuels are presented in Table 1. Miscanthus was chosen based on the current interest of the UK government in promoting the growth of miscanthus through the Energy Crop Scheme, which offers financial support to farmers for growing miscanthus as an energy crop for use in the conversion processes [19]. Miscanthus samples were milled and sieved to <2 mm size with an average size of 0.8 mm before combustion. According to Wagenaar and Vanden Heuvel [20], miscanthus samples with diameters of less than 3 mm can be fired well in a pulverised coal combustor compared to larger miscanthus particles, which tend to cause a geometrical extension of the flame in the vertical direction. Constant fuel feed rates of  $\sim 7.4$ , 8.1, 9.1, 10.2, 11.7 and 13.6 kg/h were fed through the pulverised fuel (PF) combustor with biomass additions of 0, 20, 40, 60, 80 and 100 wt.% respectively.

### 2.2. Pilot scale combustion test facility

The tests were conducted in a pilot-scale combustion rig (located at Cranfield University) which has a 100 kW<sub>th</sub> capacity pulverised fuel (PF) combustor using a  $\sim 7$ –15 kg/h feed rate. The PF combustor used a multi-fuel excess air burner to ensure complete combustion. The test rig was heated up using natural gas firing before switching to the pulverised fuels. The solid fuels were fed to the multi-fuel burner from a hopper via a pneumatic transfer system using a constant nitrogen flow rate of 30 L/min. The PF combustion unit, fuel feeding system and combustion conditions have been described in more detail by Khodier et al. [21]. Combustion gas temperatures in this rig have been measured using R type thermocouples (housed in ceramic sheaths) and infra-red pyrometers in the hotter regions, and K type thermocouples (with metal sheaths) in the cooler regions (<1000 °C).

### 2.3. Flue gas and deposit analysis

A portable high resolution multi-component Fourier Transform Infra-Red (FTIR) gas analyser was used to measure on-line the levels 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 gases. Deposits from the combustion gas stream were collected using air-cooled ceramic probes that were inserted horizontally into the side-access of the rig. The surface temperatures of the probes were maintained at  $\sim 700$  °C (Probe 1),  $\sim 600$  °C (Probe 2) and  $\sim 500$  °C (Probe 3) using compressed air passing through the centre of the probes (to simulate the surface temperatures of superheaters/reheaters in co-fired boilers). The surface temperatures of the probes were measured using K type thermocouples. A more detailed description of the probe geometry and function can be found in reference [22]. The composition of the deposits build-up on the upstream, side-stream and downstream surfaces of the probes, referred to as top, side and underside deposits, were determined using Environmental Scanning Electron Microscope (ESEM) equipped with Energy Dispersive X-ray (EDX) analysis and X-ray Diffraction (XRD).

**Table 1**  
Characterisation of elements (wt.%) on as received (AR) basis of Daw Mill coal and miscanthus.

	Daw Mill coal	Miscanthus
<i>Proximate analysis (wt.%, AR)</i>		
Moisture	4.60	10.80
Ash	4.20	4.60
Volatile matter	31.30	70.70
<i>Calorific value (kJ/kg)</i>		
Gross calorific value	25,260	17,824
Net calorific value	24,107	16,478
<i>Ultimate analysis (wt.%, AR)</i>		
Carbon	74.15	43.59
Hydrogen	4.38	4.80
Nitrogen	1.17	0.58
Oxygen	10.49	35.52
Sulphur	1.28	0.11
Chlorine	0.20	0.09
<i>Ash composition (wt.%, of total ash)</i>		
SiO <sub>2</sub>	36.80	55.85
Al <sub>2</sub> O <sub>3</sub>	23.90	3.14
Fe <sub>2</sub> O <sub>3</sub>	11.20	2.12
TiO <sub>2</sub>	1.10	0.19
CaO	12.00	8.77
MgO	2.50	3.76
Na <sub>2</sub> O	1.50	0.50
K <sub>2</sub> O	0.50	12.69
Mn <sub>3</sub> O <sub>4</sub>	0.40	0.15
P <sub>2</sub> O <sub>5</sub>	–	12.30
BaO	–	0.03

## 2.4. Thermodynamic modelling

The thermodynamic software package MTDATA (National Physical Laboratory, Teddington, London, UK) [23] has been used to model the behaviour of the trace elements present in fuel mixtures in terms of their partitioning between species in the gas phase and condensed phases (heat exchanger deposits) as the combustion gas stream is cooled. The calculations included up to 15 elements in any one run (C, H, N, O, S, Cl, Fe, Ca, Mg, K, Na, Ti, Ba, Mn and P). Previous studies have suggested that Si and Al should be omitted from such thermodynamic calculations as they are present in coal in forms that are largely unreacted in combustion environments as a result of kinetic factors [24]. These calculations were carried out using the “multiphase” module in MTDATA, combined with SGTE (Scientific Group Thermodata Europe) database. The relative values of all the elements were entered in the programme on a molar basis under the same target combustion conditions as the pilot-scale experiments. Calculations were carried out to cover the temperature range from 200 to 1300 °C with a step size of 20 °C at atmospheric pressure.

## 3. Results and discussion

### 3.1. Gaseous emissions

The mean values of major gaseous species ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{O}_2$ ) and minor species ( $\text{CO}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{SO}_2$  and  $\text{HCl}$ ) released during

2 h of stable combustion of co-firing biomass at 0, 20, 40, 60, 80 and 100 wt.% are shown in Fig. 1a and b. To compare the gases produced from the different fuel mixes, the oxygen content of the combusted gas stream was targeted to be at ~4 vol.%, with the air/fuel ratio adjusted accordingly. Under these operating conditions, it was found that the combustion efficiency was high, with only low levels of  $\text{CO}$  being measured in the flue gases (Fig. 1b). Low carbon contents in the deposits collected on probe surfaces (see Section 3.2) were consistent with this high combustion efficiency. The levels of  $\text{CO}$  showed a decreasing trend with increasing percentage of biomass co-firing up to 60 wt.%, above which  $\text{CO}$  levels increased with increasing biomass content (lower  $\text{CO}$  emissions correspond to higher combustion efficiencies). Looking at Fig. 1a, the  $\text{CO}_2$  emissions were similar for all co-firing conditions but decreased when 100 wt.% miscanthus was fired. This is what should be expected in firing miscanthus which has a lower carbon content than that of the Daw Mill coal (Table 1). The  $\text{H}_2\text{O}$  content in the combustion gas showed a linear increase from 7.7 vol.%, with 100% Daw Mill coal combustion, to 12.8 vol.%, with 100% miscanthus combustion. Miscanthus in general has higher moisture content compared to Daw Mill coal, as can be seen from Table 1; therefore, increasing the percentages of biomass co-firing will result in an increase in  $\text{H}_2\text{O}$  content in the combustion gas stream.

The emissions of minor gaseous species in Fig. 1b shows that the  $\text{NO}$  concentration decreased with increasing levels of co-firing; i.e., the highest level of  $\text{NO}$ , ~400 ppm, was found in 100% Daw Mill coal and the lowest level, ~290 ppm, was found in 100% miscan-

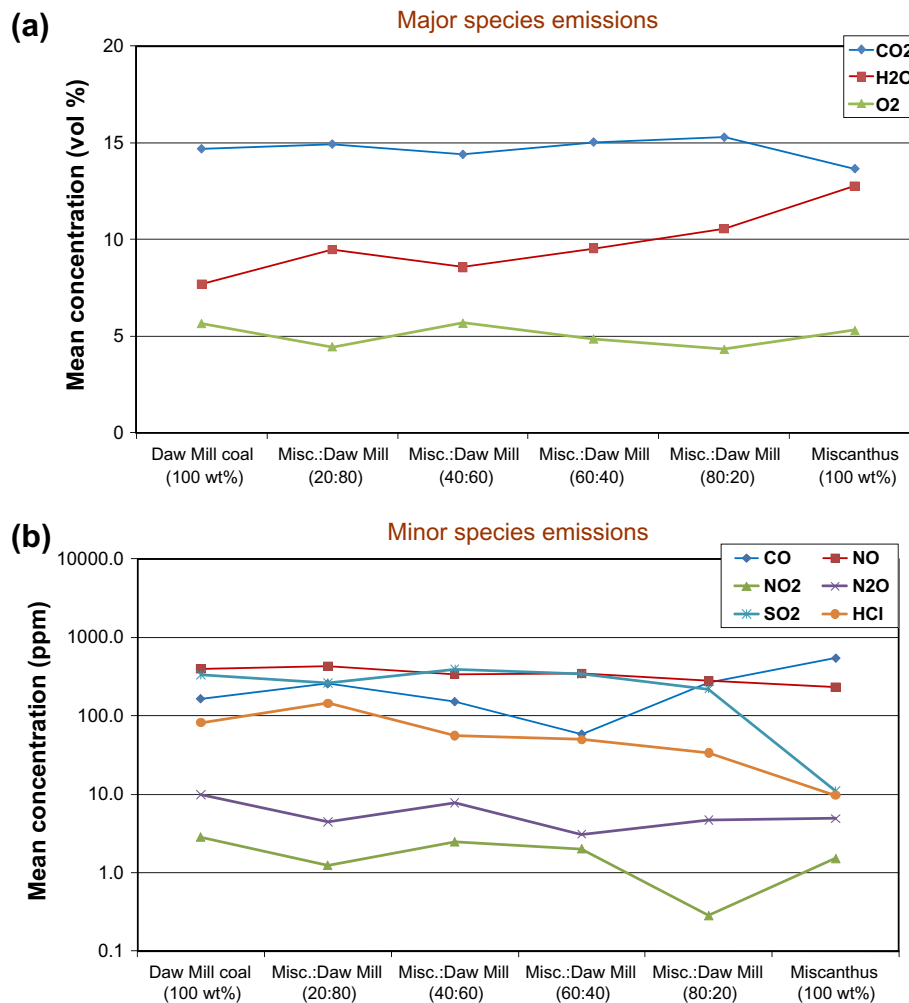


Fig. 1. (a) Major gaseous species and (b) minor gaseous species emissions from combustion of various levels of miscanthus with Daw Mill coal.

thus firing. Biomass addition to the coal contributes to  $\text{NO}_x$  reduction due to its high content of volatile matter [4,25]. In addition,  $\text{SO}_2$  concentration was the highest ( $\sim 450$  ppm) when 100% Daw Mill coal was fired, whereas using 100% miscanthus resulted in the lowest level of  $\text{SO}_2$  ( $\sim 10$  ppm). Co-firing of biomass with coal is expected to produce less  $\text{SO}_2$  as biomass contains less sulphur than coal [26]. However, the relationship between the percentages of biomass addition and  $\text{SO}_2$  reduction is not clear from the results (i.e.,  $\text{SO}_2$  emissions showed similar levels from 100% coal firing to 80% biomass firing and then a decrease to 100% biomass firing). The levels of HCl decreased with increasing the percentage of miscanthus in the fuel blends and the lowest level of HCl was found with 100% miscanthus firing ( $\sim 10$  ppm). This low level of HCl in the flue gas reflects the fact that in the ultimate analysis of this miscanthus fuel there was only a little chlorine present (Table 1).

In summary, for the co-firing conditions the  $\text{SO}_2$ , NO and HCl concentrations decreased as the miscanthus share of the fuel mix

increased. Moreover, it is worth mentioning that the levels of the major and minor gaseous species remained steady during combustion runs, except for when the fuel feeding was interrupted due to blockages caused by dirt/stones in the fuels.

### 3.2. Deposit formation and characterisation

The deposits were collected over  $\sim 3$  h of exposure at various levels of miscanthus/Daw Mill coal co-firing: 0, 20, 40, 60, 80 and 100 wt.%. As an example, Fig. 2 shows images of the deposits collected on the top and side of the coolest probe (maintained at  $\sim 500$  °C) in the left column and corresponding underside deposits in the right column. The amount of the deposits formed on the top and side surfaces (upstream and side surfaces in the gas path) decreased with increasing levels of biomass co-firing. However, the amounts of deposits formed on the underside of the probes (downstream surface in the gas path) increased with increasing levels of biomass co-firing. The increased levels of deposits on the down-

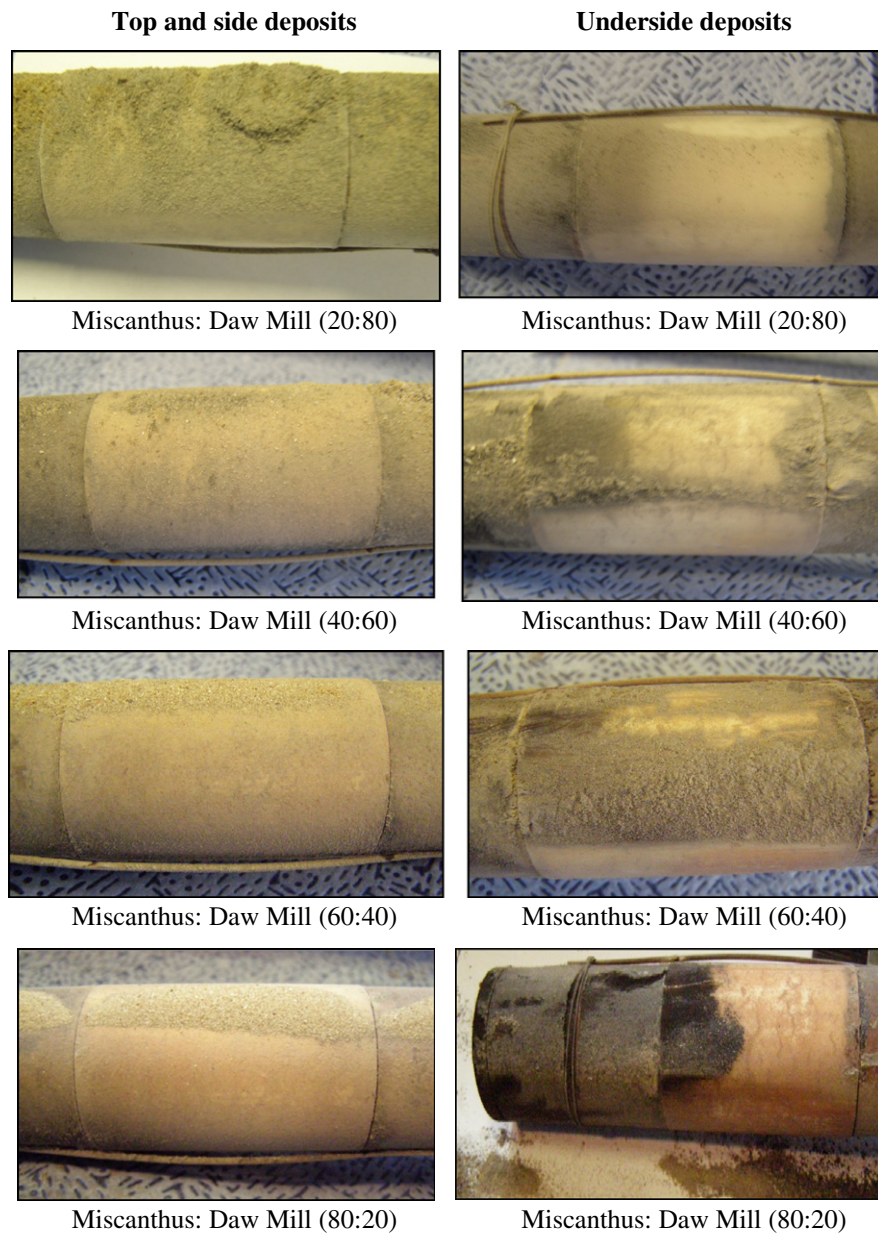
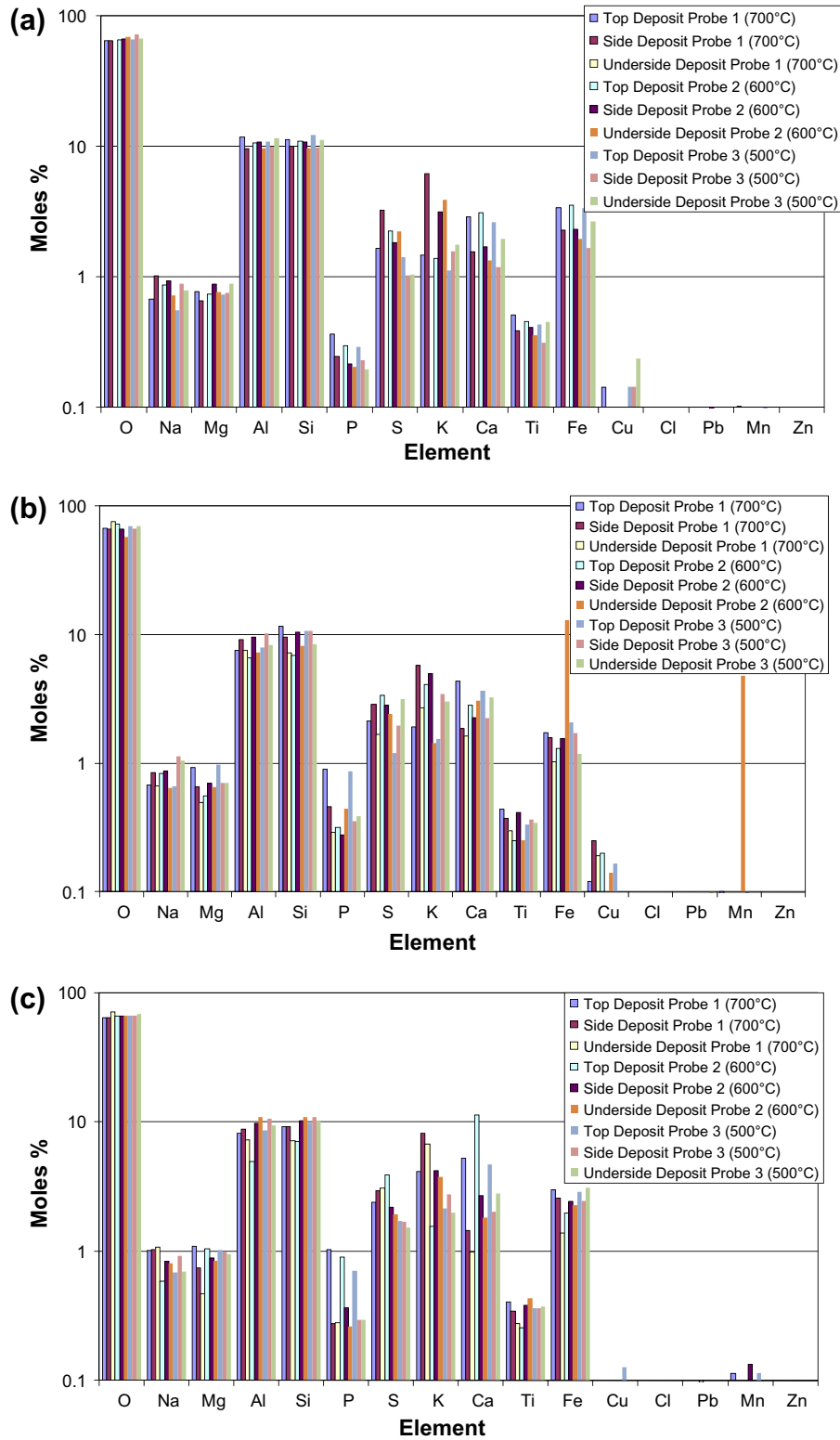


Fig. 2. Close up view of the deposits formed on probe 3 ( $\sim 500$  °C surface temperature) from co-firing various fuel mixtures.





**Fig. 3.** Elemental concentrations of deposits on the probe 1 (700 °C), probe 2 (600 °C) and probe 3 (500 °C) from combustion of (a) 100 wt.% Daw Mill coal (b) miscanthus: Daw Mill (20:40) (c) miscanthus: Daw Mill (40:60) (d) miscanthus: Daw Mill (60:40) (e) miscanthus: Daw Mill (80:20) and (f) 100 wt.% miscanthus.

stream surfaces imply a higher risk of fouling with increasing levels of biomass co-firing. Deposits form and grow as a result of both physical and chemical processes, which can involve at least five mechanisms: direct inertial impaction, condensation, thermophoresis, eddy impaction and chemical reactions [27,28]. Typically, the deposits formed on upstream surfaces are dominated by direct

inertial impaction of larger particles and the deposits on downstream surfaces are dominated by vapour condensation and eddy impaction of smaller particles [34,35].

The elemental compositions of the deposits formed on the top, side and underside of all three probes exposed at three different temperatures (700, 600 and 500 °C) were analysed by ESEM/EDX

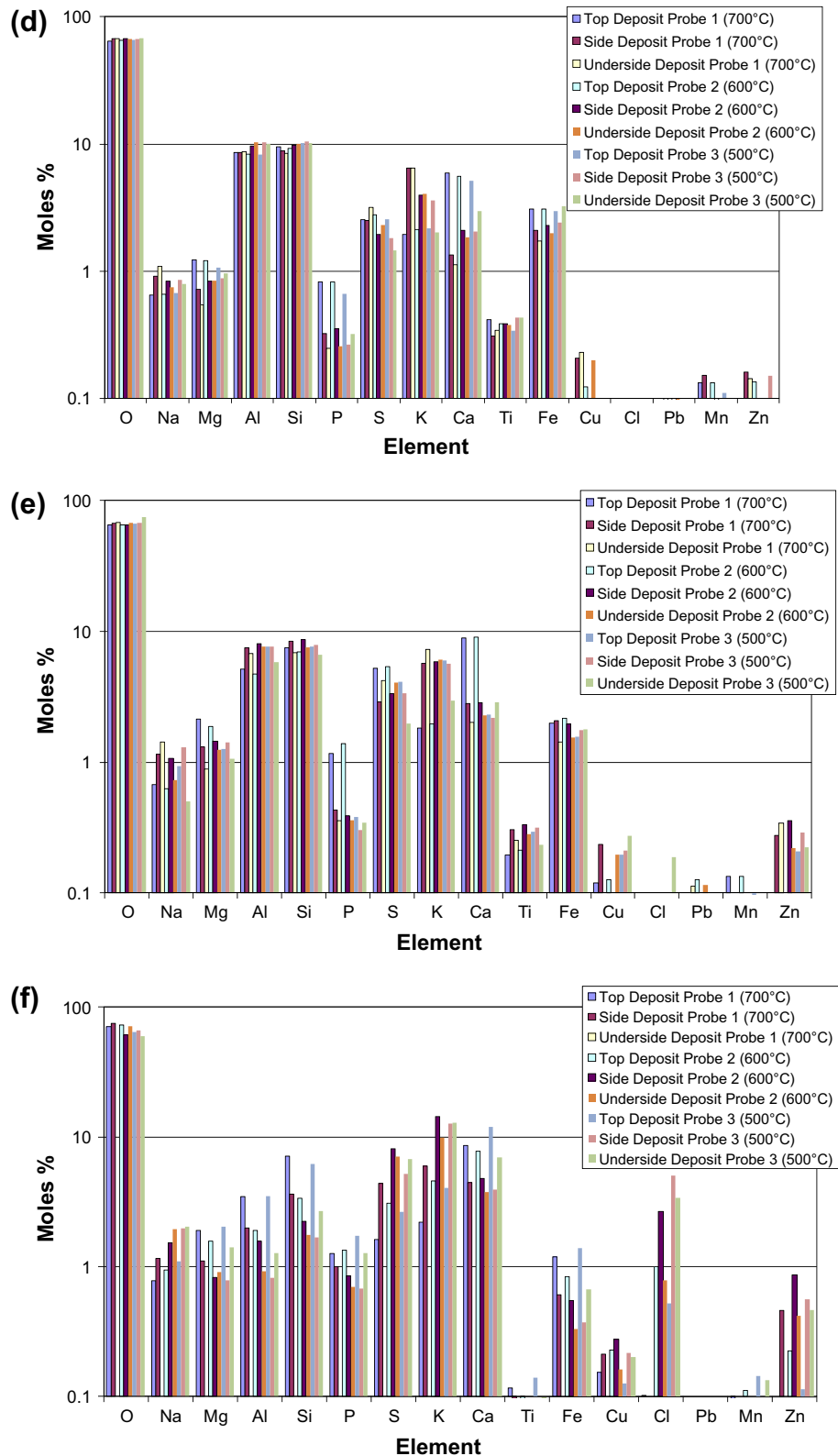


Fig. 3 (continued)

and are shown in Fig. 3. It is seen that for 100% Daw Mill coal and all co-firing conditions Al, Si, S, K, Ca and Fe were higher than other elements. The percentages of Al and Si decreased as the fuel mixtures became more miscanthus based (Fig. 3 e and f). The Fe content in the deposits showed a steady decrease with increasing miscanthus percentage in the fuel. However, it should also be

noted that the percentage of K and S in the deposits increased with increasing the levels of miscanthus in the fuel, up to 80 wt.% miscanthus. Moreover, the amount of P in the deposits also increased as the biomass fraction of the fuel increased.

Chlorine was not detected in the deposits formed by co-firing up to 60% miscanthus. A very small amount, ~0.1% mole, was de-

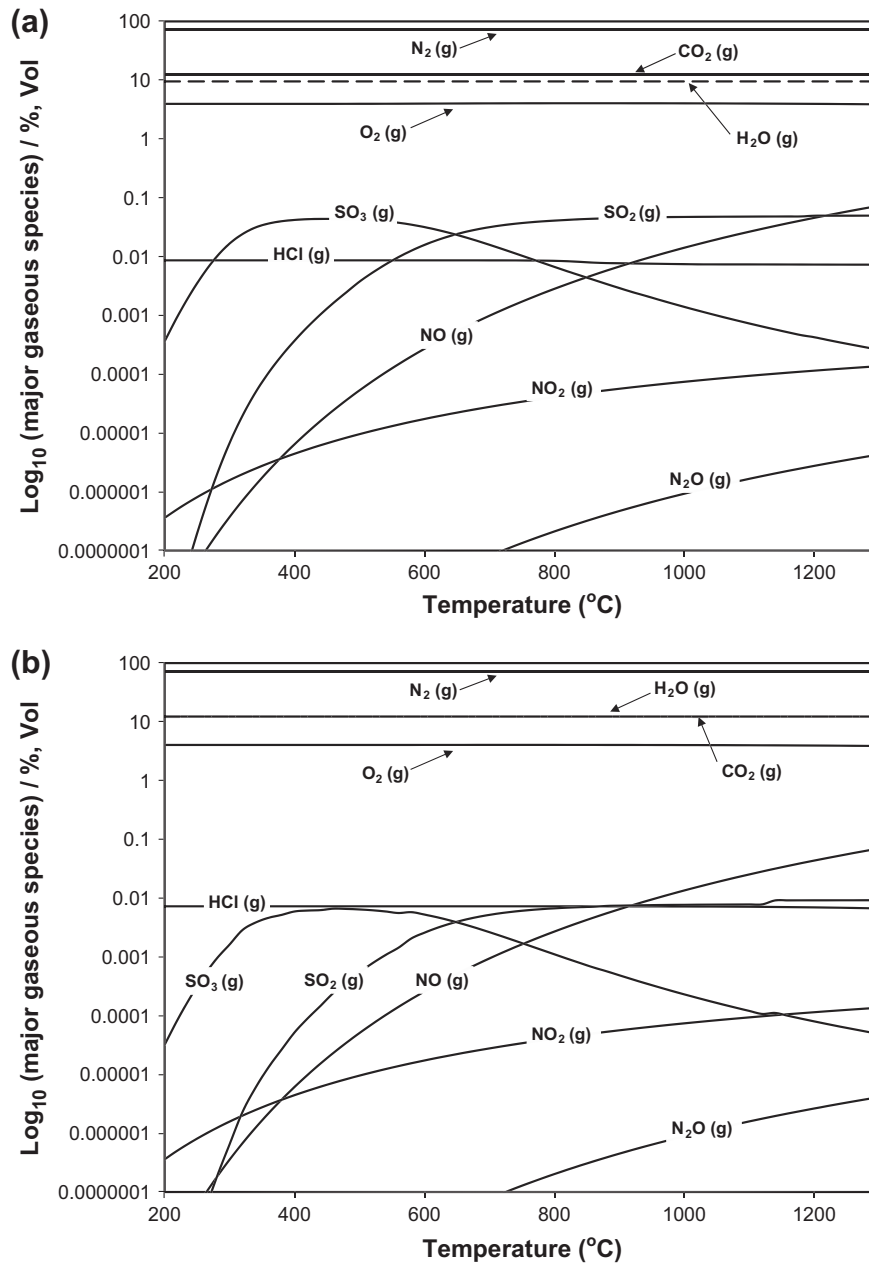


Fig. 4. Calculated major gaseous species (MTDATA) from combustion of (a) miscanthus: Daw Mill coal (40:60) and (b) 100 wt.% of miscanthus.

tected at the underside of probe 3 at 80% miscanthus co-firing). However, in contrast, much higher levels of Cl were found in the deposits only on the two cooler temperature probes (500 and 600 °C) when 100% miscanthus was used as the fuel (Fig. 3f). The amounts of Cl detected on the sides and undersides of the probes were always higher than that on the top surfaces. The presence of Cl on the side/underside of the deposit suggests that it has been deposited by condensation and/or thermophoresis mechanisms. Combined with the increased levels of K found with increased levels of miscanthus, this suggests the presence of potassium chloride (a highly fouling compound leading to high corrosion damage rates [22]) at the highest levels of miscanthus/Daw Mill coal co-firing.

XRD was used to detect the mineral phases with the higher concentrations in the deposits from the coal and miscanthus co-firing runs (not shown here). The main compounds identified by XRD included: quartz ( $\text{SiO}_2$ ), anhydrite ( $\text{CaSO}_4$ ), iron sulphate ( $\text{FeSO}_4$ ) and

haematite ( $\text{Fe}_2\text{O}_3$ ) for all miscanthus/Daw Mill coal blends (0, 20, 40, 60, 80 and 100 wt.%). The presence of sylvite (KCl) and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) were only detected on deposits from 100% miscanthus combustion. This suggests that alkali species in 100% miscanthus combustion were more mobile than in the co-firing conditions, which is consistent with results from chemical fractionation analysis [29]. Gas phase alkali species mainly contribute to deposit formation by vapour condensation reactions [30]. Alkali species can react to form alkali silicates either via residual alkali in fly ash particles (condensed-phase reaction) or between gas-phase, alkali-bearing species and condensed-phase silica or silicate. The formation of alkali silicates which have relatively low melting temperatures increases the probability that a particle impacting the probe surface will stick [29]. The presence of KCl in the deposits from 100% miscanthus firing indicates that there are significant changes in the balance of processes that form the deposits on cooled surfaces at high miscanthus co-firing levels.

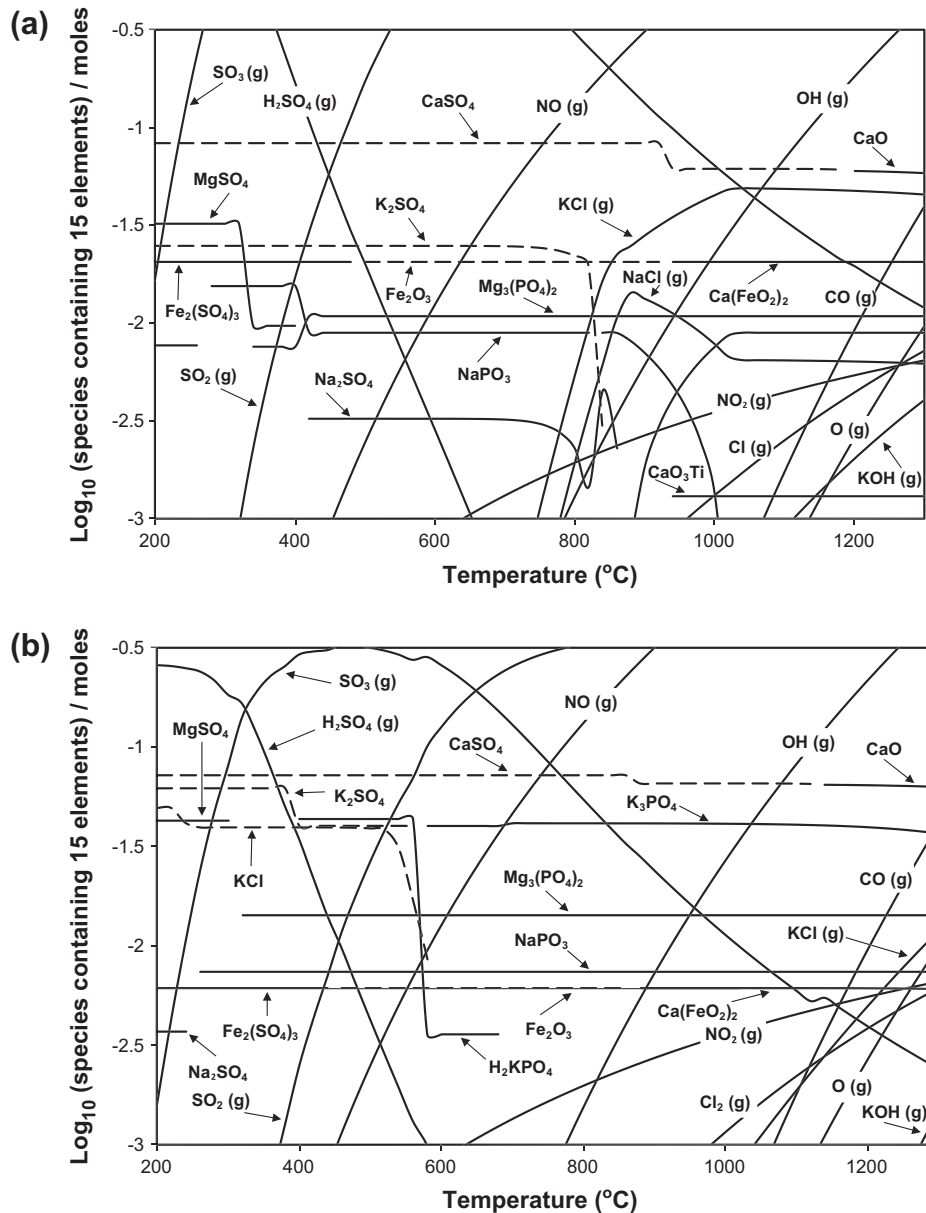


Fig. 5. Calculated gaseous & condensed species (MTDATA) from combustion of (a) miscanthus: Daw Mill coal (40:60) and (b) 100 wt.% miscanthus.

### 3.3. Thermodynamic modelling

In addition to the pilot scale experiments, thermodynamic modelling using MTDATA software was performed to try to improve understanding of the behaviour of gaseous and condensed species. Major gaseous species ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{HCl}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}$ ) from co-firing of miscanthus: Daw Mill Coal (40:60) and 100% miscanthus firing are shown in Fig. 4. In the thermodynamic modelling, the oxygen content of the combustion gas stream was targeted at 4 vol.% to keep it consistent with the pilot scale experiments. The trend of decreasing  $\text{SO}_2$ ,  $\text{NO}$  and  $\text{HCl}$  levels and increasing levels of  $\text{H}_2\text{O}$  with increasing percentage of miscanthus in the fuel mix, that was found in the pilot scale experiments, were also seen in the thermodynamic modelling.

The molar quantities of the gaseous and condensed species in equilibrium with combustion gases (200–1300 °C) for 40% and 100% miscanthus are shown in Fig. 5. The condensed species of anhydrite ( $\text{CaSO}_4$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ) were found for all the fuels mixtures.  $\text{CaSO}_4$  is stable over the temperature ranges of 200–1180 °C at 40% miscanthus addition and 200–1100 °C at 100%

miscanthus, whereas  $\text{Fe}_2\text{O}_3$  is stable over the temperature ranges of 500–920 °C at 40% miscanthus addition and 460–860 °C at 100% miscanthus combustion. Increases in the miscanthus content in the fuel decreases the temperature ranges over which the deposits are stable. It should be noted that condensed species of sylvite ( $\text{KCl}$ ) was only predicted when 100% miscanthus was used for combustion. This also supports the SEM/EDX and XRD results of the presence of  $\text{KCl}$  on the two lower temperature probes only with 100% miscanthus firing. The model outputs in Fig. 5 predicted that  $\text{KCl}$  is stable up to temperatures of ~600 °C (again consistent with the analytical results given in Section 3.2). Condensed species of  $\text{K}_2\text{SO}_4$  were predicted for all the fuel mixtures investigated in this paper. For example,  $\text{K}_2\text{SO}_4$  was present in the temperature ranges of 200–840 °C at 40% miscanthus co-firing and 200–560 °C at 100% of miscanthus firing. The condensed phases are sensitive to the amount of S in the system which makes condensed  $\text{K}_2\text{SO}_4$  the dominant species to form. Since  $\text{K}_2\text{SO}_4$  has a lower vapour pressure than  $\text{KCl}$ , it leads to condensation and deposition at high temperatures. There is an ongoing discussion [31] whether sulphation of  $\text{KCl}$  to  $\text{K}_2\text{SO}_4$  takes place in the gas phase and/or after condensa-



tion. Investigations carried out by several groups [27,31–33] based on observations in different combustion units indicate that the deposition processes for KCl and K<sub>2</sub>SO<sub>4</sub> compounds were dominated by condensation and thermophoresis mechanisms, which first form the sticky inner layer of deposits. Whereas, the outer deposit layer is dominated by Si, Al, Fe and Ca compounds (depending on the fuel composition) which build up generally by inertial impaction mechanisms and consist mainly of the individual fly ash particles.

In summary, thermodynamic modelling is a useful predictive tool for trends in gas compositions, formation of condensed phase compounds and element partitioning, which help to support the use of experimental analytical techniques (with their well-known limitations).

#### 4. Conclusions

Co-firing of miscanthus with Daw Mill coal was studied at biomass levels of 0, 20, 40, 60, 80 and 100 wt.% in a pilot scale combustion test rig. Gaseous emissions from the co-firing were measured using a Fourier Transform Infra-Red (FTIR) gas analyser. Air cooled probes were used to study the deposition behaviour at surface temperatures of ~500, ~600 and ~700 °C (to simulate heat exchanger surfaces). In addition, thermodynamic modelling of the co-firing miscanthus with Daw Mill coal was performed to provide additional information on the potential gaseous and condensed species.

The results indicated high combustion efficiency for all fuel mixes and no major operational/feeding problems were encountered during co-firing. It has been found that the addition of miscanthus to Daw Mill coal resulted in a reduction of SO<sub>x</sub>, NO<sub>x</sub> and HCl levels. The deposition on the upstream surfaces of the probes decreased with increasing biomass percentages but increased on the downstream surfaces, which indicates increase in vapour deposition processes. The concentration of K and S in the deposits increased with increasing miscanthus share in the fuel (up to 80 wt.%), particularly noticeable on the cooler probes. Cl was not detected in the deposits at lower biomass concentrations; however, when 100% miscanthus was used Cl was detected on two lower temperature probes (e.g., 600 and 500 °C). Thermodynamic modelling of the combustion process predicted that chlorine was in the form of KCl when 100% miscanthus was used, whereas in the rest of the co-firing conditions K was in the form of K<sub>2</sub>SO<sub>4</sub> in the deposits, consistent with the SEM/EDX and XRD analyses carried out.

The pilot scale rig exposures with various co-firing levels provided valuable information on gaseous emissions and deposition chemistry for use in industrial scale boilers. As the compositions of biomass fuels vary significantly depending on crop type, agricultural practices, harvest times, storage, etc., and coal compositions vary with their mine location, it is important that pilot scale tests are carried out for each specific fuel mix as part of its assessment for use in utility boilers.

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