

## Full Length Article

# Fuel flexible power stations: Utilisation of ash co-products as additives for NO<sub>x</sub> emissions control

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## ABSTRACT

This work investigated the effects of different ash co-products on the combustion of solid fuels, in particular the fuel-nitrogen behaviour: The fuel-ash additive combinations investigated were: Firstly, biomass ashes added to bituminous coals, representative of those used in power stations; Secondly, a low reactivity coal; Thirdly, a high-N biomass (olive cake) was chosen as a high reactivity fuel and studied with a power-station pulverised coal fly ash as an additive. These five solid fuels have a wide fuel ratio, FR (i.e. the ratio of fixed carbon to volatile matter content). The ash additives were a pulverised fly ash (PFA) and a furnace bottom ash (FBA) from wood pellet combustion in a UK power station. Fuels (with and without additives) were studied for nitrogen partitioning during (i) devolatilisation and for (ii) NO<sub>x</sub> formation during combustion, using two different electrically heated drop tube furnaces (DTF) operating at 1373 K. Devolatilisation was also studied via ballistic-heated thermogravimetric analysis (TGA). The extent of impact of additives on volatile yield under devolatilisation conditions was dependent on fuel ratio, high FR has the greatest increase in volatile release when co-feeding the additive. Under devolatilisation conditions, there is a correlation between volatile nitrogen and carbon conversion for all the fuels tested. Thus, additives liberate more volatile-nitrogen from the coals and also deliver enhanced carbon conversion. A mechanism is proposed whereby ultra-fine particles and vapours of reactive compounds from the additives interact with the reacting fuel/char particle and influence N-release during both devolatilisation and char burn-out. The enhanced conversion of fuel-nitrogen to volatile-nitrogen and the reduction of char-nitrogen can lead to reductions of NO<sub>x</sub> emissions in emissions-controlled furnaces. This approach could assist fuel-flexible power stations in achieving their NO<sub>x</sub> emission targets.

## 1. Introduction

In 2016, 3.8 Gtoe of coal was mined and 28.1% of global energy consumption came from coal [1]. Coal is an energy rich fuel with dry-mineral-matter-free heating values varying from 15 MJ/kg for lignite coals through to > 32 MJ/kg for anthracites [2]. Because of the energy content, it is a high value primary fuel for electricity generation. Coal however, has the highest carbon emissions of all the fossil fuels, and is also responsible for many other harmful emissions, including NO<sub>x</sub> (NO and NO<sub>2</sub>), SO<sub>x</sub> (SO<sub>2</sub>, SO<sub>3</sub>), particulate (dust and aerosols), CO, organics, and trace metals. Emissions regulations are in place to restrict the amount of these pollutants released from power generation [3]. While the UK and the EU are seeking to reduce fossil emissions by moving away from coal, much of the rest of the World have energy programmes that are dependent on coal for the foreseeable future. The general trend

around the Globe had been a reduction in thermal coal usage for electrical power production, but Global demand rose by 1% in 2017 [1].

An emission of particular concern is NO<sub>x</sub> which can lead to acid rain, photochemical smog and increased particulate matter (PM). The NO<sub>x</sub> emission level in the Industrial Emissions Directive (IED) is 200 mgNm<sup>-3</sup>, dropping to 150 mgNm<sup>-3</sup> by 2020 [3]. The values of 150 mgNm<sup>-3</sup> are not attainable for most coal combustion plants without other interventions. Historically, NO<sub>x</sub> emissions from coal have been managed by several strategies. Primary measures include low NO<sub>x</sub> burners, advanced overfire air, re-burning and exhaust gas recirculation, which, when combined can achieve NO<sub>x</sub> reductions of up to 70% [4]. These techniques not only influence the mechanism of NO<sub>x</sub> formation in the combustion chamber but also affect the combustion process. For example, when overfire air is used, it can lead to

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incomplete combustion and thus high levels of carbon can occur in the fly ash [5]. Secondary techniques, which are those employed after the combustion process, include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) and hybrid SNCR/SCR. NO<sub>x</sub> reductions as high as 90% can be achieved through secondary measures. SCR and SNCR however are most effective when used with low sulphur coals [6]. Another possible intervention is the introduction of biomass as an alternative fuel to coal, as many biomass types have lower fuel-N, compared to coal. This can result in a decrease in NO<sub>x</sub> levels, although, even at 100% biomass, 150 mgNm<sup>-3</sup> will not be easily attained without other secondary control systems. However, the high costs of implementation of SCR may be prohibitive in developing countries and for European plants that are expected to close down within the next decade. Under these circumstances, the use of additives in addition to primary NO<sub>x</sub> reduction strategies may be a more cost-effective way to comply with the stricter emission limits. An additional advantage for plants complying with the current 200 mgNm<sup>-3</sup> limit is that the use of additives could increase their fuel range.

The combined consequence of the Large Combustion Plant Directive, followed by the IED, together with incentives to decarbonise power generation, has seen the development of fuel-flexible power stations, which are managing not only coal fuel inventories, but also biomass fuel inventories, together with resultant ash co-products which can be fossil derived, biomass derived, or a mix of the two. This raises the opportunities for improving combustion performance through the addition of ash co-products in the boiler. For example, coal ash might be added in the biomass boiler to reduce deposition, corrosion or bed agglomeration problems [7,8], and, particularly pertinent to the current study, is the addition of biomass ash to the coal boiler to decrease NO<sub>x</sub> emissions. Small reductions in NO<sub>x</sub> and unburnt carbon by the addition of biomass ash additives could lead to substantial savings in operating costs or allow a widening of the fuel specification for the power plant.

There has been some prior research into the reduction of NO<sub>x</sub> in coal combustion through the action of certain metal oxides which may be present, either inherently in the ash or added separately. This addition can be in the fuel feed [9,10], or later in combustion to catalyse the NO-char reaction [11,12]. Fe-based additives have been found to improve SNCR performance (with NO<sub>x</sub> reduction seen to increase by > 10%) [13]. Alternatively coal chars and impregnated coal chars with potassium have shown promise in SCR [14–16].

Biomass fuels tend to have reactive ashes due to high content of alkali metals (i.e. potassium (K)). Besides its role in ash formation and ash related problems in boilers, potassium is a well-known catalyst for the pyrolysis reaction. Furthermore, the potassium in the biomass, or other metals such as iron, may influence the N-partitioning of the coal and consequently NO<sub>x</sub> emissions [17–19]. Indeed, the presence of Na, K and Ca (hydroxides) has been reported to enhance the formation of both N<sub>2</sub> and NH<sub>3</sub> from HCN and tar-N during coal combustion [20]. This may be via both heterogeneous and homogeneous (vapour phase) reactions. Alkali metals are often in a mobile form in combustion and can be readily released into the vapour phase during both devolatilisation and char combustion stages [21–24]. Hernández and Kilpinen, [25] modelled the influence of alkali vapours on volatile-N oxidation chemistry. They found that during staged and non-staged biomass combustion, K and Na decrease radical pool concentrations of active oxidation species (O and OH) and thereby promote reduction of NO<sub>x</sub>.

As well as influencing N-partitioning during combustion, potassium is also a well-known catalyst in char oxidation, and NO reduction by carbon is remarkably enhanced with alkali metals e.g. [12]. Other metals (e.g. iron) or mixed metal systems also impact on the NO reaction with carbon (e.g. [10]). It is proposed that NO adsorbs onto the metal sites, resulting in C(N) and C(O) surface species which react further to form N<sub>2</sub> and CO or CO<sub>2</sub>. A model is proposed in [26] whereby the steady-state surface oxygen concentration, of which the CO/CO<sub>2</sub> ratio is an indication, controls NO reduction on the carbon surface.

Thus there are a number of routes through which active metals may influence N-chemistry in combustion: (i) catalysing devolatilisation reactions and simultaneous release of N-compounds in early stages of combustion; (ii) changing the ratio of HCN, NH<sub>3</sub> and N<sub>2</sub> during tar-N cracking reactions; (iii) reacting in the gas phase to influence the homogeneous reaction routes to N<sub>2</sub> versus NO; (iv) catalysing the char oxidation reaction (v) catalysing NO reduction on char. The current work seeks to investigate the viability of using the ashes from a biomass boiler (fly ash and bottom ash) as additives to reduce NO<sub>x</sub> during coal combustion, something that has not been studied previously. The high levels of alkali and alkaline earth metals in the biomass ashes may act as catalysts to change the distribution and rate of release of N from the coal during devolatilisation and char combustion. A number of techniques, including TGA with ballistic heating and drop tube furnace (DTF), have been utilised to determine high heating rate volatile yields and volatile nitrogen release of fuels and fuels with additives.

## 2. Experimental

Data are provided in full in the results section of this paper.

### 2.1. Materials

Four coal samples were studied, three bituminous coals Shotton blend (UK), La Loma (Columbia), Galatia (USA). The bituminous coals were selected as representative of those used in power station. A steam-coal, Ffos-y-fran (UK) was chosen as a low reactivity coal. A high reactivity biomass, olive cake (Spain) was selected as a comparator. The additives studied included white wood pulverised fly ash (PFA) and a furnace bottom ash (FBA) obtained from a UK power station. Coal PFA was also studied in combination with the olive cake.

All fuels and additives were milled and sieved to between 75 and 89 μm using a Retsch PM100 Ball Mill. The additives were combined with the fuels at 15% w/w. The ash compositions of the additives and the coals were analysed by an external, accredited service laboratory.

### 2.2. Fuel analysis

Elemental analysis was carried out using an EA112 Flash Analyser in accordance with BS ISO 29541:2010 for the coals and BS EN 15104:2011 for the olive cake. Predicted high heating values (HHV) for the coals was calculated using a model given in the ASTM [27].

$$HHV = 0.341C + 1.322H - 0.12O - 0.12N + 0.06865S - 0.0153Ash \quad (1)$$

For calculating the HHV of the olive cake, equation (2) was used, as presented by Friedl et al [28]

$$HHV = 3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20,600 \quad (2)$$

where, C, H, and N correspond to the carbon, hydrogen and nitrogen contents of the fuel (dry basis %).

Proximate analyses of the coal samples were carried out following the British Standard BS1016: Section 104.1:1999 in a Carbolite MFS oven, Section 104.3:1998 in a Carbolite AAF 11/18 and Section 104.4:1998 in a Carbolite AAF 11/18 furnace, for moisture, volatile and ash contents, respectively. The fixed carbon contents were calculated by difference for all of the fuels.

The olive cake proximate analysis was carried out using the British Standards BS EN 14774-3:2009, BS EN 15148:2009 and BS EN 14775:2009 for the moisture, volatiles and ash analysis. All analyses were carried out in duplicate, and mean values are presented. Relative % errors for the proximate analyses were < 4% and for the ultimate analyses < 5%.

### 2.3. Pyrolysis in a TGA with ballistic heating

The fuels and fuel and additive blends were pyrolysed in a TA Q5000IR TGA under flowing nitrogen. For this, the samples were first heated at  $10 \text{ K min}^{-1}$ – $373 \text{ K}$  with a holding time of 30 min. The drying step was followed by ballistic heating, which resulted in a relatively high heating rate (HHR) of  $\sim 33 \text{ K s}^{-1}$ , to a final temperature of  $1273 \text{ K}$  with a holding time of 20 min.

### 2.4. Char preparation in a drop tube furnace (DTF1)

High heating rate chars were prepared from the fuels and fuel-additive blends at Leeds in a drop tube furnace (DTF1). The DTF consists of an alumina tube of  $1400 \text{ mm L}$   $65 \text{ mm i.d.}$  inserted in an electrically heated vertical furnace (Elite Thermal Systems), with three independently heated zones and an isothermal reaction zone of  $455 \text{ mm}$  (with a residence time of  $\sim 0.5 \text{ s}$ ). A schematic of the rig and further details can be found in McNamee et al. [29]. All chars were prepared at a DTF temperature set at  $1373 \text{ K}$ , under pure nitrogen at a flowrate of  $16 \text{ L min}^{-1}$  and entrained air in order to ensure an oxygen concentration of  $1.0 \pm 0.2\%$ , to prevent the biomass chars sticking to the inside walls of the reactor. The chars were collected via a water-cooled collection tube at the bottom of the reactor and two catch-pots for further analysis.

### 2.5. Combustion in a drop tube furnace (DTF2)

The fuels and their blends with additives were combusted in a DTF at Northeastern University. The DTF consisted of an electrically-heated alumina furnace (manufactured by ATS), with an inner diameter of  $3.5 \text{ cm}$  and  $25 \text{ cm}$  in length. Air was introduced to the hot zone, which was heated at  $1375 \text{ K}$ , through both the particle injector and a concentric annular space between the furnace injector and the alumina for a residence time of  $0.75 \text{ s}$ . A schematic diagram and detailed descriptions are given in [30–32]. On-line analysis allowed the monitoring of the exhaust combustion gases from the furnace, which were passed through a glass condenser in an ice-bath prior to being fed to the following analysers: a Teledyne UV-based  $\text{SO}_2$  analyzer Model T100H, a Teledyne chemiluminescent  $\text{NO}_x$  analyzer Model T200H, an  $\text{O}_2$  Horiba VIA-510 analyzer, and a California  $\text{CO}$  and  $\text{CO}_2$  analyser.

## 3. Results and discussion

### 3.1. Elemental and proximate analysis

The analysis of the fuels and additives is presented in Tables 1 and 2. The bituminous coals showed a difference in nitrogen values ranging from  $1.5\%$  to  $1.9\%$  (daf), compared to the Ffos-y-fran at  $0.96\%$  daf. The

**Table 1**  
Elemental and proximate analysis of fuels and ash additives.

	Ffos-y-fran	Shotton	La Loma	Galatia	FBA	PFA	Olive cake	Coal PFA
Carbon (% daf)	81.9	86.5	73.2	77.3	93.9	36.5	51.9	87.2
Hydrogen (% daf)	3.2	4.5	5.3	5.0	4.7	0.6	6.8	1.2
Nitrogen (% daf)	1.0	1.9	1.5	1.9	0.3	0.2	3.0	0.0
Sulphur (% daf)	0.8	1.1	0.6	1.2	0.0	0.8	0.4	0.0
Oxygen (% daf) <sup>a</sup>	13.1	6.0	19.4	14.6	1.0	61.9	37.9	11.6
Volatiles (% db)	8.1	32.3	38.8	40.0	25.7	2.9	72.3	2.3
Fixed carbon (% db) <sup>a</sup>	87.6	57.9	49.1	49.7	16.3	9.4	17.8	1.8
Ash (% db)	4.3	9.8	12.1	10.3	58.0	87.7	9.9	95.9
LOI (%)	–	–	–	–	41.4	12.3	–	2.8
Moisture (% ar)	3.9	7.4	5.4	12.4	2.4	0.4	13.4	0.5
Fuel ratio	10.8	1.8	1.3	1.2	0.6	3.3	0.2	0.8
HHV (MJ/kg db) <sup>b</sup>	28.04	31.08	25.79	27.72	15.14	–	18.90	–

<sup>a</sup> by difference.

<sup>b</sup> calculated by Eqs. (1) (coals) and (2) (olive cake).

**Table 2**  
Oxide analysis of the ash in the fuels and the additives.

Wt % db	Shotton	La Loma	Galatia	FBA	PFA	Olive cake	Coal PFA
$\text{SiO}_2$	46.7	57.3	51.0	52.8	47.4	11.2	56.0
$\text{Al}_2\text{O}_3$	28.0	22.3	19.2	17.4	18.1	1.2	23.3
$\text{TiO}_2$	1.0	1.1	1.0	0.7	0.8	0.9	0.8
$\text{Fe}_2\text{O}_3$	13.4	7.9	16.6	8.2	5.8	0.1	9.4
$\text{CaO}$	6.5	3.1	3.9	9.8	11.7	10.3	3.8
$\text{MgO}$	2.0	1.9	0.9	2.8	3.3	3.0	2.2
$\text{Na}_2\text{O}$	0.4	3.4	0.9	1.2	1.3	0.6	2.8
$\text{K}_2\text{O}$	1.9	1.8	2.4	3.5	5.9	32.3	1.7
$\text{Mn}_3\text{O}_4$	0.0	0.0	0.0	0.4	0.5	0.1	0.0
$\text{P}_2\text{O}_5$	0.0	0.3	0.1	0.9	1.2	5.0	0.0
$\text{SO}_3$	0.0	2.6	3.8	0.3	0.7	2.4	0.0

fuel ratios, FR (fixed carbon content/volatile content) for the bituminous coals ranged from 1.2 through to 1.8. The Ffos-y-fran had a fuel ratio much higher than the other coals at 10.8. Fuel ratio affects the ignitability of the coal (higher fuel ratio coals are harder to ignite because of the low volatile matter content), and therefore the minimum burner load. Fuel ratio, together with fuel nitrogen also correlate with conversion to  $\text{NO}_x$  during combustion [33]. Thus higher volatile matter is expected to promote  $\text{NO}_x$  reduction mechanisms in the primary combustion regions, although high fuel-N would favour increased concentrations of  $\text{NO}_x$  precursors in this region. The olive cake has the highest level of nitrogen at  $3.0\%$ . The fuel ratio of 0.2 is low compared to the coals, but consistent with the type of biomass.

### 3.2. Ash analysis

All of the bituminous coals and the olive cake have a similar ash contents, in the range of  $9.8$ – $12.1\%$ . The additives showed variations in carbon content, reflected in the loss-on-ignition (LOI) values and the carbon contents displayed in Table 1 (note the wt% C is on a daf basis). The ash analysis, in Table 2 was used to establish the reactive components that may act as catalysts to initiate changes in nitrogen partitioning and evolution from the fuels. Previous work has shown iron ( $\text{Fe}_2\text{O}_3$ ) can act as a catalyst and has reaction sites where nitrogen reactions can take place [10,11,26], and alkali metals and alkaline earth metals can influence gas phase chemistry [25] as well as modifying heterogeneous reaction rates [16,34]. The reactive components in the biomass FBA and PFA and coal PFA make up approximately  $18$ – $25\%$  of the ash (although they may not be present in a reactive form, and may be in different forms in the ashes from different sources). Biomass ashes have higher levels of K, Ca, Na and Mg, compared to the coals. Olive cake is higher in reactive components than the coals and the biomass ashes: For example, the potassium in the olive cake ash is  $\sim 32\%$ . The FBA in particular showed high levels of carbon, which could act to

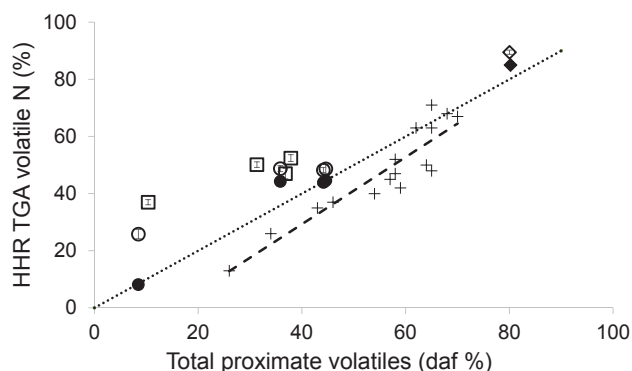


Fig. 1. Synergy of HHR (TGA) volatile N compared to total volatile matter contents. Dotted line is a 1:1 relationship. Symbols: ● Coals, ○ Coals + PFA, □ Coals + FBA, ◆ Olive cake, ◇ olive cake + coal PFA, and + Previous data from [35] (trend line for the latter given by the dashed line).

reduce  $\text{NO}_x$  to  $\text{N}_2$  by providing reaction zones on high surface areas, as seen for studies of the  $\text{NO-C}$  reaction; E.g. [4,16,26].

### 3.3. HHR volatile-N release (TGA)

Fig. 1 shows the results of HHR volatile nitrogen release from TGA (ballistic heating), compared to total volatiles (daf) measured by the proximate method. The coals under test were plotted against the trend line for previous published data from heated wire-mesh reactor experiments which have higher heating rates, and shorter residence time compared to the TGA [35]. Results from the current work for N-partitioning from pure coals and biomass fall along the 1:1 relationship, with HHR volatile nitrogen release in the range 8–45% for the coals and 85% for the olive cake. Thus for the most part volatile nitrogen release follow total volatiles, and there is a concentration of nitrogen in the char for the low volatile content coal. This is why there is a well-known relationship between  $\text{NO}_x$  and FR [4].

When the additives were mixed with the coals (and olive cake) there was a very significant change in the nitrogen released during devolatilisation. The addition of FBA or PFA both resulted in an increase in the fraction of N in the volatiles; in some cases this more than doubled compared to volatile-N from the pure fuels. The increases in HHR volatile-N release across all of the fuels indicates that catalysis is taking place with the additives. Within the TGA, the fuels and additives are held in close physical proximity and the additives clearly influence the decomposition of the coal matrix. Furthermore, as seen in previous studies [E.g. 18,20] it is possible that as the coal matrix decomposes and the volatiles are released from the fuels, they interact with the surface area of the additives, which can provide reaction zones for enhanced reduction of  $\text{NO}$  to  $\text{N}_2$ . These reaction zones could be from reactive elements within the additives. For example, [18,20] showed coals with iron on the surface could instigate a reduction of  $\text{NO}$  to  $\text{N}_2$  from char. In the case of the additives studied here, there are high levels of  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{Na}_2\text{O}$ , and elevated levels of potentially reactive carbon in the ash additives.

### 3.4. HHR volatile-N release (DTF1)

It was observed in the previous section that both additives can catalyse the release of nitrogen into the volatile phase when the fuels are reacting in a bed and the additives and fuels are in close proximity. Of interest to this work, is whether the same influence is observed when the fuel and additive particles are entrained in the DTF. Chars from DTF1 were collected and analysed for proximate and ultimate analysis. The burnout (%) is calculated using the ash tracer method, which assumes no loss of metals and ash species through volatilisation, as given in Eq. (3) [36]. Nitrogen partitioning was calculated from the char

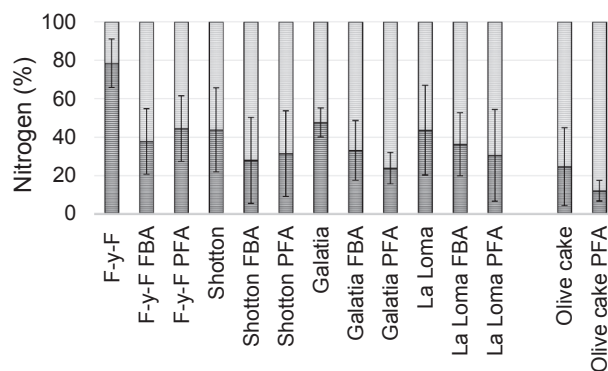


Fig. 2. Nitrogen partitioning of the fuels and fuels with additives during devolatilisation in DTF1. Dark grey = char-N %, Light grey = volatile-N %.

yields and N-contents of fuels and chars.

$$\text{Burnout} (\%) = (A_1 - A_0)10^4 / A_1(100 - A_0) \quad (3)$$

where  $A_0$  is the ash content of the coal and  $A_1$  is the ash content of the char.

Fig. 2 shows the distribution of nitrogen between volatile and char phases. The coals without additives all retained high levels of nitrogen in the chars ranging from 44 to 78% (i.e. 22–56% released into the volatiles). This is different to the results of Fig. 1 which showed that at the heating rates attained in the ballistic TGA, there is less fuel-N released into the volatiles. When additives were co-fed into DTF1 there was a change in the distribution of the nitrogen. The addition of the PFA resulted in a decrease of the nitrogen retained in the chars during devolatilisation across all four coals. The lower volatile coal (Ffos-y-fran) in particular showed a marked reduction in the char N with both additives. The FBA addition also resulted in a higher volatile-N yield. Thus, both additives showed reductions in the nitrogen retained in the char for all of the coals. A similar, although smaller trend was observed for the olive cake: The N retained in the char fell from 25% to 12% with the addition of coal PFA, as shown in Fig. 2.

The reason for the trends seen in Fig. 2 might be explained by the extent of conversion in the DTF. Literature suggests that carbon conversion (i.e. both devolatilisation and char oxidation) can be used as an indicator for nitrogen release, and there is a known correlation between carbon conversion and nitrogen devolatilisation in coals, as reviewed in [4]. Consensus of the relationship differs dependent of coal type and heating regime. Jones et al. [37] reported that nitrogen devolatilisation was slightly lower than carbon conversion, in a DTF at 1400 °C. Woi-towicz et al. [38] suggested nitrogen devolatilisation and carbon conversion was dependent on temperature profiles.

The carbon conversion for the fuels during devolatilisation in 1–2%  $\text{O}_2$  at 1373 K is given in Fig. 3. The level of conversion ranged from

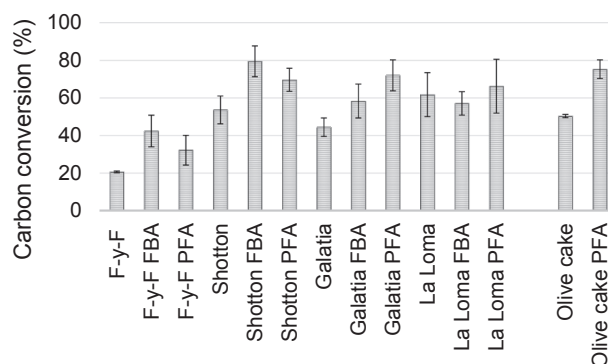
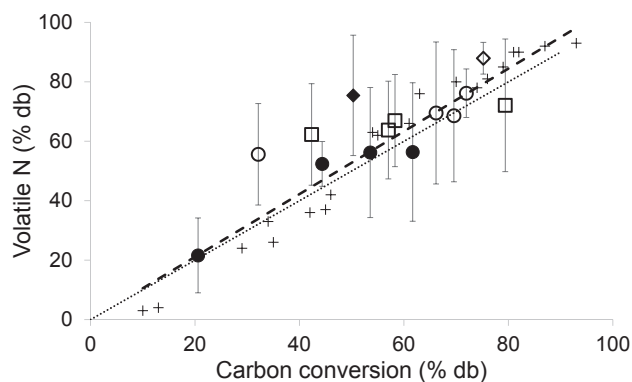


Fig. 3. Carbon conversion of the fuels and fuels with additives during devolatilisation at 1373 K in DTF1.



**Fig. 4.** Volatile N as a function of carbon conversion during devolatilisation at 1373 K in DTF1. Previous published data (+) from [39] is represented by the dashed trend line. The dotted line represents a monotonic relationship between volatile-N and carbon conversion. Symbols: ● Coals, ○ Coals + PFA, □ Coals + FBA, ◆ Olive cake, ◇ olive cake + coal PFA.

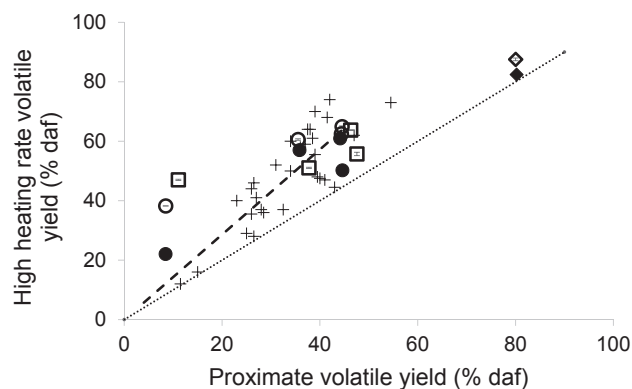
~20% for Ffos-y-fran to 62% for La Loma. A very interesting effect is observed in the presence of both of the additives, where there is a very large increase in carbon conversion- with the exception of La Loma. For example, conversion reaches to over 80% for Shotton when co-fed with FBA, and over 70% for Galatia when co-fed with PFA. A similar trend is observed for all coals, and for the olive cake when co-fed with coal PFA.

Fig. 4 shows the relationship between nitrogen partitioning and carbon conversion. Included in Fig. 4 is the trend line based on previous data presented in Kambara et al. [39]. The four coals all fall along the plotted trend line (and within the scatter of data in [39]) which is very close to the monotonic relationship given by the dotted line in Fig. 4.

When the coals are co-fed with PFA there is an increase in both the volatile N release and the carbon conversion. The general trend is for the carbon conversion and the volatile nitrogen release from the coals to move to the right on the graph but still follow the trend line. This would indicate the coals are behaving as higher volatile coals in the presence of the additive. This is an important finding, coal combustion in full-scale plant, equipped with low- $\text{NO}_x$  burners, show a general relationship of decreasing  $\text{NO}_x$  with increasing volatile matter content [4]. For Ffos-y-fran with additives there was enhanced volatile-N release compared to the carbon conversion, and these data points are therefore above the trend line (and above the scatter in the data given in [39]). The olive cake data also shows a greater volatile N release compared to the carbon conversion, and the addition of the coal PFA to this fuels increases both the carbon conversion and the volatile N release. The result draws the biomass data closer to the trend line. Across all of the fuels, and fuels with additives the general trend of volatile-N following carbon conversion is maintained. Higher values are achieved with the additives, indicating catalysis is taking place during devolatilisation. Since there is 1–2%  $\text{O}_2$  in DTF1 it is possible that the rate of char oxidation is also being increased in the presence of the additives. Nevertheless, various researchers have demonstrated that reactive elements within biomass (and coal) can participate in reactions which can result in a decrease in  $\text{NO}_x$  emissions [10–16,25,34,40]. One mechanism by which this can occur is via catalysis of the fuel-N release (i.e. enhanced fuel-N release) in early stages of combustion. During pulverised fuel coal combustion, low- $\text{NO}_x$  burners promote the release of fuel-N in low oxygen environments which enhances the formation of  $\text{N}_2$  over  $\text{NO}_x$ . Results from both TGA (ballistic heating) and DTF1 show that the additives enhance the conversion of the fuel (and concomitant release of N), which is clearly a desirable attribute to help lower  $\text{NO}_x$  emissions.

### 3.5. High heating rate volatile yields

It is well known that under conditions of high heating rates and high temperature the volatile yields increase due to the rapid cracking of the



**Fig. 5.** High temperature volatile yield compared to proximate volatile yields. Symbols: ● Coals, ○ Coals + PFA, □ Coals + FBA, ◆ Olive cake, ◇olive cake + coal PFA, and + data from previous work in [41] with trend represented by the dashed line, and 1:1 relationship by the dotted line.

coal matrix which releases volatiles before they re-polymerise to form char [39]. It was of interest to compare the results in this work to previous data, to see if similar trends were followed. The four coals, when plotted against data collated by King [41] fall along the trendline,  $y \approx 1.5x$  as shown in Fig. 5. The low reactivity Ffos-y-fran sits to the left on the graph. The three bituminous coals all sit close together between 50 and 60% total high temperature volatile yields (daf). Thus, the coals are behaving as would be expected under these conditions. The biomass data point is close to the  $y = x$  (dotted) line.

In the presence of the additives the high heating rate volatile yields generally increase relative to the proximate volatile yield, although many of the data points are still within the scatter of data from previous work. The results for olive cake showed that the addition of the coal PFA results in an increase in high temperature volatile yield, while proximate volatile yield is virtually unchanged. Ffos-y-fran data indicates that, when the additives are present, the high temperature volatile yield is increased significantly compared to the change in proximate volatile content. This shows that (i) the lower volatile coals are affected more by the additives than the more reactive coals (ii) the additives are more effective at enhancing volatile yield at high temperatures and heating rates than they are under conditions of proximate analysis.

It is interesting that enhanced volatile (and volatile-N) release happens under both fixed-bed and entrained flow conditions, where in the latter case, there may not be close contact between the reacting fuel and the additive. Daood et al [11] also saw a decrease in  $\text{NO}_x$  through fly ash addition to the coal feed for a staged, 100 kWth down-fired combustion test facility. In this case, the catalytic effect was attributed to fly ash entering the coal matrix during decomposition reactions and also interacting with volatiles as they are released. In this case, iron components within the fly ash were highlighted as potential catalytic sites, because Fe/char [19] and iron additives are known catalysts for  $\text{NO}_x$  reduction [10,26]. Similarly biomass fly ash has been shown to be effective at reducing NO at temperatures of 300–600 °C [14]. Such a mechanism could partly explain the results seen here, although the  $\text{O}_2$  concentration in DTF1 is low, and NO-carbon or NO-ash reactions are expected to be of much lesser importance because the NO concentration will be low. If the solid additive is able to interact with the coal matrix, then the alkali and alkaline earth metals may also interact with the devolatilisation step [42]. Nanoparticles of CaO and MgO are known to form during coal (and biomass) combustion [43] and it is feasible that these ultra-fine particles become embedded in the forming char particle and react. Alternatively, the alkali metal salts, and fine particles of alkaline earth metal salts may enter the vapour phase and influence gas phase reactions. Hernández and Kilpinen [25] showed a reduction of  $\text{NO}_x$  during biomass staged and non-staged combustion through the

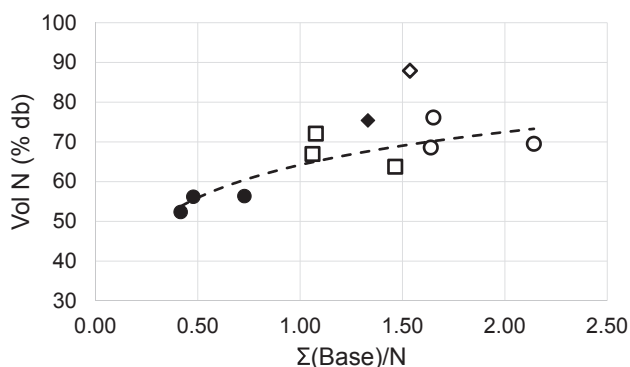


Fig. 6. Volatile N release (DTF1) as a function of mass ratio of alkali and alkaline earth metals to N-content of the feed,  $\Sigma(\text{basic components in the feed})/N$ . Symbols: ● Coals, ○ Coals + PFA, □ Coals + FBA, ◆ Olive cake, ◇ olive cake + coal PFA.

effects of K and Na. Fig. 6 demonstrates a clear effect of the alkali and alkaline earth components within the feed on the partitioning of nitrogen into the volatiles.

### 3.6. $\text{NO}_x$ emissions during combustion

Having established that the additives have a strong influence on devolatilisation (in low  $\text{O}_2$  environments), combustion in DTF2 was undertaken for most of the fuels and fuel + additive blends. The combustion emissions from DTF2 were measured in an excess air environment for all of the bituminous coals and olive cake, and for these fuels blended with appropriate additives. Values for equivalence ratios,  $\phi$  [(actual fuel/air ratio)/(stoichiometric fuel/air ratio)] were in the

range 0.4–0.6 for the coals (with and without additives), and 0.25–0.3 for the olive cake (with and without additive).  $\text{NO}_x$  measurement results are given in Fig. 7. At first inspection (Fig. 7a), a correlation is possible between  $\text{NO}_x$  emissions and FR ( $R^2 = 0.9747$ ), but work by Ren et al [31] demonstrated that there is a different correlation for biomass fuels compared to coal or torrefied biomass fuels. In fact, the  $\text{NO}_x$  emissions given in Fig. 7a are in close agreement with these previous findings, and the curves from [31] are reported in Fig. 7b for comparison. Ren et al. [31] also observed that a high-N biomass can yield higher  $\text{NO}_x$  than coal under the conditions in DTF2. One would expect that in the DTF CH radicals from the volatiles would react with NO thereby producing the well-known correlation of decreasing  $\text{NO}_x$  with decreasing FR [44]. However, for high-N fuels, a high fraction of fuel-N enters the volatiles, and for biomass, the volatiles have high O-species. Thus it is possible that for some biomass,  $\text{NO}_x$  will be more dependent upon fuel-N content. Of course, competition between  $\text{NO}_x$  formation versus reduction routes is also profoundly influenced by excess air. For the fuel lean stoichiometry used here, one would expect increased  $\text{NO}_x$  emissions, and thus it is less easy to observe the impact of the additives than it is in devolatilisation.

It should be noted that while the effects are not as large as seen in devolatilisation (DTF1) some effect of the additives was apparent: As the volatility increased (FR decreased), so there was a greater reduction in NO emissions in the presence of additive, particularly when using the PFA additive. The olive cake, with the lowest fuel ratio showed a reduction of emissions from  $0.57 \text{ kg GJ}^{-1}$  to  $0.47 \text{ kg GJ}^{-1}$  ( $\pm 0.01 \text{ kg GJ}^{-1}$ ). Co-feeding PFA (coal or biomass derived) resulted in a reduction for  $\text{NO}_x \text{ kg GJ}^{-1}$ , across all of the fuels, coals and olive cake. The PFA had higher values of alkali and alkaline earth metals compared to the FBA and the coals as shown in Table 2. Fig. 8 explores the

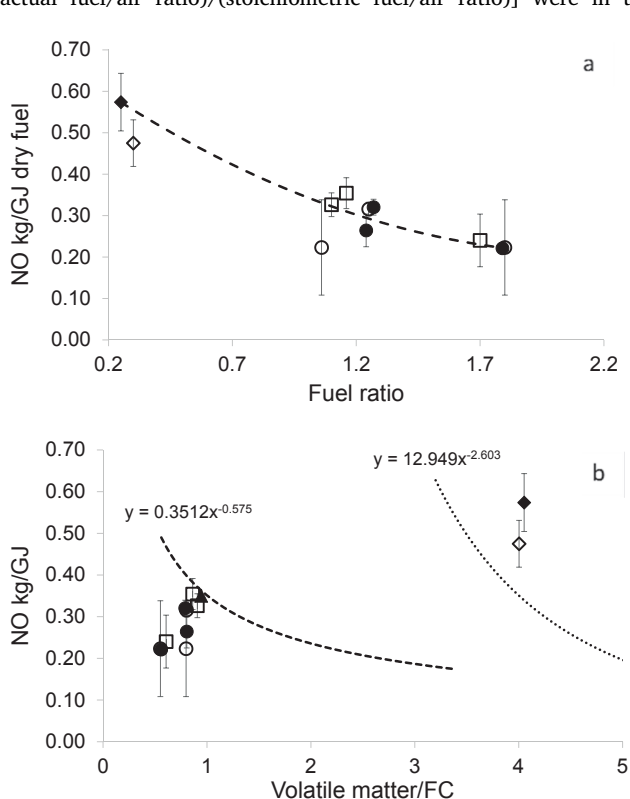


Fig. 7. Fuel  $\text{NO}_x$  emissions from combustion at 1373 K in DTF2 ( $\text{kg GJ}^{-1}$ ) as a function of (a) fuel ratio (FC/VM), (b) VM/FC. Symbols: ● Coals, ○ Coals + PFA, □ Coals + FBA, ◆ Olive cake, ◇ olive cake + coal PFA, and ▲ coal studied in [31] with trend lines based on data in Ren et al [31] for coals/torrefied fuels (dashed line) and biomass fuels (dotted line).

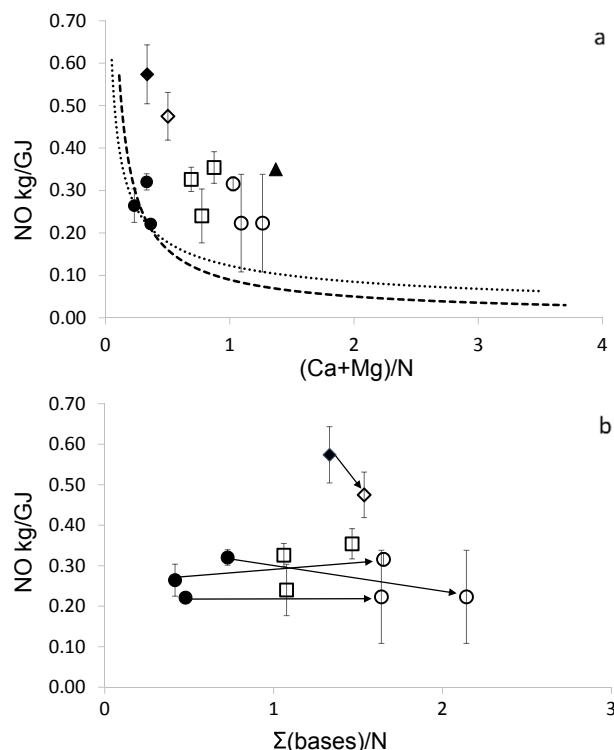


Fig. 8. NO emissions from combustion at 1373 K in DTF2 with respect to mass ratios of potential reactive elements in the feed (normalised for nitrogen in the feed). (a) alkaline earth metals (dashed and dotted lines represent the relationship for coal/torrefied biomass, or biomass respectively from [31]) (b) alkali + alkaline earth metals. ● Coals, ○ Coals + PFA, □ Coals + FBA, ◆ Olive cake, ◇ olive cake + coal PFA. Arrows denote change in NO emissions for fuels with PFA.

influence of alkali and alkaline earth metals on NO<sub>x</sub> emissions from the test in the un-staged DTF (in excess air). The curves in Fig. 8a are based on data for combustion of coals/torrefied biomass and raw biomass from [31]. A trend of decreasing NO<sub>x</sub> with increasing reactive metal components is observed, which could point to a mechanism whereby fine nanoparticles of metal oxides embed into the fuel/char particles at reactive sites. Once in close contact with the fuel matrix they can influence the heterogeneous reaction chemistry and decrease NO<sub>x</sub>. The curves and data in both Figs. 6 and 8 suggest that there is a limit to the effectiveness of this mechanism. Results for the raw fuels are in agreement with [31], and there are modest reduction in the NO emission (17% decrease in NO for the olive cake and 5% decrease in NO for the coals in the presence of PFA, which has the greatest amount of alkali and alkaline earth metals). This is demonstrated further in Fig. 8b. However, the presence of excess air in DTF2 is influencing the efficacy of the gas-phase NO<sub>x</sub> reduction chemistry. If the additives were used in a staged combustion system, then the reduced oxygen in the near burner region, together with enhanced fuel-N release in the presence of additives (as seen in DTF1 and ballistic TGA), should be conducive to NO<sub>x</sub> reduction, although the combustion would need optimising for each fuel-additive combination.

#### 4. Practical application considerations

According to the results obtained, the addition of biomass ash to coal was found to increase volatile release and thus volatile nitrogen fraction under both fixed-bed and entrained flow combustion conditions. This suggests that to see the beneficial effects of these additives, in practice the biomass ash would have to be introduced with the coal feed – whether co-milled with coal or injected closely together into the furnace. This would require optimisation of the combustion process, as mentioned in section 3.6. In addition, fouling and slagging could be an issue with injecting biomass ash into the system. It is to be noted that the feed ratio has not been optimised in this work, and it is possible that a similar benefit could be seen on NO<sub>x</sub> with lower amounts of biomass ash. Nevertheless, volatile-K from the biomass ash would be of special concern, in particular for fouling [45]. In this regard, since this ash has already been through the boiler, it may have less mobile potassium than low temperature ashed biomass ash (or a biomass fuel). Moreover, previous studies have shown that coal ash can react with volatile-K, so it is possible that coal ash could capture any remaining K as the coal burns [46]. The cost trade-off between bringing NO<sub>x</sub> emissions down and increasing of fouling and slagging propensity would have to be carefully assessed. Thus the use of biomass ash as an additive would require further study and optimisation, but it looks promising as a relatively cheap addition to NO<sub>x</sub> reduction strategies in a power station that already has a flexible fuel inventory.

#### 5. Conclusion

Experimental studies were made of four coals and one biomass, in the absence and presence of power-station ash additives. During high heating rate devolatilisation, the coals retain 44–78% of their nitrogen in the char at 1373 K. In comparison, the olive cake loses 75% of its nitrogen under the same conditions. In the presence of the ash additives, a higher loss of fuel-N is observed in the volatiles. This is most significant for high fuel ratio coal, Ffos-y-fran, where volatile-nitrogen increased from 22% to ~60% in the presence of the additives. This enhanced volatile-N release in the presence of the additives is related to the enhanced carbon conversion, and volatile-N correlates well with extent of conversion. Thus one role of the additives is to catalyse the devolatilisation (and char burning) stages. The additives all had elevated levels of the potentially catalytic species, CaO and K<sub>2</sub>O, compared to the coal ashes. The effect of the additives for decreasing NO emissions was more modest in the studies under excess air. Nevertheless, the volatile fuel-N release shows a synergy with the base

components (Ca, Mg, K, Na) in the feed (i.e. fuel or fuel + additive): When the summation of base elements increase, so the volatile-N release increases, and NO decreases. A 17% reduction in NO for the biomass, and a 5% reduction in NO for the bituminous coals was achieved even under fuel lean conditions.

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