Research article

The use of agricultural residues, wood briquettes and logs for small-scale domestic heating

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ABSTRACT

Large amounts of agricultural residues are produced annually in the UK alone, which presents a significant biomass energy resource. It has limited availability in briquetted form in the UK but is widely used, particularly in Asia. The aim of this work is to assess the emission from briquetted agricultural residues to wood fuel, including commercial wood briquettes, when utilised in a 5 kW domestic heating stove. Other straw-type materials, sugarcane bagasse, Miscanthus, were also investigated. The combustion behaviour depended on the chemical and physical nature of the briquettes. Results indicate that fuel choice is an important consideration for emission reduction. Fuel-N directly correlates to emitted NOx and all the fuels studied had NOx emissions below the EU regulation limit. While agricultural residues can be relatively high in Cl and S, there is evidence of in-situ capture of HCl and SO_2 by calcium salts in the fuel ash. Particulate emissions correlate with the volatile matter in the fuel, but also are influenced by the quality/durability of the briquette. The briquettes performed well compared to wood logs, and while there is a fuel-type influence on emissions, it is also clear that briquettes from optimised manufacture can be lower emitting than wood logs.

1. Introduction

In many countries' biomass fuels, such as wood have replaced coal for small domestic stoves in a move to decarbonisation and because it is often a convenient alternative. The extensive use of wood-derived fuels has however resulted in pressure on forest resources since, for example, biomass accounts for about 10% of the energy consumption in Europe in 2017. The use of non-woody residues such as herbaceous materials and agricultural residues is another alternative [1], but these fuels tend to be of a lower quality, and, in the UK few are approved for use in smokeless areas [2]. Furthermore, most are not approved for use in exempted appliances. Interestingly, briquettes formed from pressed wood residues are widely available in supermarkets and garage forecourts and it is therefore likely that they are in use in smokeless zones. Similarly, briquettes of waste agricultural materials such as wood, straw and bagasse are used in small stoves in countries such as China, India, Africa and Northern Europe [3–8], and are sometimes used in the UK also. In fact, in recent years there has been an increasing use of these low-grade biomass fuels more widely and this paper seeks to identify the performance of briquettes manufactured from agricultural residues (AgR) and wood residues, which could be a cost-effective alternative

fuel to wood logs.

Life cycle impacts of domestic fuels produced from agricultural residues are considerably lower than traditional fuels, as the feedstock is a by-product and does not require additional land or put strain on forestry resources [3,4,7]. However, there may be increased HCl, NO_x, SO_x and particulate emissions for certain feedstocks compared to wood logs and briquettes [5,7–9], an important consideration. Recently there has been considerable interest in the measurement of gaseous and particulate emissions [7–13], especially fine particles and their toxicity [9,10], from small biomass stoves. The influence of fuel type such as logs or pellets has also been examined [11–13]. The suitability of agricultural residue feedstocks may also be limited by high ash contents and low ash melting temperature [4,5,8]. Volatile salts (such as K-salts) condense into the emitted particulate, although they have not demonstrated cytotoxicity [4,9], and those in the solid phase can affect the melting temperature of the ash. This has been a known issue in large scale biomass heat and power generation for many years, but, for space heaters, there has been few cases reported of slagging, fouling, corrosion and bed agglomeration in small scale systems because of the lower combustion temperatures. This is not the case for pellet boilers, where ash agglomeration can be a serious problem during periods of

prolonged use at high load because of the higher operating temperatures. Agronomy may be important here as well [14–16].

There are many complex interactions between K, S, Ca and Si which affect emissions and the nature of the ash produced [8]. The sulphur content of some agricultural residues may be 10–30 times greater than wood [3]. Sulphur retention in the ash may be increased through the use of calcium-based binders [17] or inherent calcium in the ash [18,19]. Ash melting characteristics may also be improved through phosphorus based additives and blends. As mentioned above, high inorganics may also impact emissions. Wiinikka et al. [18] found that the ratio of fuel alkali to silica (K + Na)/Si was related to the amount of particulate matter (PM) formed: Alkali silicates are captured in the ash and therefore do not enter the particle phase. Briquettes from agricultural residues also have a lower density and calorific value than wood logs and wood briquettes, depending on the degree of densification by briquetting [3].

This paper forms a continuation of earlier stove combustion studies looking at the use of fuel type [20], fuel moisture content [21] and fuel pellet composition [22] and impacts on emissions. It particularly focuses on three main areas: (i) An assessment of different agricultural residues and other residues for their fuel properties, which highlights potential areas of concern for use in small-scale domestic heating; (ii) An examination of emissions of briquetted agricultural residues in a simple multi-fuel space heater; and (iii) a comparison of combustion behaviour and emissions to those seen for wood-based briquettes and logs under similar conditions. Much is known about the combustion behaviour of logs and wood pellets in small stoves and the nature of the pollutants formed. This is specially the case for the particulate material, but much less is known for the utilisation of briquettes.

2. Materials and methods

2.1. Fuels and their sources

The majority of the fuels studied here are wheat and barley straws grown in different sites at Rothamsted Research, UK, and which have been subjected to different fertilisers and growing conditions, as shown in Table 1. In addition, sugarcane bagasse and miscanthus fuels were used for comparison, the former being a residue from the sugar industry, and the latter an energy crop. Some of these were purchased in briquetted form and some were prepared from the milled straw material as detailed in the next section.

2.2. Fuel processing

For the combustion measurements and emissions testing, all the samples needed to be briquetted following milling (< 4 mm) and

Fig. 1. Photographs showing the bagasse (left), straw (centre) and Miscanthus (right) briquettes.

drying. Bagasse briquettes were made in house using a hydraulic press with a pressure of 30 MPa and a jacket temperature of 125 °C. The straw briquettes were more difficult to manufacture and were outsourced. The Miscanthus briquettes were obtained from locally sourced Miscanthus in SW England. Hence the briquette size and shape varied by fuel type, as shown in Fig. 1. The wood briquettes were commercial products made by a high-pressure thermal process.

The straw briquettes contained particles < 4 mm in length and were cylinders of about 75 mm in diam. and 60 mm in height and had a 20 mm diameter hole through the centre. Straw is inherently difficult to bind and here 10% of solid pre-gelled wheat starch was added and briquetting proceeded immediately after mixing. The durability was still not ideal, as illustrated by the crack in the straw briquette in Fig. 1. The bagasse briquettes were similar as shown in Fig. 1 but without a central hole. The Miscanthus briquettes were 60 × 40 × 40 mm blocks and contained particles < 4 mm in length. The commercial wood briquettes (logs) consisted of compressed sawdust, approximately 200 mm long, 50 mm diam. with a central 10 mm hole. They are manufactured by the application of high pressure at slightly elevated temperature and the sawdust particles are bonded together by softened, inherent lignin [6,23] giving a high-density product.

2.3. Fuel characterisation

After milling, fuels were characterized for proximate analysis using a Carbolite AAF 1100 furnace and Carbolite moisture oven in accordance with the European Standard methods (BS EN ISO 18134-1:2015, BS EN ISO 18122:2015, BS EN ISO 18123:2015). Ultimate analysis was determined in duplicate according to BS EN ISO 16948:2015, using a CE Instruments Flash EA 1112 Series elemental analyser for C, H, N, and O calculated by difference after accounting for the ash

Table 1

Agricultural residues and biomass fuels used, together with the added fertiliser, where applicable, and their origin.

Fuel	Site	Added N as ammonium nitrate (kg/Ha)	Added K as K$_2$SO$_4$ (kg/Ha)	Comments on fuel sources
Winter wheat straw	013	192		And farmyard manure added, 35 t/ha.
Winter wheat straw	093	192	90	Fertiliser added as shown.
Winter wheat straw	123	240	180	Fertiliser added as shown and 55 kg/ha Na as Na$_2$SO$_4$.
Winter wheat straw	143		90	As 093, but K added as KCl
Spring barley straw	423	144	90	Fertiliser added as shown
Spring barley straw	433	144	90	Fertiliser added and 450 kg/ha as Na$_2$SiO$_3$
Spring barley straw	723	144		N, P & K from farmyard manure
Bagasse		–	–	Brazil
Miscanthus		–	–	South-west UK (locally grown)
Commercially made 'Heatlogs' briquettes		–	–	Hardwood briquettes made by Fuel Express, HETAS Approved.
Commercially made 'Hotmax' briquettes				Softwood (pine) waste briquettes made by Hotmax, HETAS Approved.
Wood logs, spruce				18% moisture DEFRA Approved.
Wood logs, willow				10% moisture, DEFRA Approved.

and moisture contents. High heating values (dry basis) were estimated using the method previously used by us [22].

Metals analysis in the milled biomass samples was undertaken by acid digestion followed by Atomic Absorption Spectroscopy (Varian FS 240 to an accuracy ± 5%), following BS EN ISO 16967:2015. In addition, some of the fuels were analysed by an external accredited laboratory for major ash components.

2.4. Combustion and emission tests

A Waterford Stanley Oisin Multi-fuel stove (Defra exempt appliance) was used to study combustion of all fuels as described previously [20]. It is rated as having a maximum non-boiler thermal output of 5.72 kW. There is one primary air supply under the bed, which is manually controlled via a damper. The general arrangement of the test equipment was in accordance with BS EN 13240, and the stove was mounted on an electronic scale. Sampling ports were installed in the 125 mm diameter flue at a height of 1.43 m. The stove was brought up to the working temperature using a hot bed of burning charcoal. The first batch of fuel was added to the hot embers as an ignition aid. Each subsequent batch (up to four per fuel) was added when the CO_2 concentration fell to 1%. Each batch of fuel was 750 ± 100 g. The damper was kept constant for all fuels. Flue gas composition was monitored using a Gasmet 4040 FTIR instrument as before [21].

Particulate matter (PM) was determined using a gravimetric method in which a measured volume of flue gas was passed through two 47 mm Munktell Quartz filters held at 70 °C. Filters were analysed for elemental carbon (EC) and organic carbon (OC) using a thermo-optical method by Sunset Laboratories Inc. (www.Sunlab.com). Data is presented as EC/TC where TC is total carbon (EC + OC).

3. Results

3.1. Fuels analysis

Mean values of the ultimate and proximate analyses of the fuels are reported in Table 2. Details for the logs are given in reference [22].

It is clear from a comparison of the N and K contents of the straws listed in Tables 2 and 3 respectively, together with data given in Table 1 showing the addition of fertilisers, that there is poor correlation between the two. That is, for this small sample set the fertiliser does not seem to affect the K content or N content (cf Tables 1–3) of the fuels. These fuels are therefore considered to have properties that are typical of wheat and barley straw, harvested in winter and spring respectively, in the UK. Both straws have ash contents in the range 4.2–7.0 wt%. On average, the barley straws (BS) harvested in the spring have higher N- and Cl-contents than the winter wheat straw (WS). In terms of ultimate

Table 3

Metals analysis in the whole sample by Atomic Absorption Spectroscopy.

	mg/kg (db)							
Sample	K	Na	Fe	Mn	Ca	Al	Zn	Mg
WS 013	8077	104	98	44	5754	111		633
WS 093	5053	53	91	33	4374	138	42	907
WS 123	5495	55	89	31	5274	92	37	874
WS 143	5252	254	120	36	3911	60		584
BS 423	20,649	260	147	39	7298	196	43	999
BS 433	16,464	1078	156	52	7922	196	46	1014
BS 723	12,394	206	147	14	5149	217	43	617
Bagasse	2645	280	1889[a]	68	1969	3058[a]		282
Miscanthus	11,112	171	97	29	4406	23		555
Wood briq. Heatlogs	1326	23	167	8	3888	138		926

[a] The values in italics are probably high as a result of soil contamination.

and proximate analysis, Miscanthus briquettes have similar characteristics to BS, although they contained the highest chlorine of the fuels under study, Bagasse properties given in Table 2 fall within the range seen for the wheat straws.

Table 3 contains the concentration of the main inorganic elements in the fuels. Note that the alkali content (K + Na) of the BS samples are much higher than the WS samples. Miscanthus, resembles BS in terms of alkali concentrations, and Bagasse contains the lowest alkali of all the fuels (and the lowest Ca content). There is some evidence of soil contamination in the bagasse sample.

The major metals were measured by an accredited external laboratory, SOCOTEC Group, UK, using acid digestion and ICP-OES and were converted to wt% oxides in the ash and are presented in Table 4. Here only the oxides were considered but there are some chlorides, carbonates and sulphate present as well. Note that the SiO_2 content of the bagasse ash and wheat straw ash was over 60 wt%. The bagasse also contained significantly higher levels of Al and Fe which are possibly due to contamination and which will slightly affect the ash softening properties.

The high alkali and Cl found in BS and Miscanthus is likely to contribute to inorganic aerosol in combustion, whereby alkali chlorides, vaporised in the burning bed, nucleate, condense on cooler surfaces (including carbonaceous particulate) and form fine particulate which might escape the flue. As mentioned earlier, volatile salts (such as K-salts) condense into the emitted particulate, but they have not demonstrated cytotoxicity [7]. The remaining chlorine will either be emitted as HCl or be retained in the bottom ash (e.g. as calcium chloride) as observed before [20]. This issue is examined further in the next section, where data for HCl emissions from combustion of the fuels are presented.

During combustion in a small combustor such as those found in

Table 2

Ultimate and proximate analyses of samples of the fuels; the straw samples were analysed before briquetting; the other analyses are of the finished briquettes.

	wt% db					ar	wt% db			HHV, db
Sample	C	H	N	S	Cl	MC	VM	FC	Ash	MJ/kg
WS 013	44.3	6.2	0.5	0.10	0.06	6.7	82.3	12	7.0	17.62
WS 093	50.3	5.5	0.5	0.06	0.03	5.8	79.6	16.2	4.2	19.71
WS 123	47.8	5.2	0.6	0.08	0.04	8.7	78.6	16.8	4.7	19.59
WS 143	43.2	6.2	0.4	0.24	0.02	6.6	87.7	6.6	5.7	19.23
BS 423	48.7	5.1	0.9	0.10	0.11	7.4	75.1	19.0	5.9	19.75
BS 433	48.2	5.1	0.9	0.10	0.13	7.8	74.2	19.3	6.5	19.66
BS 723	47.4	5.2	0.5	0.06	0.05	7.3	76.6	18.2	5.2	19.23
Bagasse	48.2	5.6	0.3	0.03	0.01	5.9	87.5[a]		5.4	18.95
Miscanthus	47.3	5.7	0.8	0.10	0.25	9.1	87.0[a]		4.6	20.02
Wood briq. Heatlogs	49.7	5.8	0.2	0.02	0.01	6.7	90.1	8.6	1.3	19.81
Wood briq. Hotmax	49.7	6.1	0.5	0.0	–	5.5	75.8	19.1	4.9	19.8

Db: dry basis; ar: as received; MC: moisture content wt%; HHV: Higher Heating Value.

[a] Values from ECN Biomass Database [24].

Table 4
Analysis of some of the fuel ash fractions.

Sample	wt% oxides										
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Mn_3O_4	P_2O_5	SO_3
WS 013	55.8	0.3	0.2	< 0.1	11.5	1.5	0.2	13.9	< 0.1	2.1	3.1
WS 143	62.8	0.2	0.3	< 0.1	9.6	1.7	0.6	11.1	0.1	1.5	2.1
Bagasse	60.1	10.7	5	0.6	5.1	2.4	0.7	5.9	0.2	2.2	1.3
Miscanthus	33.2	0.3	0.3	< 0.1	13.4	2	0.5	29.1	< 0.1	3	3.8

domestic space heaters, the temperature remains low enough that the majority of emitted nitrogen oxides are from the nitrogen in the fuel. Thus, a correlation has been seen for NO emissions versus fuel-N content. This is also discussed in the next section, but based on the analysis in Table 2, Miscanthus and BS might be of concern because of their higher N-content. It should perhaps be noted though, that the N-content of these fuels is still lower than typical values for coal-based smokeless fuels, such as those found on the Defra-approved fuels list, and only recently discontinued.

The relative base to acid ratio may be used as an indicator of slagging/agglomeration propensity, and there is a strong variation with this for the fuels studied here and which are shown in Fig. 2. The acid component was calculated from (TiO2 + SiO_2 + Al_2O_3), and the acid component from (K_2O + Na_2O + CaO + MgO + Fe_2O_3), both terms calculated on a weight % basis.

These results show [24–26], together with the high ash content, that the straws studied have a higher tendency to form fused ash during combustion. However, there has been little evidence of slagging, fouling, corrosion or extensive bed agglomeration in small-scale low temperature systems of the type examined here. i.e. Temperatures in space heaters are usually low enough that ash agglomeration does not present a problem, but this could be an issue in pellet boilers, where prolonged operation at high load (and therefore high temperature) is likely.

3.2. Combustion properties and emission factors

3.2.1. Burning rates

The average burning rates over a whole cycle with a hot start are given in Table 5, together with results from other fuels using the same stove and experimental results. The burning rates are a function of the reactivity of the fuel and the available reactive surface area; thus, split logs would burn faster than 'unsplit' logs, the data for which is give here. Combustion of logs, after the ignition phase, undergoes essentially

Table 5
Average burning rates for the straws over the whole cycle together with some other values for logs: the errors for burning rates are ± 0.3 kg/h.

Sample	Burning rate (kg/h)	K wt% content (db)	VM wt% (db)	Reference
WS 093	2.0	5053	79.6	This work
WS 123	1.3	5495	78.6	This work
BS 423	1.4	20,649	75.1	This work
BS 433	1.5	16,464	74.2	This work
BS 723	1.3	12,394	76.6	This work
Bagasse	1.9	2645	87.5	This work
Miscanthus	1.8	11,112	87.0	This work
Wood briquette, Heatlogs	1.6	1326	90.1	This work
Wood briquette, Hotmax	1.7	–	76.0	This work
Wood logs (spruce, 18% moisture)	1.3	840	77.0	[17]
Wood logs (willow, 10% moisture	1.4	2660	82.0	[17]

two major easily defined phases, a flaming phase and a smouldering phase; the flaming phase is related to the volatile matter content, and the smouldering phase, largely to the amount of residual char which can be catalysed by the K (and Na) content. Briquettes behave slightly differently in that after an initial 'main flaming' phase the briquettes may disintegrate exposing small fuel particles which may continue flaming whist some of the charred fuel is undergoing smouldering. Thus, the conventional division into flaming and spontaneous phases is not clear. The results show that within experimental error the average complete cycle burning rates do not differ markedly between the fuel types, the mean is 1.6 kg/h. Straw 093, Miscanthus and bagasse briquettes burned more rapidly, possibly due to their high volatile matter content.

3.2.2. Emissions measurements

Emissions testing revealed large differences between the fuel types. An example emissions plot is shown in Fig. 3 for barley straw briquettes (site 423). The flaming and smouldering phases can be identified visually or by use of the modified combustion efficiency (MCE), which is defined as the ratio of CO_2 released / sum of CO and CO_2 [13]. But the distinction is not clear as previously explained because of 'disruptive combustion'. In Fig. 3 the reload points as well as approximate locations of the flaming and smouldering regions are located for the MCE plot. For these tests, MCE never dropped below 0.6 during the smouldering phases and was generally 0.9 or above during flaming. HCl, SO_2, formaldehyde and acetic acid are seen to peak in the flaming phase just after fuel addition, whereas CO and CH_4 are seen to peak in the smouldering phase. Interestingly, up to 25 ppm of N_2O is emitted alongside NO and NO_2. The phases can be approximately identified from the MCE and the variation of CO. The levels of the gaseous emissions are given in ppm at 13% O_2 and STP. These can be converted into Emission Factors which can be compared with other studies, as shown later. The bed temperature also plays a key role in emissions formation and is presented for BS 433 in Fig. 4. The high initial bed temperature is due to the charcoal used for ignition. Several cycles are shown, and these are indicated by the periodic change in both bed and
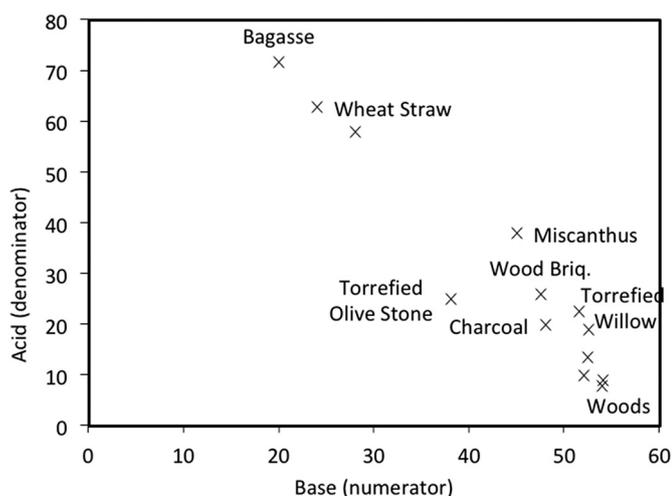
Fig. 2. Calculated acid to base ratios for the fuels in Table 4 and using data from [22,24–26].
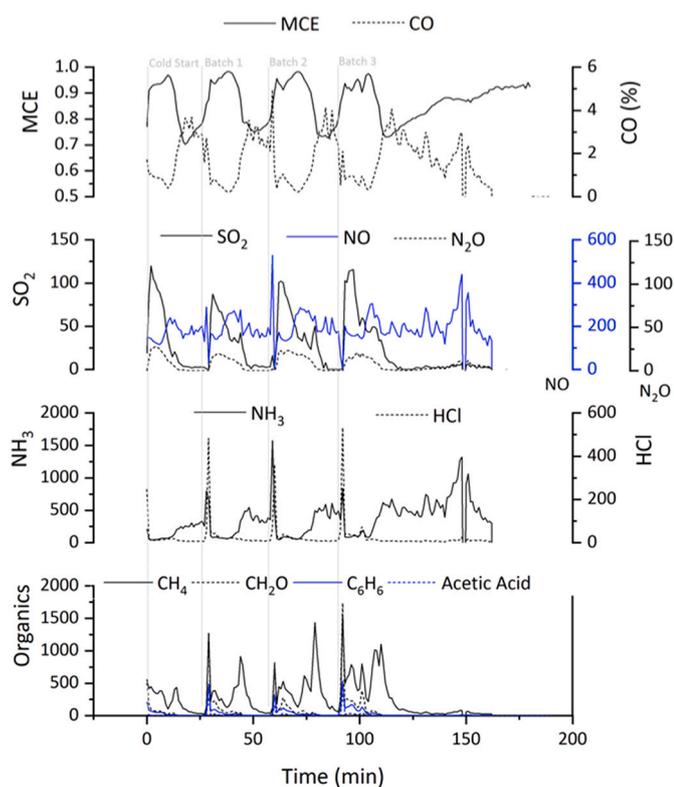
Fig. 3. Emissions profiles for BS 423 briquettes. Axes show concentrations in ppm at 13% O_2 and STP, unless otherwise stated.
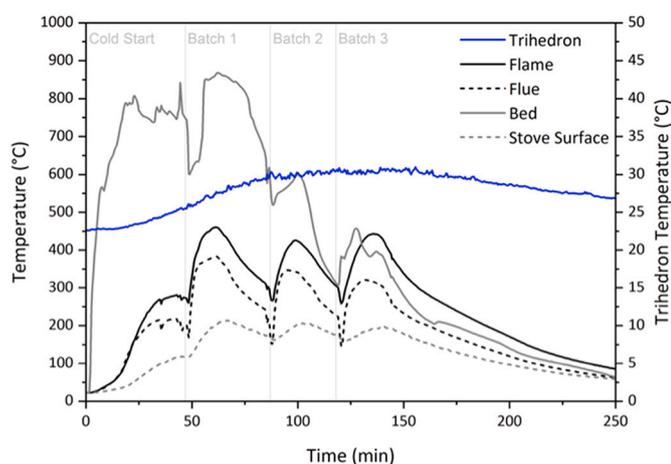
Fig. 4. Temperature profiles for BS 433 briquettes, showing an ignition cycle followed by three reload cycles.

flame temperature (defined as the gas temperature just above the bed), these occurring at approximately 50, 80 and 120 min. The flue temperatures tend to be more uniform and this is the case for the trihedron temperature, 500 mm from the stove surface, which peaks at 31 °C.

Fig. 5(a) is of a relight situation with a fresh load of briquettes placed on hot charcoal bed and undergoing flaming combustion. Ignition initially takes place from the centre of the briquette as well as the top, which acts as anchoring bluff body ignition. Fig. 5(b) shows a combustion image of the smouldering phase. The shape of the briquette remains intact until the final stages of combustion until the ash/char remnants disintegrate.

Figs. 6–8 show the emissions of the trace species NO, HCl and SO_2 for some of the samples listed in Table 1. Fig. 6 shows the NO emission for the different fuels.

Only the combustion of one straw is shown in Fig. 6 but all the straws studied here follow the same time dependence of NO formation. NO emission is constant during flaming and smouldering phases, although the magnitude varies from straw to straw. Miscanthus has a higher NO emission during flaming combustion, and this continues at a high level into the smouldering phase. In the case of bagasse emission, the ratio of flaming emission to smouldering emission is 1.5, that is, the smouldering emission is higher than the two previous cases. Wood is different, with NO being formed over the whole cycle with a slight increase towards the end of smouldering, showing that fuel-N concentrates in the char during burn-out.

The time dependences of HCl release are given in Fig. 7 and are similar for all straws, namely that emission peaks during flaming combustion, and then fall away as the char burns out. Miscanthus combustion results in a peak in HCl emission in the flaming stage and then another during the smouldering phase, possibly indicative of evaporation of KCl which react in the gas phase to form HCl. Bagasse is different: just a single small, broad emission peak is observed during the combustion process. The HCl emission for wood is very low hence the large experimental scatter and an average line are shown in Fig. 7 for the Heatlogs briquette.

The data obtained in terms of Emission Factors are given in Table 6. In addition, we have included data for some commonly used wood fuels which have been obtained using the same experimental methods for comparison purposes. High levels of HCl emissions are usually associated with high levels of potassium content in the fuel [8]. As pointed out before, this can result in corrosion, and deposit formation from salts above the combustion zone. Additionally, it can result in the formation of aerosol particles of KCl as discussed later.

Fig. 8 gives representative SO_2 emissions from the reloaded batches of different types of fuels. Sulphur dioxide is emitted throughout the combustion cycle, although higher in the flaming stage. Peak concentrations are highest for Miscanthus and barley straw, which are fuels with relatively high sulphur contents. The data for the emissions of SO_2 in terms of Emission Factors are given in Table 6. It has been previously been observed [8] that they are dependent on the amount of S in the fuel and the data given in Table 6 and Fig. 9 are consistent with this conclusion.

3.2.3. Gaseous emission factors and comparison with other fuels

The emission factors for the gases are given in Table 6 for the fuels studied and typical results for logs and other fuels burning in a similar stove under the same conditions. The results show that fuel type/ composition has a large impact on emissions. The commercial wood briquettes had the lowest emissions of all fuels, including wood logs.

Figs. 9 and 10 show the relationship between the NO and HCl emissions and N or Cl content in the fuels. In Fig. 9 the linear relationship is based on present work and data from Refs [20, 22]. It is seen that there is a relationship between NO emission and fuel-N content. There is a suggestion that torrefied fuels give lower NOx than expected based on their N-content. This is discussed further in [17] and it is thought to be due to the slower rate of combustion of the char, which promotes heterogeneous reduction of NO to N_2.

A plot of the Emission Factor for HCl against the fuel-Cl content is given in Fig. 10. It is seen that the HCl emissions are correlated to the Cl content of the fuel but only at low levels as shown by the straight line in Fig. 10, but then level off at about 0.05 wt% fuel Cl, This could indicate that chlorine is being captured in-situ by calcium in the ash. Such an effect has been observed in bed combustion [27]. This observation is consistent with that of Zeng at al [8]. The emission levels are all low so there are considerable measurement errors, which are shown in the plot.

A similar plot is observed for SO_2 emissions versus S in the fuel as shown in Fig. 11. The emissions are all below those expected based on the fuel-S content, and again indicate in situ capture in the bed, probably by reaction with calcium salts. Such an effect is well known, and
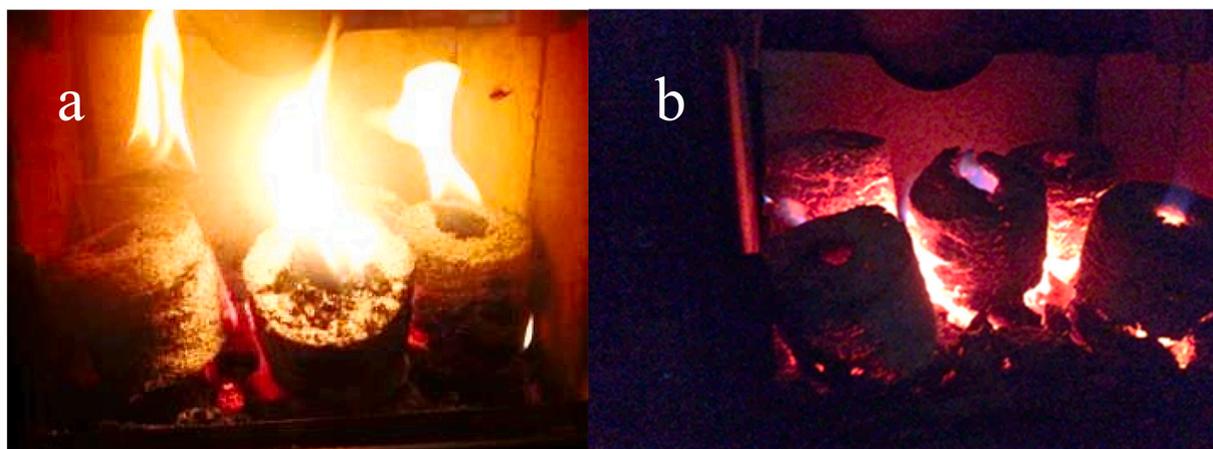
Fig. 5. Direct photograph of BS 433 briquettes (a) undergoing flaming combustion, and (b) undergoing smouldering combustion.

minerals such as limestone are often added to fluid bed combustors to capture sulphur in the combustion of high-S fuels. Except for the Miscanthus (ratio is 0.65), all the fuels studied have molar ratios of Ca/ $(2Cl + S) > 1$ showing that there is enough Ca to capture a large fraction of the Cl (as $CaCl_2$) and S (as $CaSO_4$).

3.3. Particulate emissions and comparison to other fuels-

Particulate emissions and EC/TC ratios for each fuel were obtained for several tests, averaged over the complete combustion cycle. The average PM emissions on a mass basis, EF_{PM}, together with EC/TC ratios are presented in Table 7. As was the case with Table 6, data for some wood fuels (from reference [17]) are included for purposes of

comparison.

Briquettes of wood, Miscanthus and bagasse showed the lowest PM emissions, whereas the straw briquettes gave consistently higher PM emissions, although still in the range observed for wood logs. The PM formation is a dependent on the VM content as well as the K content, since potassium salts are expected to dominate the fine inorganic particulate (not measure here) that is emitted as KCl or KOH [8,28]. That is, particulate matter emission from the combustion of biomass consists basically of fine soot particles, particulate KCl and KOH, and larger particles from ash and char [1,8,14,20,28,29].

A plot of PM on a volumetric basis versus volatile matter content, which is a reasonably accurate indication of soot formation for wood fuel, is given in Fig. 12. The lower trend line is for woody biomass
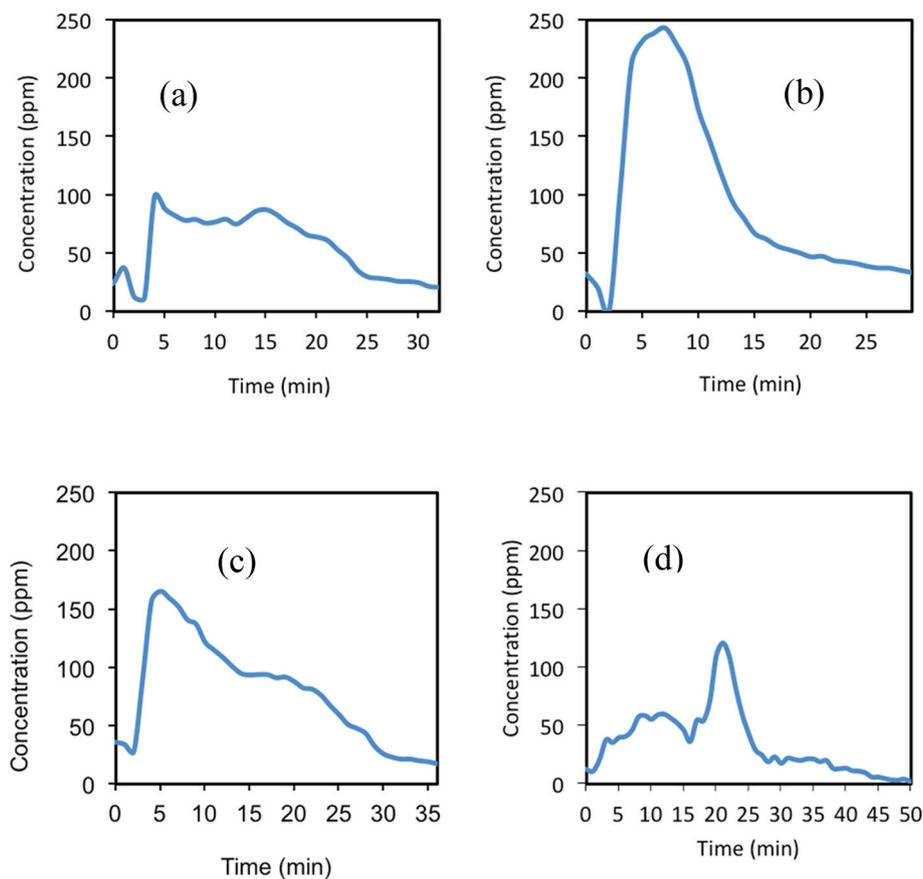
Fig. 6. NO emissions as a function of time over one batch (reload) for (a) BS 433, (b) Miscanthus, (c) bagasse and (d) Heatlog briquette.
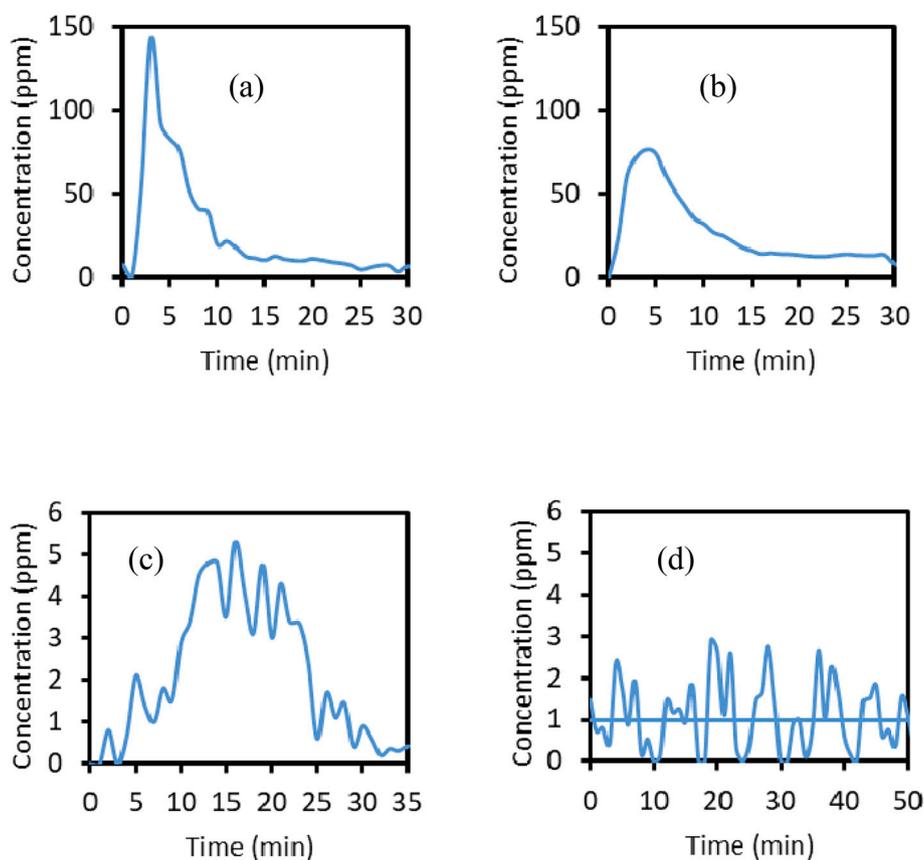
Fig. 7. HCl emissions for one (reloaded) batch for (a) BS 433, (b) Miscanthus, (c) bagasse and (d) Heatlogs briquette.

where the emission is largely from fine, gas phase generated soot particulate matter and tends to follow an almost linear relationship with VM as described before [20]; soot is only formed once the 'critical soot threshold' is reached at 8% VM. Here the PM emissions measured for the wood briquettes, bagasse and Miscanthus are consistent with previous work for woods, but the emissions for the straws are much higher i.e. higher than expected from their VM content. This probably due to two factors, the formation of particulate matter [5,7,8,29], possibly including higher fractions of inorganic particulate (not determined), and that the nature of the straw briquettes (i.e. being composed of fine particles with low density) tends to result in greater smoke formation.

Measurement was made of EC/TC determined as previously described and the results are shown in Table 7. The values are over the whole combustion cycle covering both flaming and smouldering phases. Therefore, there can be significant errors, about ± 25%, but they are consistent in magnitude with the results of Shen et al. [30]. The fuels appear to separate into two distinct groups based on EC/TC ratios. The average EC/TC ratios of the barley straw briquettes (and Miscanthus briquettes) were consistently higher than the wheat straw briquettes. It is interesting that the barley straws and the Miscanthus are the fuels with the highest concentrations of both potassium and chlorine. We can speculate that the differences in EC/TC ratios may be associated with the higher potassium content which influences the way in which EC/TC is determined. Alternatively, it could indicate that the gas phase potassium interacts with the combustion steps.

4. Discussion

Fuel properties can be influenced by many factors including biomass type, fertiliser use, soil type, and time of harvest [15,16]. The key distinction here is between the straws and their growing conditions, winter wheat vs spring barley. Spring barley straw (and Miscanthus) has higher potassium content than winter wheat. Similarly, on average,

the barley straws harvested in the spring have higher N- and Cl-contents than the winter wheat straw. This has a major effect on the fuel properties, and some emissions as discussed below.

There seems to be a good relationship between the composition of the fuels and the emission of N, Cl and PM found in previous studies. It is well known that operator and measurement methods have a significant influence on the accuracy of the values of the EF's for a combustion cycle, this is especially the case of PM where there is a sudden increase in PM on reloading. The first ignition in a cold bed can cause problems with briquettes and this was particularly the case with these straw briquettes which proved difficult to ignite using the standard firelighter method and batch testing used before [20]. Hence the measurements here were undertaken by reloading onto a hot bed of burning char. It was found that the frequency of reloading has an impact on emissions; the longer the fuel bed is left to burn out, the lower the temperature and poorer the combustion of the ensuing batch, leading to increased organic, CO and CH_4 emissions. Consequently, the measurements of Emission Factors here have considerable errors as indicated earlier in the text.

Of particular interest is the combustion behaviour of the different fuels when compared with the DEFRA limits. These limits are based on EU regulation 2015/1185 for eco-designed space heaters and are given in Table 8. It is clear for the stove used in this work and using the procedures outlined in the Materials and methods section, that: the CO limit is not met for any of the fuels; within the limits of experimental error the NO limit is met for all fuels except for Miscanthus (which has a high nitrogen content); the OGC limit is met within experimental error by the two wood briquettes, and the bagasse and Miscanthus briquettes; the particulate emission limit is met for the two wood briquettes, and the bagasse and Miscanthus briquettes. It is expected that eco-design stoves (which are required by 2022) will have significantly lower emissions because of better combustion control, but that fuel choice will remain to be an important consideration.
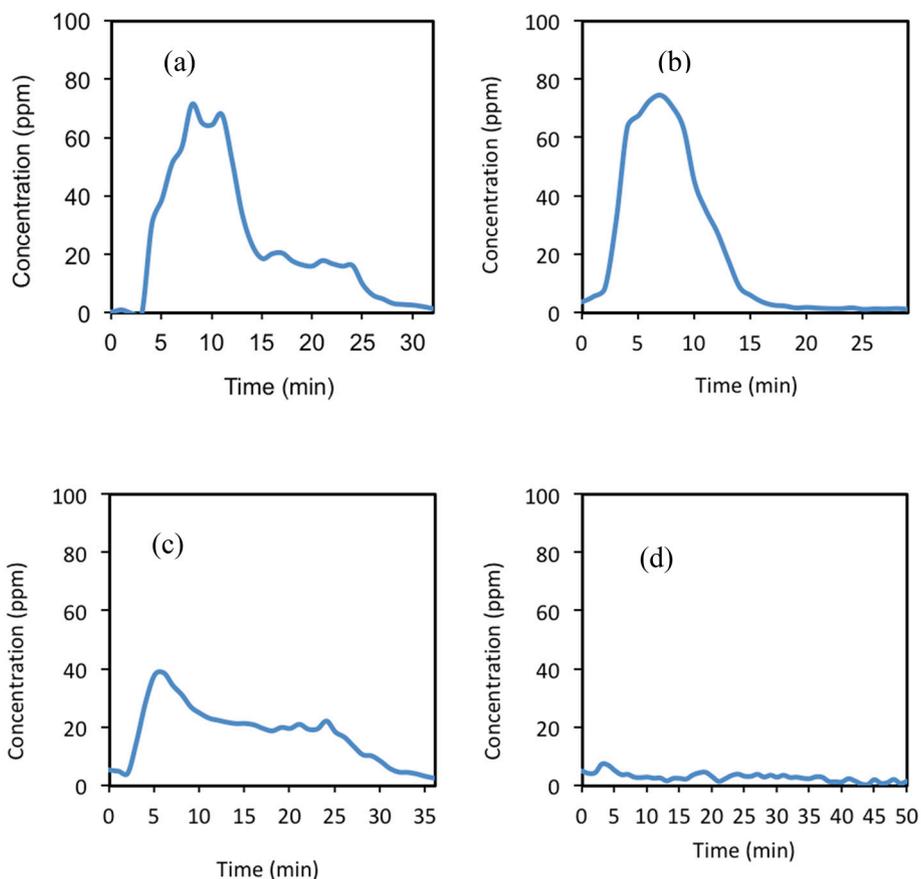
Fig. 8. SO_2 emissions over one (reloaded) batch for (a) BS 433, (b) Miscanthus, (c) bagasse and (d) Heatlogs briquette.

Table 6

Emission Factors for gases over the whole cycle for the fuels studied, g/kg$_{db.}$

Sample	CO	NOx	HCl	SO$_2$	CH$_4$	Reference
WS 093	100	2.0	0.2	0.5	0.7	This work
WS 123	150	3.0	0.4	0.6	1.4	This work
BS 423	180	3.6	0.3	0.8	2.2	This work
BS 433	180	3.4	0.3	1.2	2.4	This work
BS 723	150	2.2	0.3	0.6	1.6	This work
Bagasse	160	1.8	0.05	0.6	2.1	This work
Miscanthus	160	2.5	0.3	0.8	1.2	This work
Wood briquettes, Heatlogs	120	1.4	0.06	0.3	1.5	This work
Wood briquette, Hotmax	50.8	1.5	0.06	0.9	1.1	This work
Wood logs (spruce, 18% moisture)	110	1.2	0.6	7.3	4.2	[17]
Wood logs (willow, 10% moisture)	80	2.6	0.2	3.4	6.4	[17]

Briquettes can give cleaner combustion than wood logs, although burning rates can be faster. Burning rates are a function of the chemical nature of the biomass (and binder), the density of the briquette, the geometrical properties and the friability.

Briquette size and density varies significantly between feedstocks, and both laboratory produced and commercially made, and this is seen in Fig. 1. The commercially made extruded sawdust briquettes have densities in the range of 1000–1200 kg/m^3, whereas the density of the mechanically pressed straw and bagasse briquettes was half this. In addition, a number of issues were identified during the briquetting process largely due to the low density which can lead to cracks forming. The log fuels had densities ranging from 500 to 850 kg/m^3. Although some of the briquettes were lower in quality to the commercial wood-fuel briquettes, they still perform well compared to wood logs. Commercial systems are usually extrusion based large briquettes or 'synthetic logs' with a central hole, which assists in smooth combustion.
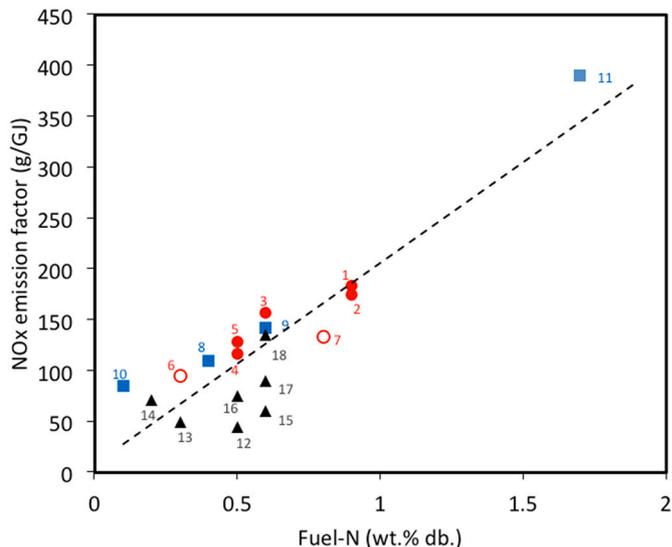
Fig. 9. Plot of the NOx Emission Factor (g/GJ) over the whole combustion cycle against fuel-N content wt% (db) is shown. Present work (●): straws, BS 423 (1), BS 433 (2), WS 123 (3), BS 723 (4) and WS 093 (5); other fuels ○, Bagasse (6) and Miscanthus (7); data from Mitchell et al. [20] (■): wood A (8), wood B (9), torrefied briquette (10), biomass blend (11); Maxwell et al. [22] (▲): torrefied spruce (12), spruce (13), wood briquette (14), torrefied olive (15), olive (16), torrefied willow (17) and willow (18).

While there is a fuel-type influence on emissions, it is also clear that briquettes from optimised manufacture are lower emitting (and less variable) than wood logs.
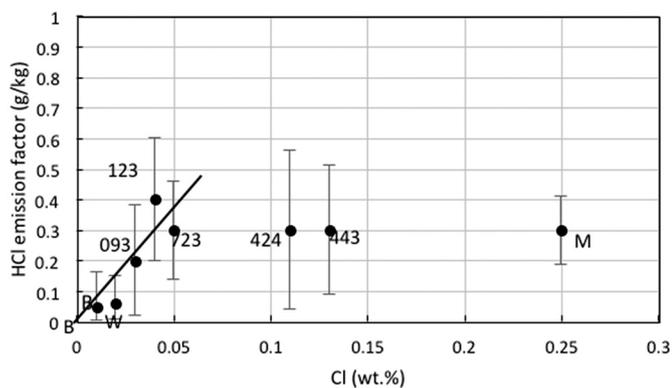
Fig. 10. Plot of HCl Emission Factor against fuel-Cl content (wt%, db). The numbers refer to the site numbers of the straw samples (see Table 1); B, bagasse; M, Miscanthus; W, Heatlogs briquette.
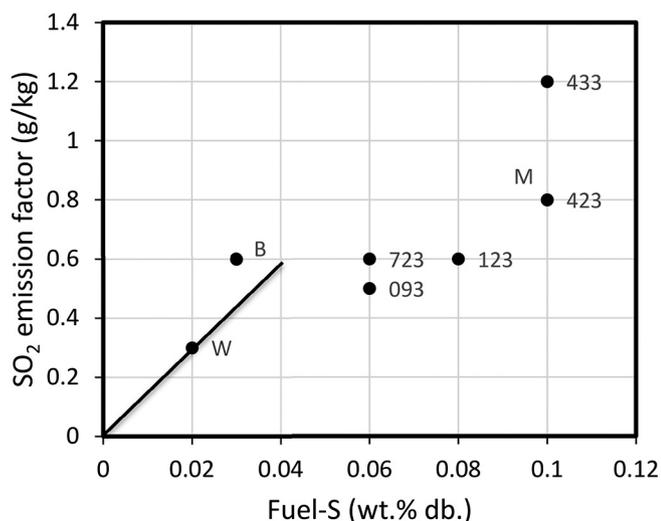
Fig. 11. Plot of SO_2 Emission Factor against fuel-S content (wt% db). The numbers refer to the site numbers of the straw samples (see Table 1); B, bagasse; M, Miscanthus; W, Heatlogs briquette.

Fig. 12. Plot of the Total PM Emission Factor (g/MJ) over the whole combustion cycle against fuel-VM content wt% (db) is shown. Present work: straws (●), BS 423 (1), BS 433 (2), WS 123 (3), BS 723 (4) and BS 093 (5); Other Fuels: ○, bagasse; (6) and miscanthus (7); data from Mitchell et al. [20] (■): wood A (8), wood B (9), torrefied briquette (10), biomass blend (11), smokeless coal (12), low smoke coal (13), coal (14) and peat briquette (15); data from Maxwell et al. [22] (▲): wood briquette (16), torrefied willow (17) and willow (18), spruce (19). Solid line and dashed line are trends for wood logs and coal-based fuels respectively, from [20]. Dotted line is new trend line for cereal straw briquettes from this work.

5. Conclusions

A number of agricultural residues, wheat straw, barley straw, bagasse, as well as Miscanthus, have been burned in briquetted form in a simple multi-fuel space heater following testing protocols laid out in European and British standard testing methods for emission measurement. Results are compared to those observed from commercial wood-based briquettes and previous studies of wood logs as well as briquettes

of torrefied biomass. The materials were first compared in terms of fuel properties. For the samples studied here, fertiliser has not affected the K and N contents of the resultant spring barley straw and winter wheat straw. Both straws have high ash contents, and the spring harvested barley straw has higher N and Cl contents than the winter harvested wheat straw. The Miscanthus and bagasse briquettes under study had fuel characteristics resembling barley straw and wheat straw respectively. The ash characteristics of the agricultural straws indicate a higher tendency to form fused ash during combustion, but there was no evidence of this during the combustion testing.

All the fuels, laboratory-produced briquettes, commercial briquettes, and logs, had similar complete-cycle burning rates, but there were large differences in emissions depending on fuel type, whereby the fuel-N, and VM content correlate with the emissions of NO and particulate matter respectively, although in the latter case, briquette density and durability also had an impact. Interestingly, the high-Cl and high-S fuels correlated with HCl and SO_2 emissions only at low concentrations, and this provides evidence of in situ capture of these gases by the inherent calcium salts in the inorganic material.

Results indicate that fuel choice is an important consideration for

Table 7
Average whole cycle PM Emissions as Emission Factor (EF_{PM}) and EC/TC ratios, together with values from Table 2 for VM and Cl, and K from Table 3.

Sample	VM wt% (db) (from Table 2)	EF_{PM} g/kg	EC/TC	K wt% (db) (from Table 2)	Cl wt% (db) (from Table 2)
WS 093	79.6	6.4	0.36	5053	0.03
WS 123	78.6	6.7	0.34	5495	0.04
BS 423	75.1	5.0	0.49	20,649	0.11
BS 433	74.2	4.8	0.41	16,464	0.13
BS 723	76.6	5.2	0.46	12,394	0.05
Bagasse	87.5	3.0	0.32	2645	0.01
Miscanthus	87.0	2.7	0.54	11,112	0.25
Heatlogs briquette	90.1	3.0	0.34	1326	0.01
Hotmax briquette	76.0	2.4			
Wood logs (spruce, 18% moisture)	77.0	4.2	0.1	840	
Wood logs (willow, 10% moisture)	82.0	6.4	0.34	2660	

The errors in the Emission Factors are ± 1; and for EC/TC are ± 25%.

Table 8
Table showing the DEFRA limits compared to the other fuels studied here.

Species	DEFRA limit all at 13% O_2	WS 123	Miscanthus	Bagasse	Heatlogs	Hotmax	Spruce logs	Willow logs
CO	1500 mg/m^3	8800	8500	8900	9000	7081	9100	7000
NO expressed as NO_2	200 mg/m^3	255	255	180	150	168	150	225
Organic gaseous C, OGC	120 mgC/m^3	150	140	200	160	186	400	200
Particulates	2.4 g/kg dry matter	6.7	2.7	3.0	3.0	2.4	4.2	6.4

The errors in our measurements are CO $\pm$ 4000 mg/m^3, NO_2 $\pm$ 30 g/m^3, organic gaseous compounds $\pm$ 100 mgC/m^3, particulates $\pm$ 1.0 g/kg.

emission reduction from the domestic sector. Fuel-N directly correlates to emitted NOx, but even so, all the fuels studied here (N-content ranged from 0.2–0.9 wt%, dry basis) had NOx emissions below the EU regulation 2015/1185 (Eco 2022-design) limit. The briquettes perform well compared to wood logs, and so while there is a fuel-type influence on emissions, it is also clear that briquettes from optimised manufacture are lower emitting (and less variable) than wood logs.

Data availability

The data related to this work are available upon reasonable request.

Declaration of competing interest

The authors declare that they do not have any known conflicting interests that could influence the work in this paper.

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