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Repurposing lignin rich biorefinery waste streams into the next generation of sustainable solid fuels

Martin J. Taylor[a,*], Karl Hornsby[a], Kin Wai Cheah[a,b], Peter Hurst[c], Simon Walker[d], Vasiliki Skoulou[a,*]

[a] School of Engineering, Chemical Engineering, University of Hull, Cottingham Road, Hull HU6 7RX, United Kingdom
[b] School of Computing, Engineering and Digital Technologies, Teesside University, Borough Road, Middlesbrough TS1 3BA, United Kingdom
[c] Biorenewables Development Centre, Unit 1 Hassacarr Ln, Chessingham Park, York, YO19 5SN, United Kingdom
[d] Jesmond Engineering Ltd, Baffin Way, Brough HU15 1YU, United Kingdom

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ABSTRACT

Value added lignin rich waste sludges from biorefinery processes are, as yet untapped valuable feedstocks that can be reformed into clean, high quality solid fuels. By water washing sludges produced from base hydrolyzed waste, a material stripped of water-soluble alkali and alkaline earth metals (ash) can be obtained. This work shows how leached bagasse, barley and wheat straw sludges can be valorised into clean, low ash solid biofuels that can be used to supplement global energy demands. Repurposed lignin rich sludges of 1.00–2.00 mm particle size feedstocks were found to exhibit calorific values +17.3 %, +16.8 % and +11.7 % for bagasse, wheat, and barley straw sludges, respectively higher than their untreated waste counterparts. Additionally, by employing densification in the absence of a binder, <0.25 mm particles of leached sludge feedstocks were found to experience 16.0 % (bagasse), 12.0 % (wheat) and 4.0 % (barley) increases to their calorific values. This provides options for sustained energy from waste production and consumption campaigns, diversifying feedstock options for green solid fuels

1. Introduction

As greater quantities of bio-renewable feedstocks, especially those rich in lignin, are consumed globally for energy generation, either directly or indirectly [1,2], we must diversify our solid fuels options as a matter of urgency. This will allow us to achieve a smooth transition from fossil fuels to clean low carbon energy utilization. The European Union have already developed a strategy to target new technologies for the production of renewable fuels from agricultural by-products and biodegradable wastes, especially for energy production [3]. It is estimated that there is ~950 million tons of biomass produced annually in Europe. In this continent there are already leading countries which have capitalized on energy from waste, including Austria, Poland, Denmark and Sweden who have sourced biorenewable options directly for energy [3,4]. However, as global energy consumption continues to increase, with a projected usage of 247 exajoules by 2050 [3], leading consumers including the United States of America, China, India and Japan will need to consider the European approach to augment their current energy mixtures, including biorenewables solid fuels such as lignin. Rich in lignin wastes are a prime option for short term substitution of the traditional fossil based solid fuels, due to their high abundancy and renewability, as well as low competition with food and feed markets. However, their varied nature and wide variation of physicochemical characteristics are a drawback for their immediate use as "drop in" materials for energy production, especially in terms of their varying moisture and ash content, as well as chemical structure [5–7]. Thermochemical transformations of solid fuels emerging from woody or herbaceous biomass waste are not new concepts, having been exploited for energy and materials such as charcoal since ancient history via CO_2 emitting processes. The method of which this is accomplished have changed throughout the centuries where they have been refined and optimized, developing innovative low carbon energy and fuels production processes such as gasification for syngas and fast pyrolysis for bio-oil production [8]. This often involves the use of a single waste stream to avoid operational problems that an energy generation process is built around. However, to lower the carbon footprint and increase the energy production capacity of the process, one must investigate the use of blended lignin rich feedstocks: this is where multiple pre-treated

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* Corresponding authors.
E-mail addresses: Martin.Taylor@hull.ac.uk (M.J. Taylor), V.Skoulou@hull.ac.uk (V. Skoulou).

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materials can be combined into a single feed or even in a co-feed energy generation process. This is important as generally lignin rich biomass wastes have a lower calorific value compared to traditional coal or lignite (brown coal) fuels at 26.0–32.0 MJ/kg and 19.0–23.0 MJ/kg, respectively [9–13]. This is compared with a variety of biomass feedstocks such as switchgrass (16.2 MJ/kg), tobacco (16.3 MJ/kg), almond shells (20.0 MJ/kg), dried rice straw (16.5 MJ/kg), beech wood (18.1 MJ/kg) and pine wood (18.8 MJ/kg) [13–15]. Co-feeding is used as a method of diluting fossil fuels (coal) with lignin rich biomass-derived fuels or mixing different lignin rich waste streams, as a result alleviating our heavy reliance on non-renewable fossil fuels.

Commonly, alternative fuels refer to the use of forestry wastes such as dead woods, only recently have much lower quality ash-rich agricultural wastes been considered for bioenergy production. This being said, there is still an extensive range of underutilised lignin rich waste streams, especially from those generated in current energy/fuels from waste processes, agricultural and agro-industrial activities. However, much like commonly used lignocellulosic wastes and coal before this, there is an overarching issue that affects the waste to energy sector, ash. The mineral content that remains after the thermochemical conversion process, are the non-combustible inorganic components that have no calorific value and tend to cause reactor shutdowns and physical pretreatment equipment wear [16]. This can involve general operational drawbacks such as corrosion and erosion in the form of acidic/basic surface deposits on the reactor lining/refractory. These must be routinely removed to limit long term reactor degradation, ultimately resulting in intensive labour costs and an inefficient process. Specific ash components have been found to have catalytic properties which can drive various beneficial thermochemical reactions and promote for example syngas production during gasification [17–19]. However, a major concern with ash components such as K, Na, Ca, Mg, Cl and S are their reactivity with reactor bed media, especially when using fluidised bed technologies [7,20]. This is where low melting temperature eutectic mixtures can cause ash fusing, leading to severe reactor bed material agglomeration, hindering fluidisation in terms of gas medium flow rate and poor heat transfer/mixing [21,22]. Eventually, through bed material fusing and adhering to the reactor surface, the fluidised bed reactor is forced to shut down for cleaning and maintenance. This is a major expenditure at an industrial scale, not just for cost of repairs but a loss of revenue through energy production. Other elements such as chlorine and sulphur are often linked with corrosion related issues, as well as environmental pollution as these elements when released are both toxic and harmful emissions. By reacting with H_2 generated through the thermochemical decomposition of lignocellulosic biomass, chemicals such as hydrochloric acid (HCl) and hydrogen sulphide (H_2S) can be formed, therefore a drive to reduce such species is vital to create a sustainable and clean energy production process. With this in mind there is a continuous interest in developing simple, scalable, and low energy methods of reducing the inorganic ash constituents in waste streams [6], this becomes more vital as fuel supplies diversify to newer alternative solid fuels.

One such waste stream is the sludge fraction from the bio-ethanol production process. During the prelude to fermentation, a lignocellulosic biomass feedstock is usually pre-treated, often with acid or base [5,23]. Such a pre-treatment technique serves for delignification, the weakening of the interactions from the lignin backbone which surrounds cellulose and hemicellulose, allowing for greater accessibility to sugar components [23]. During this time intermolecular interactions such as hydrogen bonding in the cellulose components are disrupted which cause a decrease in cellulose crystallinity [6]. After which a hydrolysis reaction can take place and allow for the liberation of the valuable sugar molecules from the cellulose and hemicellulose components. Hydrolysis reactions for lignocellulosic biomass wastes are routinely carried out using a few methods. These range from acid/base pre-treatments, including the Scholler-Madison process which used sulphuric acid (H_2SO_4) for sugar liberation from wood [24]. Alternatively, pressure induced processes such as steam or CO_2 explosions, enzyme facilitated hydrolysis or even via mechanical extrusion are commonly used sugar removal techniques [25]. After this is completed, the sugar extracted sludge or solid residue is removed from the process and often repurposed for agri-feed or committed to the land. However, the disposal onto land is not sustainable as naturally decomposing the sludge is a carbon emitting process.

In this work, we investigate the potential of repurposing high moisture, ash and lignin sludges generated post hydrolysis of parent lignocellulosic feedstocks into solid fuels for thermochemical processing. By assessing three different feedstocks, each with varying ash and lignin contents, the possibility of utilising pre-treated sludges for lowering the carbon footprint of the waste to energy industry will be addressed. The virgin feedstocks include barley straw, wheat straw and sugar bagasse. These residues will be compared in a raw and leached form against sugar extracted sludges and a pre-treated (modified) sludge, to show the variation in feedstock physical/chemical structure and thermal decomposition. In turn, it will be determined if there is a solid fuel improvement in terms of calorific value so that the sludges can be used for direct energy production (combustion). The feedstocks themselves are variable in nature, each containing different physical and chemical structures as well as different ash compositions.

2. Experimental section

Due to the various feedstock processing steps used for this work, an experimental framework is presented in Fig. 1. The subsequent sections below detail the preparation steps for reformed feedstocks [A], [B], [C] and [D].

2.1. Feedstock preparation

Locally sourced barley straw, wheat straw and sugar bagasse were milled using a Retsch GM200 Grindomix Knife Mill at 10,000 rpm for 1 min, followed by sieving and separating using a Retsch AS200 Vibratory Sieve Shaker, reclaiming the 1.00–2.00 mm, 0.75–0.55 mm and <0.25 mm particles. Each fraction was individually pre-treated via water washing (leaching) in deionized water using a Heidolph Hei-Tec hotplate at 50 °C, mixing at 700 rpm for 24 h at a ratio of 10 g L^{-1}. The temperature was monitored using a Pt1000 thermocouple based in the leachate. The leached feedstocks were separated from their leachates and dried under *vacuo*. This was followed by drying in a Fisherbrand gravity convection oven for 24 h at 105 °C (Feedstock [A], Fig. 1).

2.2. Sludge preparation

The raw feedstocks were milled using a Retsch SM300 cutting mill fitted with a 1.00 mm screen. The 1.00 mm particles were pre-treated

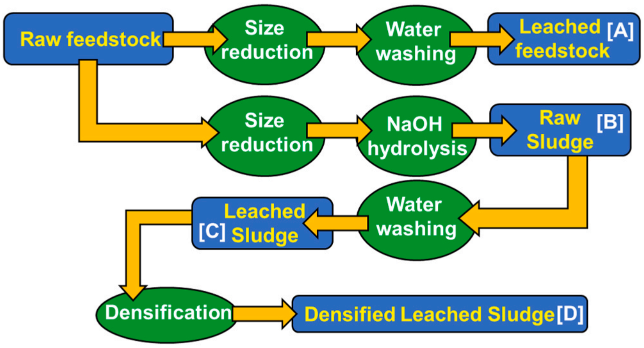

Fig. 1. Feedstock experimental framework showing the production routes to [A] Leached feedstock, [B] Raw Sludge, [C] Leached Sludge and [D] Densified Leached Sludge.

with 10 M NaOH solution (Fisher Scientific) for 0.5 h at 90 °C in a 10 L Universal Process Machine (RoboQbo 15–4). This was followed by pressing to remove excess water, followed by drying at 105 °C in a Genlab OV/100/F/DTG oven. The dried sludges were milled using a Retsch GM200 Grindomix Knife Mill, 10,000 rpm for 1 min, then sieved and separated using a Retsch AS200 Vibratory Sieve Shaker, reclaiming the 1.00–2.00 mm, 0.75–0.55 mm and <0.25 mm particles (Feedstock [B], Fig. 1). This was followed by leaching and drying in the same methods used for the standard feedstocks (Feedstock [C], Fig. 1). The dried sludges were then thermochemically tested in a loose powder and pelletized form. Pellets of ~1.00 g were individually created using a 12 mm diameter die using a Retsch PP 25 pellet press in the absence of a binder at 9.5 tonnes of pressure (Feedstock [D], Fig. 1).

2.3. Feedstock characterisation

Proximate analysis was carried out using a LECO 701 thermogravimetric analyser at ~1.00 g scale where moisture, devolatilization, ash and higher heating value (HHV) were measured and calculated using Equation S1. The proximate analysis method used was as follows: ambient to 107 °C at a rate of 3 °C/min under nitrogen, holding for 15 min before heating from 107 °C to 950 °C at 5 °C/min, holding for 7 min before cooling to 600 °C. This was followed by an ashing phase in air from 600 °C to 750 °C at 3 °C/min, before cooling to ambient conditions. Fixed carbon was calculated by subtracting the final ash mass from the initial sample mass prior combustion. Ultimate analysis of all feedstocks was acquired using a LECO Truspec CHN combustion analyser using sample sizes of 50.00–70.00 mg. FTIR spectra were obtained using a Thermo Scientific Nicolet iS5 with a PIKE MIRacle single reflection horizontal ATR accessory. Scanning Electron Microscopy (SEM) images were acquired via a Zeiss EVO 60 instrument at 10^{-2} Pa and an electron acceleration voltage of 20 kV. Powders were adhered to a coated conductive carbon tape and attached to the specimen holder. Bomb calorimetry was carried out on sample sizes between 0.80 and 1.00 g using a Parr 6200 Isoperibol calorimeter fitted with a Parr 1108 P oxygen combustion vessel with an O_2 pressure of 450 psi. Sugar analysis was carried out by Celignis, samples (~300 mg) were hydrolysed in sulphuric acid in a pressurised environment at 121 °C for 1 h. Once cooled the hydrolysates were filtered and washed with deionised water, the solutions were then diluted before analysis on a Dionex ICS-3000 system that is equipped with electrochemical, conductivity, and ultraviolet-visible detectors.

3. Results and discussion

3.1. Feedstock characterisation

The proximate and ultimate analysis for all the feedstocks, across all particle sizes, in both raw and pre-treated (leached) forms are shown in Tables 1, 2 and 3, respectively. From Tables 1–3, there is a clear correlation between particle size and ash content where the large particle size (1.00–2.00 mm) has a lower ash content compared to the smallest size tested (<0.25 mm). This is shown for all feedstocks where bagasse ash increases from 1.52 wt% to 4.99 wt%, when comparing the largest particle size with the smallest. A similar trend is shown for both barley and wheat straw residues but not to the same magnitude. After leaching, all feedstocks were seen to undergo ash extraction where bagasse and barley straw specifically at 1.00–2.00 mm were lowered to <0.9 wt%. The straws were seen to have a much higher ash content than the bagasse, which is attributed to their high potassium concentrations, this is common with straw feedstocks [7]. Potassium is readily soluble in water and easily extracted under the leaching conditions used in this work. However, bagasse has been shown in the past to not contain high concentrations of water-soluble elements [26]. In fact, bagasse is rich in both iron and aluminium, these are more problematic for simple water washing and a more fitting pre-treatment method is required such as physicochemical technologies, including assisted leaching have been shown in the past to decrease Fe content in woody waste [6]. By reducing the ash components in all the feedstocks there was a clear increase in higher heating value (HHV), known as the gross calorific value (Equation S1) and lower heating value, known as the net calorific value (LHV) (Equation S2), where a significant increase was seen for wheat straw. In Tables 1–3, the raw sludges are denoted as the materials that underwent base pre-treatment (10 M NaOH) to hydrolyse the sugar components, with no further pre-treatment. As can be seen, across the board the ash in all raw sludges are higher than the raw feedstocks themselves. This is due to a high impregnation of Na attributed to the base pre-treatment. The bagasse sludge ash increased by 27.49 %, 64.50 % and 16.29 % for 1.00–2.00 mm, 0.55–0.75 mm and <0.25 mm, respectively, as compared with the raw bagasse feedstock. Barley straw sludge also saw an increase in ash by 49.16 %-53.40 % across each particle size. Finally, wheat straw sludge, which albeit saw an increase in ash, was to a lower magnitude at 32.21 %–49.71 %, across the particle sizes investigated, where alike the other feedstocks saw the largest ash content for the smallest particle size investigated. Directly related with ash content is the HHV, for all the raw sludges there has been a clear reduction in the HHV in comparison with the raw feedstocks, as shown in Tables 1–3, the increase in ash content across all investigated

Table 1

Proximate and ultimate analysis of raw / leached bagasse and bagasse sludge, at three different particle sizes.

Size (mm)	Feedstock		Moisture (wt%)	Volatile (wt%)	Fixed Carbon (wt%)	Ash (wt %)	Ash+* (%)	HHV (MJ/ kg)	LHV (MJ/ kg)	C (wt %)	H (wt %)	N (wt %)	O** (wt %)	C/H ratio	C/N ratio
1.00–2.00	Bag	Raw	7.16	78.04	8.84	5.96	-	12.43	15.67	45.40	6.16	N/D	48.44	7.37	-
		Leached	5.99	79.24	11.36	3.41	-	12.73	16.39	46.20	6.27	N/D	47.53	7.37	-
	Bag S	Raw	7.04	75.54	9.20	8.22	27.49	12.04	14.51	43.20	5.91	N/D	50.89	7.31	-
		Leached	1.80	81.73	14.01	2.46	-	13.22	17.23	45.70	6.30	N/D	48.00	7.25	-
0.55–0.75	Bag	Raw	7.56	77.54	12.93	1.97	-	12.53	16.08	45.00	6.27	0.07	48.66	7.18	667.66
		Leached	5.54	79.52	13.57	1.37	-	12.87	16.43	47.00	6.21	N/D	46.79	7.57	-
	Bag S	Raw	6.74	77.60	10.11	5.55	64.50	12.41	15.26	42.60	6.02	0.09	51.29	7.08	480.54
		Leached	1.49	81.49	13.45	3.57	-	13.16	17.10	46.10	6.28	N/D	47.62	7.34	-
<0.25	Bag	Raw	7.43	73.52	13.09	5.96	-	11.88	14.15	41.10	5.86	0.23	52.81	7.01	181.18
		Leached	6.06	79.31	11.22	3.41	-	12.74	15.88	44.50	6.08	0.01	49.41	7.32	3717.63
	Bag S	Raw	6.92	76.60	9.36	7.12	16.29	12.22	14.40	40.20	5.79	0.11	53.90	6.94	358.80
		Leached	2.59	73.86	15.70	7.85	-	12.01	14.52	42.80	5.89	N/D	51.31	7.27	-

Bag – Bagasse, Bag S – Bagasse Sludge, HHV – Higher Heating Value (gross calorific value), LHV – Lower Heating Value (net calorific value).

* Ash+ – The increase in ash after base pre-treatment as compared with the virgin equivalent feedstock on a dry basis.

**O – calculated by the CHN + ash difference

N/D – Not detectable

Table 2
Proximate and ultimate analysis of raw / leached barley straw and barley straw sludge, at three different particle sizes.

Size (mm)	Feedstock		Moisture (wt%)	Volatile (wt%)	Fixed Carbon (wt%)	Ash (wt%)	Ash+* (%)	HHV (MJ/kg)	LHV (MJ/kg)	C (wt%)	H (wt%)	N (wt%)	O** (wt%)	C/H ratio	C/N ratio
1.00–2.00	B	Raw	9.58	76.25	11.09	3.08	-	12.26	14.91	44.30	5.97	0.40	46.25	7.42	110.71
		Leached	5.06	83.60	10.46	0.88	-	13.40	16.98	47.30	6.15	0.10	45.57	7.69	460.25
	B S	Raw	5.30	84.49	3.60	6.61	53.40	13.25	16.68	43.00	6.11	0.19	44.09	7.04	224.08
		Leached	2.82	86.06	9.67	1.45	-	13.75	18.54	46.20	6.51	0.00	45.84	7.10	-
0.55–0.75	B	Raw	9.92	75.81	11.00	3.27	-	12.18	15.52	43.70	6.25	0.46	46.32	6.99	94.29
		Leached	5.01	84.89	9.11	0.99	-	13.55	17.28	48.30	6.18	0.26	44.27	7.82	187.21
	B S	Raw	5.09	79.33	9.11	6.47	49.46	12.64	15.67	42.20	6.03	0.05	45.25	7.00	874.07
		Leached	2.03	85.56	10.96	1.45	-	13.72	18.37	46.20	6.46	0.05	45.84	7.15	893.10
<0.25	B	Raw	10.14	76.41	9.52	3.93	-	12.22	15.84	43.50	6.35	0.52	45.70	6.85	82.97
		Leached	5.87	89.10	3.59	1.44	-	14.00	18.51	44.90	6.41	0.30	46.95	7.00	151.02
	B S	Raw	5.33	81.99	4.95	7.73	49.16	12.90	16.37	43.00	6.16	0.18	42.93	6.98	240.18
		Leached	2.17	85.12	10.97	1.74	-	13.65	18.22	45.80	6.44	0.13	45.89	7.11	354.00

B – Barley straw, B S – Barley Straw Sludge, HHV – Higher Heating Value (gross calorific value), LHV – Lower Heating Value (net calorific value).
* Ash+ – The increase in ash after base pre-treatment as compared with the virgin equivalent feedstock on a dry basis.
**O – calculated by the CHN + ash difference
N/D – Not detectable

Table 3
Proximate and ultimate analysis of raw / leached wheat straw and wheat straw sludge, at three different particle sizes.

Size (mm)	Feedstock		Moisture (wt%)	Volatile (wt%)	Fixed Carbon (wt%)	Ash (wt%)	Ash+* (%)	HHV (MJ/kg)	LHV (MJ/kg)	C (wt%)	H (wt%)	N (wt%)	O** (wt%)	C/H ratio	C/N ratio
1.00–2.00	W	Raw	8.98	76.24	11.30	3.48	-	12.26	15.71	43.80	6.27	0.22	46.23	6.99	198.23
		Leached	2.30	85.12	11.11	1.47	-	13.65	17.74	45.50	6.28	0.09	46.66	7.25	503.21
	W S	Raw	6.31	78.73	8.04	6.92	49.71	12.51	15.73	42.90	6.12	0.18	43.88	7.01	243.02
		Leached	2.11	85.72	10.44	1.73	-	13.72	18.52	46.20	6.51	N/D	45.56	7.10	-
0.55–0.75	W	Raw	8.58	75.41	11.74	4.27	-	12.14	15.79	43.40	6.36	0.26	45.71	6.82	170.04
		Leached	5.10	84.31	9.39	1.20	-	13.47	17.43	45.50	6.28	0.02	47.00	7.25	2372.26
	W S	Raw	6.39	78.36	8.26	6.99	38.91	12.46	15.60	42.60	6.10	0.27	44.04	6.98	160.51
		Leached	2.39	83.72	12.33	1.56	-	13.48	18.04	46.20	6.46	0.05	45.73	7.15	893.10
<0.25	W	Raw	9.01	74.42	11.54	5.03	-	11.97	15.45	42.70	6.32	0.47	45.48	6.76	90.48
		Leached	5.48	80.06	12.28	2.18	-	12.90	16.87	45.40	6.35	0.28	45.79	7.15	160.24
	W S	Raw	6.33	76.72	9.53	7.42	32.21	12.24	15.40	42.20	6.13	0.32	43.93	6.88	130.12
		Leached	2.56	83.07	11.77	2.60	-	13.35	17.80	45.80	6.44	0.13	45.03	7.11	354.00

W – Wheat Straw, W S – Wheat Straw Sludge, HHV – Higher Heating Value (gross calorific value), LHV – Lower Heating Value (net calorific value).
* Ash+ – The increase in ash after base pre-treatment as compared with the virgin equivalent feedstock on a dry basis.
**O – calculated by the CHN + ash difference
N/D – Not detectable

materials is indicated in the tables as Ash+, this directly compares the raw sludges with the raw virgin feedstock. As sodium is highly soluble in water, the sludges were all found to benefit from water washing or leaching. This physicochemical pre-treatment was able to reduce the ash content of the wheat and barley sludges to levels similar to the leached equivalent feedstocks shown in Table 2 and Table 3. However, bagasse possessed a slightly higher ash content than the leached feedstock equivalent. After leaching, all sludges have a higher HHV and LHV than the standard leached feedstocks, suggesting that along with ash removal there has been some alteration to the chemical structure, such as sugar extraction, this is evidenced in Table 4 as there has been a clear decrease in hexosans and pentosans. The cellulose, hemicellulose and lignin components were shown in the past to be 35.0 wt%-39.0 wt%, 23.0 wt%-30.0 wt%, 12.0 wt%-16.0 wt%, respectively for wheat straw, 36.0 wt%-43.0 wt%, 24.0 wt%-33.0 wt%, 6.3 wt%-9.8 wt%, respectively for barley straw and 25.0 wt%-45.0 wt%, 28.0 wt%-32.0 wt%, 15.0 wt%-25.0 wt%, respectively for bagasse [27]. This data shows that wheat and barley straws were modified the most, as naturally bagasse is a far hardier feedstock and exhibited the least reduction in sugar units. Barley straw sludge was found to contain 12.78 % and 29.86 % less cellulose (hexosans) and hemicellulose (pentosans) derived molecules, respectively. Wheat Straw lost less sugar units with 7.90 % and 17.53 %, respectively. Whereas leached bagasse sludge contained 1.36 % less hexosans and 3.15 % less pentosans than the raw bagasse feedstock.

Table 4
Cellulose and hemicellulose reduction following base pre-treatment and subsequent leaching for <0.25 mm feedstocks.

Feedstock	Cellulose decrease (%)*	Hemicellulose decrease (%)**
Leached Bagasse Sludge	1.36	3.15
Leached Barley Straw Sludge	12.78	29.86
Leached Wheat Straw Sludge	7.90	17.53

* Components consisting of glucan, galactan, rhamnan and mannan units
** Components consisting of xylan and arabinan units

From Tables 1–3, one can also observe that the C/H and C/N ratios for all leached feedstocks, regardless of biomass type and particle size were found to be improved as compared with their raw counterparts, which indicates its higher energy content and justifies their suitability to be used as sustainable solid fuel alternatives for bioenergy production. For the C/N ratio of the leached feedstocks, a higher C/N ratio indicates there will be less NO_x emissions produced downstream during thermochemical conversion. The C/H ratio improved for the leached sludges which is in line with carbon removal in the form of sugars during base pre-treatment, evidenced further in Table 4. Lower C/H ratios mean that leached feedstocks will produce less CO_x and higher H_2 concentrations during thermochemical conversion, meaning a more efficient material. In comparison with other common feedstocks, the sludges derived from wheat and barley straws exhibit C/H ratios lower than 7, on a dry basis. This is much lower than the ratios seen for poplar (7.5), acacia (7.2) and pine (7.1) [28]. In comparison with bagasse sludges, they were found to present a C/H ratio lower than poplar and ceder. Collectively, the leached sludges demonstrated lower C/H ratios than switchgrass (7.5) and red ceder (7.6). However, sorghum (great millet), a cereal straw comparable to wheat straw was previously shown to present a C/H ratio of 6.4, lower than the leached sludges [29]. The short coming to this feedstock is that it has >5 wt% of ash, much higher than the leached sludges shown in this work [29].

Fourier Transform Infrared Spectroscopy (FTIR) in Fig. 2 shows overlaid spectra for raw and leached feedstocks, as well as the raw and leached sludges for bagasse (Fig. 2**a**), barley straw (Fig. 2**b**) and wheat straw (Fig. 2**c**). Fig. 2**a** shows the effect of leaching on the bagasse structure, there appears to be no meaningful change to the feedstock except for a strong feature at 1739 cm^{-1} (blue square). This feature has been depicted as a C-O stretch for acetyl and ester linkages in lignin and hemicellulose [30]. The C-H stretch feature shown at 2846–2915 cm^{-1} (green dotted square) has been shown to lose its resolution after leaching and especially after NaOH pre-treatment. This structural alteration is more prevalent for barley straw (Fig. 2**b**) but appears to be unchanged until the sludge is leached for wheat straw (Fig. 2**c**). Barley straw was found to maintain a feature at 1736 cm^{-1} (red dotted line) after leaching, this is known to be a C═O stretch in hemicellulose. This feature was lost due to the NaOH pre-treatment, however for wheat straw (Fig. 2**c**) this was still visible for raw sludge but was hydrolysed in the leaching process. A similar observation was made for the lignin aromatic C-O stretch at 1250 cm^{-1} (royal blue dotted line).

Delignification through the base pre-treatment appeared to have a slightly stronger effect on the barley straw than the wheat straw, albeit both feedstocks were chemically altered through the sugar liberation process, echoed by Table 4, especially as barley straw was found to lose the greatest amount of hexosans and pentosans during pre-treatment. Finally, the dominant feature at 1038 cm,$^{-1}$ attributed to C-O, C═C and C-C-O stretching for cellulose, hemicellulose and lignin were seen to reduce in intensity for barley and wheat straws after base pre-treatment, indicating that there has been heavy disruption to chemical bonding around the cellulose and hemicellulose components [6,31,32].

The structural and textural properties of all the feedstocks and sludges were investigated using Scanning Electron Microscopy (SEM). The surface morphology of bagasse at each particle size, raw, leached, and raw sludge is shown in the supporting information in Figures S1A-Figure S1I across the three particle sizes investigated. The effect of leaching over 24 h appears to have caused some structural alterations where the surface has begun to fragment, prevalent in Figure S1D and Figure S1E which are leached bagasse at 1.0 mm-2.0 mm and 0.75 mm-0.55 mm, respectively. Figures S1G-Figure S1I are the raw bagasse sludge which has undergone substantial surface alterations. The topography of the particles has become distorted and splayed in comparison with the raw feedstocks, additionally the ordered channels have become less prominent than the ones observed in Figure S1A and Figure S1B. A remarkably similar change to the surface composition of barley straw is shown in Figure S2A-Figure S2I, this is echoed further in Figure S3A to Figure S3I for wheat straw, which shows the raw, leached, and raw sludge feedstocks. Between the two straws the surface structure of the wheat straw is more fragmented, especially at the ends of the particles where the pore openings are located. This is the most evident for Figure S2G and Figure S3G which are the 1.0–2.0 mm raw sludges of barley straw and wheat straw, respectively.

Fig. 3 shows an array of SEM images of the leached sludge feedstocks across the three particle sizes where Fig. 3**A-3 C** are bagasse, Fig. 3**D-3 F** are barley straw and Fig. 3**G-3I** are wheat straw, compared with the leached feedstocks, the leached sludges appear to be substantially different where the surface topography of each feedstock is heavily altered, as well as the pore openings at the ends of the grains which have become irregular in shape. There appears to also be some delamination for the barley straw, specifically where individual fibres have fragmented on the surface of the particles. There are minimal differences between the raw and leached sludges suggesting that the leaching process causes no further physical effects to the sludge structure.

Additional to imaging, energy dispersive x-ray spectroscopy measurements were taken of ash residues from the 1.00–2.00 mm residues. Here, the feedstocks were combusted at 750 °C in air using a LECO TGA 701 and the ash was imaged in the same way as the feedstocks. Averaged EDX data is shown in Table S1, here point analysis was carried out across a number of sample regions. It is clear from the leaching aspect of the pre-treatment that in each case, there is a full removal of chlorine from the feedstocks. It is also observed that there are overall reductions in Na, K, Ti (bagasse), Fe (bagasse) and Al (bagasse). For elements such as S and Si, often regarded as difficult elements to remove, augmented technologies have been shown to be effective in the past [6,33,34]. Whereas for the full removal of Ca, Mg, Fe, Al, Ti and Mn an acidic pre-treatment would beneficial.

3.2. *Thermochemical reactivity*

Each of the feedstocks were probed by bomb calorimetry to assess their calorific values. This was carried out on loose powders of raw, leached, raw sludge and leached sludge across the three particle sizes; it was also carried out on densified leached sludges made from <0.25 mm particle sizes. Lab scale densification took place at room temperature, using dried powders, without incorporation of a binder, specifically to investigate whether the sludges benefit from densification, in terms of their calorific values. Fig. 4 shows the variation in calorific value depending on the feedstock and physical state, raw, leached, raw sludge, leached sludge or densified leached sludge, where **(a)** is 1.00–2.00 mm, **(b)** 0.55–0.75 mm and **(c)** <0.25 mm. Fig. 4 shows that by grouping the feedstocks together per particle size there is rapid understanding for

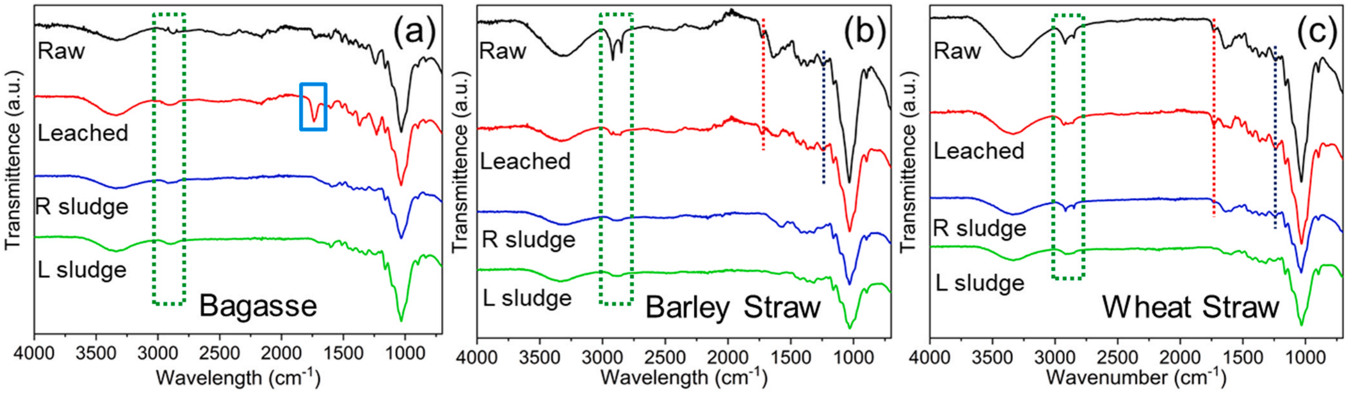

Fig. 2. Overlaid FTIR spectra for (a) bagasse, (b) barley straw and (c) wheat straw, showing the effect of pre-treatment on the chemical structure.

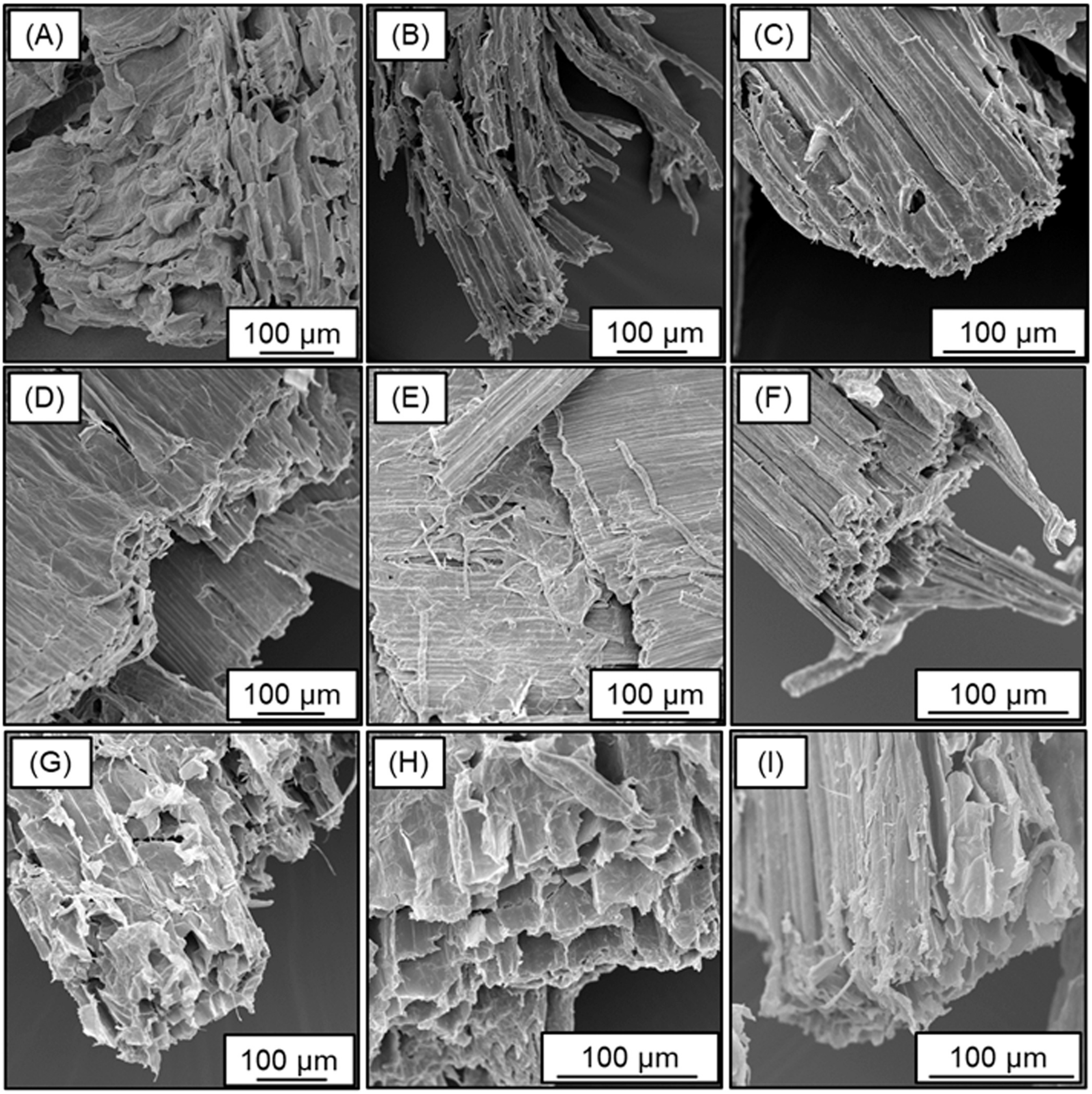

Fig. 3. Scanning Electron Micrographs of leached sludge feedstocks across all particle sizes where (A) is bagasse 1.00–2.00 mm, (B) bagasse 0.75–0.55 mm, (C) bagasse <0.25 mm, (D) barley straw 1.00–2.00 mm, (E) barley straw 0.75–0.55 mm, (F) barley straw <0.25 mm, (G) is wheat straw 1.00–2.00 mm, (H) wheat straw 0.75–0.55 mm and (I) wheat straw <0.25 mm.

how each physicochemical or chemical pre-treatment effects the energy storage potential. Across the feedstocks there is a clear benefit to the calorific value after conventional leaching where barley straw, specifically, experienced a promotional effect of +13.7 %, +14.0 % and +15.5 %, for 1.00–2.00 mm (Fig. 4**a**), 0.55–0.75 mm (Fig. 4**b**) and <0.25 mm (Fig. 4**c**), respectively. There was also a strong advantageous effect of leaching on the calorific value of wheat straw where +9.7 %, +7.2 % and +7.6 % for 1.0–2.0 mm, 0.55–0.75 mm, and <0.25 mm, respectively was seen. This effect was far subtler for the bagasse where for 1.00–2.00 mm there was a slight negative effect, while increasing by 3.6 % and 3.9 % for 0.55–0.75 mm and <0.25 mm, respectively.

As expected through the increase in ash after NaOH pre-treatment, there was a stark decrease in calorific value for all raw sludge feedstocks, across each particle size. This means that irrespective of sugar extraction, the higher ash content reduces the usefulness of a sludge for direct energy generation via combustion. As a result, without further processing of these sludges, they cannot be considered as efficient alternative and clean solid fuels. Therefore, water washing or leaching is a necessary requirement to reduce the ash contaminants, by doing so the leached sludges can be considered as clear alternative solid fuel candidates. Fig. 4 shows the calorific value of bagasse, barley straw and wheat straw before and after water washing. From Fig. 4, the calorific value of the sludge was improved after water washing. For instance, the calorific values of bagasse, barley straw and wheat straw sludge for

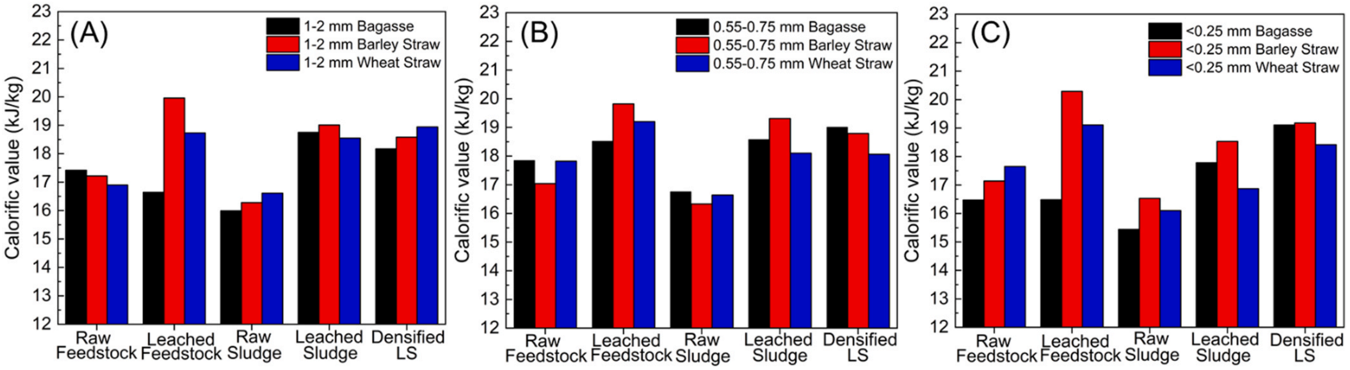

Fig. 4. Calorific value (kJ/kg) of raw and sludge feedstock (bagasse, barley straw, and wheat straw) in the form of raw, leached, and densified leached sludges (LS) at different particle sizes (A) 1.00–2.00 mm, (B) 0.55–0.75 mm, (C) <0.25 mm.

1.00–2.00 mm after leaching were significantly improved by 17.3 %, 16.8 % and 11.7 %, respectively. The same promotional effect on the calorific values can also be seen for the 0.55–0.75 mm and <0.25 mm sludges. However, it is worthwhile to point out that the promotional effect of water washing on the calorific value of wheat straw sludge is somehow less prominent than bagasse and barley straw sludge, with only 11.7 %, 8.8 % and 4.8 % for 1.00–2.00 mm, 0.55–0.75 mm and <0.25 mm, respectively. Densification was employed to further increase the energy storage potential of the <0.25 mm feedstocks. It was found that although not significantly effective for the 1.00–2.00 mm and 0.55–0.75 mm leached sludges, the smallest particle size for all three feedstocks benefited further from densification in the absence of binder by 16 %, 12 % and 4 % for bagasse, barley straw and wheat straw, respectively.

Thermogravimetric analysis was carried out on all feedstocks investigated. Figure S4 and Figure S5 show the 1st derivative plots indicating the maximum mass loss for a specific temperature for 1.00–2.00 mm and 0.75–0.55 mm, respectively. Fig. 5 shows the DTG curves for the smallest feedstock size (<0.25 mm), where Fig. 5**a** is bagasse, Fig. 5**b** is barley straw and Fig. 5**c** is wheat straw. This data shows the effect of pre-treatment on both the thermal decomposition pathways and the temperature required for the sample to devolatise. The raw feedstocks in each figure (black), indicate two distinct peaks, the first being the depolymerization of hemicellulose and pectin [35,36] which is found at 284.3 °C, 271.2 °C and 261.1 °C for bagasse, barley straw and wheat straw, respectively. This means that more energy is required for this initial reaction to take place and follows the trend of higher energy requirements for higher lignin content. Isikgor et al., indicated that bagasse had higher lignin than the other used feedstocks [27]. The second peak and major degradation feature for the raw feedstocks is found at 349.1 °C for bagasse, and ∼315 °C for both barley and wheat straws. The effect of water washing the raw feedstocks has been shown in Fig. 2 to have a minimal effect on the chemical structure of the feedstocks, except for ash removal (Tables 1–3**)**. Fig. 5 shows that leaching (red) does not alter the initial hemicellulose depolymerization as the peak is visible and in the same position for all feedstocks. However, for barley and wheat straws the major peak was found to shift to a higher temperature, indicating that removing the ash components delays the thermochemical decomposition. The increase in temperature was found to be +25.8 °C and +26.3 °C for barley and wheat straw (Figs. 5**b** and 5**c**), respectively. This being said, the leaching process improved bagasse, allowing it to decompose 17.3 °C lower than its raw feedstock equivalent. As the feedstocks were chemically pre-treated in NaOH, residual sludge was infused in Na, increasing the ash of the feedstock (Tables 1–3**)**. Although the increased ash content was found to lower the feedstock calorific values (Fig. 4), the high Na content was found to alter the thermal degradation pathways by removing the initial peak due to the removal of sugars (Table 4), the major degradation pathway was also found to shift to a lower temperature. This value was found to be 317.2 °C for bagasse and ∼305 °C for both barley and wheat straws. The similar temperatures for barley and wheat straw map with the major degradation temperature similarities for both raw and leached feedstock, reducing the temperature of the degradation by 9.8 °C and 9.6 °C for barley and wheat straws, respectively from their raw counterparts (Fig. 5**b** and Fig. 5**c**). The shift in temperature was more profound for the bagasse sludge (Fig. 5**a**), reducing by 31.9 °C from the raw feedstock. It has been shown in the past that Na cations impregnated into feedstocks catalyze pyrolysis reaction pathways [37,38]. In the previous kinetics work by Saddawi and their group, the concentration of Na and K impregnated into the biomass showed a significant effect on the biomass decomposition kinetic expressions, where a clear acceleration in pyrolysis reaction rate was observed for alkali metal-impregnated biomass [38]. Post processing in the form of water washing was found to remove this catalytic effect and the temperature of major degradation was found

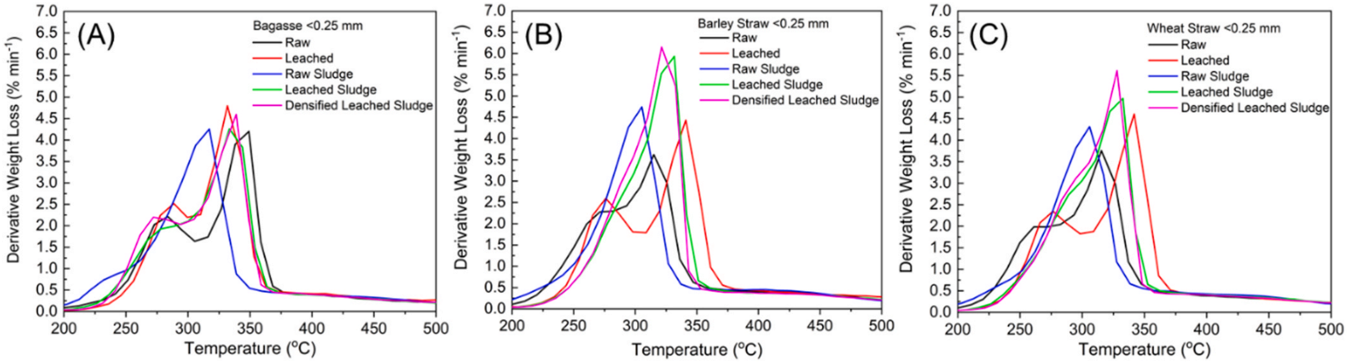

Fig. 5. Thermogravimetric analysis of (A) bagasse, (B) barley straw and (C) wheat straw in raw, leached, raw sludge, leached sludge and densified leached sludge forms using a <0.25 mm particle size.

to return to that like the raw feedstocks. This shift also shows that for bagasse the initial peak is once again visible, albeit to a lesser degree than the raw and leached feedstocks. This agrees with Table 4 that the base pre-treatment was not effective at removing a substantial amount of sugar components from the bagasse. It is believed that due to the higher lignin content in this feedstock, there is a greater interaction or supportive backbone with the cellulose and hemicellulose components, meaning that the naturally resistant lignin protects the sugar units from hydrolysis [39]. This structural reinforcement leads to low accessibility to crystalline cellulose, preventing removal or alteration to amorphous cellulose [5,39]. The leached barley sludge (Fig. 5**b**) shows that the initial peak has been reduced and appears as a mild shoulder in the major decomposition, this feature is more pronounced for leached wheat straw sludge (Fig. 5**c**) inferring that more hemicellulose is present. By liberating the ash and hemicellulose from the feedstocks, the major degradation pathway for the leached sludges is higher than the raw feedstocks and raw sludges, for all investigated lignocellulosic materials. This is extenuated further for the densified sludges, by compacting the leached sludge feedstock at 9.5 tonnes of pressure. Again, in all cases not only were the calorific values found to increase (Figs. 5**a**-5**c**), the DTG curves show much larger peaks, albeit at the same temperature as the leached sludges, across for all feedstocks (Figs. 5**a**-5**c**) resulting in the order of highest to lowest for barley straw, wheat straw and bagasse, respectively.

4. Conclusions

Lignin rich wastes have an exciting potential to become the feedstock of the future for low carbon, sustainable solid fuels. After extracting the useful sugar units for downstream valorisation, residual lignin sludges can be diverted from direct land usage, avoiding all the environmental problems associated with their direct spread on land such as leachates, bad odours, and CO_2 emissions. By post processing in an efficient way to reform the sludges into a feedstock to produce a higher calorific value, low ash solid fuel. In this work, base hydrolysis (NaOH) was used to pre-treat wheat straw, barley straw and bagasse waste streams, remove sugar components, and as a knock-on effect incorporate Na into the feedstock matrix, increasing the ash content. Due to the high water solubility of Na, water washing (leaching) was employed to de-ash the sludge materials. It was found that the leached sludges had enhanced calorific values of up to 17 % higher than their raw waste equivalents. These new solid fuels not only have reduced nitrogen content due to the leaching process and will therefore emit less NO_x during the direct energy generation process, their lowered inorganic content means that there will be less reactor fouling, corrosion over long term usage and reduction in de-fluidisation (bed fusing), if used in conjunction with a fluidised bed reactor at an industrial scale. Additionally, post processing was found to lower the C/H ratios meaning that these new feedstocks can be effective for both gasification and combustion, exhibiting lower CO_x emissions as well as other pollutants. The calorific value of leached bagasse sludge was found to possess lower calorific values than the barley and wheat straw sludge equivalents, while possessing a higher C/H ratio. This means that leached bagasse sludge is better suited to gasification, depending on cold and hot gas efficiency, whereas the other two upgraded sludges could be better used in clean combustion processes.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Vasiliki Skoulou reports financial support was provided by Engineering and Physical Sciences Research Council. Martin Taylor reports financial support was provided by Research England. Vasiliki Skoulou reports financial support was provided by Research England. Kin Wai Cheah reports financial support was provided by Engineering and Physical Sciences Research Council. Vasilki Skoulou reports a relationship with Engineering and Physical Sciences Research Council that includes: funding grants. Kin Wai Cheah reports a relationship with Engineering and Physical Sciences Research Council that includes: funding grants. Vasiliki Skoulou reports a relationship with Research England that includes: funding grants. Martin Taylor reports a relationship with Research England that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.scenv.2024.100123.

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