PRETREATING LIGNOCELLULOSIC BIOMASS WASTES FOR THE NEXT GENERATION OF SOLID FUELS

Karl Hornsby[1,2], Martin J. Taylor[1,2], Peter Hurst[3], Simon Walker[4] and Vasiliki Skoulou[1,2]*
[1] Energy and Environment Institute, University of Hull, Cottingham Road, Hull, HU6 7RX, United Kingdom
[2] B³ Challenge Group, Department of Chemical Engineering, University of Hull, Cottingham Road, Hull, HU6 7RX, United Kingdom
[3] Biorenewables Development Centre (BDC), Chessingham Park, Dunnington, York, YO19 5SN, United Kingdom
[4] Jesmond Engineering Limited, Brough Business Centre, Skillings Lane, Brough, HU15 1EN, United Kingdom
* Corresponding author: V.Skoulou@Hull.ac.uk

Abstract

To assist in the measures to combat climate change and considerably reduce the use of fossil fuels, three abundant lignocellulosic biomass wastes have undergone physicochemical pre-treatments to reform them into alternative solid fuels. By leaching wheat straw, barley straw and bagasse waste, there has been a profound effect on their calorific values and lowering of their mineral (ash) content without sacrificing their carbonaceous structures. It was found that by water washing over 24 h at 50 °C, the calorific values of wheat straw and barley straw increased by 10 % and 14 %, respectively, as a result of their de-ashing.

Introduction

As we move away from fossil fuels we endeavour to find alternative solid fuels. One such possibility is the upgrading of the underutilised lignocellulosic biomass wastes. A carbon neutral approach that can be adapted and optimised to assist in both the impending energy crisis, and everting climatological disaster caused by carbon emitting processes. By characterising and pre-treating a range of feedstocks, a more varied group of lignocellulosic biomass options can be made available for the Energy to Waste (EtW) industry. However, these solid wastes are not drop in fuels. To unlock their true potential they must be physically, chemically or physicochemically pre-treated to reform them into non-problematic solid fuels.[1,2] One such option is leaching, otherwise known as water washing. This is where a waste material is immersed in water and mixed at a variable speed and temperature. Here, the water will enter the material and exit carrying dissolved mineral ions into the liquid phase. As a result, the ash content of lignocellulosic biomass wastes can be radically lowered.[3] Ash, specifically elements such as K, Na, Mg, S and Cl are major culprits for damage to thermochemical reactors. Various inorganic deposits can adhere to the reactor walls which have been proven corrosive and create issues with reactor heat transfer. Additionally, during Fluidised Bed (FB) operation of industrial scale EtW technologies, low melting point eutectic mixtures can form which will interact with the bed material and cause de-fluidisation. This is where the FB reactor is forced to shutdown, as eutectic mixtures cause bed material fusing which restricts gas flow, proceeding via a sudden pressure drop inside the bioenergy system. To determine the extent of de-ashing, the LECO TGA 701 (**Figure 1**) was employed due to its versatile nature and the ability to process a high sample throughput. Moreover, by handling a large sample size (~1 g) a more representative sample can be processed than commonly used in smaller scale instruments.


Figure 1: The LECO TGA 701

Materials preparation

Three lignocellulosic biomass wastes; wheat straw, barley straw and bagasse were blended in a Knife mill (Retsch GM 200) for 1 min at 10,000 rpm. The resulting powders were separated and the 1-2 mm fraction was retrieved using a Retsch AC 200 sieve stack. Each feedstock particle size was then leached in deionised water at a ratio of 10 g/L at 50 °C and 400 rpm for 24 h. The slurry was separated and dried under *vacuo* before drying in a Fisherbrand Gravity Convection Oven at 105 °C for 24 h, according to ASTM standards.

Feedstock characterisation

Fourier Transform Infrared (FTIR) spectra were obtained using a Thermo Scientific Nicolet iS5 with a PIKE MIRacle single reflection horizontal ATR accessory (**Figure 2**). Scanning Electron Microscope (SEM) images were acquired via a Zeiss EVO 60 instrument at a pressure of 10^{-2} Pa and an electron acceleration voltage of 20 kV (**Figure 3**). Raw and leached samples were adhered to a coated conductive carbon tape and attached to the specimen holder, where a 10 nm thick coating of graphite was added to the surface. Bomb calorimetry was carried out using a Parr 6200 Isoperibol calorimeter.

Parallel feedstock processing

To maximise the data quality and acquisition six, ~1 g samples of raw and leached waste were analysed per heat cycle. A standardised LECO procedure for biomass was used consists of a moisture phase in air from ambient to 107 °C at a rate of 3 °C/min. Holding for several minutes before adding crucible lids for the removal of volatiles. This stage was carried out under N2 from 107 °C to 950 °C at 5 °C/min, holding for 7 min before cooling to 600 °C. After the lids were removed the ashing phase was carried out in air from 600 °C to 750 °C at 6 °C/min before cooling to ambient conditions, the proximate analysis for each feedstock is summarised in **Table 1**.

Results and Discussion

Table 1 shows the effect of water washing on the three lignocellulosic biomass wastes. It is clear that the ash has significantly reduced across all feedstocks as result of water washing. Specifically, 71 % for wheat straw, 72 % for barley straw and 45 % for bagasse. The straw feedstocks, known for their high K and other water soluble elements benefited from the leaching pre-treatment. Whereas leaching was not as efficient for bagasse, known for its high Fe and Al content. This being said, Fe is not a known element for causing eutectic mixtures, instead known for its catalytic properties for gasification.[4] This being leaching has benefited an increase in heating values (HHV) for all feedstocks, specifically for wheat and barley straws.

TABLE 1: PROXIMATE ANALYSIS OF BIOMASS WASTE, BEFORE AND AFTER WATER WASHING (LEACHING) USING THE LECO TGA 701

Feedstock		Moisture (wt %)	Volatile (wt %)	Fixed Carbon (wt %)	Ash (wt %)	HHV (MJ/Kg)
Wheat Straw	Raw	7.67	71.68	16.55	4.11	16.99
	Leached	2.90	79.66	16.23	1.21	18.15
Barley Straw	Raw	10.06	70.20	16.60	3.13	16.79
	Leached	3.88	79.63	15.61	0.88	17.63
Bagasse	Raw	6.63	76.19	15.78	1.52	17.41
	Leached	3.18	81.21	14.65	0.84	17.76

FTIR spectra shown in **Figure 2** all show for the most part there is negligible structural differences between raw and leached feedstocks, indicating that carbonaceous matrix is mostly unchanged. However, a mild decrease in a feature at 1600 cm^{-1} for wheat straw does indicate that the leaching process has carried out some delignification. Additionally, for both barley and wheat straws, a change to the double feature at 2900 cm^{-1} indicates that some of the cellulose linkages have been hydrolysed.

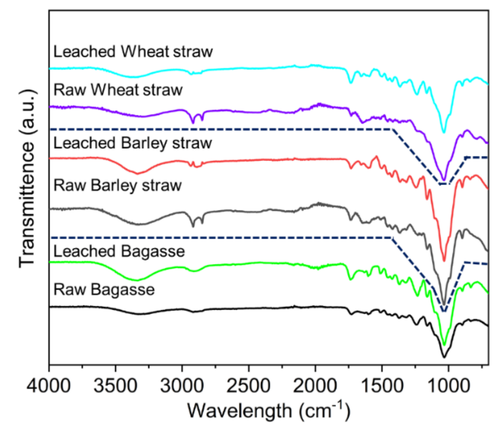

Figure 2: Stacked FTIR spectra showing a lack of structural alteration before and after leaching, for all feedstocks.

Figure 3 shows SEM images for both raw and treated wheat straw (**Figures 3a** and **3b**), barley straw (**Figures 3c** and **3d**) and bagasse (**Figures 3e** and **3f**). All images were taken at the same magnification and show the effect of leaching over 24 h. The surface morphology for all feedstocks appears to have changed. This can be in the form of cracking or separating or through ruptures in the feedstock wall. It is believe that these surface opening could prove beneficial for gas diffusion throughout the feedstock during thermochemical conversion. Surface ruptures appeared to be more apparent for barley straw and bagasse. This is evidenced in **Figures 3d** and **3f** where high contract dots have appeared along the channels. This being said, the surface morphologies are relatively similar across the feedstocks.

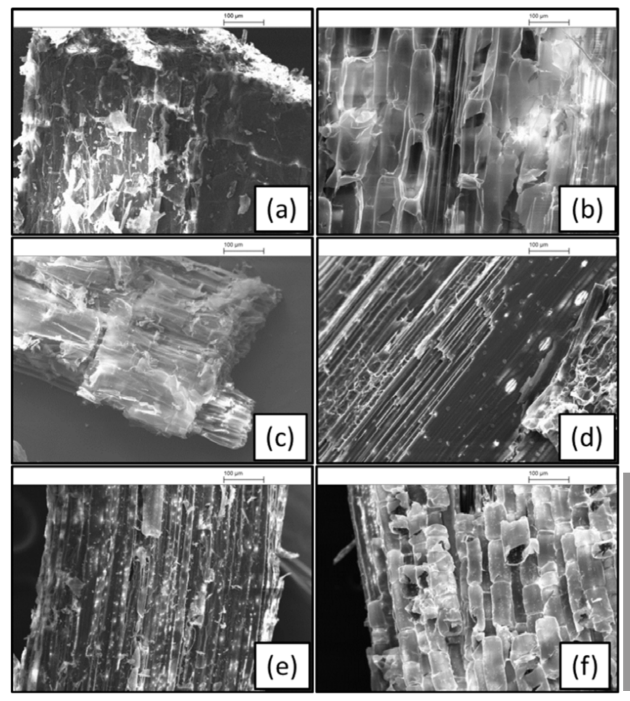

Figure 3: SEM images of (a) Raw Wheat straw, (b) Leached Wheat straw, (c) Raw Barley straw, (d) Leached Barley straw, (e) Raw Bagasse and (f) Leached Bagasse.

The upgraded waste feedstocks once leached represent better solid fuels. This is because of their clean decrease in ash content (**Table 1**) and no major decrease in carbon structure (**Figure 2**). To further characterise these materials bomb calorimetry was carried out, as shown in **Figure 4a** and a further inspection into the DTG curves produced during thermogravimetric analysis (TGA) (**Figures 4b** and **4c**). The information supplied by these curves informs how the structure of the material has changed after the pre-treatment of leaching and if there is greater overall mass loss at a given temperature. **Figure 4a** shows that the calorific value of each feedstock has changed after leaching. For wheat and barley straw this has been a positive alteration where an increase in calorific value of 10 % and 14 % are shown, respectively. Bagasse on the other hand, although possessing less ash has suffered from a negative effect by 5 %. This being said, data from the LECO TGA 701 has shown that bagasse has a larger maximum mass loss at 350 °C than the other feedstocks both raw and leached. Additionally, due to the fine temperature control across all samples, **Figures 4b** and **4c** show two distinct peaks for each feedstock, the first at ~270 °C and the second between 300-350 °C. These peaks are indicative of depolymerisation of hemicelluloses and pectins (inital peak) and the degradation of cellulose (major peak).

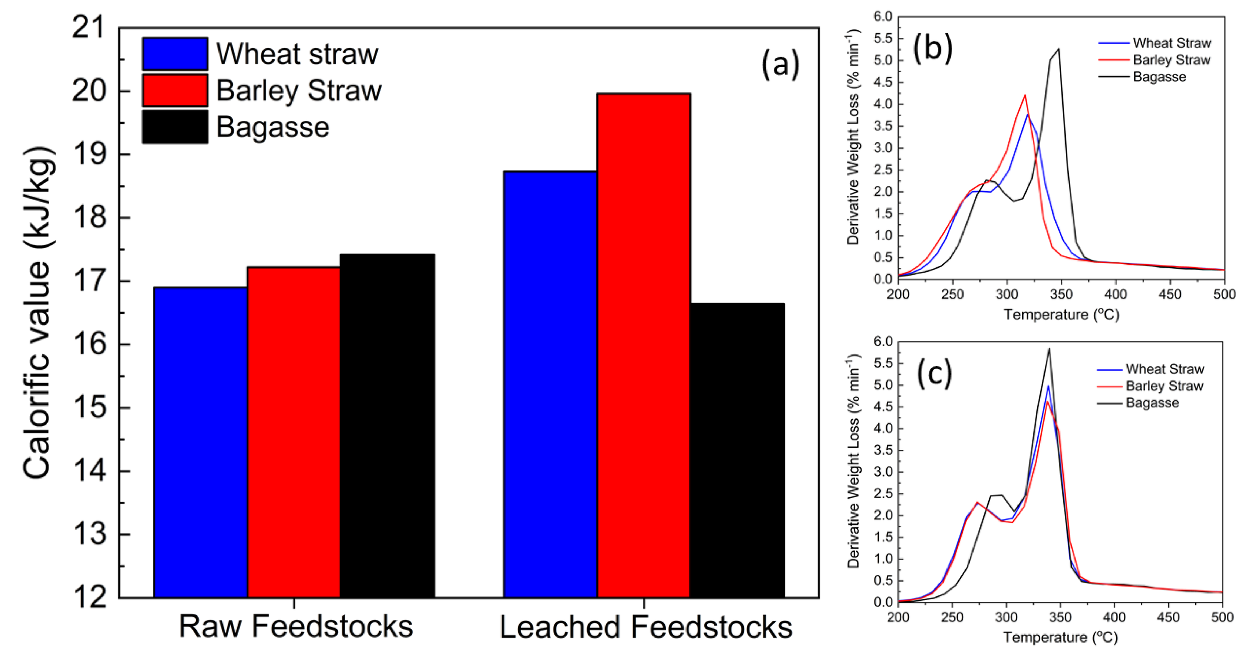

Figure 4: (a) Bomb calorimetry of raw and leached feedstocks, (b) DTG curves for all raw feedstocks and (c) the effect of leaching on the DTG curves for each feedstock.

Conclusions

In the quest to find alternative solid fuels to replace existing fossil based fuels, three different feedstocks provide an option after pre-treatment for ash removal. By using a cheap and scalable technology such as conventional water leaching, it has been found to remove a large quantity of the undesirable ash components from cereal straws and bagasse. As a result, improving the heating value and for the straws their calorific value by over 10 %. Due to a relatively low temperature used for the leaching pre-treatment, there was no large loss of sugar content from the feedstocks, as shown by FTIR. Ultimately demonstrating that leached barley straw is a strong contender for the future, when not used in competitive markets, due to its low ash content and higher calorific value. Bagasse however is the weakest feedstock under the conditions shown due to its high ash content and low calorific value.

Acknowledgements

All authors are greatly acknowledge the THYME project (UKRI, Research England) for funding. We would like to especially thank Mr Timothy Dunstan for the acquisition of HRSEM images and Jesmond Engineering for fruitful discussions.

References

1. Taylor, M. J.; Alabdrabalameer, H. A.; Michopoulos, A. K.; Volpe, R.; Skoulou, V., Augmented Leaching Pretreatments for Forest Wood Waste and Their Effect on Ash Composition and the Lignocellulosic Network. *ACS Sustainable Chemistry & Engineering* **2020**, 8 (14), 5674-5682.
2. Taylor, M. J; Alabdrabalameer, H. A; Skoulou, V., Choosing Physical, Physicochemical and Chemical Methods of Pre-Treating Lignocellulosic Wastes to Repurpose into Solid Fuels. *Sustainability* **2019**, 11, 3604.
3. Alabdrabalameer, H. A.; Taylor, M. J.; Kauppinen, J.; Soini, T.; Pikkarainen, T.; Skoulou, V., Big problem, little answer: overcoming bed agglomeration and reactor slagging during the gasification of barley straw under continuous operation. *Sustain Energ Fuels* **2020**.
4. Skoulou, V.; Zabaniotou, A., Fe catalysis for lignocellulosic biomass conversion to fuels and materials via thermochemical processes. *Catalysis Today* **2012**, 196 (1), 56-66.