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Augmented Leaching Pre-treatments for Forest Wood Waste and Their Effect on Ash Composition and the Lignocellulosic Network

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ABSTRACT: By augmenting conventional leaching technologies for the removal of ash constituents from lignocellulosic waste residues, a cleaner and energy efficient solution can be provided for critical industrial problems such as, biomass feeding, defluidization and reactor corrosion. It has been found that not only are inorganic constituents (ash) effectively removed by coupling a physicochemical technology with conventional leaching, the intermolecular interactions within the lignocellulosic matrix can be modified, as shown by a variable crystallinity index (PXR) without the loss of physical bonding (FTIR). Ultimately, this allowed for a greater thermochemical transformation of cellulose, hemicellulose and lignin for all technologies used; conventional leaching, indirect/directed ultrasound and microwave. However, the use of directed ultrasound was found to be the standout, energy efficient technology (8.6 kJ/g) to radically improve the thermochemical transformation of wood waste, especially in the reduction of fixed carbon at high temperatures. It was also found to be efficient at removing vital eutectic mixture causing elements, a common cause of thermochemical reactor damage and shut downs, including Si, a notoriously difficult element to remove via leaching. In comparison, hotplate leaching and microwave use 39 and 116 times more energy, respectively. The integration of this technology into the energy production sector will prove vital in the future due to its scalability, as compared with microwave alternatives which are currently not suitable for large scale operations. Additionally, the residence time required for directed ultrasound was found to be negligible as compared to the various other physicochemical techniques, 0.1 h opposed to 4 h.

KEYWORDS

Biomass; Solid fuels; Energy assessment; Multi-parameter analysis; Enhanced leaching processes; Waste-to-energy; Clean technology

Introduction

As the transition from fossil fuels commences to combat climatological catastrophe, various alternate methods of energy production have been exploited such as, solar, wind (on and offshore), nuclear, hydro, geothermal and bio-renewables.¹⁻³ Globally these alternate energy sources have been investigated in different ways. An example of such is the United Kingdom who in 2017 have switched their energy consumption mix to 31% renewables. However, of this percentage where natural gas and nuclear energy are dominant, only 9.4% is from biomass waste derived operations.⁴⁻⁵ This fraction is attributed to energy generated through thermochemical and biochemical methods such as, combustion and gasification vs anaerobic digestion.⁶ This percentage is slightly higher than the overall global energy consumption of 9% for biomass waste derived processes.⁷ One of the major indicators for why very little biomass waste is used in comparison to other renewable technologies is the ash constituents present in the waste feedstock. This is variable

depending on the type of lignocellulosic biomass waste used, be this wood based, examples being, pine,⁸ eucalyptus,⁹ oak,¹⁰ poplar,¹¹ beech wood¹²⁻¹³ or olive kernel wood.¹⁴ Or other non-wood, herbaceous wastes such as, wheat straw,¹⁵ sugarcane straw,¹⁶ switchgrass¹⁷ and bagasse.¹⁸

Between the two categories of lignocellulosic waste substrates there is not only a difference in the hemicellulose: lignin ratio but also a stark difference in the inorganic elements present.¹⁹ Major elements generally found in the ash/fly ash of decomposed lignocellulosic wastes are K, Na, P, Ca, Mg, S, Cl and Si.^{4, 20-21} Some of which are capable of catalyzing thermochemical gas phase reactions such as K, Na, Ca and Fe, as well as the depolymerisation of cellulose in low metal concentrations.^{4, 22-25} There are many others that are instrumental in causing fluidised bed reactor agglomeration via eutectic mixtures, these compounds have lower melting points than standard oxide based materials.²⁶ One of the most common problematic mixtures of parent ash constituents in biomass

waste is K and Si. These are present in the form of silica or silicates, either from the inherent Si content of the waste substrate or attributed from the reactor bed material, the usual culprit being cheap and readily abundant silica sand.²⁰ Bed agglomeration is where the bed material grains have been fused together, restricting heat and mass transfer, ultimately preventing thermochemical conversion. This process leads to the restriction of the carrier/product gas through the system, ending in pressure instability leading to operational shut down. Not only will this cause the production of low carbon fuel to slow down or even stop but can also cause irreversible damage to the reactor itself. This can include erosion and corrosion to the heat exchanger surfaces of the reactor, ceramic filters of the gas cleaning system, turbine blades and reactor walls due to slagging.^{20, 26-27} High levels of Cl in the biomass waste feedstock will also lead to the production of KCl in the gas phase which will react with S. This forms highly acidic sulphates on the reactor walls after cooling down or in cold spots in the reactor system.²⁰⁻²¹ Often, these inorganic compounds will act as particulate traps where they will collect other gas phase contaminants, increasing the size of the slagging deposits.^{20-21, 27}

In-situ methods of mitigating problematic inorganic based compounds have been explored heavily in the literature.^{21, 28} Initially, a lower reaction temperature can be carried used. This is where gasification takes place below 800 °C to avoid the formation of K and Si eutectic mixtures.⁴ However, this leads to a drop in both production and product selectivity as the gasification reactions are promoted at temperatures higher than 750 °C.²⁹ Various additives or bed material compositions can be used to alter aspects of the thermochemical reaction, this involves changing the product mix by varying the H₂/CO ratio, or via catalyzed transformations. Also, the heat balance, oxygen transport or the ability to trap/react with inorganic based ash components are modified.²⁴ However, in some cases an enhanced oxygen mobility has been found to increase the concentration of CO₂ found in the gas product mix.²⁴ Examples of bed materials commonly used in fluidised bed systems are dolomite (CaMg(CO₃)₂), bauxite (Al₂O₃.nH₂O), olivine (Mg, Fe)₂SiO₄ and quartz sand (SiO₂).^{24-25, 28, 30-31} These compounds have had a large amount of success in lowering ash related problems, albeit presenting a new issue: a higher cost for industrial practice compared to plain silica (quartz) sand. For further justification of use, materials such as olivine, once it has been thermally processed in air can be useful for tar cracking.²⁴ Whereas the inert material, quartz sand, is prone to forming eutectic mixtures with alkali ash constituents as mentioned previously.

An alternative, ex-situ method of overcoming the build-up of inorganic compounds inside the reactor, as well as negating the occurrence of bed agglomeration is to remove them from the waste feedstock prior to use. This can be efficiently carried out by leaching the waste substrate, often referred to industrially as washing.³²⁻³³ This technology has been used for coal pre-treatments for a number of decades.³⁴⁻³⁵ Seen as a chemical pretreatment method, leaching is often carried out in demineralized water where the substrate is suspended and mixed. Overtime the liquid medium will diffuse into feedstock's porous network and remove inorganic elements, forming a mineral rich leachate. As a result of this process being carried out the internal lignocellulosic structure will swell. This causes an increase to the pore volume and available surface area.⁴ Previously, it has been found that temperatures up to 90

°C are effective at reducing the concentration of elements such as S, K and Cl by up to 90%.³⁶⁻³⁷ However, when operating at high temperatures, organic aspects of the feedstock such as hemicellulose (sugars) will begin to be solubilized (a loss of valuable carbon units). Therefore, low temperature leaching is the preferred method of removing alkaline and alkali metals, as well as being less energy intensive.

In this work we will investigate the effect of conventional leaching of inorganic components from forest wood and how this process can be augmented by different technologies, without causing a detrimental effect to the carbon network in the form of bond breaking and the loss of potential fuel components. This will be carried out by combining the chemical pre-treatment with various physicochemical technologies such as microwave irradiation, previously used for extracting metals from ores³⁸ and direct/indirect ultrasound, used in the past for leaching sugars and proteins from biomass.³⁹ Additionally, the surface and bulk substrate structure will be analyzed to determine the full effect of the leaching process on the lignocellulosic waste material via ICP-OES, PXRD, FTIR, SEM and TGA. Moreover, an analysis on the energy consumption of each technology has been carried out in order to assess the amount of energy consumed to pre-treat the lignocellulosic waste. Conclusions can then be drawn to determine the least energy intensive pre-treatment method. The technologies and assessment reported in this work may be applicable in the future of low carbon energy generation. Finally, and in order to evaluate the overall performance of the alternative examined pre-treatment technologies, a multi-parameter assessment based on six selected indicators was carried out. All of which are of high importance and need to be taken into consideration for energy from waste investors interested in low carbon footprint energy generation.

Materials and Methods

Raw forest wood waste, all taken from the same source, (locally sourced pine) was physically pre-treated using a Luvele LPPB 2200 W Power-Plus blender (knife mill) followed by sieving fractions of the desired particle size (<250 µm) using a Retsch vibratory sieve shaker. The ultimate (C, H, N, S and calculated O content) and proximate analysis (moisture and volatile content) as well as the higher heating value, HHV, is reported in **Table 1**. For all data acquired, the process was carried out in triplicate to account for potential feedstock variability. The ultimate analysis of the forest wood was carried out using a Fisons Instruments EA 1108 CHNS elemental analyzer, sample sizes for this characterization was between 2-3 mg, the elemental composition was to found to be similar across 3 different samples. From this data, there was only a broad variation in nitrogen content. The ash component was measured by heating 1 g of untreated wood waste in a muffle furnace (Carbolite AAF 11/3 ashing furnace, in air). Here, the material was heated at 10 °C/min and held for 2 h at 600 °C. The proximate analysis took place under thermogravimetric (Perkin Elmer TGA4000) conditions under N₂ flow where moisture and devolatilization was measured in triplicate. The proximate analysis thermal method used was; 30 – 105 °C (5 °C/min, held 0.3 h), 100 – 600 °C (10 °C/min, held 0.5 h) and 600 – 900 °C (10 °C/min, held 0.3 h). Fixed carbon was calculated by using the ash content acquired from the muffle furnace approach (**Equation S1**). Inorganic content of the raw and pretreated forest wood were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Thermo Fisher

7400). The samples were digested via microwave (CEM Discover-S microwave system) in 4 mL HNO₃ (Romil SPA grade 70%) at 200 °C, followed by aqueous dilution. Bulk compositions were measured to be ±10-20 %, dependent on element response. FTIR spectra were obtained using a Thermo Scientific Nicolet iS5 with a PIKE MIRacle single reflection horizontal ATR accessory. 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. Powders 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. The crystallinity of the cellulose component was monitored via Powder X-ray diffraction (PXRD) measurements using monochromated Cu K α radiation ($\lambda = 0.1542$ nm) on a PANalytical Empyrean series 2 diffractometer. Subsequent analysis of the diffractograms was performed in HighScore Plus (2013, PANalytical B.V.) with the ICDD's PDF-2 2012 database. The energy (electricity) consumed per experiment has been measured with the aid of a Brennenstuhl PM231 LCD Plug in Energy Meter.

Table 1 – Averaged ultimate and proximate analysis of the untreated wood waste

Untreated Forest Wood	
Ultimate analysis (average wt%, dry basis)	
Carbon	48.19 ± 0.57
Oxygen*	44.73 ± 0.15
Hydrogen	6.35 ± 0.03
Nitrogen	0.48 ± 0.31
Sulphur	0.00 ± 0.01
Ash	0.74 ± 0.11
Proximate analysis (average wt%, dry basis)	
Moisture	5.5 ± 1.14
Volatiles	76.5 ± 0.93
Fixed Carbon	17.3 ± 0.38
HHV(MJ/kg)	17.5 ± 0.41

*Calculated by the difference

Augmented Pre-treatment Technologies

Individual samples of finely milled pine wood was immersed in deionized water (10 g/L) and subjected to various methods of physicochemical pretreatment to extract ash constituents. The technologies used were conventional hotplate leaching at 45 °C, 700 rpm (to disrupt the surface tension of the water and homogenise the process) for 2, 4 and 24 h (Heidolph Hei-Tec hotplate). The broad variation in leaching time was carried out due to elements such as S, P, Mg and Fe possessing a higher solubility in water value.⁴ This means that a longer extraction time is required to maximise removal. Indirect ultrasound (SLS U300) was used where the forest wood waste was suspended in water inside a glass beaker. The vessel was then placed on the base of the unit and the sweeping action of the device was carried out over 2, 3 and 4 h periods. Directed ultrasound utilised a Branson Digital Sonifer 450 operating at 25% amplitude at a depth of 75% into the conical sample holder. This was where the probe underwent a number of cycles, pulsing for

20 seconds and resting for 20 seconds. Total residence times completed were 2, 4, and 6 min. Residence time was limited for this technology to reduce chances of potential sample degradation. Finally, microwave irradiation was carried out using an Ethos EX Microwave-Assisted Extraction System, 1200 W with a rotary vessel reactor system over 2, 3 and 4 h, operating with an output of 500 W. An above ambient temperature (45 °C) was used so that microwave extraction could be viable. This temperature was used for all technologies with the exception of directed ultrasound, this occurred at room temperature. Upon leaching completion for all technologies, the forest wood was separated from the leachate via vacuum filtration and subsequently dried in a Memmert UN75 circulating oven at 105 °C for 24 h.

Thermal Degradation Measurements

The effect of pre-treatment on the rate of thermal decomposition, moisture, volatile, fixed carbon and ash content was monitored by thermogravimetric analysis using a Perkin Elmer TGA4000 under a nitrogen flow at 30 mL/min. This was carried out using a stepwise heating profile, starting from 30 – 105 °C (5 °C/min), held for 10 min at 105 °C, 105 – 600 °C (10 °C/min), held for 20 min at 600 °C and 600 – 900 °C (10 °C/min), where it was held finally for 20 min.

Results and Discussion

After pre-treatment, the substrates underwent ICP-OES where a broad array of elements were followed such as Ca, Fe, K, Mg, Na, P, S and Si. **Figures S1a-S1d** show the effect of the augmented leaching technologies over time. **Table 2** presents the overall element extraction at the maximum time monitored. Here, it is shown that all technologies facilitate an ash removal of over 66%. It also shows that the conventional hotplate and microwave have similar capabilities for overall inorganic reduction of 77.9% and 77.3%, respectively. However, the specific elements removed from each method are highly variable, depending on the technology used and for how long. For elements with a high water solubility e.g. Na, K and P, the levels of extraction are similar for all technologies, where as shown in **Figures S1a-S1d**, there is no benefit from a prolonged leaching pre-treatment. All technologies were also efficient at the removal of Ca from the waste wood, a highly abundant element in softwood.⁴⁰ It was found that both forms of ultrasound pre-treatments retarded the extraction of Ca marginally overtime, proving to be 10% less effective than conventional hotplate, as shown in **Figure S1**. There is a clear advantage to the use of directed ultrasound for the removal of the often troublesome, or tricky to extract elements Fe, S and Si. Specifically, the high intensity directed ultrasound was able to extract 75% of the Si component during a short residence time of 6 min. Microwave irradiation was also found to remove Si, albeit it was 37.5% after 4 h. It has been documented in the past that Si removal from biomass waste is notoriously difficult, requiring high leaching temperatures for only partial removal.⁴¹ This is the reason why after 24 h of continuous hotplate leaching under mild conditions there was no detectable decrease in Si concentration (**Table 2**). For Fe, the directed ultrasound probe was found to remove 72.7% after 2 min (**Figure S1d**), for this element the maximum Fe was removed after a short residence time as the prolonged pre-treatment had no further effect. For conventional hotplate and microwave irradiation, the removal of Fe from the wood waste is time dependant (**Figure S1a and S1c**). Resulting in the same level of extraction after 4 h

(microwave) and 24 h (conventional hotplate). For this element as well as Si, the indirect ultrasound technology was not appropriate, presenting no detectable decrease after 4 h of sustained operation. Interestingly, ultrasound as a physicochemical technology reduced S by the same magnitude after 4 h (indirect) and 6 min (direct), both more effective than conventional leaching but marginally less effective than microwave augmented extraction.

Table 2 – Summary ICP-OES data showing the effect of conventional and enhanced leaching of softwood waste at the maximum residence time investigated.

Technology	Pre-treatment Time (h)	Inorganic Reduction (%)	Element Removal From Raw Wood Waste (%)							
			Ca	Fe	K	Mg	Na	P	S	Si
Conventional Hotplate	24.0	77.9	76.3	54.5	96.9	81.8	N/A	N/A	41.7	N/A
Direct Ultrasound	0.1	76.3	76.3	72.7	96.9	77.3	N/A	N/A	75.0	75.0
Indirect Ultrasound	4.0	66.0	66.4	N/A	93.8	68.2	N/A	N/A	75.0	N/A
Microwave	4.0	77.3	73.3	54.5	95.8	81.8	N/A	N/A	83.3	37.5

N/A represents a value below detection limit

Although a prolonged residence time for the augmented leaching technologies was not essential for all the monitored elements (**Figures S1a-S1d**), the lignocellulosic network does appear to be effected over time, namely the crystalline region of cellulose. This is where the glucose monomers of the cellulose are connected by glycosidic linkages as well as intermolecular interactions such as hydrogen bonding. Such arrangements present areas of high ordering known as crystalline, whereas regions where there is limited ordering are known as amorphous. The benefit of reducing the crystallinity of the cellulose is that less energy could be required to thermally decompose the biomass waste, compare to if not pre-treated.⁴² However, a downside to lowering the crystallinity of cellulose is that the solubility of the substrate in water increases.⁴³ This means that carbon content could be lost from the feedstock into the leachate. The crystallinity index (Crl) of the raw/pre-treated wood substrates can be calculated as a percentage by monitoring the loss in peak intensity for the crystalline cellulose (002) feature via PXRD. This is then used as part of Segal's equation shown in Eq. 1.⁴⁴

$$\text{Eq 1. } Crl\% = \left(\frac{I(002) - I(AM)}{I(002)} \right) \times 100$$

Figure 1 shows an arrangement of PXRD diffractograms observing the effect of the pre-treatment technology on the Crl, this was calculated by componentizing the peaks to determine the amorphous and crystalline regions.⁴⁴⁻⁴⁵ **Figure S2** shows a fitted diffraction pattern once the background had been subtracted. **Table 3** shows that prior to any pre-treatments the inherent Crl of the untreated wood waste is 82.1%. **Figure 1** shows that the indirect ultrasound pre-treatment, although efficient for the removal of sulphur (**Table 2** and **Figure S1b**), it is not an effective technology at reducing the crystallinity index of the wood waste. This value after 4 h as reported in **Table 3** is 77.5%, this is a drop of 4.6% from the untreated wood. **Table 3** does clearly show that a decrease in Crl is directly related with the residence time of each augmented biomass waste pre-treatment technology. For all the technologies operated up to 4 h, hotplate, microwave and indirect ultrasound, the calculated Crl values were 74.5%, 69.5% and 77.5%, respectively. This shows that the microwave was the most effective method of reducing the

Ultimately, the data presented in **Table 2** shows that as a technology, the sweeping action of indirect ultrasound is not an effective method of enhancing leaching. However, by directing the ultrasound into the substrate in short cycles is very effective. Not only is this favourable due to a short residence time, it was found to be more efficient than conventional hotplate or indirect ultrasound, in terms of S and Si removal.

crystallinity of cellulose. However, the directed ultrasound probe in terms of residence time requirements proved to be the most effective for disrupting the intermolecular interactions within the cellulose network. Diffraction patterns of all pre-treatment technologies used across all residence times are presented in **Figure S3a-3d**.

Bonding of the organic matrix was observed by FTIR, here depending on features in the spectra, various functional groups can be assigned. Unlike PXRD, this technique doesn't just consider cellulose features.

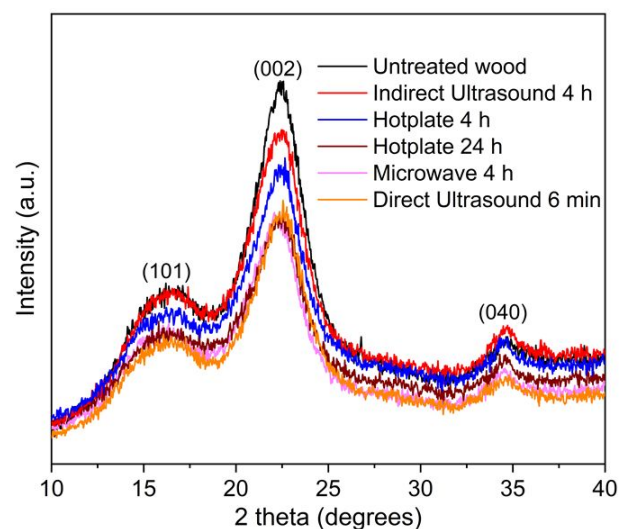


Figure 1 – Stacked PXRD diffractograms of untreated and pretreated wood waste showing the effect of the augmented technology on the Crl.

Table 3 - The effect of the leaching technology on the cellulose crystallinity over time, Crl – Crystallinity Index

Technology	Time	Crl (%)
Untreated wood	-	82.1
Conventional Hotplate	2 h	75.0
Conventional Hotplate	4 h	74.5

Conventional Hotplate	24 h	68.2
Direct Ultrasound	2 min	74.2
Direct Ultrasound	4 min	72.7
Direct Ultrasound	6 min	70.9
Indirect Ultrasound	2 h	78.6
Indirect Ultrasound	3 h	78.1
Indirect Ultrasound	4 h	77.5
Microwave	2 h	79.4
Microwave	3 h	77.5
Microwave	4 h	69.5

This means that each pre-treated biomass waste material can be scrutinized for its lignin and hemicellulose bonding as well as bonding to the cellulose component.

Figure 2 shows an arrangement of FTIR spectra for the untreated wood and all of the pre-treated substrates investigated at the maximum residence time used. The assignment of each band is in a very close proximity to various other data presented in the literature.⁴⁶⁻⁴⁷ The first band, starting from lowest wavenumber and working upwards is 1032 cm^{-1} which is attributed to C-O, C=C and C-C-O stretching for cellulose, hemicellulose and lignin. The stretch at 1162 cm^{-1} is assigned to an asymmetrical C-O-C for cellulose and hemicellulose. An aromatic ring vibration specific to guaiacyl alcohol, one of the molecules indicative of lignin was seen at 1270 cm^{-1} .^{4, 46-47} However, there was no band observed $\sim 1327 \text{ cm}^{-1}$ for syringyl alcohol, another fingerprint of lignin.⁴⁶ This is because syringyl alcohol is specific to hardwood, the data suggests that this forest wood waste belongs in fact to the softwood family, indicating the subtle differences of woody biomass waste species. The terms hard and soft are not typecast to the material's tensile strength as the name would suggest. Instead, hardwood is typically from broad leaved trees, e.g. eucalyptus.⁴⁸ Whereas softwood is generally sourced from trees without these leaves such as pine, the feedstock used for this work.⁴⁸ Other lignin specific aromatic ring vibrations were isolated at 1505 cm^{-1} and 1593 cm^{-1} .⁴⁹ The band at 1730 cm^{-1} highlighted in **Figure 2** has been identified as a ketone/aldehyde C=O stretch for hemicellulose.^{47, 49} Finally, the broad O-H stretch at 3347 cm^{-1} is attributed specifically to a softwood band position for lignin, this shifts to a higher wavenumber (3421 cm^{-1}) for hardwood.⁴⁶⁻⁴⁷

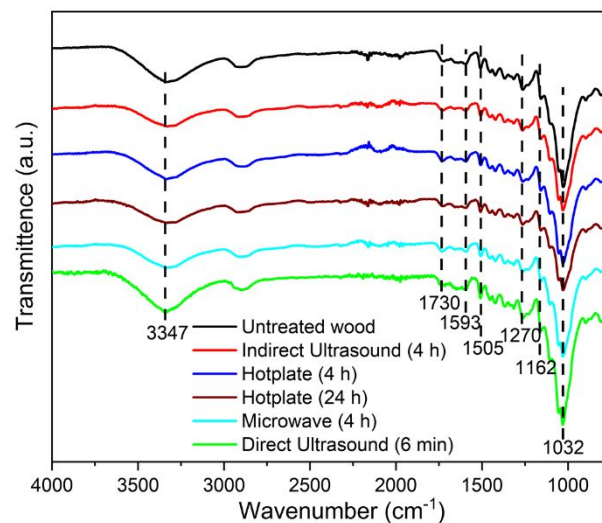


Figure 2 – Overlaid FTIR spectra of untreated and pre-treated wood waste, dashed lines indicate various cellulose, lignin and hemicellulose functional groups.

The take home message from these spectra are that all of the features present in the untreated wood waste are identifiable in every pre-treated sample. This infers that the various pre-treatment technologies irrelevant of residence time are not removing hemicellulose or lignin features, and therefore chemical bonding remains unchanged and there is no obvious change to the carbon content post leaching.

Figure 3 shows an array of high resolution SEM images in the order of the least to most destructive augmented technology. **Figure 3a** shows the surface structure of the untreated wood, well ordered channels are clearly shown with no obvious fracturing. **Figure 3b** is the first of the pre-treated samples, indirect ultrasound after 4 h. This has shown that there has been a pressure build up within the lignocellulosic waste causing stomata like structures to form suggesting that the cell wall of the wood has begun to burst open (yellow circle). Above these surface alterations there is also signs of cracking along the channel with some slight separation (yellow square). Interestingly, the indirect ultrasound technology was found to have negligible effect on the Crl (**Figure 1, Table 3**), it could mean that the technology is surface specific. The indirect ultrasound technology operates in a sweeping motion, this had a dampened effect as the substrate suspension was housed in a glass beaker, and this means that the energy travelling across the device will be diminished at the centre of the sample holder. **Figure 3c** shows the effect of microwave irradiation on the softwood material. Although at a higher magnification than the other images presented, there is a greater surface destructive effect (red square) as compared with indirect ultrasound as is the frequency of 'stomata' (blue circle). For this technology the sample is heated from the inside-out. It appears that as pressure has built up, the cell wall has ruptured and as a result there is build-up of wood around the centre of the stomata structure, similar to a volcanic eruption. There is also more evident substrate separation for this technology as the once ordered channels have fractured. This technology alongside conventional hotplate leaching over 24 h and directed ultrasound at 6 min, **Figures 3d** and **3e**, respectively present Crl values similar to one and other (**Table 3**). **Figure 3d** although operating at a far higher residence time to the

other technologies, it presents a more distorted surface morphology as compared with **Figure 3a**. Here, the ordered channels have been warped and fractured causing surface splintering. There is also a substantial stomata concentration along a number of the channels (purple square). However, this pales in comparison to the effect of directed ultrasound pulsed over a 6 min period (**Figure 3e**). The effect of this technology appears to have less of an effect to the surface morphology in terms of channel fracturing and splintering, it has had a notable effect on stomata concentration (green squares). The ordered channels have been saturated by micron sized ruptures, this concludes that there has been a substantial pressure build-up within the cell wall causing it to burst. There is also the presence of micro fibrils (yellow arrows) which suggests that the cellulose has undergone deterioration of the cell wall.⁵⁰ This is not obvious in **Figures 3b, 3c** and **3d**, as a

result, this aspect of surface manipulation could be specific to directed ultrasound under the conditions used.

Figure 4 illustrates the electrical energy consumption normalized per gram of wood waste for each pre-treatment technology assessed in this work. These results indicate that the most energy intensive pre-treatment technology is the microwave (997.5 kJ/g), followed by conventional hotplate (336.0 kJ/g), indirect ultrasound (96.0 kJ/g) and finally directed ultrasound (8.6 kJ/g). By directing the ultrasound output to a single point (directed ultrasound) the energy output is substantially decreased. This infers that direct ultrasound used 2.56% of the energy used for the conventional leaching. Comparing the ultrasound technologies, indirect ultrasound consumed more than 11 times of the energy than the directed equivalent.

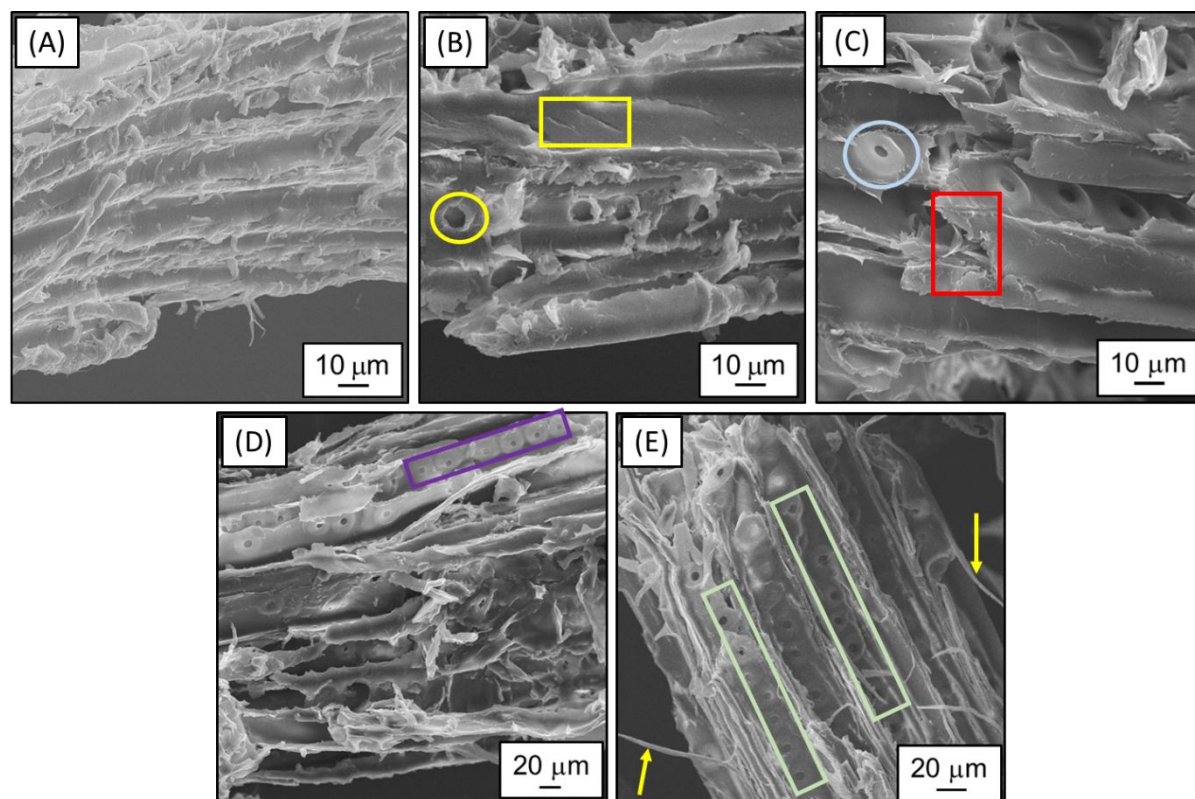


Figure 3 – SEM images of untreated and pre-treated wood waste where: (A) untreated wood waste, (B) indirect ultrasound after 4 h, (C) microwave irradiation after 4 h, (D) conventional hotplate stirring after 24 h and (E) directed ultrasound after 6 min.

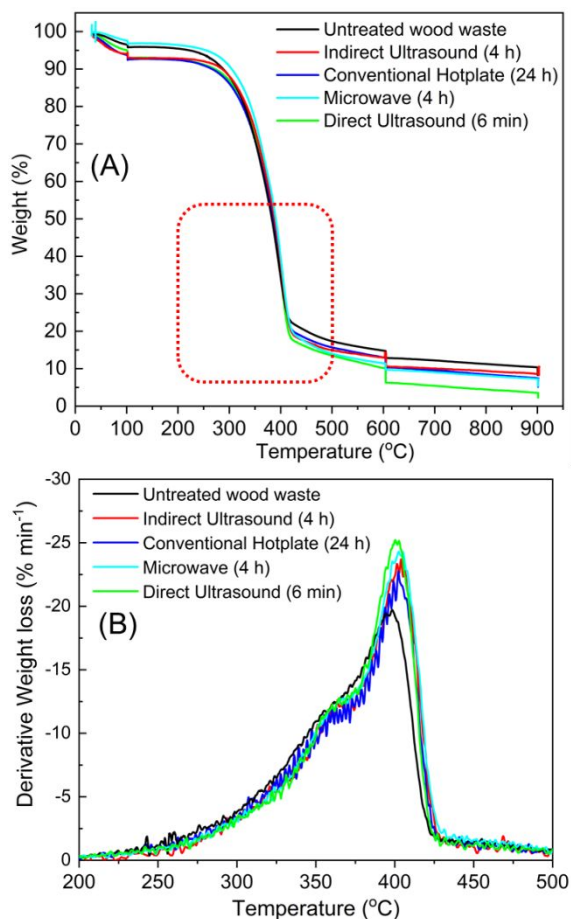


Figure 5 – Thermogravimetric analysis under N_2 across all technologies at the maximum residence time, where (A) is an overview of the reaction profile, and (B) presents the derivative weight loss profile, highlighted by a red dashed square in Figure 5a.

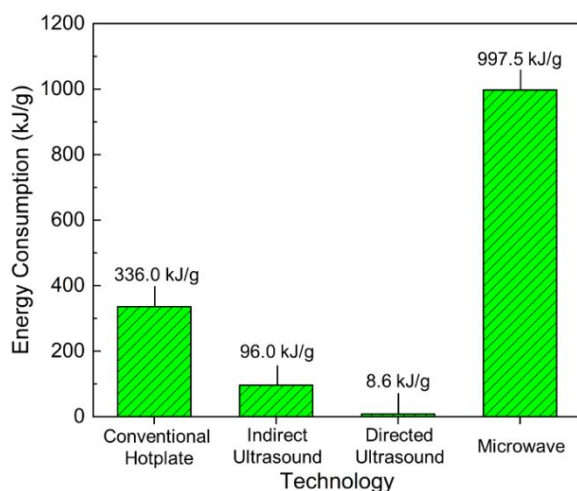


Figure 4 – Energy consumption per gram of wood waste for each examined pre-treatment technology

Microwave assisted leaching is an energy intensive process as the power consumed during the initial heating process is incredibly high. When at the leaching temperature the system pulses periodically to maintain the temperature, energy is however used for sample rotation to ensure homogenous heating, during non-pulse periods this energy is wasted. The

electricity requirements of the microwave technology leads to almost 116 times more energy consumed, as compared to the directed ultrasound. This means that the directed ultrasound pre-treated is the most energy efficient method. Thermochemical reactions were carried out under TGA conditions in flowing N_2 . By utilizing a single heating ramp rate ($20\text{ }^\circ\text{C}/\text{min}$) during the temperature range of $100 - 400\text{ }^\circ\text{C}$, the light volatile molecules derived from the cellulose and hemicellulose components are released.⁵¹ Higher, at $600\text{ }^\circ\text{C}$ lignin components in the form of heavy volatiles are then decomposed. **Figure 5a** provides an illustration of the overall reaction profile where the moisture is released from the sample at $100\text{ }^\circ\text{C}$. This is variable for each of the samples as all of the pre-treated biomass waste, with the exception of the microwave pre-treatment, have a lower moisture content as compared to the raw wood waste. The reaction profile for volatiles released is identical for all materials up to $\sim 400\text{ }^\circ\text{C}$. This means that the energy required for the second stage of the process to be carried out is not changed. This therefore infers that the pre-treatment processes used are not dramatically altering the lignocellulosic matrix, albeit each effecting the CrI and surface morphology. Instead due to the subtle differences in the weight loss % per min observed in **Figure 5b**, it can be suggested that there has been substantial disruption to the intermolecular interactions within the lignocellulosic matrix, agreeing with the decreases in CrI (**Table 3**). For the case of directed ultrasound as a pre-treatment technology, the highest rate of sample weight % loss is observed (**Figure 5b**), **Figure 5a** also shows that less fixed carbon remains. This is represented by a 51 % decrease on sample weight at $600\text{ }^\circ\text{C}$ when compared with untreated wood. However, for the other three technologies used the decrease in weight (%) at this temperature is very similar

at $\sim 24\%$. This means that the directed ultrasound has also disrupted the lignin interaction within the matrix, without removing any of the chemical bonding, as seen in **Figure 2**.

The conventional and enhanced leaching technologies used in this work were assessed for their large scale feasibility using six characteristic indicators, these represent their equal physical parameters, respectively. The indicators have been presented and analytically discussed previously in the manuscript. The first gauge is the required pre-treatment time, in industrial applications the pre-treatment time should be minimum in order to ensure continuous feed rates, reducing feedstock storage and processing areas (logistics). The following three characteristics deal with the capability of the technology to extract inorganic components, expressed as inorganic reduction efficiency (IRF), the removal of sulphur and silicon constituents. The IRF expresses the percentage of the inorganic elements that are extracted from the waste solid matrix. The IRF criterion should be maximised in order to minimize potential operational issues such as corrosion phenomena, sulphur-based emissions, as well as eutectic mixture creation and related de-fluidization events.^{4, 41} The last two characteristics taken into consideration are the crystallinity index and the energy consumption required for the pre-treatment technology. The crystallinity index in our case expresses the easiness of thermochemical decomposition. The lower the crystallinity of the carbonaceous matrix, the less energy required for thermal decomposition of the improved solid fuel. The energy consumed during the pre-treatment process of the biomass waste should be a minima to offset the energy production, improving the cost effective nature of both the solid fuel and

production process, this is imperative for the waste-to-energy generation industry.

These characteristic indicators have been translated into quantitative key factors by dividing each parameter with the minimum or maximum counterpart, deducing the best performing technology per criteria mentioned previously, thus a key factor equal to 1.0 indicates the best performance. Values of the key factor above (>1) or below this (<1), represent the time discrepancy of the best performing characteristic indicators that should be minimized and maximized, respectively. Table 4 summarizes the quantitative key factors per parameter and their average value. More specifically, the ultrasound technologies are both promising as these leaching enhancements have the lowest average value. In contrast, microwave and conventional hotplate technologies are the most inefficient as their average value is

26.5 and 47 times higher than direct ultrasound, the best performing technology, respectively. In addition, it is interesting that the direct ultrasound technology achieves an average value of 0.99 indicating only 0.01% discrepancy from the best performance limit. This is due to the fact that the directed ultrasound technology achieves the lowest pre-treatment time and energy consumption factors, compared to the competitive alternatives such as conventional hotplate and microwave.

Conclusions

Industrial scale low carbon energy generation based on woody waste should demonstrate an efficient, stable and non-problematic long-term operation. When alternative solid fuels such as woody wastes are exploited in the fluidised bed reactors, initial physical pre-treatments to increase the surface area: volume ratio is a necessary requirement.

Table 4 – Results of the multi-parameter assessment of the conventional and alternative biomass waste pre-treatment technologies on the leaching of softwood waste (ideal value: 1.0)

Technology	Pre-treatment Time	Inorganic Reduction	Element Removal From Raw Wood Waste		Crystallinity	Energy Consumption	Average
			S	Si			
Conventional Hotplate	240.00	1.00	0.50	0.00	1.00	39.07	46.93
Direct Ultrasound	1.00	0.98	0.90	1.00	1.04	1.00	0.99
Indirect Ultrasound	40.00	0.85	0.90	0.00	1.14	11.16	9.01
Microwave	40.00	0.99	1.00	0.50	1.02	115.99	26.58

Variations in the pre-treatment used can be tailored to meet required specifications (e.g. feeding capabilities, elemental composition, particle size and moisture content). The pre-treatment of pine wood waste was carried out using augmented leaching techniques. This is where a mild temperature of 45 °C was used in the presence of conventional stirring, microwave irradiation and indirect ultrasound. Directed ultrasound was also carried out in the absence of water heating. The pre-treated wood was found to contain dramatically less inorganic components across all technologies (>66%). However, extended residence times for all techniques was not required for inorganic extraction, it was proved that reduction in ash constituents reached a maxima at the first time point, this is due in part to the elemental solubility in water. This is the reason why the reduction in S is dependent on time (high solubility in water), even for the direct ultrasound technology. Directed ultrasound was also the only enhanced leaching technology that could effectively remove Si. As well as ash component removal, there has been varying differences to the structure and surface morphology of the substrate. It was found that the crystallinity index decreased in direct relation to residence time, for every technology. The maximum decrease of ~13 % was observed for conventional hotplate (24 h), microwave (4 h) and directed ultrasound (6 min). This is where the intermolecular interactions (i.e. Van der Waals interactions and hydrogen bonding) within the cellulose network have been disrupted. FTIR studies provided clear indication that the chemical bonding throughout the substrate remained unchanged when compared with untreated wood waste. However, the surface morphology of the feedstock was found to be markedly different for each technology. For directed ultrasound, the once clearly defined channels begun to rupture, forming micro fibrils. Ultimately, the effect of pre-treatment technology benefitted the rate of mass loss for the cellulose and hemicellulose light volatile region (~400 °C, **Figure 5**). This was most prolific for microwave (4 h) and directed ultrasound (6 min), the latter being the most energy efficient techniques used (**Figure 4** and **Table 4**). For directed ultrasound, there was also a clear reduction in char yield (decrease of 51%) as compared with the parent wood waste. However, for the future of the energy production sector, form the augmented technologies investigated, directed ultrasound is the most promising to be scaled up for industrial scale biomass waste pre-treatment. It is already applicable at scale in other industrial practices. As shown in this work, this enhanced technology had the highest performance rate based on the multi-parameters assessment evaluation. In this assessment it was found that microwave irradiation was very poor, with the exception of rapid S removal.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Additional graphs presenting ICP-OES, PXRD data over time as well as the method of CrI determination is shown.

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