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Tailoring Product Characteristics in the Carbonisation of Brewers' Spent Grain through Solvent Selection

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Abstract

Agricultural, food and other biomass wastes represent an untapped resource of hydrocarbonaceous material with potential for valorisation into fuels and chemical products. A key challenge in this area is directing the characteristics of the products for different applications. Here, the use of different solvents – water and simple alcohols – is shown to directly impact on the products arising from the carbonisation of brewers' spent grain (BSG). Unprocessed BSG was carbonised using water, methanol, ethanol and 2-propanol under pressure. The synthesised biochar was analysed using infrared spectroscopy, thermogravimetic analysis, elemental analysis and bomb calorimetry. Biochar synthesised in alcohol solvents exhibited significantly different properties to that produced via conventional hydrothermal carbonisation (HTC) in water. HTC yielded a biochar with reduced heteroatom content and more favourable properties for application as a solid fuel. The alcohol solvents yielded greater quantities of water soluble oil (WSO), with the yield increasing with alcohol chain length. These trends are correlated with physical properties such as dielectric constant and increased solubility of organics in higher carbon number alcohols. These results show that the choice of solvent can direct the properties of synthesised chars for specific applications or can maximise the yield of bio-oil for fuel.

Keywords: *carbonization, sub-critical water, hydrochar, spent grains, solvent effects*

1.0 Introduction

Over recent decades, thermochemical conversion technologies and processes have been extensively studied as a path for valorisation of biomass feedstocks to produce a large variety of different materials and fuels [1]–[3]. Under the umbrella term of hydrothermal processing; carbonisation, liquefaction and gasification have been widely studied. Hydrothermal carbonisation (HTC) is a thermochemical process which has been used to produce solid fuels, adsorbents, electric double layer capacitors, catalysts and other carbonaceous materials from a large variety of different waste feedstocks such as agricultural waste, food waste, sewage sludge and plastics [4]–[11]. HTC requires low temperatures (180 – 260 °C) and moderate pressures (20 – 100 bar) using only water as the solvent [12]. One of the major advantages that hydrothermal carbonisation gives is the capability for direct processing of wet feedstocks with high moisture content without the need for a pre-drying step [13].The relatively modest operating conditions and flexibility of feedstock mean that HTC has significant potential in the valorisation of many different waste materials with high moisture contents into high value carbons and renewable liquid fuels.

When the solvent employed is not water but an organic solvent, the reaction conditions are described as solvothermal, rather than hydrothermal [14]–[17]. In either case, the feedstock can undergo carbonisation, liquefaction or gasification based on the processing conditions and target product. Sulfonated carbon catalysts have previously been synthesised from cellulose, lignin and glucose in both hydrothermal and "alcohothermal" conditions using water or ethanol respectively with processing conditions of 260 °C for 20 hours. [14]. Elemental analysis of the biochars produced from glucose and lignin showed that they presented a higher carbon and oxygen content and a lower hydrogen content when ethanol was used as the reaction medium as compared to those synthesised in water. Elsewhere, porous carbon materials have been produced from sugarcane bagasse in different mixed ethanol/water systems, a process considered analogous to the well-established organosolv process which is used by the paper processing industry to solubilise lignin and hemicellulose [15]. In that work, the ethanol/water mixtures examined were 0, 8.8, 23.5, 49.4 and 100 mol% ethanol under mild conditions of 180 °C for 20 minutes. BET isotherms showed that the synthesised biochar had the highest surface area at 8.8 mol% ethanol. FT-IR analysis of the biochars showed that the spectral region associated with hemicellulose showed the greatest depletion in intensity in the 100% ethanol system, whilst the peak assigned to cellulose was most reduced in the 8.8 mol% ethanol/water mixture [15]. Other feedstocks investigated using mixed alcohol/water systems include forestry wastes such as pinewood. The processing of pinewood has been performed at 320 °C for short residence times of 15 minutes in different methanol/water mixtures (0, 9.4, 30.6, 65.5 and 100 mol%) [16]. These data showed a maximum bio-oil yield (56%) and minimum biochar yield (12%) at 30.6 mol% methanol/water; while the largest biochar yield (46%) and lowest bio-oil yield (25%) were achieved in the water system. This shows that alcohol/water mixtures have the potential to be used not only to control the properties of biochar but also to optimise the yield of the desired product.

Brewers' spent grain (BSG) is a low value by-product of the brewing industry and is produced in large quantities throughout the year [18]–[22]. In the brewing process, filtered liquor is subsequently converted into beer, while the left-over BSG is currently either predominately sent to landfill or used as animal feed due to its high sugar and protein content [23]. HTC of BSG has previously been investigated, both in terms of the distribution of organic products in the liquid phase and biochar quality [24]–[27]. Analysis of the dissolved organic chemicals has shown acetic acids to be the most abundant, accounting for more than 50 wt% of the organic products, whilst lactic, formic and propionic acid are also formed in substantial amounts. Additionally, there are many different minor products encompassing a wide range of carboxylic and fatty acids, oxygen-functionalised phenols and phenolic acids, benzenediols and cyclopentenone derivatives [25], [27]. HTC of BSG also results in the formation of a solid biochar which – when compared to BSG – has an increased energy density, reduced oxygen and hydrogen content, increased fixed carbon content and decreased ash content; these changes improve the combustion efficiency of the solid material [28]. Previous studies have measured a higher heating value (HHV) between 20.6 and 22.3 MJ kg^{-1}for BSG, while the HHV of the BSG-derived biochar can be between 24 – 34 MJ kg^{-1} depending on the processing temperature and retention time [26], [28]. HHV is a measure of the gross calorific content of a material and is defined as the amount of heat released by a specified quantity once it has been combusted [29].

The objective of this research was to investigate the direct carbonisation of BSG conducted in water or in simple alcohols; and to further investigate the impact of alcohols of different chain-length. Specifically, it is desired to develop an understanding of the influence of the solvent upon the characteristics of the synthesised products and to correlate this with the physicochemical properties of the solvent. Ultimately this will allow the tailored synthesis of products with desired properties through the judicious selection of solvent. To the best knowledge of the authors this is the first report on the effect of mixed alcohol/water systems on the carbonisation of BSG, however the findings are applicable to a wide range of biomass feedstocks. Herein, the influence of the solvent systems was evaluated through considering differences in the yields of biochar and of water soluble oil (WSO). The latter is used in liquefaction studies as a proximate marker for the yield of bio-oil [30]. Additionally, the physical structure of the biochar was analysed for elemental and proximate composition as well as HHV. While single component solvents are employed herein, in practice the reaction medium is best considered as a mixed alcohol/water system as a result of the moisture content in the raw biomass which is released during processing.

2.0 Experimental

2.1 Materials

BSG was provided by Thornbridge Brewery (United Kingdom) and used as received in all carbonisation reactions. The moisture content of the BSG was determined gravimetrically, whereby unprocessed BSG was weighed and then dried in an oven (105 °C, 24 hrs), after which the dried BSG was then weighed, with the mass difference assumed to correspond to the moisture content [31]. The moisture content of the BSG was calculated at 75 wt%. Methanol (≥98%), ethanol (≥99%) and 2-propanol (≥99%) (all Sigma-Aldrich, UK) were used as received. Helium (99.99%, BOC) was used to pressurise the reaction vessel to the pressure stated in Section 2.2. Deionised water was purified using a Suez L300130 instrument to <1M Ω cm.

2.2 Carbonisation procedure

Carbonisation was performed in a 100 ml EZE-Seal Hastelloy C-276 pressure vessel (Parker Autoclave Engineers) fitted with a MagneDrive stirrer and heated using a ceramic band heater (Figure 1). Raw BSG (5 g) was processed in four different solvents: deionised water; methanol; ethanol; and 2-propanol (8.75 g). When accounting for the moisture content of BSG this gives the following mol% alcohol/water mixtures - methanol: 58 mol%; ethanol: 49 mol%; 2-propanol: 43 mol%, assuming that all water is liberated from BSG during reaction. These mixtures were processed under helium (30 barg, room temp) ramping to 250 °C and holding at that temperature with stirring (500 rpm). After holding at 250 °C for 30 min, the reaction was quenched in a water-ice bath; and biochar was subsequently separated using vacuum filtration. The choice of experimental parameters was based on preliminary screening studies and selected to maximise yield of the desired solid carbonaceous product [32]. The synthesised biochar was subsequently washed with deionised water and dried in an oven (105 °C, 24 hrs). The aqueous phase was heated (100 °C, 15 min) to remove excess solvent and to determine the WSO yield [30]. The HTC experiments were performed in triplicate in order to determine the run-to-run experimental variation and quantify experimental error.

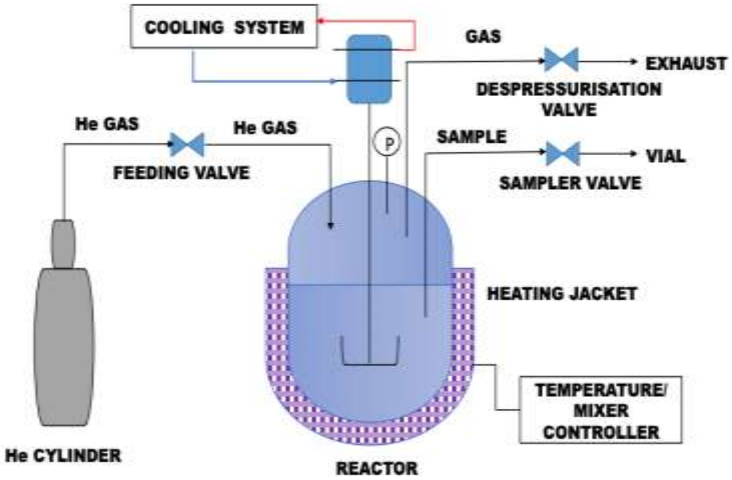

Figure 1: A schematic diagram of the experimental apparatus

The product yields and conversion were determined by Equations (1) – (4), where Y_X represents the yield of product X and M_X represents the mass of product X. Conversion was determined based on the solid residue remaining. All yields were calculated on a dry basis of BSG:

$$Y_{\text{biochar}}\ (\text{wt\%}) = \frac{\text{M biochar}}{\text{M BSG}} \times 100\% \qquad (1)$$

$$Y_{\text{bio-oil}}\ (\text{wt\%}) = \frac{\text{M bio-oil}}{\text{M BSG}} \times 100\% \qquad (2)$$

$$\text{Conversion (wt\%)} = 100 - \text{Residue (wt\%)} \quad (3)$$

$$Y_{\text{gas}}\text{ (wt\%)} = 100 - (Y_{\text{bio-oil}}\text{ (wt\%)} + Y_{\text{biochar}}\text{ (wt\%)}) \quad (4)$$

2.3 Biochar Analysis

Thermogravimetic analysis (TGA) was performed using a PerkinElmer TGA 400. Analysis commenced at 40 °C with continuous heating at 2 °C min^{-1} up to 900 °C under a constant flow of air at 50 ml min^{-1}. Gravimetric and differential thermogravimetic measurements were collected to determine the moisture, volatile and ash content of the biochar. Functional groups present on the biochar were analysed using Fourier transform-infrared spectrometry (FT-IR) performed on a Shimadzu IR Affinity-IS with a 4000 – 400 cm^{-1} range, averaged over 16 scans and with a resolution of 4 cm^{-1}. The higher heating value of the biochar was measured using a Parr 6200 oxygen combustion calorimeter equipped with a Parr water handling system; heat combustion was calculated from temperature observations before, during and after combustion. Benzoic acid was used as a standard for calibration for calorific content determination. CHN elemental analysis was conducted using a Flash 2000 organic elemental analyser (Thermo Scientific) fitted with a MAS 200R carousel autosampler. The sample was combusted under pure oxygen at 900 ºC and combustion products were analysed using a GC column equipped with TCD. Data were analysed using Eager Xperience software version 1.1.

3.0 Results and discussion

3.1 Effect of alcohol solvents on solid and organic yield from carbonisation

Conversion of BSG to WSO and gaseous products on a dry weight basis was calculated for each different solvent system and is shown in Figure 2; the solid residue is considered as biochar. The conversion increased in alcohol solvents as compared to water: methanol giving the highest conversion at 82%, followed by 77%, 75% and 72% for ethanol, 2-propanol and water respectively (Figure 2(a)). The WSO yield was 29% when using 2-propanol, decreasing to 25% for ethanol and 23% for water, with methanol producing the lowest yield at 16% (Figure 2(b)). The differences observed in the product distribution suggest that different solvents are advantageous depending on the application, with 2-propanol being favourable for liquefaction and methanol for gasification.

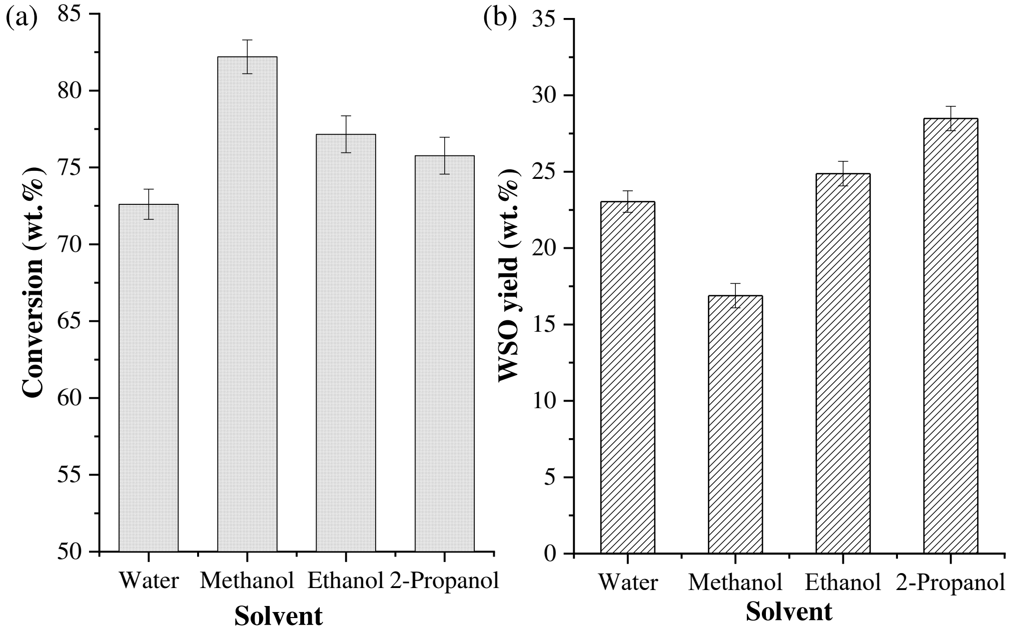

Figure 2: Comparison of (a) conversion to WSO and gas-phase products and (b) WSO yield from the direct carbonisation of raw BSG in water, methanol, ethanol and 2-propanol. Reaction conditions:250 °C, 30 min, initial P_{He}= 30 barg, 10 wt% dry solids. Error bars are calculated on the basis of triplicate experimental studies of the HTC system.

It is important to note that while single component solvents are added, the reaction medium in fact consists of a mixed alcohol/water system due to the presence of moisture within the BSG feedstock. If all of the moisture is released during processing then the molar compositions are 58 mol% methanol, 49 mol% ethanol and 43 mol% 2-propanol in water. Alcohol/water mixtures are non-ideal solutions and exist in different structural domains depending on their composition, as previously described by Li *et al.* [25]. A composition exists at which the non-ideality of the solution is maximised, characterised by extended hydrogen bonded networks between alcohol and water molecules. At room temperature, this composition is 30, 15 and 10 mol% for methanol, ethanol and 2-propanol respectively. Above these concentrations of alcohol, a further transition point occurs at 70, 60 and 50 mol% respectively, describing the point at which the mixture consists of independent small water clusters within a larger network of alcohol molecules with little interaction between alcohol and water molecules. Therefore, prior to heating, the compositions that exist with the present work all coincide with a system where an extensive hydrogen-bonded network of mixed alcohol and water molecules exists, and in all cases is in excess of the maximum structuring of alcohol/water networks. It is therefore assumed that dissolution and reaction of BSG in all solutions follows a similar mechanistic pathway where interactions with both alcohol and water molecules are crucial, rather than, e.g. preferentially segregating into a molecularly homogeneous (single component) phase.

The results obtained for conversion and WSO yield can be related to known physical properties of the solvents. Methanol gives the highest total conversion of BSG to WSO and gas-phase products, followed by ethanol, 2-propanol and then water. Solvent molecule size has previously been correlated with solvation capacity in carbonisation processes [33]. Smaller molecules provide a larger entropic force towards dissolution and can diffuse mole easily through a polymeric structure such as lignocellulosic biomass. In addition to the ability to access the internal structure of BSG, the self-diffusion coefficients of the alcohols follow the trend methanol >> ethanol > 2-propanol [34]. Mass transfer may therefore play a crucial role in the extent of conversion obtained. That water shows lower conversion than the alcohol solvents can be ascribed to the fact that it has, even under hydrothermal conditions, a more extensive hydrogen bond network, which in turn results in an anomalously high dielectric constant; ~30 F m^{-1}at 250 °C [35]. A higher dielectric constant will reduce the capacity of the solvent to solubilise large organic molecules arising from the degradation of BSG which itself has an expected dielectric constant of ~2 F m^{-1}[36]. At elevated temperatures the dielectric constant of methanol is 6.02 F m^{-1}(240 °C), while those of ethanol and 2-propanol are 4.20 (240 °C) and 3.75 F m^{-1}(230 °C) respectively [37]. As the alcohol solvents actually exist as a mixture with biomass-derived water, the true dielectric constant of the medium will be slightly higher than for the pure alcohols, however the trend between the solvents will likely be maintained. The WSO yield increases with alcohol chain length through the series methanol (16%), ethanol (25%) and 2-propanol (29%). This is reflective of the increased extent of conversion in the shorter-chained alcohol solvents, resulting in a greater extent of reaction and increased yields of gas-phase products. The gaseous yields, determined by difference (Equation 4), are 66, 52, 46 and 49% for methanol, ethanol, 2-propanol and water respectively. Note that water gives a higher yield of both WSO and gaseous products than might be expected from the lower conversion observed. While water may be less effective than the alcohols at solubilising larger organics, the extensive hydrogen-bond network will increase its efficiency at shuttling hydrogen and hence acting as a hydrogen-donor, when compared to the alcohols.

3.2 Changes in physical properties of biochars in different alcohol/water mixtures

FT-IR spectroscopy of the dry BSG and biochars yields information regarding the functional groups present on the surface of the materials (Figure 3). The broad peak at ~1030 cm^{-1} can be attributed to the β-glycosidic bond vibration in cellulose, the absorbance at ~572 cm^{-1} represents lignin, and the absorption at 1638 cm^{-1} can be attributed to unconjugated carbonyl (C=O) bonds of xylan in hemicellulose [38]. In all biochars obtained, these peaks from lignocellulosic material (572 cm^{-1}, 1030 cm^{-1}, 1638 cm^{-1}) are diminished compared to the dry BSG.

This indicates decomposition of the cellulose, hemicellulose and lignin content of BSG for every solvent system used and the synthesis of carbon rich coke/char deposits. The water system biochar showed a larger decrease in these lignocellulosic peaks than the biochars formed in alcohol solvents, and hence a greater extent of carbonisation within the solid residue. This is in agreement with the results presented in Section 3.1, where the greater ability of the alcohol solvents to solubilise organic species resulted in higher conversions to WSO and gaseous species than that observed in water. While the alcohol solvents preferentially degrade BSG to smaller organics, water instead provides a medium for the solid-state conversion of BSG to char through polymerisation reactions [39]. As a result, biochar-derived from the alcohol media has a greater structural similarity to raw BSG than biochar formed under aqueous conditions, consistent with the spectra presented in Figure 3. Specifically, peaks at 572 and 1030 cm^{-1}, characteristic of lignin and cellulosic material respectively, which are present in the spectrum of BSG are retained in the spectra of alcohol-derived biochars. In contrast these peaks are absent or significantly diminished for the biochar synthesised in water.

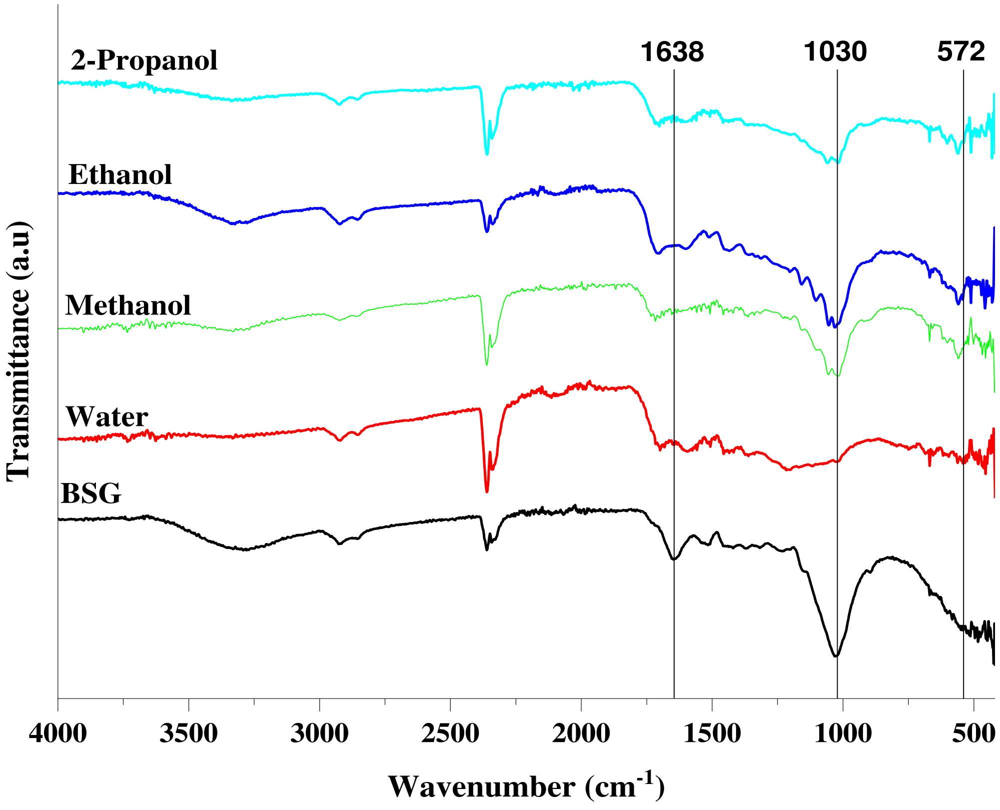

Figure 3 FT-IR spectra of dried BSG and biochars obtained from the direct carbonisation of raw BSG in water, methanol, ethanol and 2-propanol.Reaction conditions: 250 °C, 30 min, initial P_{He} = 30 barg, 10 wt% dry solids. Spectra are offset for clarity.

Further examination of the β-glycosidic bond vibration (1030 cm^{-1}) shows that this peak is completely eliminated from the spectra in the water system (Figure 4), showing that cellulose is completely degraded. In contrast, for the biochars produced in the alcohol solvents the peak is still present; with the least degree of reduction in methanol and the greatest in 2-propanol.

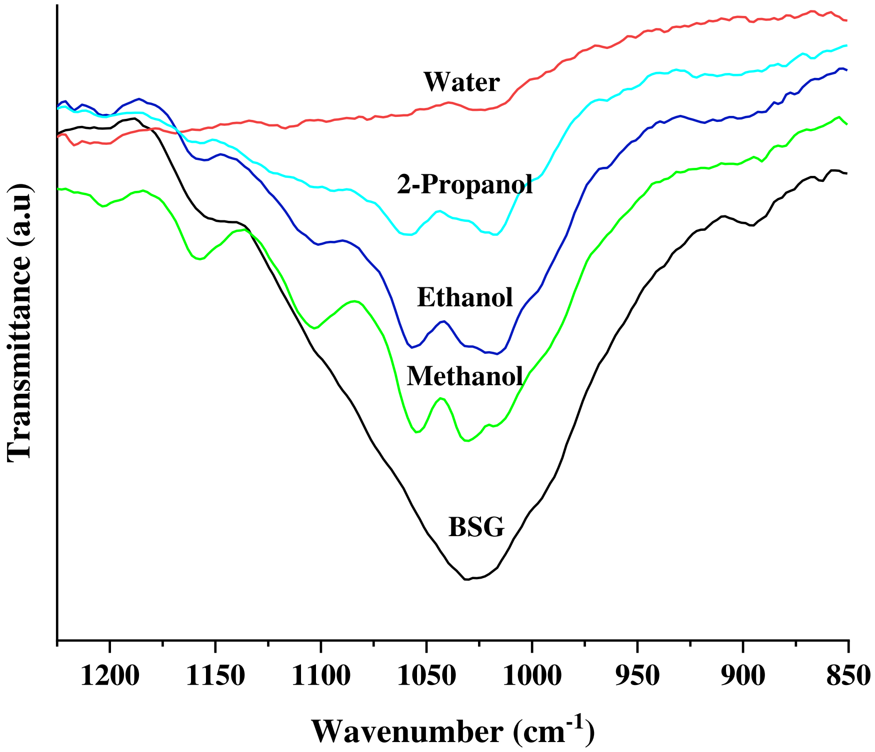

Figure 4. FT-IR spectra in the region 850 – 1250 cm^{-1} for dried BSG and biochars obtained direct carbonisation of raw BSG in water, methanol, ethanol and 2-propanol. Reaction conditions: 250 °C, 30 min, initial P_{He} = 30 barg, 10 wt% dry solids.

Thermogravimetic analysis (TGA) of the biochar and dried BSG was used to quantify the moisture, volatile, fixed carbon and ash content of the materials (Figure 5). Previously reported carbonisation of BSG in water (HTC) shows a reduction in ash content, increase in fixed carbon and decrease in moisture and volatile matter [28]. The biochar obtained from water supports literature findings: ash content and volatile matter has decreased, and fixed carbon content has increased substantially. Conversely the alcohol solvents decreased the percentage of fixed carbon, and moisture content but increased the proportion of volatile matter and ash compared to dried BSG. This increased volatiles content reduces the combustion efficiency of the biochar and increases pollutant emission when used as a solid fuel [40]. The increased ash content significantly influences the transport, handling and management costs associated with the process; it is also influential in corrosion and slag formation [41]. This shows that these alcohol solvents produced biochar with inferior properties to that of traditional HTC biochar for fuel applications, and is in agreement with FT-IR data (Figures 3 and 4) where a greater extent of carbonisation was observed in water. Ash from lignocellulose is generally comprised of ionically complexed silicon, potassium, calcium, sulphur, and chlorine [42]. As such, water, having a more ionic character than the alcohols, is more effective at extracting these components.

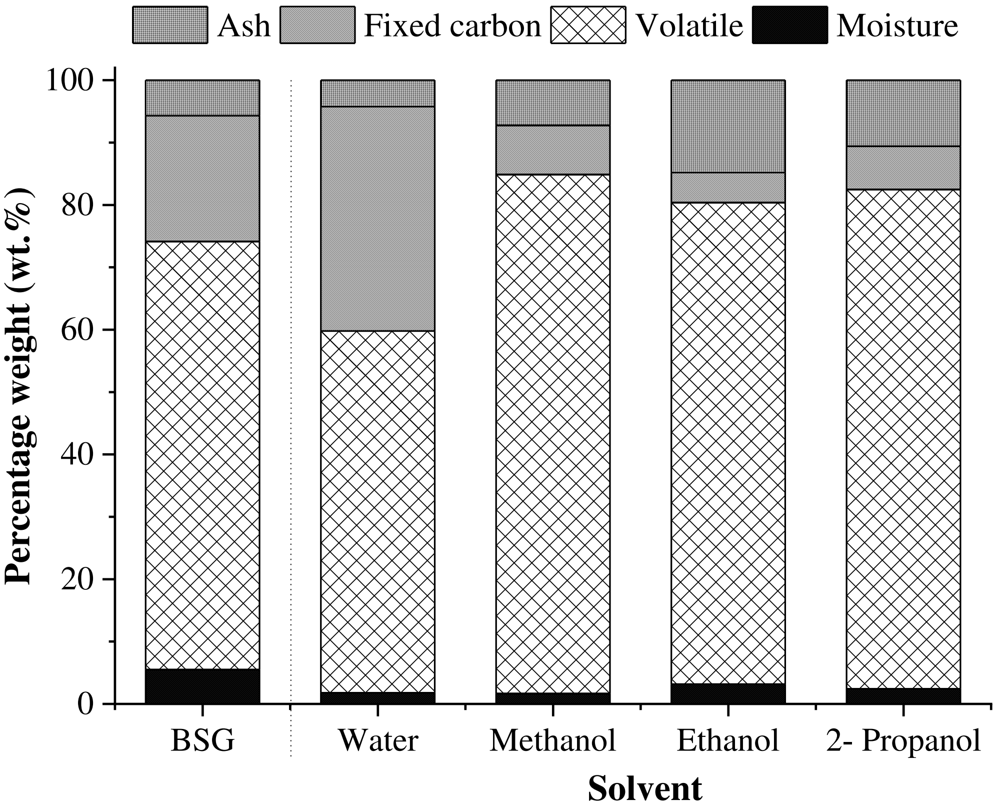

Figure 5.*Thermogravimetic analysis (TGA) of raw BSG and biochar from direct carbonisation of raw BSG in water, methanol, ethanol and 2-propanol. Reaction conditions: 250 °C, 30 min, initial P_{He}= 30 barg, 10 wt% dry solids.*

Elemental analysis of the dried BSG and biochars obtained in the different solvents was performed in order to provide a full analysis of their carbon, hydrogen, and nitrogen content (Table 1). These data were used to calculate H/C and O/C ratios, which give valuable insight into the quality of the carbon for use as a solid fuel. Generally, a fuel with low H/C and O/C ratios is desirable because of the reductions in energy loss, smoke and water vapour during the combustion process. The water system produces a solid biochar with increased carbon and oxygen content and decreased H/C and O/C ratios compared to BSG which improves its combustion properties [28], [43], in agreement with TGA analysis showing a greater fixed carbon content per unit mass.

Table 1 Elemental analysis, O/C and H/C ratios and high heating values (HHV) of dried BSG and biochars from direct carbonisation of raw BSG in water, methanol, ethanol and 2-propanol. Reaction conditions: 250 °C, 30 min, initial P_{He}= 30 barg, 10 wt% dry solids.[26], [28]

Individual element and the molar ratio	**Biochar produced in a different alcohol/water systems**				
	Dry BSG	Water	Methanol	Ethanol	2-Propanol
	Analysis (wt%)				
Carbon (C)	47.2	63 ± 1.6	54.8 ± 0.8	48.8 ± 0.5	55.1 ± 0.3
Hydrogen (H)	8.2	5.2 ± 0.1	5.3 ± 0.3	4.43 ± 0.3	4.2 ± 0.2
Nitrogen (N)	3.3	3.5 ± 0.5	3.8 ± 0.5	3.31 ± 0.1	4.3 ± 0.6
Oxygen (O)[a]	41.0	24± 2.0	28.8 ± 0.1	28.6 ± 0.1	25.9 ± 0.7
	H/C and O/C ratio (molar ratio)				
H/C ratio	2.07	0.99	1.17	1.09	0.91
O/C ratio	0.65	0.29	0.38	0.44	0.35
HHV (MJ kg^{-1})	17	25	19	17	21

The alcohol/water mixtures produce biochars with 8.2 ± 2.4, 14.2 ± 2.1and 7.9 ± 1.9 wt% lower carbon content than the water biochars for, methanol, ethanol and2-propanol respectively but with a higher oxygen content of 4.8 ± 2.1, 4.6 ± 2.1 and 1.9 ± 2.7 wt%. This implies that the biochars produced in the alcohols have a greater degree of functionalisation than that produced in water. If this translates to an increase in surface oxygen moieties, these have the potential to act as adsorbent and active sites in applications as sorbent or catalyst/catalysts support; and hence alcohols may present a more attractive medium in the synthesis of materials for these applications. HHV of the synthesised biochars increases after reaction, from an initial value of 17 MJ kg^{-1} for dried BSG. The largest HHV (25 MJ kg^{-1}) is obtained for the char formed in water, in agreement with the greater extent of carbonisation indicated by elemental analysis and FT-IR studies. Among the alcohol solvents, 2-propanol produces the biochar with the highest HHV (21 MJ kg^{-1}), again consistent with the results from other characterisation techniques presented herein. For further evaluation of the biochars as solid fuel alternatives the molar ratios of the H/C and O/C can be plotted on a van Krevelen diagram where the higher quality coals are further into the bottom left corner near anthracite (Figure 6).

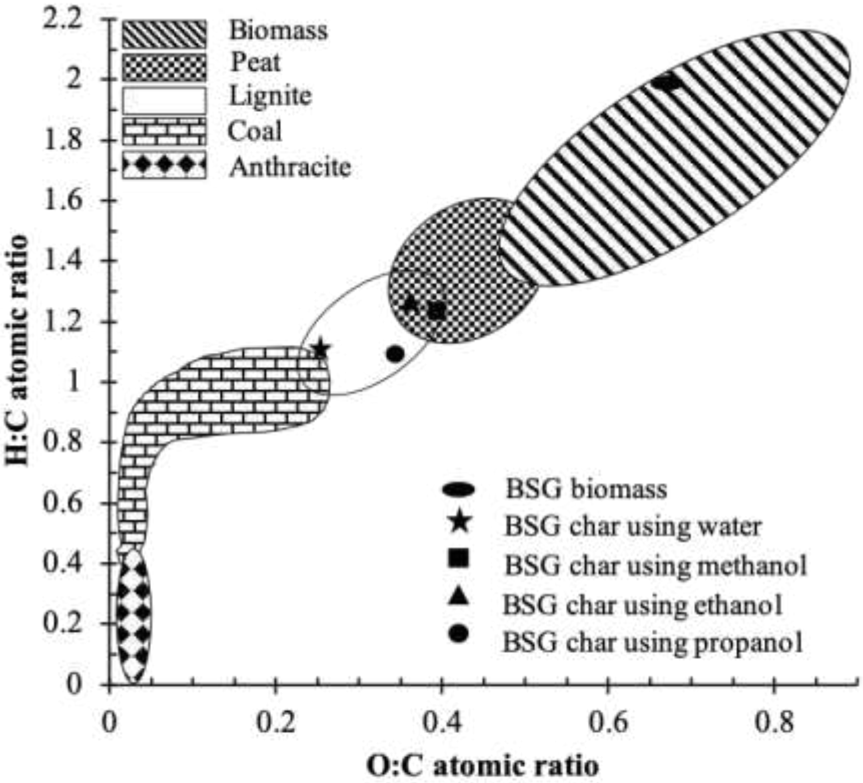

Figure 6.van Krevelen diagram adapted from McKendry (2002) and plotted point for the raw BSG and biochars from direct carbonisation of raw BSG in water, methanol, ethanol and 2-propanol. Reaction conditions: 250 °C, 30 min, initial P_{He} = 30 barg, 10 wt% dry solids.

The water biochar shows the best capacity for use as a solid fuel alternative when visualised on the van Krevelen diagram, when compared to any of the alcohol/water biochars and is nearly within the range of coal. Both methanol, and ethanol only produced biochars within the expected range of peat which is far below what is required for modern fuel applications. Of the alcohols, 2-propanol gave the biochar which had the best properties for fuel applications being comparable to types of lignite.

4.0 Conclusion

The selection of solvent for the carbonisation of BSG is shown to have a significant effect on the structure and composition of the produced biochar, and on the production of liquid and gaseous by-products. Water is shown to be the most effective solvent in terms of degrading the lignocellulosic structure of the initial biomass to form a char with high carbon content and good potential for application as a solid fuel. For other applications however, such as adsorption or catalysis, where the presence of heteroatoms is advantageous, then the use of alcohol solvents may be preferred. The alcohol solvents were also seen to be more effective at producing a liquid-phase product, namely water soluble oil, and gaseous products. If a bio-oil or permanent gases are the desired product, then the use of alcohol solvents is beneficial. This may be due to the greater ability of the alcohol solvents to solubilise and stabilise larger organic molecules derived from BSG in solution. Among the alcohol solvents the conversion of liquid- and gas-phase products decreased with chain length through the series methanol, ethanol and 2-propanol; however, the yield of liquid-phase products (rather than gas-phase products) increased through that series. These results show that, while water remains the most common medium for liquid-phase carbonisation, liquefaction and gasification processes, the judicious choice of an alternative solvent provides a means to direct the reaction towards alternative products and/or materials with differing physical properties. The difference in product distribution is ultimately controlled by the physical properties of the solvent and therefore an increased understanding of these at elevated temperature and pressure, in particular in mixtures with water to account for the release of moisture from biomass during processing, will facilitate the rational and holistic design of processing environments in the future.

Acknowledgments

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