



# Fate of inorganic material during hydrothermal carbonisation of biomass: Influence of feedstock on combustion behaviour of hydrochar



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## ABSTRACT

A series of high moisture content biomass have been processed by hydrothermal carbonisation (HTC) in a batch reactor at two temperatures (200 °C and 250 °C). The feedstocks processed include food waste, secondary sewage sludge, AD press cake, microalgae, macroalgae and a fibre derived from municipal derived wastes. In addition, three lignocellulosic biomass including miscanthus, willow and oak wood have been processed under identical conditions. The yields and properties of the resulting hydrochars including their HHV, CHNS, mineral content and ash fusibility properties have been determined and compared with their starting biomass. Typical char yields for lignocellulosic material range between 58 and 70 wt% at 200 °C and reduce to 40–46 wt% at 250 °C. The behaviour and mass balance is however very feedstock dependent and the higher lignin biomass produce higher yields of hydrochar. There is a significant upgrading of the energy density of the hydrochars with calculated HHV ranging from typically 24 MJ kg<sup>-1</sup> at 200 °C to 28–31 MJ kg<sup>-1</sup> at 250 °C for lignocellulosic material. The exception is for sewage sludge and AD press cake which result in a significant solubilisation of organic matter. A significant removal of alkali metals is observed and this in turn changes the ash chemistry upon combustion. This change in ash chemistry has been shown to change the ash melting behaviour and the hemisphere temperatures (oxidising conditions) were seen to increase substantially. A number of predictive slagging and fouling indices have been used to evaluate the influence of the ash chemistry on the fuel combustion behaviour and this combined with the ash fusion testing has shown that HTC reduces the potential fouling and slagging in some of the resulting hydrochars if combusted.

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## 1. Introduction

Biomass is becoming an attractive energy resource as it offers benefits in terms of its potential sustainability and carbon neutrality. However when compared to solid fossil fuels such as coal, biomass suffers due its low bulk density, high moisture content, low calorific value and high hydrophilic nature. This combined with milling difficulties brought about through the fibrous nature of biomass means that the handling properties of raw biomass negatively influence the economics of biomass. This has prompted considerable interest in pre-treatment of biomass which may help overcome some of these limitations. One such process is torrefaction which has received increasing interest in recent years. Torrefaction is a thermal process that involves the heating of biomass between 250 °C and 300 °C in an inert atmosphere; driving out moisture and low calorific components to increase

the fuels calorific value [9]. Torrefaction however requires a dry feedstock and enhances ash within the biofuel. Hydrothermal carbonisation (HTC) is an alternative option and involves the processing of wet biomass in hot compressed water [6]. It has previously been used as a method to simulate natural coalification in coal petrology but with the emergence of biomass as a future energy source, it now shows potential as a biomass pre-treatment, as it produces a coal like product called hydrochar.

The aim of HTC is to produce a coal like hydrochar which is: (i) more energy dense, (ii) easily friable and (iii) more hydrophobic than the starting material. This is achieved by reducing the oxygen and hydrogen content of the feed (described by the molecular O/C and H/C ratio), destroying the colloidal structures and reducing the hydrophilic functional groups. During HTC, the biomass is submerged in water and is subjected to high temperatures at pressures which prevent the water from evaporating. Under these conditions, water undergoes changes at the molecular level which in turn influence its solvation power, viscosity and polarity [24]. As the water is heated and compressed, its density and polarity change reversing its properties from a highly polar hydrogen-

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bonded solvent to properties more like a non-polar solvent such as hexane [24]. Under these conditions, the water provides a medium for a complex series of reactions which involve the removal of hydroxyl groups through dehydration, removal of carboxyl and carbonyl groups through decarboxylation, and cleavage of many ester and ether bonds through hydrolysis [6].

For lignocellulose based biomass, the net result is the macromolecule becoming increasingly aromatised with phenolic structures derived from the dehydration of lignin and aromatisation of carbohydrates derived from the hemicellulose and cellulose. Condensation and polymerisation of the fragments from the main macromolecules also occur, forming humic acid and bitumen based molecules which tend to re-adhere to the hydrochar [6]. The detailed nature and the relative significance of the above mechanisms appear strongly dependent on the type and composition of the feed [6]. Food waste and microalgae for example have a different biochemical composition (comprising of protein, carbohydrate and lipid) to that of lignocellulosic biomass which comprise of hemicellulose, cellulose and lignin. The proportions of the biochemical components also influence the degradation temperature. For lignocellulosic biomass, hemicellulose appears to degrade first, at temperatures generally below 200 °C, cellulose degrades at 200–230 °C and lignin degrades between 220 °C and 260 °C [23,16,25]. In order to produce a coal like product using hydrothermal processing, a reaction temperature of between 200 °C and 250 °C is typically used [6]. Above 250 °C the yield of solid products decrease and give way to a crude oil like product as the conditions favour a process known as hydrothermal liquefaction (HTL). The transition between HTC and HTL appears to be feedstock dependent, with some HTC studies using temperatures above 250 °C. Temperature appears to be the most dominant parameter in HTC although the efficiency of the hydrothermal process is also influenced by the percentage of solids in the feed [16,6], with increased carbon loss into the water phase with increasing water within the reaction [16].

The benefits of the HTC process in terms of combustion are brought about through the low H/C and O/C ratios along with the reduced fraction of volatile matter in the combustible carbon in comparison to the starting biomass. These changes result in increased combustion efficiency, along with reduced pollutant emissions, smoke and water vapour during the combustion process [17,11]. The process has also been shown to influence the ignition temperature and burn out temperatures of the hydrochar, with temperatures increasing with increasing HTC process temperatures, while the activation energy, the critical energy required to start combustion, has been shown to decrease [22]. This can be of particular benefit when blending with low rank coals as it can improve the combustion of low rank coal [22].

While the handling improvements brought about through HTC are well documented, there has been less research into the fate of inorganic material in the biomass during HTC. Inorganics are a particular issue for biomass during combustion, pyrolysis and gasification as large amounts of alkali and alkaline metals, particularly potassium and sodium, along with sulphur and chlorine influence ash chemistry and influence the behaviours of the fuel in terms of its tendency to corrode equipment and cause slagging and fouling [12]. The main cause of slagging is attributed to the reactions of alkali metals with silica to form alkali silicates, which melt and soften at temperatures as low as 700 °C [28]. The cause of the fouling is attributed to the reaction of the alkali metals with sulphur which form alkali sulphates which can be deposited on heat transfer and combustor surfaces. Chlorine within the ash is very corrosive to stainless steel and can also react with silicates and the alkali metals to form an undesirably stable slag [19]. Demineralization of the fuel through dissolution of these alkali salts into the process water during HTC could potentially remove a large fraction of the

fuel mineral content thereby reducing the above mentioned ash problems.

Previous work by Saddawi et al. [28] has demonstrated that simple washing of biomass in distilled water (at room temperature and pressure) can remove simple ionic salts such as alkali earth chlorides which dissolve easily. Washing in solutions such as ammonium acetate can further increase recovery, recovering inorganic elements which are bound to the organic structures of the biomass with ionic bonds, though ion exchange. Finally washing in a hydrochloric acid solution dissolves alkali earth carbonates, sulphates and sulphides. Consecutive leaching using these three methods can subsequently remove the ionic bonded inorganics from the biomass structure, leaving only silicates and elements bound to the organic matrix with covalent bonds [28]. During HTC, the subcritical conditions of water have a lower density and viscosity than that of water under normal conditions [31] and as such, removal of simple ionic salts within the biomass matrix can be enhanced. The increased dielectric content [1], increased ionic dissociation constant [2] and lower pH [6] of the subcritical water could also aid the removal of ionic bonded inorganics though ion exchange and dissolve the inorganic salts, thus removing ionic bonded inorganics from the biomass structure. The modification of the biomass structure during HTC will also further aid the removal of the inorganic material.

Reza et al. [25] investigated the fate of inorganics during HTC for miscanthus, corn stover, switch grass and rice hull. The results have shown reductions in the amount of calcium, sulphur, phosphorus, magnesium and potassium in the original biomass when the biomass is processed under hydrothermal conditions at 200 °C, 230 °C and 260 °C. Removal of silicon appears limited at 200 °C and 230 °C although there was some indication that silicon content starts to decrease when the lignin starts to degrade at 260 °C. It should be noted that despite a decrease in the inorganic content relative to the starting biomass, the overall concentration of inorganics within the char can increase.

In addition to combustion, it has been suggested that HTC derived hydrochars could have other applications in soil amendment or as absorbents for heavy metals due to the high surface chemical functionality [16,8,30]. This investigation has investigated a large number of feedstock including wet biomass wastes such as food waste, anaerobic digestion (AD) press cake, sewage sludge, fibre derived from organically separated municipal wastes and greenhouse waste, a number of terrestrial biomass such as miscanthus, oak and willow and the aquatic biomass: microalgae and macroalgae. The feedstock investigated have a diverse biochemical composition and wide ranging level of inorganics. This work seeks to understand the fate of inorganic material, the production of high energy density biofuels, and following HTC the prediction of fouling behaviour during combustion.

## 2. Methodology

### 2.1. Materials

Samples of willow, miscanthus, oak, greenhouse waste, food waste, secondary sewage sludge, AD press cake, macroalgae (*Laminaria Hyperborea*), microalgae (*Chlorella* spp.) and fibre derived from municipal waste were used in this investigation. The sample sizes ranged from 1 × 1 cm to 2 × 1 cm cuttings for willow and oak, 1 × 1 cm cuttings for miscanthus, macroalgae, food waste and greenhouse waste, 600–1200 µm for municipal solid waste derived fibre, sewage sludge and AD press cake and a freeze dried powder for microalgae. Samples were air dried before treatment and used as received for HTC on the assumption that in an industrial process, HTC would be conducted on chipped fuels to avoid

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