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Mild hydrothermal conditioning prior to torrefaction and slow pyrolysis of low-value biomass



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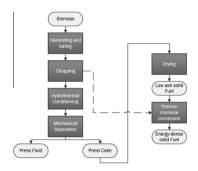
HIGHLIGHTS

Mild hydrothermal conditioning reduces the ash content in the biomass.

- Hydrothermal conditioning has a big impact on the yield of thermochemical conversions.
- Heating values similar to those of high-volatile bituminous coals can be produced.

G R A P H I C A L A B S T R A C T

Overview of the experimental set-up: thermochemical conversion of mild hydrothermally treated biomass and not treated biomass.



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ABSTRACT

The aim of this research was to establish whether hydrothermal conditioning and subsequent thermochemical processing via batch torrefaction or slow pyrolysis may improve the fuel quality of grass residues. A comparison in terms of fuel quality was made of the direct thermochemical processing of the feedstock versus hydrothermal conditioning as a pretreatment prior to thermochemical processing. Hydrothermal conditioning reduced ash content, and particularly nitrogen, potassium and chlorine contents in the biomass. The removal of volatile organic matter associated with thermochemical processes can increase the HHV to levels of volatile bituminous coal. However, slow pyrolysis only increased the HHV of biomass provided a low ash content (<6%) feedstock was used. In conclusion, hydrothermal conditioning can have a highly positive influence on the efficiency of thermochemical processes for upgrading low-value (high-ash) biomass to a higher quality fuel.

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1. Introduction

Grass obtained from mowing roadside verges or nature management areas is regarded as waste in many cases due to its abundance in the summer months and limited disposal options.

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Incineration and landfilling may be legally restricted, and composting may not be financially attractive (Faaij et al., 1997). A technical procedure has been developed by the University of Kassel to reduce the concentration of chlorine and other elements in seminatural grassland biomasses (Wachendorf et al., 2009). The aim of this method, referred to as "integrated generation of solid fuel and biogas from biomass (IFBB) technology", is to yield a high quality product for combustion by reducing the concentration of elements detrimental to the combustion process. Biomass is washed with warm water at 40 °C and subsequently dewatered using a screw press. This way, the biomass is separated into a mineralrich, low-fibre fluid, which can be used in anaerobic digestion (Richter et al., 2009; De Moor et al., 2013) and a solid press cake high in lignin and cellulose but lower in minerals than the feedstock (Hensgen et al., 2012, 2014). The technique is suitable for different input materials such as semi-natural grasslands or urban waste (Hensgen et al., 2011, 2012). It has also been observed that of all the investigated types of substrates, soluble minerals such as K and Cl end up in the press fluid (Hensgen et al., 2012; Richter et al., 2010).

Torrefaction and slow pyrolysis are two related processes in which heat is applied to the biomass in an oxygen-free environment in order to either partially or completely break down the complex biological polymers. Consequently, these processes convert the biomass into different product fractions, i.e., a solid product, condensable vapours and permanent gases. In the case of biomass torrefaction, the solid product is referred to as "torrefied biomass". In the case of slow pyrolysis this product is called "char". If intended for fuel applications the universal term is charcoal. The difference between the two processes is that torrefaction employs milder temperatures (200 °C-300 °C) in comparison to slow pyrolysis (350-800 °C) (Mohan et al., 2014). The different temperatures affect the proportions in which the solid, gaseous, and liquid products are formed as well as the quality of these products (Prins et al., 2006a,b). Typically, the thermal devolatilization of biomass results in an increase in the heating value of the solid product. Other properties that are improved include the grindability, hydrophobicity. aromaticity and biological stability, ie, resistance to rotting (Mohan et al., 2014; Ndibe et al., 2015; Ahmad et al., 2014). The improvement in these properties means that the torrefied biomass or char could theoretically be used as a "drop-in" substitute for fossil coal in existing combustion and gasification processes (Bergman et al., 2005). In some cases, existing coal-based power plants have been modified to run on renewable fuels such as pine pellets, but this can reduce the power output of the process. By first upgrading the biomass to torrefied biomass or char, the increased higher heating value of the feed could reach closer to the original coalbased thermal capacities of such modified power plants.

The nitrogen and sulphur present in the biomass forms NO_X and SO₂, respectively, during combustion. Generally, biomass-derived fuels contain less nitrogen and sulphur in comparison to coals resulting in comparatively lower NO_X and SO₂ release (Ndibe et al., 2015). The inorganic materials present in the biomass, including alkali metals, trace metals, and chlorine amongst others, largely remain in the solid and are effectively concentrated since the total solid mass is reduced through torrefaction and slow pyrolysis. The amount of inorganic compounds removed during torrefaction and pyrolysis is known to increase with increasing temperatures (Olsson et al., 1997). Despite the fact that the ash content of biomass streams is in some cases lower than the fossil coal content, the specific inorganic materials present in biomass may be harmful to combustion and gasification processes or act as pollutants when flue gases are released to the atmosphere. The presence of chlorine is known to contribute to hightemperature corrosion of process equipment as it promotes the volatilization of alkali-metals, which in turn increases the rate of alkali-chloride deposit formation (Davidsson et al., 2007). If the material to be combusted contains significant levels of sulphur, corrosion is further enhanced by the presence of sulphur dioxide in the flue gas (Nielsen et al., 2000). Even in the absence of corrosion, increased deposit formation on heat transfer surfaces of the combustion equipment will reduce thermal efficiency. The presence of certain inorganic elements can reduce the ash fusion temperature, thereby increasing slagging in grate-fired boilers and causing particle agglomeration in fluidised beds (Turn et al., 1997; Seggiani, 1999). In addition to alkali and earth-alkali metals, the fate of heavy metals, which are known to be elevated in verge grass, also needs to be determined, since the release of heavy metals to the atmosphere should be avoided during the combustion of verge grass and verge grass-derived fuels.

To reduce the release of inorganic materials during either torrefaction or slow pyrolysis or during the utilisation of the torrefied biomass and char, inorganic materials can be leached from the biomass by water-washing (Dayton et al., 1999). This reduces corrosion and fouling, and has also been shown to favourably increase the ash fusion temperatures during the combustion of torrefied biomass (Saddawi et al., 2012). Alternatively, minerals such as bauxite, kaolinite, limestone, and magnesium oxide can be added to the combustion process to stabilise the alkali metals in the solid phase and prevent or reduce the formation of volatile alkali chlorides (Saidur et al., 2011).

Joshi et al. (2014) investigated the effect of mechanical dewatering on the torrefaction of grass biomass. They found that it had little effect on the mass loss curves obtained by thermogravimetry, but that the mechanical separation of the natural juices in the grass led to a reduction in the mineral content of the torrefied biomass.

Instead of focusing on the kinetics of thermochemical conversion, our work presented here focuses on the fuel properties of the solid products generated through both the torrefaction and the slow pyrolysis of grasses that have undergone hydrothermal conditioning. The properties of interest are the higher heating value, the inorganic material content within the torrefied biomass, and the slow pyrolysis char.

2. Methods

2.1. Biomass types

In this study, different types of biomass were considered.

Willow: Willow, grown as short rotation coppice, was harvested in Lommel (Belgium) after growing for two years in a Cd and Zn contaminated field (Van Slycken et al., 2013). The wood and bark were then dried and chopped into pieces of 1 mm.

Ryegrass: English ryegrass grown in Lommel (Belgium) on the same field, was harvested in April 2014 and was dried in open air in the field for two weeks. Thus, the grass was exposed to rain and has undergone some degree of natural leaching.

Silage 1: Biomass from Flanders was harvested in "Provinciaal Domein: De Gavers, Harelbeke" (a recreation and nature conservation area) in the middle of June 2013 from a grassland of about 1 ha with the most abundant species being *Holcus lanatus*. The biomass was properly ensiled for 6 months before analysis.

Silage 2: In Wales, the grass was harvested in "Craflwyn, Nant-gwynant, Gwynedd" (a nature conservation area in North Wales) and the most abundant species were Juncus acutiflorus, Deschampsia flexuosa, and Holcus lanatus. The grass was mown on 27-08-2013 and baled the next day. The biomass was properly ensiled for 6 months before analysis.

Silage 1 and silage 2 were also treated with the IFBB technology (press cake 1 and press cake 2), as described below, before they were treated thermochemically.

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