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Research paper

The role of lignin in the densification of torrefied wood in relation to the final product properties

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ABSTRACT

Biomass properties can be improved for heat and power applications through combined torrefaction and pelleting. Good pellet quality in terms of durability, density, moisture absorption, fines production and heating value paired with a low power consumption in the pellet mill render the densification process of torrefied materials challenging. The aim of this study is to identify the lignin components/intermediates and the corresponding mechanisms during torrefaction of wood that play a role in pelleting behaviour and pellet quality. The importance of lignin lies in its ability to act as a natural binder during densification.

Structural differences caused by torrefaction of spruce and poplar (270 °C, 32–45 min) were studied by using NMR and TD-GC/MS as well as by pressing single pellets. Spruce chips were torrefied (280 °C, 35–45 min) and conditioned in steam in a pilot plant. The products were ground on a 4-mm sieve and densified in a single-pellet press, where differences in the measured responses were explained on basis of their lignin properties. The lignin was isolated from the spruce samples by organosolv fractionation and characterised in terms of amount, molecular weight distribution (SEC) and glass-transition temperature (DSC).

The results of the tests and analyses indicate that torrefied softwood should be densified immediately after production. Furthermore, pellet quality of the torrefied material was found to depend on the binding ability of its lignin in the presence of moisture during densification. Additionally, storage of torrefied spruce prior to densification causes reduced binding ability of its lignin leading to pellets of lower quality.

1. Introduction

Dry torrefaction is a thermochemical pre-treatment process typically performed in the temperature range of 200–300 °C. The chemistry behind torrefaction involves mainly the removal of oxygen from the biomass structure after exposure to a hot, oxygen-deficient atmosphere. Extensive reviews on the technology are described in Refs. [1,2]. Latest developments towards market introduction are given in Ref. [3].

The parameter widely used in the literature to express the conversion of biomass during torrefaction is the anhydrous weight loss (AWL), defined by:

$$AWL = \left(m_{dry} - m_{torr}\right) / m_{dry} \times 100\% \tag{1}$$

where m_{dry} is the mass of the initial dry biomass and m_{torr} is the mass of the torrefied biomass.

The solid product can be further densified into pellets or briquettes obtaining a solid bioenergy carrier with a high energy density, better adjusted to logistics and end-use requirements [4–6].

Experience gained by the Energy Research Centre of The Netherlands (ECN) on pilot and demonstration scale has shown that dry torrefied poplar can be readily compressed to high quality pellets, while the pelleting of dry torrefied spruce is more challenging (high die temperature, high power consumption and unstable operation). This is confirmed by other researchers who investigated differences in pelleting of torrefied hardwood and softwood [7]. Furthermore, elaborate pelleting tests demonstrated that lower-quality pellets result from torrefied material that has been stored for a longer period of time after its production.

Binders are often added in order to increase pellet quality or to minimise pellet quality variations. A review is included in Ref. [8]. However, the use of supplementary binders would increase operational costs as well as, in the case of starch-based binders, affect

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the food chain. Instead, lignin which is one of the major constituents of the biomass feedstock itself, is the main component acting as a binder during pelleting and is essential to achieve a good pellet quality [9]. The quality of a pellet can be determined by various parameters, such as pellet density, heating value, moisture uptake, mechanical durability, and production of fines upon handling. In this study, a net pellet density increase is used to express the observed effects on pellet quality (see Section 2.2.3).

Lignin consists of three basic monomer types, depicted in Fig. 1. The principal monomer in softwood lignin is coniferyl alcohol. The corresponding aromatic ring is linked to one methoxyl group and referred to as a guaiacyl unit (G). Hardwood lignin consists of two main monomers: coniferyl alcohol and sinapyl alcohol. The aromatic ring of the latter is referred to as a syringyl unit (S) and has a methoxyl group at both the C-3 and C-5 positions. Fig. 2 outlines the main functional groups and numbering in lignin macromolecules. The different monomers are linked in various ways during lignin synthesis in plants, via a series of oxidative coupling reactions [10].

Recently, researchers have investigated the role of lignin in the densification of raw [9,12–15] and torrefied biomass [16–18]. Li et al. [16] investigated the pelleting behaviour of torrefied sawdust compared to untreated sawdust. They used a single-pellet press to measure the energy consumption during pelleting and compared the properties of the resulting pellets in terms of moisture absorption, pellet density and pellet hardness. They concluded that energy consumption during pelleting was higher for torrefied sawdust than for untreated sawdust. Also, pellet hardness and moisture absorption decreased with torrefaction severity.

Research has also focused on lignin transformation and lignin chemistry during wood torrefaction [19–23]. Rousset et al. [19] studied the structure and mode of assembly of lignin, hemicellulose and cellulose of beech and spruce wood during thermal treatment up to 280 °C and 8 h of residence time. The treated samples were extracted using a Soxhlet extractor and the lignin content of the samples was determined using the Klason method. To evaluate the structural changes induced by the thermal treatment thioacidolysis was used. The results showed intense structural transformations of lignin during thermal treatment, with cleavage of β-O-4 bonds and severe re-condensation reactions. Shang et al. [20] investigated the grindability of wheat straw torrefied at 200–300 °C and residence times of 0.5–3 h. They used ATR-FTIR to study the structural changes of lignin, cellulose and hemicellulose caused by the thermal treatment and to interpret the grindability results. They concluded that the removal of hemicellulose during torrefaction is the main reason that torrefied wheat straw demonstrates a good grindability (measured in HGI equivalent).

Pommer et al. [21] studied the decomposition products during torrefaction of hardwood and softwood species by using different experimental set-ups: by on-line analysis of the torrefaction gas produced during lab-scale torrefaction and continuous pilot plant tests as well as by using a Py-GC/MS equipped with a cold trap. They investigated the type of organic condensable species present in the torrefaction gas as a function of torrefaction temperature. Using these methods they could assign specific lignin decomposition products to type of wood. Wen et al. [22] examined the chemical and structural transformations of bamboo lignin during thermal treatment at 200–300 °C by using elemental analysis, XRD, FT-IR and by applying quantitative NMR techniques. Their results showed that during thermal treatment lignin undergoes reactions of depolymerisation, demethoxylation, bond cleavage and condensation.

However, very little information exists on the direct relationship between lignin transformations during torrefaction and the effect this has on densification of the torrefied material [17,18]. Stelte et al. [17] studied the pelleting properties of torrefied wheat straw by quantifying the biomass constituents with varying torrefaction conditions and by examining the fracture surface areas of pellets produced in a single pellet press by ATR-FTIR and SEM microscopy. Their results show that most structural changes occur in the temperature range of 250–300 °C, with torrefaction temperatures up to 250 °C resulting in mechanically strong pellets with higher heating value and reduced moisture adsorption. A similar study was realised by these researchers for the case of torrefied spruce wood where results indicated a relationship between the plastic flow of amorphous polymers and the formation of solid bridges during pelleting [18].

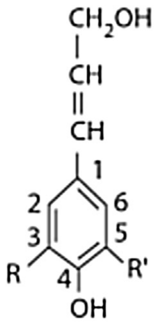
In addition, little is known on the effect of storage of torrefied material on its subsequent behaviour during densification.

The research described in this paper aims at a better understanding of the physical, chemical and structural transformations that lignin undergoes during torrefaction and their effect on the subsequent densification of the torrefied material. This is done by torrefaction of wood samples and densification in a single-pellet press. In addition, lignin was extracted from the wood samples and characterised. The work described in this paper provides an improved understanding of the role of lignin in the densification of torrefied wood. It contributes to decreasing densification costs, which still form a barrier for broad market introduction of torrefaction [24].

2. Materials and methods

2.1. Materials

In this study, two types of wood were used, namely spruce (softwood) and poplar (hardwood). Debarked and chipped spruce



Substituents	Name	Location
$R = R' = H$	*p*-coumaryl alcohol	Compression wood, grasses
$R = H, R' = OCH_3$	coniferyl alcohol	Hardwoods and softwoods
$R = R' = OCH_3$	sinapyl alcohol	Hardwoods

Fig. 1. Lignin monomeric building blocks [11].

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