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May 2017
ECN-W--17-011

Biomass and Bioenergy xxx (2017) 1–15

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

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

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ARTICLE INFO

Article history:
Received 2 September 2016
Received in revised form
7 May 2017
Accepted 11 May 2017
Available online xxx

Keywords:
Torrefaction
Lignin
Pellet
Storage
Densification
Pellet quality

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:

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

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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http://dx.doi.org/10.1016/j.biombioe.2017.05.005
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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].

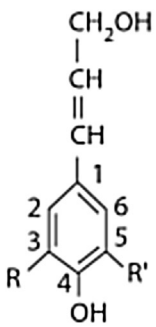
In addition, little is known on the effect of storage of torrefied material on its subsequent behaviour during densification.

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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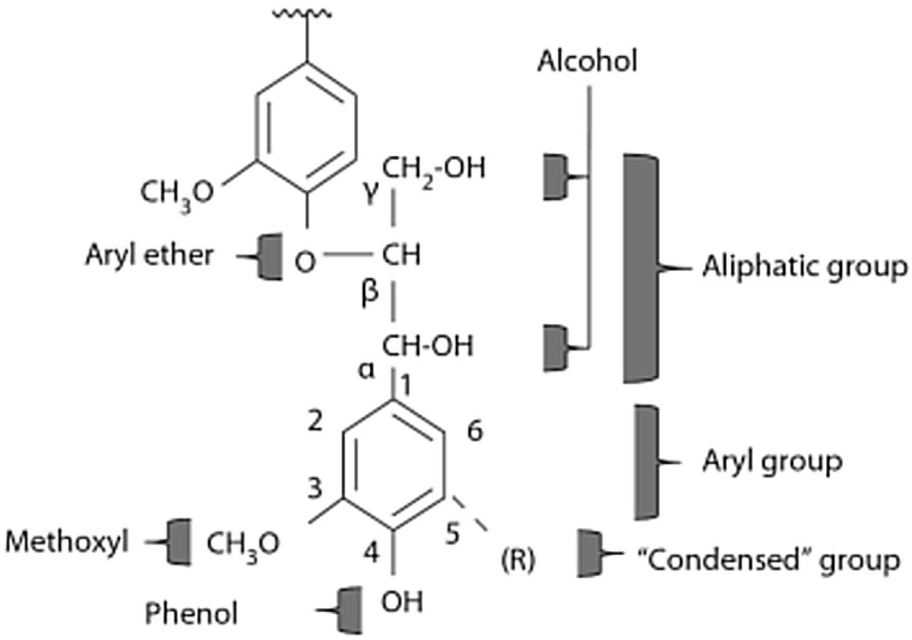

Fig. 2. Lignin functional groups and numbering [11].

and poplar wood were obtained from Norway and The Netherlands, respectively. The spruce wood was of the genera Picea abies, supplied by Andritz (DK). The poplar wood was of the family Salicaceae of the genera Populus, supplied by van den Broek B.V. (NL). The wood chips were delivered in dimensions of >2 × 2 × 2 mm to ≤40 × 40 × 15 mm (dimensions given by supplier).

In the series of tests performed to examine the effect of storage on the torrefied material, fresh torrefied spruce and poplar were compared to their corresponding 'aged' samples. Storage time is expressed throughout this paper as an 'ageing' effect and the samples that are stored at ambient conditions (air, moisture) until pelleting are referred to as 'aged' samples.

Fresh torrefied samples of both, spruce and poplar chips were produced in a batch torrefaction reactor at a temperature of 270 °C and a residence time of 45 min. These samples were subsequently ground in a Retsch cutter mill using a 4-mm sieve and immediately stored in a glovebox under a N_2 atmosphere. They were compared to torrefied samples which had been stored indoors, at ambient conditions.

The aged torrefied chips derived from poplar wood have been produced in the torrefaction pilot plant (T = 270 °C, t = 35 min) during week 11 in 2009 and stored in an open wooden cube box in an indoor storage facility. These torrefied chips were stored for 4 years and 8 months until they were ground in a Retsch cutter mill using a 4-mm sieve and pelleted using a single pellet press. The aged torrefied chips derived from spruce wood have been produced in the same pilot plant during week 24 in 2013 (T = 270 °C, t = 32 min) and were stored in a closed metal bin, placed in an indoor storage room. They were stored for 6 months until the chips were ground in a Retsch cutter mill using a 4-mm sieve and pelleted in a single pellet press. The analyses of the raw and torrefied samples used in this study are shown in Table 1.

The 'aged' samples were pelleted in a single-pellet press after drying at 105 °C in an oven, and were compared in densification behaviour to their corresponding samples that were not dried. Fresh torrefied samples were also exposed to indoor ambient conditions (T = 20 °C, RH = 55%) for 24 h to absorb moisture before pelleting in order to investigate the effect of moisture during densification. The spruce and poplar samples were torrefied in two different set-ups; the aged samples were produced in the pilot reactor and the fresh torrefied samples in the batch reactor. Although temperature set points were similar, there were differences in residence time and mode of operation. As a consequence, materials produced in the pilot reactor have undergone a relatively higher torrefaction severity, i.e. higher AWL and calorific value, than the materials produced in the batch reactor as also observed by the data in Table 1.

Furthermore, another series of additional torrefaction tests was conducted with spruce in order to examine the effect of torrefaction and steam conditioning on the lignin chemistry and the resulting pellet quality. Torrefied material was produced in the pilot plant at 280 °C and 36 min. This material was compared to torrefied material from the same pilot tests that had also been conditioned in steam by using an on-line pilot add-on set-up. These set-ups and material handling are described further in Section 2.2. These materials were also exposed to indoor ambient conditions (T = 20 °C, RH = 55%) for 24 h to absorb moisture before being pelleted. This was done in order to investigate the effect of moisture on pellet quality.

The experimental plan of the two series of torrefaction tests and analyses is summarised in Fig. 3 and Fig. 4.

2.2. Experimental set-ups

2.2.1. Batch torrefaction reactor

Batch torrefaction tests were performed in a fixed-bed reactor, shown in Fig. 5. The reactor consists of a vertical cylinder with an internal diameter of 16.5 cm and an effective length of 100 cm. The reactor is directly heated by supplying preheated nitrogen through a distributor plate at the bottom, while trace heating is applied to minimise heat losses. Off gases are led to an incinerator. The reactor is divided into three sections, separated by perforated plates. Each section can be loaded with a maximum of 1.5 kg of raw, dry feedstock depending on material density. To measure the bed

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Table 1
Properties of raw and torrefied materials on dry basis. The analyses results given are an average of three samples.

Material	Torrefaction T (°C)|t (min)	C (%)	H (%)	N (%)	O (%)	Ash (%)	HHV (MJ kg^{-1})	AWL (%)
Spruce wood raw	–	48	6.4	0.1	47.5	0.1	19.7	–
Spruce wood, batch reactor	270 | 45	55	6.0	0.1	40.5	0.3	21.7	12.0
Spruce wood, pilot reactor	270 | 32	54	6.0	0.1	41.2	0.3	22.1	19.8
Poplar wood raw	–	48	6.2	0.1	45.0	0.5	19.2	–
Poplar wood, batch reactor	270 | 45	53	5.9	0.1	40.0	0.6	20.8	17.9
Poplar wood, pilot reactor	270 | 35	52	6.0	0.1	41.0	0.6	21.1	23.1
Spruce wood, pilot reactor	280 | 36	53	6.0	0.1	41.0	0.4	22.5	28.5
Spruce wood, pilot reactor, steam conditioned	280 | 36	52	6.1	0.1	42.0	0.4	22.5	28.5

All of the element and ash data is a mass fraction of the dry materials.

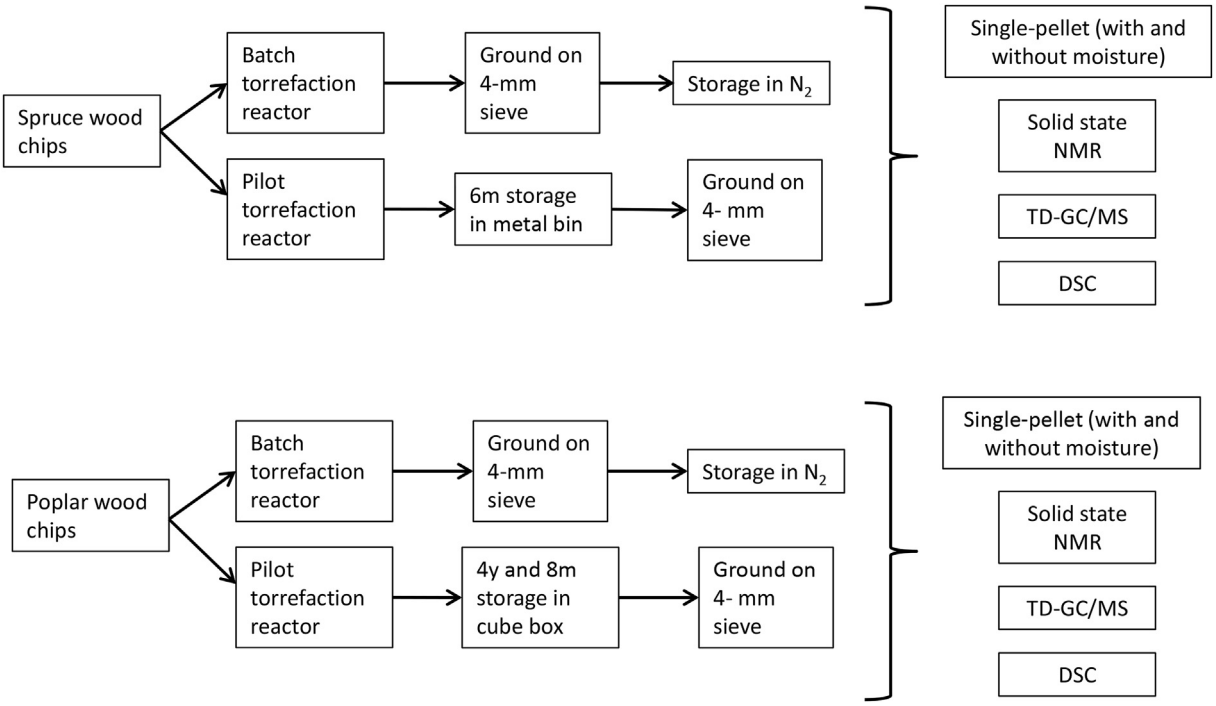

Fig. 3. Experimental plan 1st series of tests.

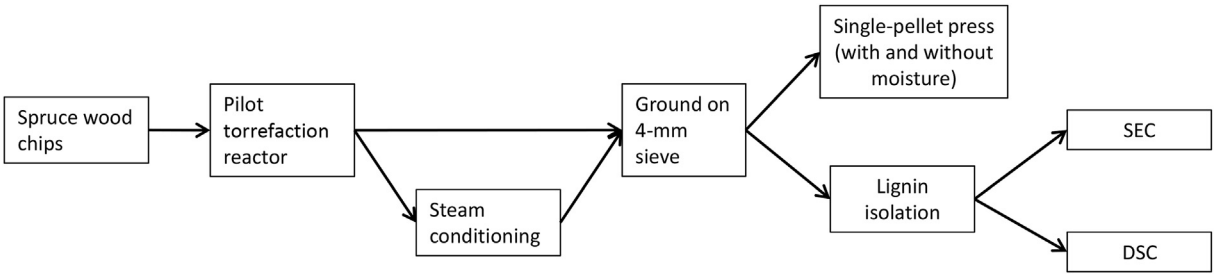

Fig. 4. Experimental plan 2nd series of tests.

temperatures in the reactor, nine thermocouples are placed inside the reactor at different radial positions and different heights. Pressure sensors are placed in the bottom and top of the reactor. All temperatures, gas flows and pressures are logged, allowing for off-line data analysis. For the experiments, the residence time was fixed at 45 min and the nitrogen flow rate was 650 L min^{-1} measured at STP of 298 K and 101.35 kPa. The residence time is defined as the time the material has been exposed to a temperature higher than 200 °C. After 45 min have passed, the electrical heating is switched off and the reactor is cooled down to room temperature by the flowing nitrogen. The reactor is opened from the top and a mechanism attached to the reactor is used to tilt the reactor vessel.

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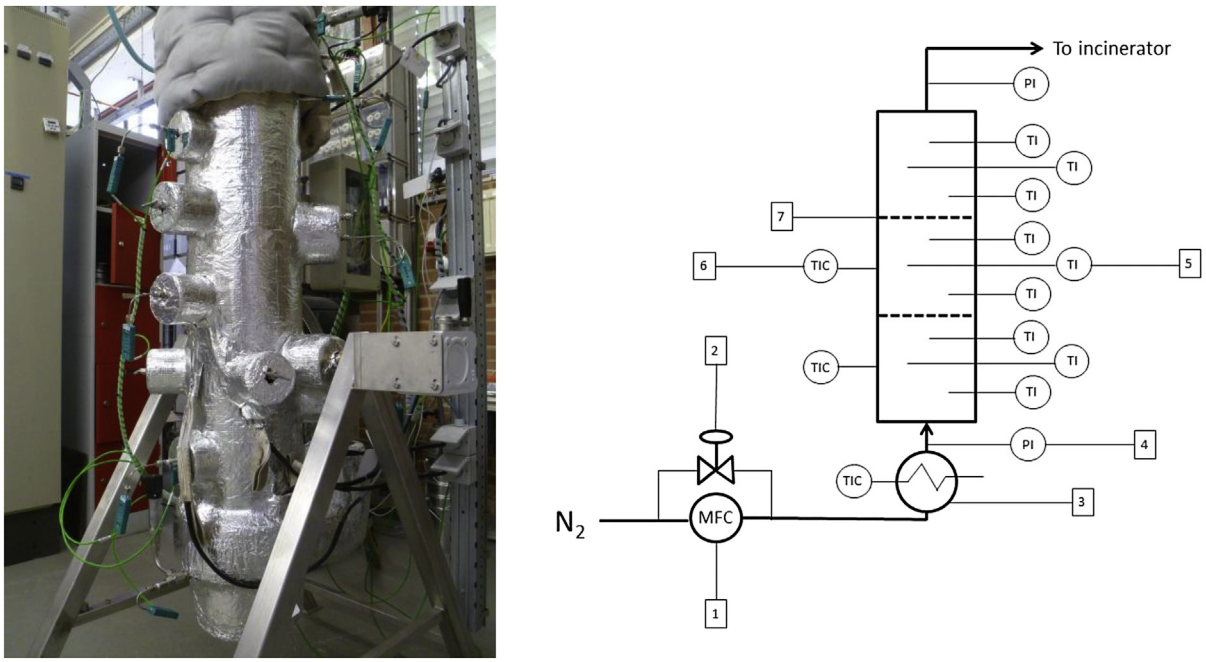

Fig. 5. Image of batch torrefaction reactor and process scheme. 1 = Mass Flow Controller (MFC), 2 = Safety valve, 3 = N_2 flow heater, 4 = Pressure Indicator (PI), 5 = Temperature Indicator (TI), 6 = Temperature Indicator & Controller (TIC), 7 = Perforated plate.

This allows emptying the reactor and collecting the torrefied material section by section. Spruce and poplar chips were dried at 105 °C prior to torrefaction and the torrefied chips were ground before storage under N_2 atmosphere.

2.2.2. Pilot-scale torrefaction tests and pilot add-on conditioning set-up

The torrefaction pilot plant used for the production of the 'aged' samples of torrefied spruce and poplar chips is situated at ECN's research facilities and has a nominal production capacity of approximately 50 kg h^{-1}. More details on the pilot torrefaction plant can be found in Ref. [25].

Post-torrefaction conditioning was performed during operation of the pilot plant. This test was done using a slip stream of 23.5 kg h^{-1} of torrefied material from the pilot torrefaction reactor. The set-up used is shown in Fig. 6. During pilot plant runs on spruce, hot torrefied material (torrefied chips) was collected directly from the product screw conveyor, which is used to transport the torrefied material out of the reactor and into the product bunkers. Sliding valves were used to divert hot torrefied material into the conditioning vessel, which was first flushed with N_2. The vessel was heated with an electric jacket. The sliding valves remained open for 12 min to collect torrefied wood chips and after these were closed, conditioning of the material took place through addition of 4 g min^{-1} steam to the conditioning vessel for about 3 h. The temperature inside the vessel was recorded (T = 154–171 °C)

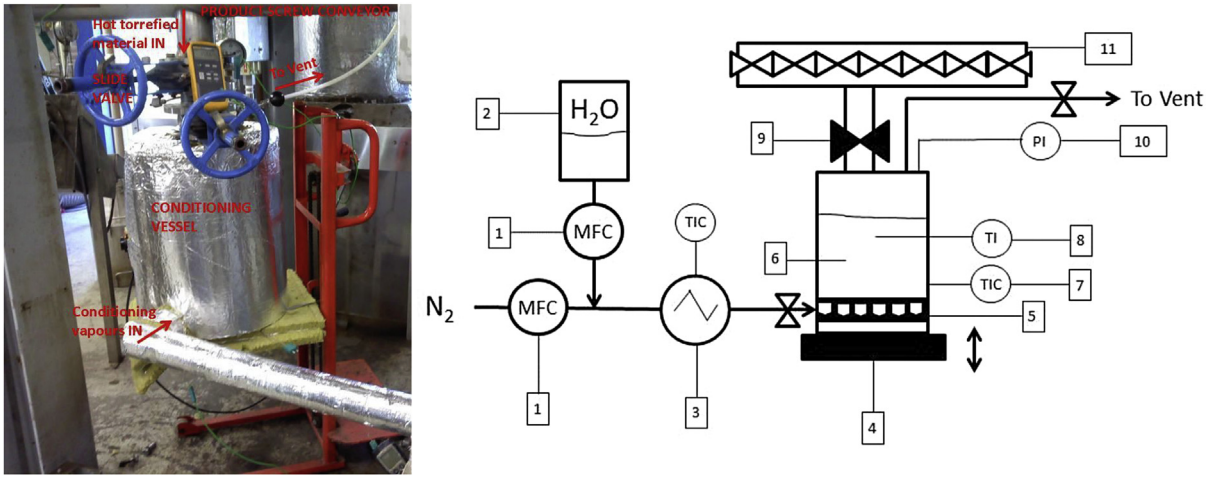

Fig. 6. Image and process scheme of pilot add-on set-up used for hot conditioning tests in steam. 1 = Mass Flow Controller (MFC), 2 = Water supply, 3 = Heater, 4 = Insulated vessel base, 5 = Distribution plate, 6 = Fresh torrefied material, 7 = Temperature Indicator & Controller (TIC), 8 = Temperature Indicator (TI), 9 = Sliding valve, 10 = Pressure Indicator (PI), 11 = Pilot plant product screw.

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and the pressure was regulated. After cooling down, the steam-conditioned torrefied chips were ground and dried at 105 °C in an oven. These dry solids were then either directly pressed into a single pellet or left overnight to absorb moisture as described in Section 2.1.

2.2.3. Single-pellet piston press

Single pellets were pressed in a lab-scale piston press (Struers Prontopress) which is shown in Fig. 7. The piston diameter is 17 mm and individual pellets are pressed batch wise by introducing approximately 3 g of material. An oven around the piston allows for pelleting temperatures up to 300 °C and the applied pelleting pressure is adjustable. In this study, pelleting conditions of T = 100–170 °C and P = 65 MPa were used for all produced pellets. Dry samples from all materials produced were pressed into pellets. Directly after pressing, the pellets had dimensions of H = 10.0–14.1 mm and D = 17.0–17.3 mm. If the initial material was in the form of chips, it was ground in a Retsch cutter mill using a 4-mm sieve prior to pelleting. Some materials were also pressed into pellets without prior drying ('aged' samples) or after moisture absorption in order to study the effect of moisture.

The single pellet's dimensions (height and diameter) and weight were determined directly after pelleting as well as after two weeks of exposure to indoor ambient air (T = 20 °C, RH = 55%). After two weeks of exposure, it was observed that single pellets tend to elongate and absorb moisture from the ambient air (see Fig. 7). This is also known as the 'spring-back effect' [26], which has been used as a measure of pellet quality and durability by other researchers [13]. Distinct cracks can also be seen in the pellet, showing that quality further decreases also in terms of durability and production of fines. This also gives a measure of material hydrophobicity, because good quality pellets do not absorb moisture. These parameters were combined into a definition for pellet quality. Pellet quality is defined by the net density improvement (NDI) after two weeks exposure to indoor ambient conditions:

$$NDI\ (\%) = \left(\left(\rho_p - \rho_{p,ref}\right) \Big/ \rho_{p,ref}\right) x100\% \quad (2)$$

where ρ_p is the measured density of a pellet after two weeks of exposure to indoor ambient conditions and $\rho_{p,ref}$ is the measured density of a pellet pressed from a reference sample (raw or torrefied spruce/poplar) after two weeks of exposure to indoor ambient conditions. The reference sample is defined in each case in the accompanying text to Figs. 11 and 16, where the NDI definition is used. Pellet durability is estimated by an attempt to manually break the pellet after the 2 weeks exposure. A good pellet durability indicates that the pellet could not be broken and a poor pellet durability indicates that the pellet could be broken into pieces.

2.3. Experimental methods

2.3.1. Solids analyses

The elemental analysis was performed with the Element Analyser FLASH 2000 (Thermo Scientific) and the ash content was determined using a Nabertherm LV5/11/B180 oven. CHN mass fractions of the dry material were determined according to EN 15104 and the ash mass fraction of the dry material was defined according to EN 14775. The oxygen mass fraction was also analysed and therefore, the sum of elements does not add up to exactly 100%. The higher heating value (HHV) of the samples was determined using a Parr 6300 Calorimeter according to standard EN 14918. The measured standard deviations of samples varied between 0.5 and 4.5% (n = 3).

2.3.2. Nuclear magnetic resonance (NMR)

^{13}C Solid state NMR analysis was performed on raw and torrefied (fresh and aged) samples of spruce and poplar in order to study the changes in the chemical structure of lignin during thermal treatment. This technique has been used successfully by other researchers [27–29].

The NMR spectra were measured on a 300 MHz solid state NMR spectrometer using a 7.5 mm double resonant chemagnetics APEX probe, tuned at 75.45 MHz for carbon. Spectra were obtained using ramped CPMAS at an rf-field of 55 kHz for carbon and 51 kHz for protons. Proton decoupling during acquisition was accomplished with a Spinal-64 sequence at an rf-field of 55 kHz, optimised to a pulse width and phase of 9 μs and 7°, respectively. MAS speeds were 4 kHz. A 2DPASS sequence was used where the spinning sidebands are separated from the centerband in a second dimension. The spectra used contained the centerband only, without any spinning sidebands.

2.3.3. Thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS)

Thermal desorption coupled with GC/MS was used on samples of torrefied (fresh and aged) spruce and poplar to study the decomposition products of the lignin, hemicellulose and cellulose contained in the samples.

The thermal desorption unit used was a Gerstel Thermal Desorption Unit coupled with GC/MS. The amount of sample used in each analysis was ca. 8 mg of sample ground in a Retsch cutter

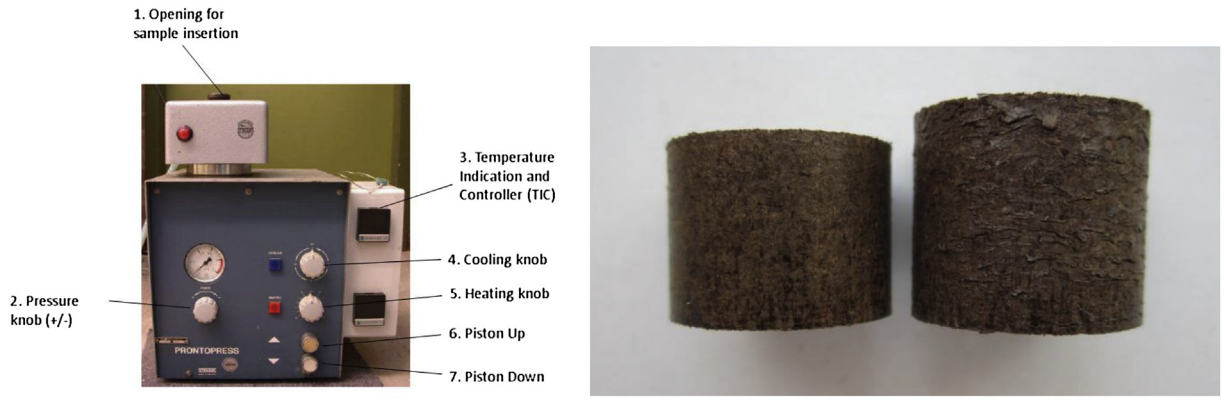

Fig. 7. Left: Struers Prontopress for single pellet pressing. Right: Example of torrefied poplar pellet elongation after two weeks exposure to indoor ambient conditions.

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mill using a 0.25-mm sieve and weighed into a Gertsel desorption tube (dimensions: OD 6 mm (ID 4 mm), length 60 mm). Quartz wool was applied in the tube to keep the sample in place. The sample was heated up at 260 K/min to 290 °C with an isothermal time of 2 min.

A Gerstel cooled injection system (CIS) (cold trap) was used at −100 °C in order to capture all components and inject them into the column for separation (injection temperature 275 °C). Desorbed compounds were separated on a 30-m Phenomenex Zebron ZB-WAXplus fused silica capillary column (0.25 mm i.d. and 0.25 μm film thickness). The GC oven was programmed to start at 50 °C for 5 min, ramped to 245 °C at 10 K/min. The MSD was operated in full scan from M/z 29 to 400.

The GC/MS chromatograms were analysed by utilising AMDIS deconvolution software and NIST library search.

2.3.4. Lignin isolation

Initial trials to determine the glass-transition temperature of in-situ lignin were not very successful because of various parameters affecting the signal (Section 3.1.4.). Therefore, it was chosen to isolate the lignin by means of low-temperature organosolv fractionation and then further characterise its properties by Size Exclusion Chromatography (SEC) and Differential Scanning Calorimetry (DSC). These analytical techniques give information on the molecular weight of the lignin and its glass-transition temperature, respectively. Both lignin properties have been associated with the densification behaviour of lignocelluloses [9,13,18].

During organosolv, biomass is treated thermally in the presence of an organic solvent. This treatment process leads to biomass fractionation including effective delignification of the biomass. The recently developed low-temperature ketone-based organosolv process yields a lignin fraction that is less-condensed (higher in β-O-4 linkages) than classical ethanol-based organosolv fractionation [30,31]. In the context of this work, condensed lignin is a form of lignin where ether bonds have been cleaved and replaced by C-C bonds. Also, the term 'lignin condensation' is used to describe condensation reactions of lignin fragments in general, i.e. reactions not only between lignin fragments (as described above), but also reactions between a lignin fragment and proteins, extractives, furfural, etc. The product of these reactions is also known as 'pseudo-lignin'.

The resulting product is thus assumed to better resemble native lignin, although it should be realised that the organosolv process: (1) affects the lignin by some additional condensation and possible reactions with the solvent used and (2) isolates only a part of the total lignin present. Nevertheless, substantially more lignin is assumed to be condensed during torrefaction than during isolation by low-temperature organosolv. In the case of torrefied samples, the condensed lignin formed during torrefaction will likely remain to a large extent in the pulp. Given the lignin modifications inherently associated with lignin isolation, future studies should look into alternative techniques for in-situ lignin characterisation such as Dynamic Mechanical Thermal Analysis (DMTA).

In this work, lignin was isolated from (torrefied) wood using aqueous acetone (60% mass fraction of acetone in water) at a temperature of 150 °C and 120 min reaction time, using H_2SO_4 as catalyst. The set-up used was a 0.5 L autoclave reactor (Büchi Glas Uster AG, Switzerland). After cooling down, the slurry is filtered and the solid cake is oven-dried at 50 °C. The filtration liquid is added to an excess of distilled water causing the lignin to precipitate. After centrifugation, the lignin sedimented on the bottom is separated from the excess liquid. After placing the lignin in a water bath at 60 °C, it shrinked and formed a thin crust. After removal of the expelled liquor, the lignin was oven-dried at 60 °C and stored for further analyses (SEC and DSC). Fig. 8 shows a schematic of the procedures and fractions obtained.

2.3.5. Size Exclusion Chromatography (SEC)

Molar mass distribution of isolated lignin samples was determined using alkaline SEC. The molar mass distribution of a lignin may affect its glass-transition temperature and provides information on how large the polymer is.

Alkaline SEC was performed with a column, consisting of a hollow tube tightly packed with extremely small porous polymer beads, TSK gel, Toyopearl HW-55. HW-55 has been designed for biomolecules between 1.000 and 700.000 Da. The collected fractions were examined by ultraviolet (UV 254 nm) spectroscopy detection. A conventional calibration with sodium polystyrene sulfonate (1.1–666 kg mol^{-1}) was used. More details on the method used can be found in Ref. [32].

2.3.6. Differential Scanning Calorimetry (DSC)

Torrefied samples as well as isolated lignin samples were characterised by using DSC for determination of the glass-transition temperature of the lignin (T_g). This temperature gives an indication of the thermal properties of the lignin which are relevant to densification behaviour. The glass transition is the reversible transition in amorphous materials, such as lignin, from a hard and relatively brittle 'glassy' state into a viscous or rubbery state as the temperature increases. The glass-transition temperature (T_g) of a material characterises the range of temperatures over which this glass transition occurs. The T_g of lignin is strongly affected by the presence of moisture in the sample and therefore, all lignin samples were dried at a mild temperature (50 °C) prior to DSC analysis.

The DSC equipment used was a Netsch DSC 200 F1 Phoenix. The gas flow was nitrogen at 20 cm^3 min^{-1} measured at STP of 298 K and 101.35 kPa. A commonly used approach to determine the T_g of lignins has been used [33,34]. The specific temperature programme used for glass-transition temperature determination is given in Fig. 9. The transition is observed in segment nr.6, where the sample is heated up from −50 °C to 200 °C. Sample mass used per measurement was 10–20 mg in an aluminium crucible.

From the experimental methods described in this section, the solids analyses, TD-GC/MS, lignin isolation, SEC and DSC analyses were carried out at ECN's facilities while the NMR analyses were done at the Radboud University of Nijmegen, at the Institute for Molecules and Materials.

3. Results and discussion

3.1. Torrefied softwood vs. hardwood

3.1.1. Effect of storage

Single pellets were pressed from the dry or dried torrefied materials at different pelleting temperatures and Fig. 10 presents the obtained densities vs. pelleting temperature. This shows that pellet density increases with increasing pelleting temperature. Also, the densification behaviour of the different torrefied samples is similar. Specifically for the 115–125 °C pelleting temperature range, the density values are within a 3.5–5% range. Therefore, their densification baseline is the same and these samples can be compared to each other in this pelleting temperature range, although produced in different set-ups.

Fig. 11 shows the results on density improvement (NDI) obtained by single pellet pressing of moisture containing torrefied poplar and spruce samples. This is defined by eq. (2) in Section 2.2.3. These tests were realised in order to examine the effect of moisture on pellet density improvement between a fresh torrefied and an aged torrefied sample. This was done for poplar containing a

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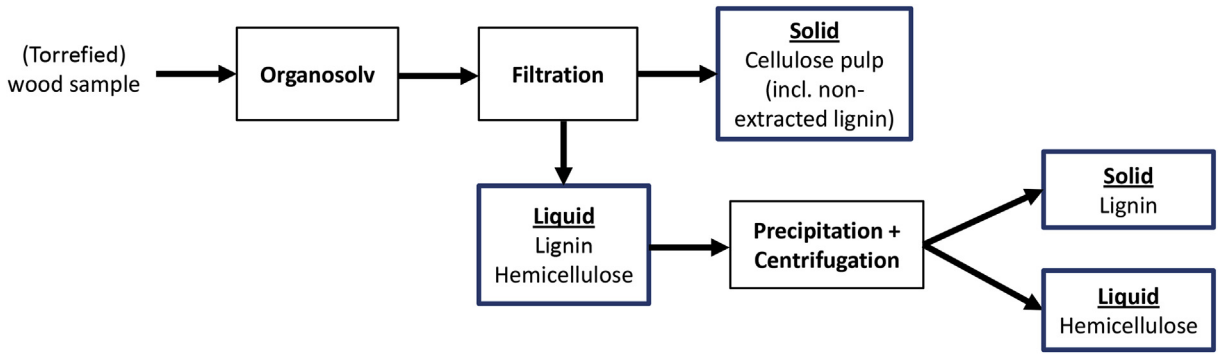

Fig. 8. Organosolv treatment procedure and obtained fractions.

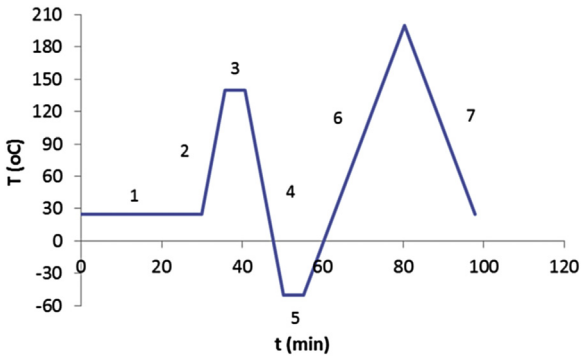

Fig. 9. Temperature segments of DSC program for T_g determination. 1 = isotherm at 25 °C for 30 min, 2 = heating up to 140 °C at 20 K min^{-1}, 3 = isotherm at 140 °C for 5 min, 4 = cooling down to −50 °C at 20 K min^{-1}, 5 = isotherm at −50 °C for 5 min, 6 = heating up to 200 °C at 10 K min^{-1}, 7 = cooling down to 25 °C at 10 K min^{-1}.

mass fraction of 3.5–5% moisture and for spruce containing a moisture mass fraction of ca. 2%.

The reference samples used for the density improvement calculation according to eq. (2) were dry poplar samples and dry spruce samples, respectively. 'Aged' samples are defined as torrefied samples that have been stored indoors before being pelleted as described in Section 2.1.

In Fig. 11 it can be seen that presence of moisture in the torrefied material has a positive effect on pellet density when the material has been fresh torrefied, independently of wood type. However, after ageing, the two wood types show different behaviour. The presence of moisture in aged poplar results in a density improvement comparable to the fresh torrefied poplar. On the contrary, the presence of moisture in aged spruce showed no similar improvement in pellet density when compared to the fresh torrefied spruce sample. This occurs despite the fact that aged torrefied spruce had been stored for a shorter period of time than aged poplar (storage time poplar: 4 years and 8 months, storage time spruce: 6 months). This effect and the underlying mechanism are not yet fully understood.

3.1.2. *Characterisation by ^{13}C solid state NMR*

Fig. 12 presents the results of ^{13}C NMR performed on poplar samples of raw, untreated biomass and after torrefaction (fresh and aged material). When comparing the curve of untreated poplar with the curve of torrefied poplar, the most important changes that occur related to lignin, are: (1) the slight decrease of the signal at 54–55 ppm, which corresponds to lignin methoxyl groups (peak nr.3 |Fig. 12B) and (2) the decrease of the signal at 152 ppm (peak

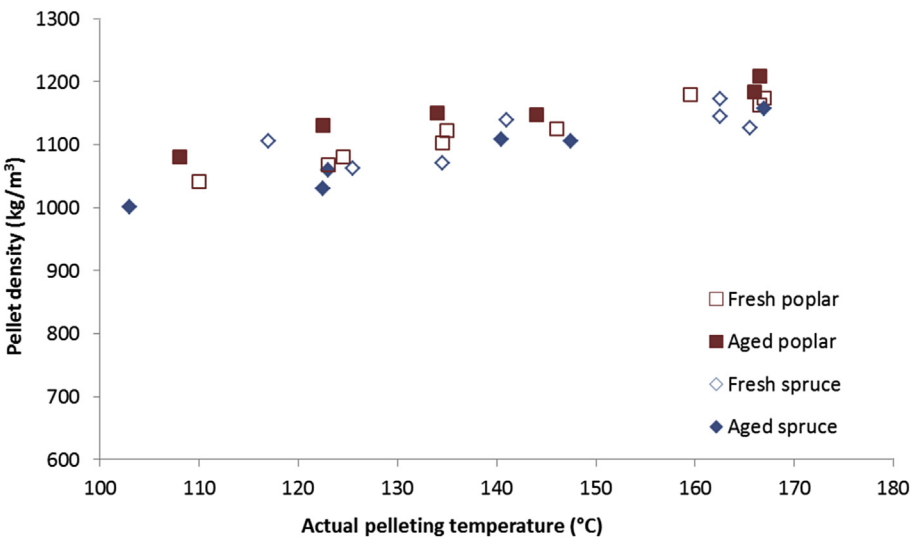

Fig. 10. Pellet densities of aged and fresh torrefied spruce and poplar samples vs. pelleting temperature.

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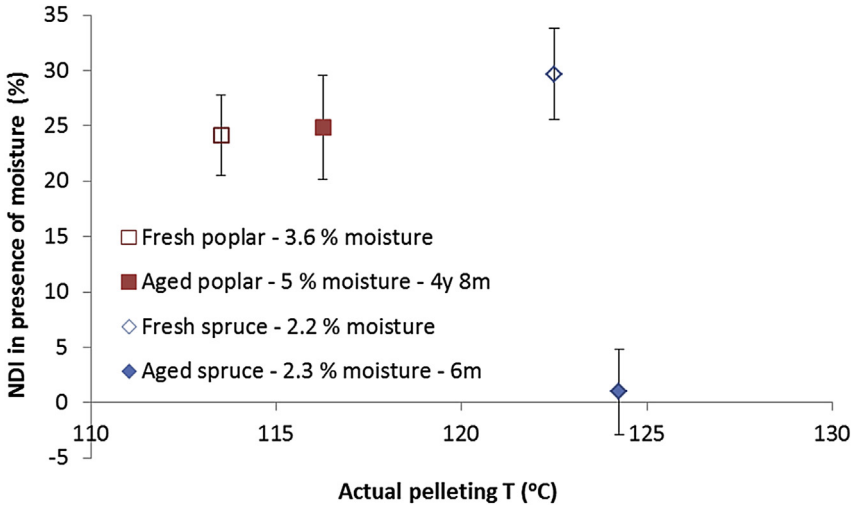

Fig. 11. Net density improvement (NDI) of poplar and spruce pellets of undried aged torrefied samples and fresh torrefied samples after moisture absorption.

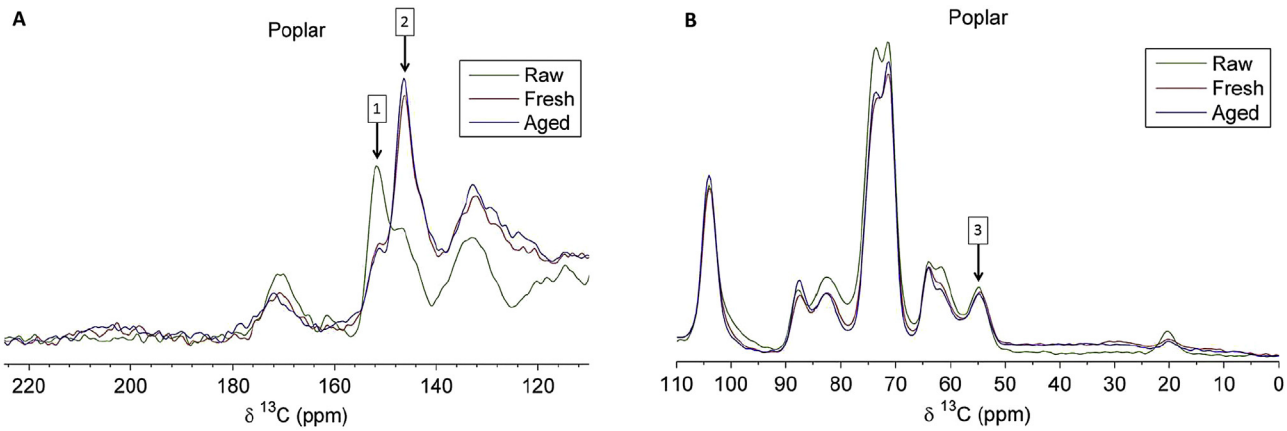

Fig. 12. ^{13}C NMR results of raw, fresh torrefied and aged torrefied poplar. **A:** Spectrum range 110–220 ppm, **B:** Spectrum range 0–110 ppm.

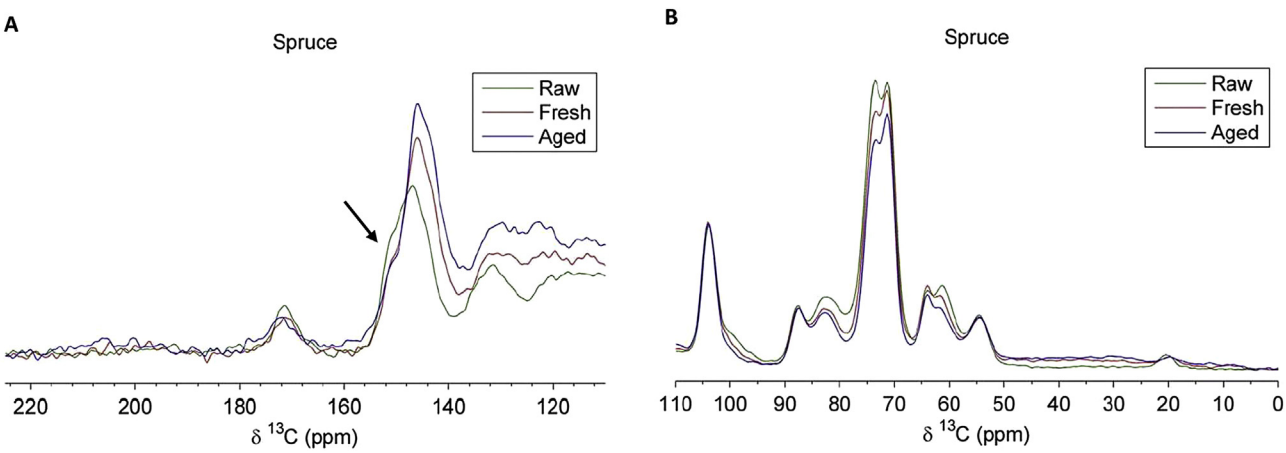

Fig. 13. ^{13}C NMR results of raw, fresh torrefied and aged torrefied spruce. **A:** Spectrum range 110–220 ppm, **B:** Spectrum range 0–110 ppm.

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nr.1 |Fig. 12A) with a simultaneous increase of the 146 ppm signal (peak nr.2 |Fig. 12A). The changes correspond to demethoxylation and cleavage of the ether linkages in lignin, respectively [27]. The decrease of the rest of the signals corresponds mostly to hemicellulose decomposition and to a lesser extent to cellulose degradation. No significant structural changes related to lignin have been observed between a fresh torrefied and an aged torrefied poplar sample.

Fig. 13 shows the obtained ^{13}C NMR results for spruce and the effect that torrefaction and storage of torrefied material have on material structure. The most prominent changes in signals related to lignin are displayed by the shape of the shoulders observed at 140–160 ppm (indicated by an arrow in Fig. 13A). This indicates cleavage of the ether linkages in softwood lignin [27,28]. The increased peak intensity at 144 ppm for the aged torrefied spruce sample compared to the fresh torrefied spruce could indicate some changes in the direct chemical environment of the carbon bond. However, since the changes are not substantial and the analytical method is qualitative, no hard conclusion can be drawn.

3.1.3. Characterisation by TD-GC/MS

Results from thermal desorption analyses coupled with GC/MS are given in Fig. 14 and Fig. 15 for torrefied poplar and torrefied spruce, respectively. The TD-GC/MS method only gives qualitative results and thus exploratory and preliminary trends. True quantification in lignins still remains difficult. However, the same amount of sample was used for the four analyses enabling comparison among samples.

In the chromatograms in Figs. 14 and 15 the peak abundance is plotted against the retention time in the GC column. The increase of the baseline around 25 min in all four chromatograms is due to the temperature gradient in the column. In Fig. 14, the aged poplar sample contains 4-hydroxy-3-methoxybenzaldehyde (or vanillin) and 4-hydroxy-3,5-dimethoxybenzaldehyde (or syringaldehyde) (relevant peaks also indicated in Fig. 14) which are products of lignin oxidation reactions [35]. This suggests that during storage of the torrefied material, lignin reacts with oxygen from air. Also, in the chromatograms of torrefied poplar, some components appear which are products of lignin degradation (phenol and 1,3-dimethoxy-2-hydroxybenzene) occurring during thermal desorption.

In Fig. 15, no large differences can be observed between the fresh torrefied spruce and the aged sample. Furthermore, 4-hydroxy-3-methoxybenzaldehyde (or vanillin) was detected in the aged spruce sample, which means that the lignin in this case has also undergone some reactions with atmospheric oxygen during storage. The aged spruce sample was stored in a closed metal bin as described in Section 2.1. As the TD-GC/MS results indicate, the sample has reacted with oxygen present in the container. If the sample's exposure to the limited oxygen source (closed bin) would have played a positive role in its densification behaviour we would have observed this in the results shown in Figs. 10 and 11. However, this is not the case.

Based on peak intensities, both aged torrefied poplar and spruce samples seem to contain lower concentrations of components than their corresponding fresh torrefied samples related to hemicellulose decomposition in the range of 10–20 min retention time, such as acetic acid and 2-furanmethanol (furfuryl alcohol). This is probably caused by the fact that the aged samples, which are a product of pilot torrefaction tests, have been exposed to a higher torrefaction severity than the fresh torrefied ones. This difference is also discussed in Section 3.2.1.

When comparing peak intensities between the poplar and spruce samples, torrefied poplar samples contain, in general, higher concentrations of lignin and hemicellulose decomposition products than torrefied spruce samples (noted by the difference in range of the y-axis between Figs. 14 and 15). This implies that hardwood (lignin) decomposes more extensively than softwood (lignin) at the

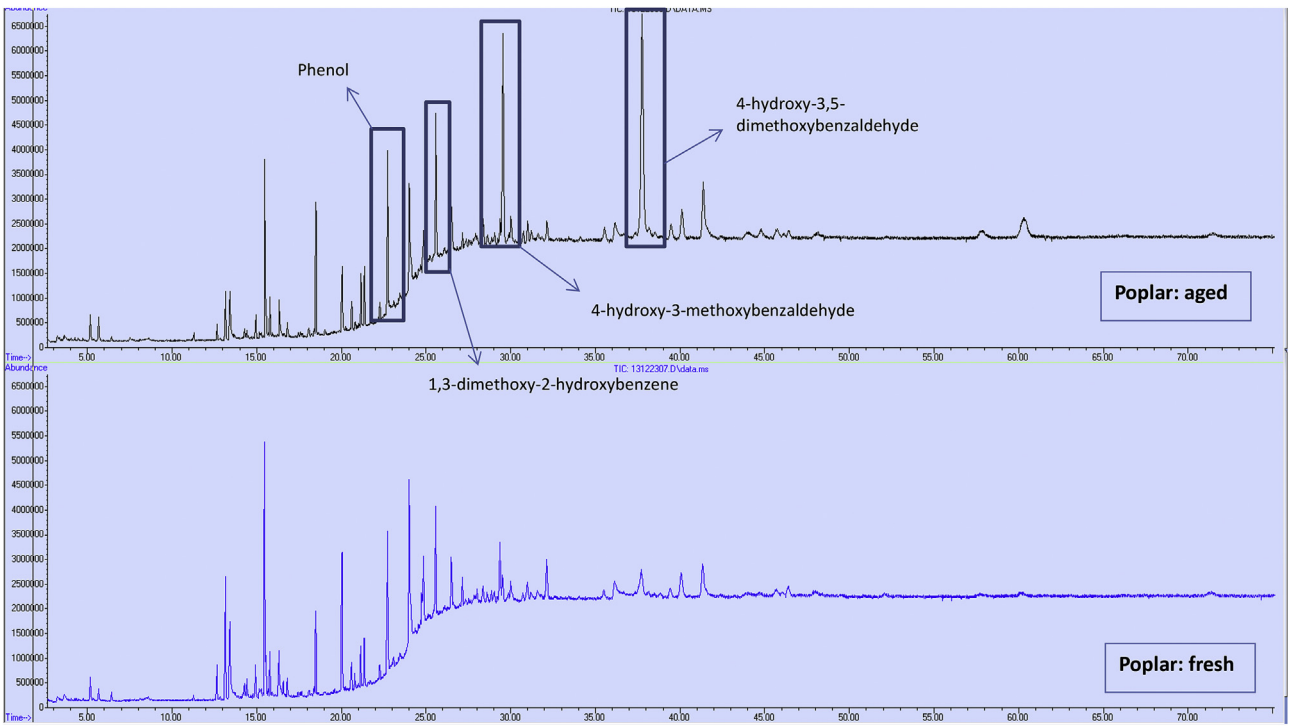

Fig. 14. TD-GC/MS data for aged (top) and fresh torrefied poplar (bottom). Scale on y-axis (abundance) ranges from 0 to 6.5 × 10^6 (arbitrary units).

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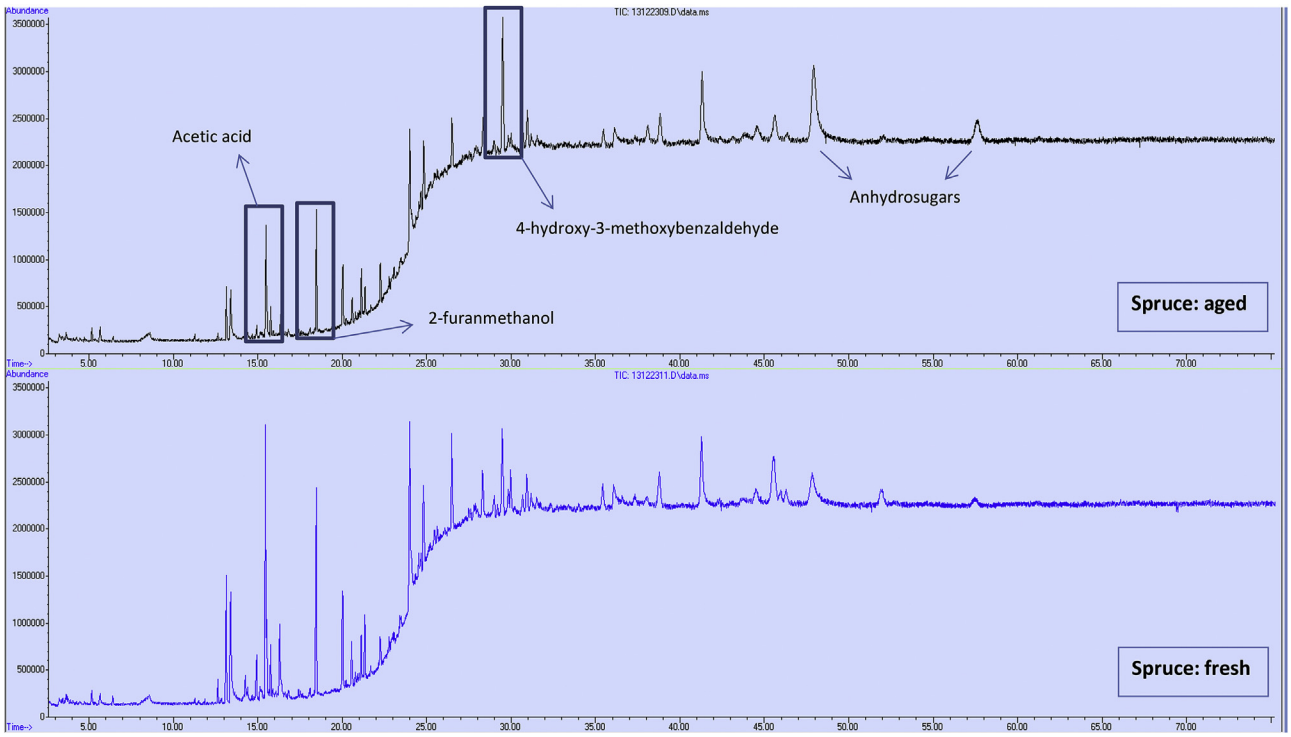

Fig. 15. TD-GC/MS data for aged (top) and fresh torrefied spruce (bottom). Scale on y-axis (abundance) ranges from 0 to 3.5 × 10^6 (arbitrary units).

same thermal decomposition conditions applied during torrefaction. This is in agreement with the literature where it is stated that thermal modification causes more evident structural changes in hardwood than in softwood lignin [27]. There seems to be a link between lignin syringol content, and therefore S units, and β-O-4 (aryl ether) abundance in the lignin molecule. These are moieties that have a relatively low bond energy. This makes hardwood lignins, which have a higher syringol content than softwood lignins to depolymerise more readily [36]. Other reactions taking place are demethoxylation and crosslinking reactions (in the literature also referred to as 'lignin condensation' [37]) by the formation of C-C bonds between aromatic sub-structures. Between S units in hardwood lignins, crosslinking reactions are less likely to occur because methoxyl groups occupy the C-5 and C-3 positions of the aromatic ring. Given the higher G-content of softwood lignins, torrefaction of softwood leads possibly to a more cross-linked structure of its lignin.

3.1.4. Characterisation by Differential Scanning Calorimetry (DSC)

Further analyses performed were DSC measurements for determination of the glass-transition (softening) temperature, T_g, of the in-situ lignin. Cellulose was used in the empty reference crucible in an effort to correct for the remaining cellulose content of the sample. A transition could be measured at an average temperature of 108 °C, but the signal was quite weak and the T_g did not vary among the samples tested. According to the literature, when trying to measure the T_g of in-situ lignin, indeed weak transition signals are observed. This occurs because of the bonds of lignin with other carbohydrates inside the biomass matrix, restricting free rotation/movement of the lignin macromolecule [38]. Therefore, in the continuation of this study, lignins were isolated from the materials by using organosolv and the T_g of isolated lignins was measured. These results are further described and discussed in Section 3.2.3.

3.2. Behaviour of softwood lignin

3.2.1. Densification of torrefied softwood in presence of moisture

From the results presented and discussed so far, it is evident that softwood lignin transformation during torrefaction, is key for understanding its densification performance. Therefore, some additional torrefaction tests were conducted, namely torrefaction and torrefaction combined with direct steam conditioning. These materials were all fresh torrefied and storage time between production and pelleting was minimal. The effect of moisture on pellet quality was investigated and the lignin from the torrefied samples was isolated by organosolv and characterised.

Fig. 16 shows the pellet density results using the single pellet piston press for spruce samples that have undergone various thermal treatment conditions. In order to evaluate the torrefaction methods used in terms of pellet quality, the net density improvement definition (NDI) and a measure of pellet durability were introduced in Section 2.2. In Fig. 16 the reference density chosen is that of an oven-dried (at 105 °C) raw spruce pellet pressed in the temperature range of 115–125 °C and exposed to indoor ambient air for two weeks at T = 20 °C and RH = 55%. The moisture mass fraction of the samples was ca. 2%. The trend in durability of the pressed pellets is included in Fig. 16.

Torrefaction improves density by ca. 20% compared to raw spruce. When moisture is added to a (fresh) torrefied spruce sample by absorption from the ambient air, the density improvement increases to 50% and the resulting pellet shows good durability. After exposure of the pellet to ambient air conditions, the torrefied sample contained a 3% moisture mass fraction, while the pellet with added moisture contained a 1.3% moisture mass fraction. This difference in moisture uptake supports the observations on pellet durability.

Steam conditioning of the fresh torrefied spruce also shows a net density improvement, but comparable to that of torrefaction

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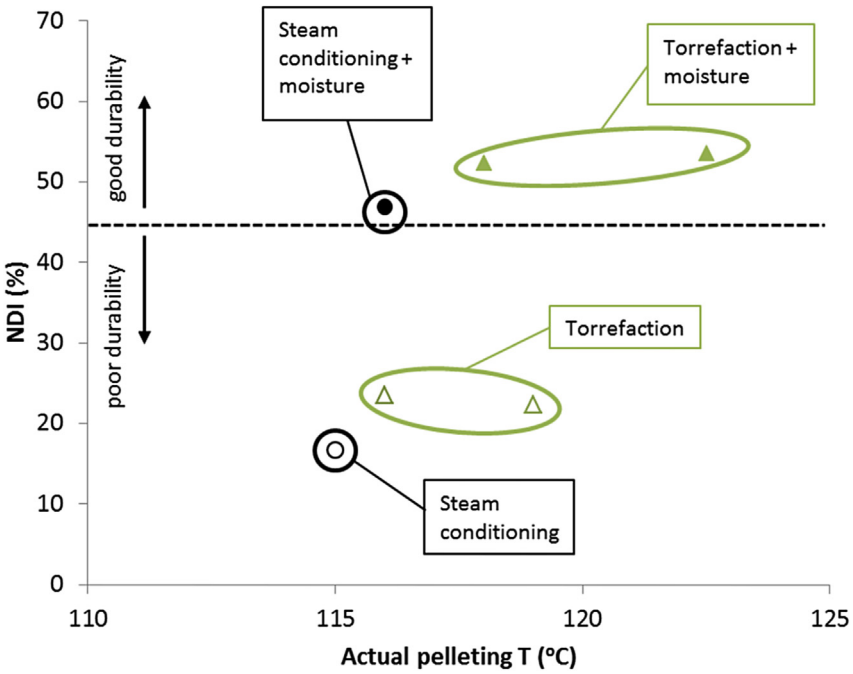

Fig. 16. Net density improvement (NDI) of torrefied spruce pellets as a function of the measured pelleting temperature. The effects of moisturising through direct steam conditioning and moisture addition are shown. Empty markers indicate pellets pressed from dried samples and filled markers indicate pellets pressed from samples containing moisture.

only. Also, a similar effect to the torrefied sample is observed when moisture is added to the steam conditioned torrefied sample. After exposure of the pellet to ambient air conditions, the steam conditioned torrefied sample contained a 2.5% moisture mass fraction, while the corresponding pellet with added moisture contained a 1% moisture mass fraction. Also in this case, the moisture uptake by the pellet supports the observations on pellet durability.

Steam conditioning of the fresh torrefied spruce does not further aid densification in this case. Steam conditioning is widely used by most commercial pellet or briquette producers as a means to add heat and moisture to the dry particles of a feedstock in order to lower power requirements of the pellet mill and to produce pellets of higher mechanical durability [39]. In our case, the steam is added to the fresh torrefied material which is afterwards cooled down again before being pressed into single pellets. It is highly possible that an improvement in pellet quality and durability would be observed if the torrefied spruce would be directly densified after steam conditioning (hot densification). However, current set-up limitations did not allow for such an experiment. This subject is part of ongoing research and will be published elsewhere.

3.2.2. *Lignin isolation*

Samples obtained from the torrefaction and conditioning tests were treated by organosolv in order to obtain the different lignin fractions. Fig. 17 presents the dry mass fractions of raw spruce and thermally treated (and/or steam conditioned) spruce samples as

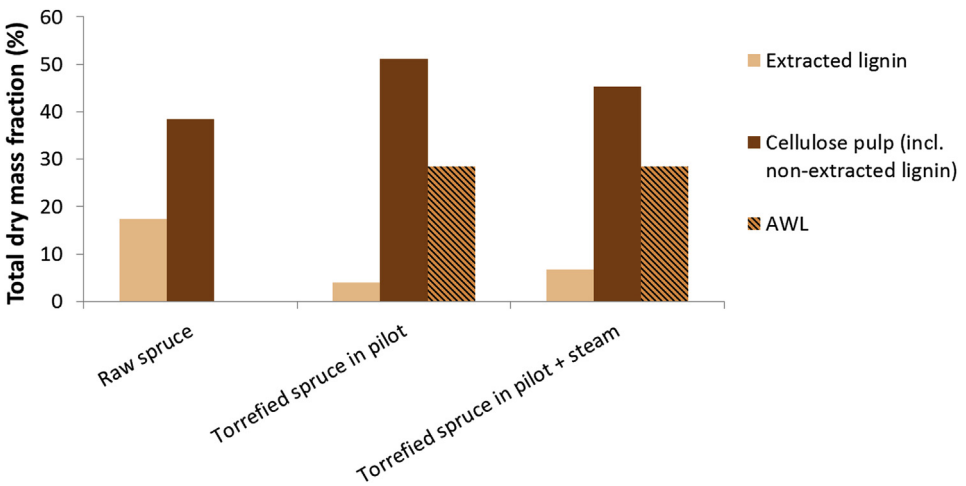

Fig. 17. Quantification of total mass fractions of raw and torrefied spruce samples. The fractions 'extracted lignin' and 'cellulose pulp' correspond to the solid fractions obtained by organosolv as shown in Fig. 8. AWL is a property of the organosolv feed and defined by eq. (1).

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quantified after (torrefaction and) organosolv. The cellulose pulp is obtained by weighing the dry solid residue after filtration (Section 2.3.4, Fig. 8). The anhydrous weight loss (AWL) is also included in Fig. 17 as a measure of torrefaction severity according to eq. (1).

The lignin produced by this specific organosolv process is of high purity and is assumed to consist primarily of native lignin not condensed during torrefaction. This lignin fraction is supposed to play a crucial role in the proper downstream densification of the material. The rest of the lignin (non-extracted) in the torrefied wood exists in a condensed form and its glass-transition temperature is considered to be higher than temperatures used in practice for densification of softwoods [33].

As a hypothesis it is assumed here that the higher the amount of extractable lignin present in the material, the more there is available to potentially act as the binding constituent during pelleting. In Fig. 17 it can be seen that the extractable lignin decreases upon torrefaction resulting in a smaller amount of potentially available lignin for subsequent densification. Torrefaction of raw spruce seems to cause its lignin to condense, considering that the cellulose fraction remains intact at the relatively low torrefaction temperatures used in this study. This is shown in Fig. 17 by the increase in the fraction denoted as 'cellulose pulp'. This is in agreement with findings by Wen et al. [22] who concluded that G type of lignin units, largely present in softwoods are more prone to condensation reactions.

Samples from spruce that was torrefied in the pilot plant both with and without steam conditioning were obtained from the same pilot-scale torrefaction tests, which is also reflected by the same fraction converted by torrefaction (AWL) of these two samples in Fig. 17. The latter sample had also been conditioned in steam directly after production in a slipstream of the pilot plant. Some small differences can be observed between their extracted lignin and cellulose pulp fractions. However, such small differences could also originate from experimental errors and can therefore not lead to solid conclusions concerning the effect of steam conditioning on lignin reactions/transformations.

3.2.3. Lignin characterisation by SEC and DSC

Table 2 presents the results from the SEC analyses performed on the organosolv lignins of the materials. The results are expressed in terms of weight average (M_w) and number average (M_n) molecular weights and the polydispersity index (D).

SEC results show that all organosolv lignins have relatively low molecular weights and their polydispersity does not vary significantly among the samples. This shows that torrefaction and steam conditioning do not significantly alter spruce lignin in terms of molecular weight distribution. Furthermore, conditioning of the torrefied spruce with steam does not seem to influence this further. Results are in agreement with statements found in the literature on M_w of softwood lignin determined by SEC at a value of 3.0 kg mol^{-1} [32,40].

DSC analyses were performed in order to determine the glass-transition temperature (T_g) of the various organosolv lignins obtained and the results are given in Table 3. The T_g value of lignin is used as an indication of its softening point which can be used as a prediction for the formation of strong covalent bonds during pelleting of the material. For amorphous polymers such as lignin, its T_g is one of the major parameters that influence its viscoelastic properties [41].

Table 3
Glass transition temperature (T_g) of organosolv lignins of raw and thermally treated spruce samples.

Sample	T_g (°C)
Organosolv lignin raw spruce	125
Organosolv lignin spruce torrefied in pilot	150
Organosolv lignin spruce torrefied in pilot + steam conditioning	140

The glass-transition temperature of raw spruce lignin is 125 °C, which is in the same range with values found in the literature for softwood lignin [42]. Torrefaction causes the glass-transition temperature of lignin to increase to 150 °C. Moreover, conditioning of the torrefied material in steam did not seem to influence the levels of the glass-transition temperature of the lignin significantly.

The T_g value of a lignin depends on various factors such as molecular weight (distribution), interchain hydrogen bonding, crosslinking and change of chemical structure depending on lignin isolation method [11,33]. In our case, the same lignin isolation method was used and the lignins had similar molecular weight (distributions) as seen in Table 2. Therefore, changes in hydrogen bonding and crosslinking seem to be responsible for the observed differences.

3.3. Summary of findings in relation to existing knowledge

Responsible for the strongest pellet binding action are the formation of both covalent bonds and the existence of H-bonds [15,41]. Covalent bonds during pelleting can be achieved once the polymer is cooled down after the pelleting temperature has exceeded the glass-transition temperature of the active lignin (fragments) [8]. Furthermore, the existence of hydrogen bonds contributes to this effect by aiding water molecules to attach to hydrophilic groups (such as −OH) of the material's matrix, causing segmental motion to occur easily further lowering the material's softening point [11].

In raw wood, the combination of the amount of active lignin and its low glass-transition temperature, as well as availability of hydrogen bonding sites by both lignin and hemicellulose present are all contributing to a good pellet quality. During torrefaction, decomposition of hemicellulose decreases the amount of the hydrogen binding sites which results in a structure that reduces the lignin binding ability in the presence of moisture during pelleting (Fig. 16). Moreover, hydrogen binding sites also decrease because of dehydration and demethoxylation reactions that lignin undergoes. In addition, lignin condensation reactions seem to dominate the net reaction products of softwood lignin and thus decrease the amount of lignin that possesses the favourable properties for downstream pelleting while causing its glass-transition temperature to increase (Fig. 17, Table 3).

Nevertheless, the mechanism of the effect of storage on

Table 2
Molecular weight and polydispersities of organosolv lignins of raw and thermally treated spruce samples.

Sample	M_w (kg mol^{-1})	M_n (kg mol^{-1})	D (M_w/M_n)
Organosolv lignin raw spruce	3.5	1.4	2.5
Organosolv lignin spruce torrefied in pilot	3.1	1.4	2.2
Organosolv lignin spruce torrefied in pilot + steam conditioning	3.1	1.4	2.3

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torrefied softwood is not yet fully understood. Based on the rest of the results in this study it is plausible to assume that oxygen affects the hydrogen binding sites causing no positive effect in the binding ability of lignin in the presence of moisture during pelleting (Fig. 11) and/or affects the lignin structure leading to higher glass-transition temperatures. This could be related to the anti-oxidant properties that the lignin itself possesses since lignins can act as radical scavengers [43].

4. Conclusions

The main conclusions of this study can be summarised as follows:

- The results support that hardwood lignin decomposes to a greater extent than softwood lignin during torrefaction at 270 °C and 32–45 min
- Torrefied wood, and especially softwood, in this study produced at 270 °C and 32–45 min, should be densified immediately after production in order to achieve the highest attainable pellet quality
- During storage of torrefied wood, lignin fragments seem to react with atmospheric O_2. As a consequence, the binding ability of softwood lignin reduces leading to pellets of lower quality. This effect is not yet fully understood and subject to further research
- Conditioning of fresh, hot torrefied material with steam does not result in any measurable pellet improvement when compared to dry torrefaction only
- Pellet quality of a material depends on the ability of its lignin to act as a binder in the presence of moisture during densification
- A single-pellet piston press could be used to simulate results obtained on industrial scale
- Glass transition measurements of in-situ lignin by using DSC were not successful due to weak transition signals.

Overall, it was established that understanding and controlling lignin chemistry is a prerequisite for an optimum combination of biomass torrefaction and densification of torrefied wood.

Acknowledgements

This work was financially supported by the Dutch Ministry of Economic Affairs as part of the biomass research program of ECN. The authors like to thank Dr. E.R.H. van Eck, from the Radboud University of Nijmegen, Institute for Molecules and Materials for performing and giving input on the solid state NMR analyses. The feedback of A.T. Smit and P.J. de Wild on organosolv fractionation and the lignin characterisation work is gratefully acknowledged.

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