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Bioenergy II: Biomass Valorisation by a Hybrid Thermochemical Fractionation Approach*

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Abstract

The need for green renewable sources is adamant because of the adverse effects of the increasing use of fossil fuels on our society. Biomass has been considered as a very attractive candidate for green energy carriers, chemicals and materials. The development of cheap and efficient fractionation technology to separate biomass into its main constituents is highly desirable. It enables treatment of each constituent separately, using dedicated conversion technologies to get specific target chemicals. The synergistic combination of aquathermolysis (hot pressurised water treatment) and pyrolysis (thermal degradation in the absence of oxygen) is a promising thermolysis option, integrating fractionation of biomass with production of valuable chemicals. Batch aquathermolysis in an autoclave and subsequent pyrolysis using bubbling fluidised bed reactor technology with beech, poplar, spruce and straw indicate the potential of this hybrid concept to valorise lignocellulosic biomass. Hemicellulose-derived furfural was obtained in yields that ranged from 2 wt% for spruce to 8 wt% for straw. Hydroxymethylfurfural from hemicellulose was obtained in yields from 0.3 wt% for poplar to 3 wt% for spruce. Pyrolysis of the aquathermolised biomass types resulted in 8 wt% (straw) to 11 wt% (spruce) of cellulose-derived levoglucosan. Next to the

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furfurals and levoglucosan, appreciable amounts of acetic acid were obtained as well from the aquathermolysis step, ranging from 1 wt% for spruce to 5 wt% for straw. To elucidate relations between the chemical changes occurring in the biomass during the integrated process and type and amount of the chemical products formed, a ^{13}C -solid state NMR study has been conducted. Main conclusions are that aquathermolysis results in hemicellulose degradation to lower molecular weight components. Lignin ether bonds are broken, but apart from that, lignin is hardly affected by the aquathermolysis. Cellulose is also retained, although it seems to become more crystalline, probably due to a higher ordering of amorphous cellulose when the samples are cooled down after aquathermolysis. These NMR results are in agreement with thermogravimetric analyses results.

KEYWORDS: biomass, lignocellulose, beech, poplar, spruce, wheat straw, aquathermolysis, pyrolysis, value-added chemicals, TGA, GC/MS, NMR

INTRODUCTION

The adverse effects of the increasing use of fossil fuels on our society demands the use of renewable sources. Biomass can be converted to energy, fuels and chemicals by a variety of processes, but no individual process is without drawbacks (Briens et al., 2008). The complexity and heterogeneity of biomass present a major obstacle to chemical utilisation. The main constituents hemicellulose, cellulose and lignin are strongly interconnected by a variety of physico-chemical bonds that makes it difficult to separate them as individual constituents in high yields. Efficient and cost-effective fractionation technology opens up the possibility to treat each constituent separately, using dedicated conversion technologies to get specific target chemicals. A biorefinery in which the fractionation is combined / integrated with subsequent processing steps, offers the best solution for a cost-effective and environmentally sound valorisation of biomass.

Thermolysis is heat treatment to convert the biomass into chemicals according to differences in thermochemical stability between the main biomass constituents. However, a careful selection of process conditions is necessary to ensure a selective degradation of the chosen biomass constituent. At the same time a premature degradation of the other fractions should be prevented. The fact that the individual biomass constituents react differently at specific temperatures to yield different spectra of products can be exploited to extract value-added chemicals from biomass (Merritt and White, 1943; Shafizadeh, 1983). Degasification of biomass during a discontinuous step-wise temperature rise in auger and fluidised bed reactors has been studied to explore the production of chemicals. Because of limited product yields, it was concluded that alternative approaches are needed to obtain higher yields, e.g. by application of specific biomass pretreatment procedures. (De Wild et al., 2008).

Hemicellulose can be quantitatively removed from biomass by treatment with hot pressurised water (Richter, 1956; Lora and Wayman, 1978; Bonn et al., 1983; Garrote et al., 1999; Mosier et al., 2005; Liu, 2008; Yu et al., 2008). The treatment results in water soluble oligomeric and monomeric sugars and their degradation products such as furfural and hydroxymethyl furfural, both of which are valuable chemicals (Lehnen et al., 2001; Zeitsch, 2000). The formation of these products is catalysed by acetic acid, originating from the acetyl groups of hemicellulose. Water soluble components like alkali metal ions are leached out from the solid biomass. Without the catalytic cracking activity of the alkali metals, cellulose can be depolymerised to levoglucosan in good yields (Ponder et al., 1990; Scott et al., 2000). Levoglucosan is a promising chemical building block for a variety of products (Witczak, 1994).

Cellulose and lignin are relatively unaffected by the hot water treatment, although lignin can be solubilised as well, especially when the reaction products are continuously removed from the solid biomass (Bobleter et al., 1981). The amount of dissolved lignin depends on temperature and reaction time. Longer reaction times and/or higher temperatures render the lignin insoluble due to recondensation reactions (Lora and Wayman, 1978, Biermann et al., 1984). The recondensed structures could be thermally more stable than the parent material and less prone to thermal degradation under conditions where cellulose does degrade. This implies that in a subsequent pyrolysis step a more selective depolymerisation of cellulose is possible, resulting in enhanced yields of levoglucosan and less lignin-derived degradation fragments when compared to direct pyrolysis of the original feedstock.

The scope of the research described in this article is a study on a hybrid thermolysis concept for the production of furfural and levoglucosan from biomass. These chemicals were identified as promising value-added chemicals that can be produced from the carbohydrate fraction of biomass by direct thermochemical conversion (Werpy and Petersen, 2004). The hybrid concept is presented in Figure 1 and involves a synergistic combination of hot pressurised water treatment (aquathermolysis) and (fast) pyrolysis in which the fractionation of the lignocellulosic biomass is integrated with the production of valuable chemicals. Aquathermolysis focuses on the production of furfural from the

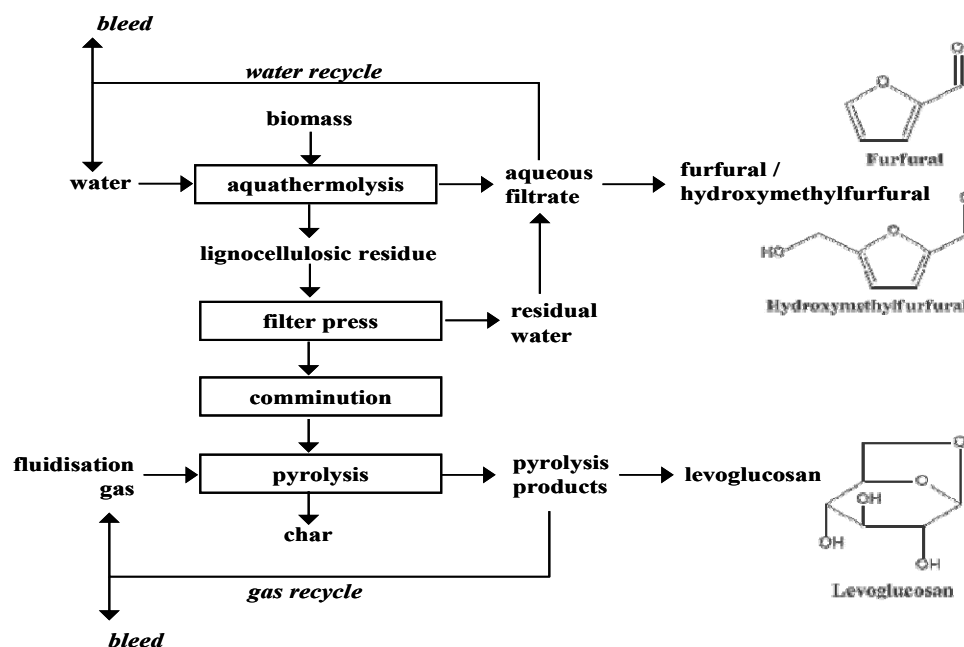


Figure 1 – Hybrid thermolysis concept for the production of chemicals from biomass.

hemicellulose while a subsequent pyrolysis of the lignocellulose residue is meant to selectively convert cellulose into levoglucosan.

MATERIALS AND METHODS

FEEDSTOCKS

Commercially available beech wood was obtained from Rettenmaier, Germany (Räuchergold, particles of 0.75 – 2 mm). The poplar wood was provided as 4 x 4 cm chips from freshly debarked and chipped trunks by the Dutch pulp- and paper mill of Mayr-Melnhof in Eerbeek, the Netherlands. Spruce was purchased as dry (moisture content approx. 4 wt%) sawdust (0.5 – 2 mm) from Bemap Houtmeel in Bommel, the Netherlands. Finally, the wheat straw was provided by Abengoa Bioenergy New Technologies (ABNT), Spain. The solid residues from the aquathermolysis treatment served as feedstock for the subsequent pyrolysis trials.

CHEMICAL CHARACTERISATION

All solid feedstocks have been chemically characterised by proximate, (moisture, volatile fraction, ash), ultimate (C, H, N, O, HHV), elemental (metals) and biochemical analysis using standard chemical analysis methods.

Moisture, volatiles and ash content were determined with an oven, using an ISO-17025 certified protocol. The ultimate analysis was conducted using an Interscience Carlo Erba element analyser for C, H, N and O and a bomb-calorimeter for the higher heating value. These measurements were performed under ISO-17025 too. Inductively coupled plasma (ICP) equipment from Spectro and an atomic emission spectrometer (AES) from Vista were used to determine elements in the biomass.

The milled samples were extracted using soxhlet-extraction with ethanol / toluene 2:1, 96% (v/v) ethanol and hot water at boiling temperature for one hour. The extracted samples were dried at 60°C for 16 hours. The total weight loss after the extractions is attributed to the extractives content in the biomass. The content of neutral sugars and lignin in the solid feedstocks was analysed according to modified TAPPI methods (Teunissen et al., 1993; TAPPI method T222, 1983; TAPPI method T249, 1985; TAPPI useful method UM250, 1983). For beech, indicative values for its biochemical content have been taken from the literature (Fengel and Wegener, 2003).

Liquid and gaseous products from the aquathermolysis and the pyrolysis experiments have been analysed using standard chemical analysis methods. Most organics were measured with a TRACE-GC-ULTRA GC/MS with DSQ-II mass spectrometer, Hydroguard pre-column, Zebron ZB-WAXplus column (30 m x

0.25 mm, film thickness 0.25 micron), split injection and calibration with internal standards.

Monomeric glucose and xylose were determined after sulphuric acid hydrolysis with a HPLC Agilent 1100 system with refractive index detection and a MetaCarb 87P (300 x 7.8 mm) column at 80°C. ABB NDIR spectrometers (Advance Optima, CALDOS – MAGNOS) were used for on-line monitoring of CO, CO₂, CH₄. Finally, Karl-Fischer titration was applied to analyse the water content in the liquid organic samples.

THERMAL CHARACTERISATION

The thermal behaviour of the feedstocks under (slow) pyrolysis conditions was investigated by thermogravimetric and differential thermogravimetric analyses (TGA/DTGA) with a Mettler Toledo TGA 850, featuring automated temperature control, weight monitoring and data acquisition. Results were interpreted using the procedure, described by Grønli et al. (Grønli et al., 2002).

From the DTGA curves a temperature of 350°C was selected as most appropriate for the bubbling fluidised bed tests. Details can be found elsewhere (De Wild, 2008).

STRUCTURAL CHARACTERISATION BY ¹³C CP/MAS NMR

The effects of the aquathermolysis and pyrolysis on beech, spruce and poplar were studied using cross-polarization, magic-angle-spinning (CP/MAS) NMR methods. For poplar and spruce, four different pretreated samples were measured: dried wood, the product after aquathermolysis at 200 °C, the product after pyrolysis of the wood at 350 °C and the product of pyrolysis of the aquathermolysed sample. For beech, the fresh unmodified wood, its aquathermolysed residue and the product from pyrolysis of the aquathermolysed residue were measured. The sawdust particles were sufficiently small to be tightly packed in the NMR rotor, the other samples were ground before they were measured.

All CP/MAS spectra were recorded on a Chemagnetics CMX-300 instrument at 75.475 MHz. The probe used was a HX, 4 mm MAS probe, the magic angle of which was set by maximizing the number of rotational echoes in the free induction decay (FID) signal of ⁷⁹Br of KBr. The spinning speed used was 5000 Hz. A CP contact time of 1.0 ms was used for all measurements.

During cross-polarisation, magnetization is transferred from proton to carbon, improving resolution and signal intensity of carbon spectra. RF field strengths for CP were 75 kHz for ¹H and 72 kHz for ¹³C. The strength of the ¹H decoupling field was 69 kHz.

To help clarification of the spectra, dipolar dephasing (DD) was used to distinguish between carbons adjacent to protons and carbons which are only weakly coupled to adjacent protons, like methyl and quaternary carbons. Proton spin-lock measurements were used to distinguish parts of the spectrum with high and low molecular order, i.e. amorphous and crystalline fractions in the biomass (Newman and Hemmingson, 1990).

AQUATHERMOLYSIS

Aquathermolysis experiments have been conducted in 0.5 litre (internal volume) stainless steel reactor vessels of commercially available autoclaves (Büchi) equipped with automated stirring, process control and data acquisition.

In a series of screening tests with beech wood chips at a liquid / solid (wt%) ratio of 5 and an (arbitrarily) reaction time of 30 minutes, the yield of furfural was determined as a function of temperature in the range 160°C-230°C. Subsequently the effect of the reaction time on the furfural yield was determined in the range of 15 - 120 minutes. Further aquathermolysis experiments of the dried and comminuted (1 mm average size) fresh biomass samples were conducted at a reaction temperature of 200°C. Samples were heated up to the reaction temperature at approximately 6°C/min with pressurised ultra-pure (double demineralised) water at a liquid / solid (wt%) ratio of 5 (beech) and 10 (other feedstocks). After 30 min of treatment at 200°C under approximately 16 bar(a) saturated steam pressure, they were cooled down to room temperature at approximately 6°C/min and depressurised to atmospheric pressure. The biomass-water mixture was stirred throughout the whole experiment (approx. 100 rpm). Subsequent vacuum filtration over a Whatman glasfibre micro-filter yielded an aqueous filtrate and a wet solid residue. To remove adhering organic and inorganic material, the solid residue was washed with excess water whereafter it was dried under air at 104°C overnight. In Figure 2 the experimental procedure is drawn.

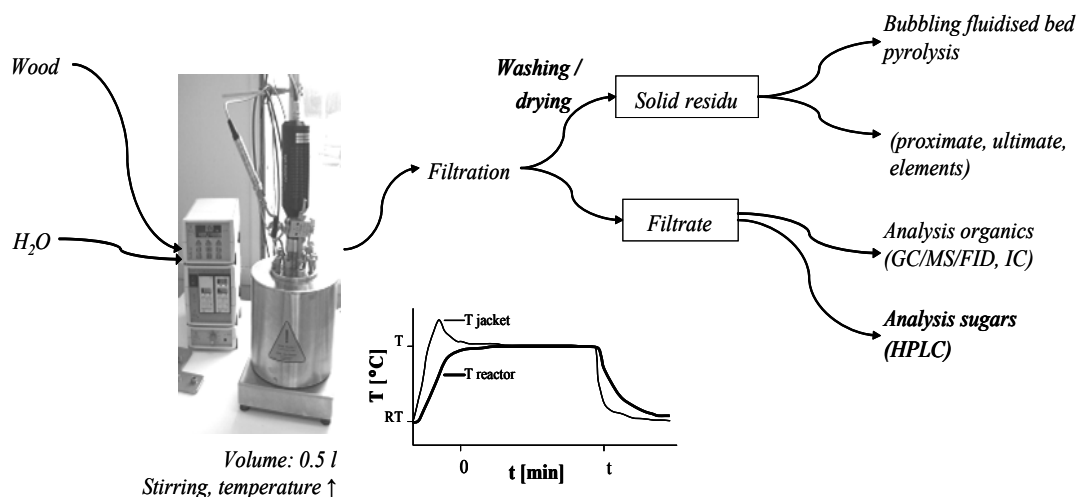


Figure 2 – Experimental procedure aquathermolysis.

BUBBLING FLUIDISED BED PYROLYSIS

Bubbling fluidised bed (BFB) reactor technology offers excellent heat and mass transfer characteristics that enable fast heating of the biomass particles, typically at a rate of thousands of degrees per minute. This favours depolymerisation reactions of the cellulose in the biomass, resulting in high yields of levoglucosan, especially after removal of the innate (alkali) metal cracking catalysts (Diebold and Bridgwater, 1999). In contrast, slow heating promotes the formation of char.

Pyrolysis experiments have been conducted with fresh and aquathermolysed feedstocks at 350°C in a fully automated 5 kW_{th} atmospheric pressure, 1 kg/hr bubbling fluidised bed test facility (Figure 3) equipped with screw feeding and pyrolysis product sampling (condensable and non-condensable gases and aerosols). The superficial gas velocity was set at approximately two-three times the minimum fluidization velocity (0.1 m/s at NTP) and the residence time of the liberated pyrolysis products in the hot zone (including the heated particle filter) is 2 – 4 sec. Further details of the experimental set up and procedures, including product analysis, have been published previously (De Wild, 2008).

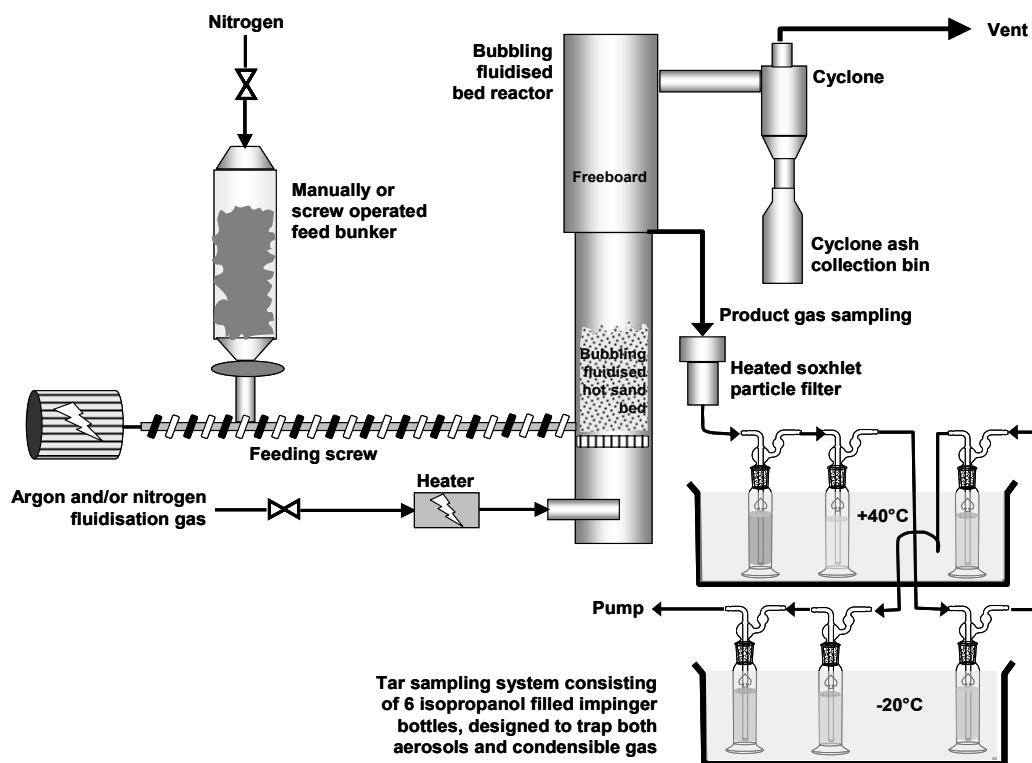


Figure 3 - Schematic of the bubbling fluidised bed test rig.

RESULTS AND DISCUSSION

CHEMICAL ANALYSIS OF THE FEEDSTOCKS

Table 1 contains the results of the chemical analysis of the selected feedstocks.

Table 1 – Biochemical, proximate, ultimate and ash elements analysis results for the feedstocks used in this study.

Parameter	Unit	Beech ¹	Poplar ²	Spruce ³	Wheat straw ⁴
Hemicellulose	wt%, d.b.	28.3*	18.3	20.5	26.8
Cellulose	wt%, d.b.	41.2*	39.4	38.8	35.8
Extractives	wt%, d.b.	2.3*	3.6	3.2	10.9
Lignin	wt%, d.b.	22.2*	24.8	26.4	21.7
Ash(550)	wt%, d.b.	0.72	1.05	0.17	8.32
Ash(815)	wt%, d.b.	0.48	0.83	ND	7.58
H ₂ O	wt%, a.r.	~ 10	~ 54	~ 7	~ 8
Volatiles	wt%, d.b.	84	84	85	73
Cl	mg/kg, d.b.	19	25	36	5209
HHV	kJ/g, d.b.	18.4	18.8	19.2	17.6
C	wt%, d.b.	46.1	47.4	47.2	43.8
H	wt%, d.b.	5.99	6.06	6.19	5.4
N	wt%, d.b.	<0.05	<0.05	<0.05	0.2
O	wt%, d.b.	45.6	45.8	46.4	41.7
Al	mg/kg, d.b.	11.5	3.31	39.8	71.7
Ba	mg/kg, d.b.	14.0	4.66	10.2	55.5
Ca	mg/kg, d.b.	1795	2554	767	1723
Co	mg/kg, d.b.	126	37.3	24.2	2.0
Fe	mg/kg, d.b.	15.6	22.0	35.1	61.8
K	mg/kg, d.b.	1214	1597	346	13629
Mg	mg/kg, d.b.	325	418	113	842
Mn	mg/kg, d.b.	42.4	7.12	158	27.2
Na	mg/kg, d.b.	7.56	233	10.2	36.9
P	mg/kg, d.b.	68	37.7	35	372
S	mg/kg, d.b.	120	154	57.2	570
Si	mg/kg, d.b.	65.5	27.7	95.6	24110
Sr	mg/kg, d.b.	3.83	9.01	3.32	49.3
Zn	mg/kg, d.b.	3.07	21.78	14.5	6.2

* Values taken from literature (Fengel and Wegener, 2003), d.b. = dry base, ND = not determined, HHV = higher heating value 1. Beech (*Fagus spec.*), 2. Mixture of European poplar species (*Populus*) 3. European spruce (*Picea abies*), 4. Spanish wheat straw

The main difference is the much higher ash and extractives content in the straw compared to the woody biomass samples. Particularly, the amounts of chlorine, sulphur, calcium, potassium and silicon are high. This is expected to have a large effect on its thermal degradation behaviour under pyrolysis conditions. Especially alkali metals are known to catalyze the thermal breakdown of carbohydrates (Evans and Milne, 1987; Nowakowski et al., 2007).

AQUATHERMOLYSIS

Aquathermolysis experiments with beech, poplar, spruce and straw were conducted at 200°C reaction temperature and 30 minutes reaction time to study the effect of hot compressed water treatment on the removal and conversion of hemicellulose. The composition of the aqueous filtrate from the aquathermolysis experiments was analysed by GC/MS and HPLC. The fresh dried feedstocks and the dried aquathermolysed residues were compared using elemental (ICP), thermogravimetric and ¹³C solid-state NMR analyses.

Aquathermolysis of beech, poplar, spruce and straw at 200°C

The reaction conditions for the aquathermolysis experiments were determined from the results of a series of screening tests with beech wood chips in the range of 160°C - 230°C. A reaction temperature of 200°C-210°C was found to give the highest yield of furfural. The results are presented in Figure 4 that serves as a representative example for the other feedstocks. The effect of reaction time appeared to be less pronounced in the range of 15 – 60 minutes (not shown). A time of 30 minutes was chosen for all further experiments.

From Figure 4 it is obvious that both the yields of hydroxymethylfurfural (HMF) and furfural increase strongly above 190°C. Furfural is predominantly formed from the hemicellulose C₅-sugars. HMF is a degradation product of C₆-sugars that also occur in the hemicellulose. Above 220°C the HMF yield seems to level off, indicating that most of the hemicellulose-derived C₆-sugars have been converted before the onset of any significant HMF formation from cellulose-derived glucose. At temperatures above 230°C, cellulose progressively degrades in hot pressurised water (Garrote et al., 1999). To achieve a high furfural yield with limited decomposition of cellulose, a reaction temperature of 200°C has been chosen for further experiments. Table 2 presents the results of the experiments with beech, poplar, spruce and straw. For all feedstocks the mass balance closes within 5 % (due to minor losses when transferring the contents of the autoclave to the filtration set up).

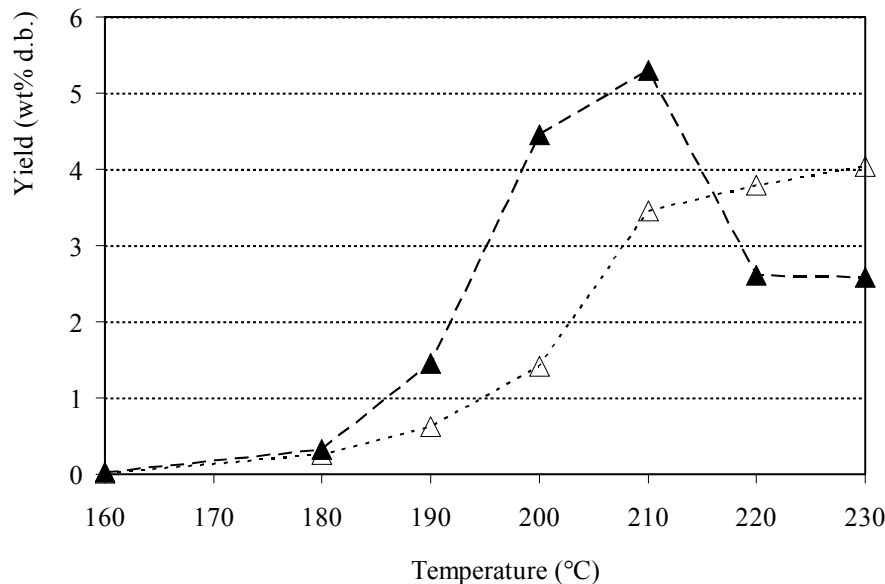


Figure 4 – Furfural (▲) and hydroxymethylfurfural (Δ) yield as function of reaction temperature for aquathermolysis of beech (30 minutes reaction time).

As can be seen from Table 2, the amount of solubilised material is - except for straw - somewhat higher (4 to 5 wt%) than the cumulative amount of hemicellulose, extractives and ash in the fresh feedstock. When it is assumed that the solubilised fraction mainly originates from hemicellulose, extractives and ash minerals, this indicates that (small) parts of the cellulose and lignin were solubilised as well. The higher content of lignin in the residue when compared to the lignin content in the feedstock (based on lignin+cellulose) and the appearance of (small) amounts of glucose and phenolic compounds in the filtrate points in this direction too. For straw, the situation is different; the solubilised fraction is less than the sum of hemicellulose, extractives and ash. It is likely that at least part of the -high-silicon containing- ash remains in the solid residue. From Table 2 it is obvious that a significant amount of the main ash metals calcium, potassium and magnesium is leached out during the aquathermolysis. Approximately 75 wt% of the calcium and more than 90 wt% of the potassium and magnesium dissolves in the hot pressurised water. For beech, the amount of calcium in the residue is higher than the amount in the fresh material. The reason for this is not clear but might be due to sample inhomogeneity and/or filtrate pollution. The solubilised amount of the feedstocks is partially accounted for by the measured organics. The amount that can not be accounted for, is attributed to reaction water, gas, leached out ash metals, and unidentified organic matter (extractives, secondary reaction products and oligomeric substances).

Table 2 – Analysis results of the fresh materials and the products from the aquathermolysis of beech, poplar, spruce and straw at 200°C, 30 min and a liquid / solid ratio (wt%) of 5 (beech) or 10 (other materials). All results are presented as weight percentages of the dry feedstock weight.

Fresh and dried solid before treatment	Beech	Poplar	Spruce	Straw
Hemicellulose (wt%, normalised)*	29.9	21.0	23.0	25.9
Cellulose (wt%, normalised)*	43.5	45.2	43.6	34.6
Extractives (wt%, normalised)*	2.4	4.1	3.6	10.5
Lignin (wt%, normalised)*	23.4	28.5	29.6	21.0
Lignin, based on the sum of lignin and cellulose (wt%)	35	39	40	38
Ash (550°C) (wt%, normalised)*	0.8	1.2	0.2	8.0
Hemicellulose + extractives + ash (wt%)	33	26	27	44
Ca (mg/kg)*	1795	2554	767	1723
K (mg/kg)*	1214	1597	346	13629
Mg (mg/kg)*	325	417	113	842
Dried residue after treatment				
Solubilised fraction (wt%)	37	31	31	38
Lignin content solid residue (wt%)	49	42	46	ND
Ca (mg/kg)	3071	652	165	ND
K (mg/kg)	104	40	15	ND
Mg (mg/kg)	33	30	8	ND
Aqueous filtrate (wt%)				
Methanol	0.53	0.30	0.26	0.12
Formic acid	0.48	0.40	0.23	1.04
Acetic acid	2.99	1.71	0.85	4.55
Hydroxyacetaldehyde	ND	ND	ND	0.00
Hydroxyacetone	0.31	0.14	0.09	0.54
Other C2-C4 oxygenates	0.12	0.12	0.08	0.14
Furfural	5.52	3.49	1.92	7.54
Hydroxymethylfurfural	1.21	0.33	2.95	0.53
Levoglucofan	0.01	0.01	0.03	0.79
Xylose	1.80	3.40	2.70	ND
Glucose	0.90	1.10	2.60	ND
Phenols	0.09	0.20	0.05	0.74
Others	2.73	1.87	1.69	2.28
Total measured organics	16.69	13.06	13.45	18.27

* Taken from Tables 1a and 1b; the original biochemical analyses results from Table 1a were normalised to 100% in order to compare them with the biochemical analyses results for the dried residues.

Thermal analysis

To illustrate the effects of the aquathermolysis on the thermal behaviour of the lignocellulosic biomass, the thermal analysis results for fresh beech and spruce as well as treated beech and spruce are compared in Figure 5.

From the figure it is clearly visible that both for beech and spruce the aquathermolysis results in the loss of the low-temperature shoulder (200-325°C), a higher weight loss rate around 350°C and in a shift of the main peak of the TGA curve at about 350°C towards higher temperatures. The low-temperature shoulder in the DTG curve for both woods can be attributed to the (thermal degradation of) hemicellulose. The maximum of the DTG curve originates from cellulose (Grønli et al., 2002). Weight loss due to the degradation of lignin is observed over a broad temperature range (200°C – 500°C) and cannot be distinguished from hemicellulose and/or cellulose degradation. Apparently, both beech and spruce have lost a significant part of the hemicellulose fraction due to the aquathermolysis process.

The shift of the main peak of the thermal analysis curves indicates that the aquathermolysed material is thermally more stable than the fresh biomass. This effect is most pronounced for spruce. The higher weight loss rate of the treated samples might be due to the higher content of cellulose and the absence of hemicellulose that normally has a structure-stabilising role in the wood.

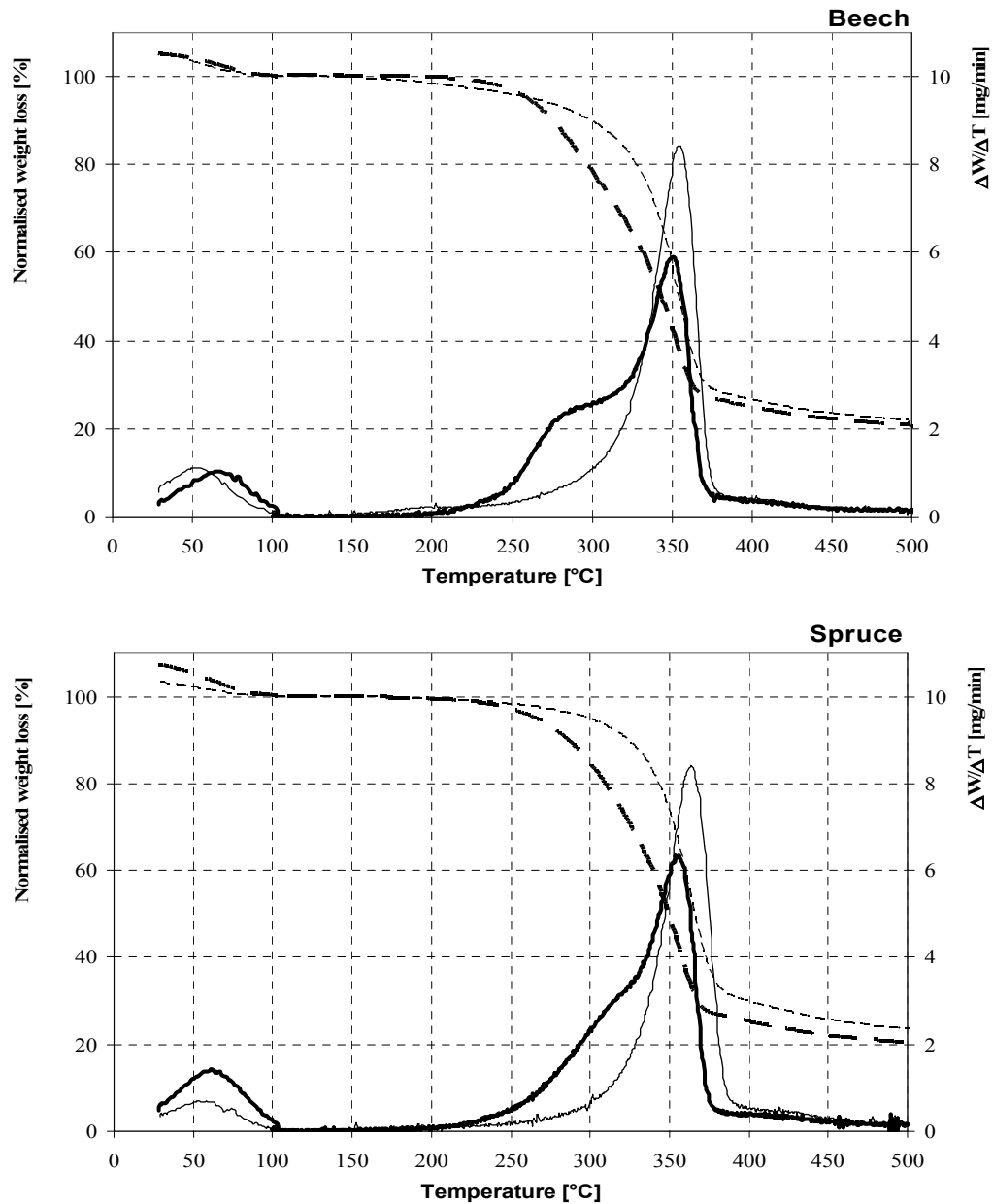


Figure 5 – Comparison of thermal analysis of beech (top) and spruce (below) before and after aquathermolysis.

- - - TGA before aquathermolysis — DTGA before aquathermolysis
 - · - · TGA after aquathermolysis — DTGA after aquathermolysis

BUBBLING FLUIDISED BED PYROLYSIS

As the second stage in the hybrid thermolysis concept, bubbling fluidised bed pyrolysis was applied to the solid residues from the aquathermolysis to investigate type and yield of the main products from the (fast) thermal degradation of the aquathermolysed feedstock at a reactor temperature of 350°C. Emphasis was on the combined formation of furfural, hydroxymethylfurfural and levoglucosan from the hybrid aquathermolysis – pyrolysis process as compared to the formation of these components from a direct pyrolysis of the unmodified feedstocks.

According to a CEN accredited and approved Technical Specification for the measurement of tar in biomass gasification, the volatile pyrolysis products (permanent and condensable gases (including water) and aerosols) were measured by sampling 10% - 20% (v/v) of the bulk product gas stream from the reactor, using isopropanol filled impinger bottles and subsequent off-line analysis by GC/MS (Van de Kamp et al., 2006, de Wild et al., 2008). The tar measurement method was designed to efficiently trap both condensable gases and aerosols. In general its collection efficiency is better than 99%.

Table 3 gives a breakdown of the major degradation products from the aquathermolysis, the subsequent pyrolysis of the aquathermolysed residue and the direct pyrolysis of beech, poplar, spruce and wheat straw. Most mass balances close within 10% - 15%. The deviations from 100% are caused by experimental errors and the amount of aquathermolysis reaction water that was not determined. Yield results from the pyrolysis experiments are calculated from the analysis results of a relatively small part of the total product. Due to sample flow variations, the average error is estimated to be around 10 wt%.

In general, Table 3 shows that the combination of aquathermolysis and pyrolysis produces more organics and less char when compared to the direct pyrolysis. The amount of liberated permanent gases from the aquathermolysis – pyrolysis combination is probably also lower when compared to the amount of gas from the direct pyrolysis. This was deduced from the observation of the small residual overpressure (1 – 3 bars) after the aquathermolysis experiments.

Figure 6 presents the yields of the main thermal degradation products from the direct pyrolysis at 350°C and the two-stage aquathermolysis (200°C) - pyrolysis (350°C) experiments with the beech, poplar, spruce and straw feedstocks. The presented yields present 35% - 60% of all detected components. The Figure shows that the combination aquathermolysis (A) – pyrolysis (P) generates higher yields for the target chemicals furfural, hydroxymethylfurfural (HMF) and levoglucosan than via direct pyrolysis (P). Yields of 7-11 wt% have been determined for levoglucosan, relatively independent of the feedstock.

The lower yield of levoglucosan from straw might be attributed to its higher content of alkali ash metals. Furfural is another target chemical that has been obtained in significant yields (up to 8 wt% from straw).

Differences between the furfural yields from the different feedstocks are probably correlated with the hemicellulose C₅ - sugar content that is highest for straw and beech and lowest for spruce. Aquathermolysis of spruce yields a significant amount of HMF (3 wt%) that probably originates from the dehydration of the hemicellulose C₆ - sugars mannose, galactose and glucose. Phenols are undesired products in the final product mixture because of anticipated difficulties with separating them from target species like furfural. Their yields are generally low, in between 1%-2%. Except for straw, the yield of phenols from aquathermolysis – pyrolysis seems to be smaller than the yield of phenols from the direct pyrolysis. An explanation might be the formation of recondensed lignin-like structures during the aquathermolysis. It is likely that this material is thermally more stable than the native lignin. This has also been found in NMR investigations described in the next section.

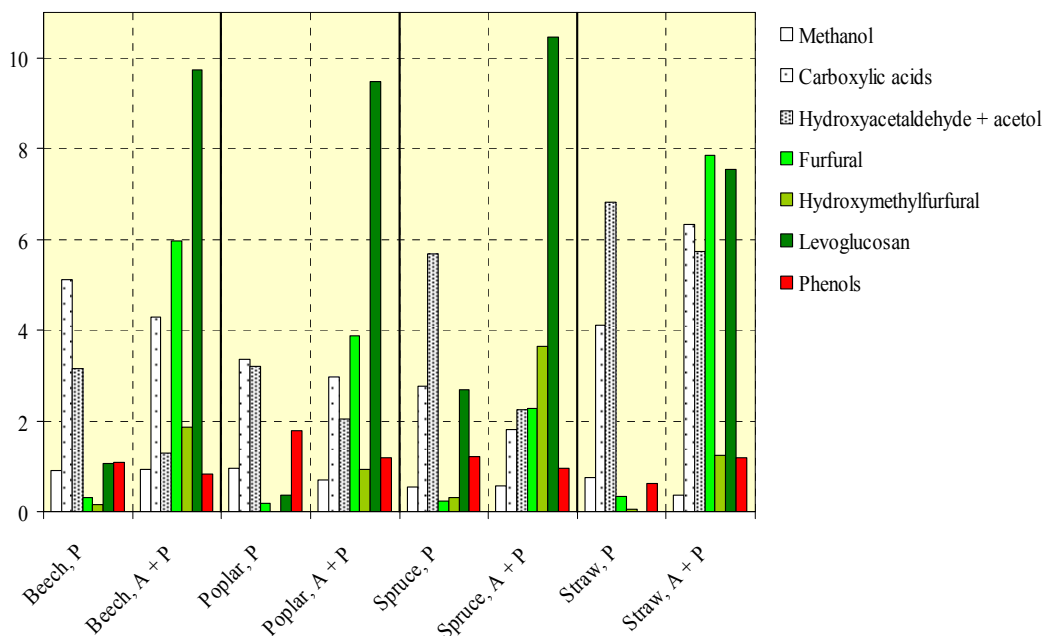


Figure 6 – Product yields (in wt% based on the dry weight of the fresh unmodified material) from the pyrolysis and combined aquathermolysis – pyrolysis of beech, poplar, spruce and straw. *P* = Pyrolysis, *A* = Aquathermolysis.

Table 3 – Breakdown of the product composition from aquathermolysis and pyrolysis experiments

Thermolysis products ¹	Beech				Poplar				Spruce				Straw			
	A ²	P ³	A+P	DP ⁴	A	P	A+P	DP	A	P	A+P	DP	A	P	A+P	DP
Permanent gases	ND	4.5	ND	16.7	ND	9.1	ND	16.7	ND	4.6	ND	9.3	ND	5.8	ND	14.6
CO	ND	2.5	ND	11.6	ND	5.7	ND	10.1	ND	2.4	ND	4.9	ND	3.8	ND	9.6
CO ₂	ND	2.0	ND	5.0	ND	3.0	ND	6.0	ND	2.1	ND	4.3	ND	2.0	ND	5.0
CH ₄	ND	0.0	ND	0.1	ND	0.4	ND	0.7	ND	0.1	ND	0.1	ND	0.0	ND	0.0
Condensables	ND	40.6	ND	46.9	ND	62.5	ND	45.8	ND	44.7	ND	54.4	ND	52.7	ND	78.7
Water	ND	18.1	ND	18.4	ND	38.0	ND	17.6	ND	18.2	ND	18.6	ND	14.4	ND	41.4
Organics	19.1	22.5	41.6	28.5	16.4	24.5	40.9	28.3	16.6	26.5	43.1	35.8	29.3	38.3	67.6	37.3
Methanol	0.50	0.42	0.92	0.90	0.30	0.39	0.69	0.95	0.30	0.26	0.56	0.55	0.12	0.24	0.36	0.75
Carboxylic acids ⁵	3.47	0.79	4.28	5.10	2.1	0.86	2.96	3.34	1.1	0.72	1.82	2.77	5.6	0.75	6.35	4.11
HAA ⁶ +acetol	0.31	1.30	1.61	3.16	0.1	2.03	2.13	3.20	0.1	2.25	2.35	5.67	0.5	5.74	6.24	6.81
Furfural	5.52	0.25	5.77	0.31	3.49	0.28	3.77	0.17	1.92	0.28	2.2	0.22	7.54	0.25	7.79	0.33
HMF ⁷	1.21	0.65	1.86	0.16	0.33	0.62	0.95	0.00	2.95	0.63	3.58	0.31	0.53	0.71	1.24	0.05
Levoglucosan	0.01	9.73	9.74	1.07	0.01	9.49	9.5	0.36	0.03	10.5	10.5	2.68	0.79	7.53	8.32	0.00
Phenols ⁸	0.09	0.75	0.84	1.09	0.20	0.98	1.18	1.77	0.05	0.92	0.97	1.21	0.74	0.45	1.19	0.62
Others ⁹	7.99	8.61	16.6	16.7	9.87	9.85	19.7	18.5	10.2	10.9	21.1	22.4	13.5	22.6	36.1	24.6
Solid residue	63	17.6	17.6	22.3	69	5.98	5.98	25.3	69	18.0	18.0	26.4	62	5.2	5.2	21.7
Mass balance	ND	100	82	86	ND	113	94	88	ND	97	84	90	ND	103	93	115

- All yields are in wt% and based on the dry input weight of the fresh, unmodified feedstocks
- A = Aquathermolysis
- P = Pyrolysis of the aquathermolysed residue
- DP = Direct Pyrolysis of the fresh, dried feedstock
- Carboxylic acids = sum of acetic acid and formic acid
- HAA = HydroxyAcetAldehyde
- HMF = HydroxyMethylFurfural
- Phenols = sum of Methoxyphenol, 4-Methylguaiacol, Phenol, 4-Ethylguaiacol, P-cresol, Eugenol, 4-Ethylphenol, 4-Propylphenol, 2,6-Dimethoxyphenol, Isoeugenol, 4-Methylsyringol, 2,6-dimethoxy-4-(2-propenyl)-phenol, Vanilline, Aceto-vanillone, Pyrocatechol, Syringaldehyde, 4-hydroxybenzaldehyde, 2-Methoxyhydroquinone, 4-Hydroxybenzylalcohol, Acetosyringone, 4-Hydroxy acetophenone, Hydroquinone, Resorcinol and Coniferylalcohol
- Others = several organic substances including glucose, xylose (see Table 1a) and extractives (Table 2). The latter are not measured but are expected to dissolve completely during the aquathermolysis

A high yield of the desired chemicals in the product mixtures from the aquathermolysis and the pyrolysis stages is important to facilitate their efficient separation. Figure 7 presents the yields of the major products / product groups from the aquathermolysis and the subsequent pyrolysis of beech, poplar, spruce and straw. In addition, a comparison with the product yields from a direct pyrolysis of the unmodified, dried material is made. From Figure 7 it is obvious that in all cases the staged approach of a hot pressurised water treatment followed by a bubbling fluidised bed pyrolysis results in higher yields for the selected chemicals when compared to direct pyrolysis.

For straw it is remarkable that both its direct pyrolysis and the pyrolysis of the residue from the aquathermolysis generates high amounts of hydroxyacetaldehyde and acetol. This can be ascribed to the relatively high content of alkalies, especially potassium, in the feedstock (see Table 1 for the content in fresh straw). It is known that these metals catalyse secondary degradation of the primary pyrolysis products from the carbohydrates (Scott et al., 1995). Apparently, the aquathermolysis treatment of straw does not leach out as much of the alkalies when compared to the other feedstocks.

Another interesting observation is the fact that – for all the tested feedstocks - hydroxyacetaldehyde and acetol are virtually absent in the product mixture from the aquathermolysis. In the hot liquid water environment the dissolution of the metal ions from the biomass probably prevails above their catalytic cracking effect. This might implicate that in a ‘dry’ pyrolysis of alkali-metal containing biomass, the secondary catalytic cracking takes place in and/or on the surface of the pyrolysing biomass because of mass transfer limitations of the devolatilising carbohydrate fragments. The alkali metals do not volatilise from the biomass under the relatively mild temperature conditions.

The hybrid aquathermolysis – pyrolysis concept results in higher selectivities for furfural and levoglucosan when compared to the direct pyrolysis approach as is illustrated in Table 4 for the four feedstocks. Selectivity is defined as the mass fraction of the chemical in the detected organic product mixture.

Table 4 – Selectivities for the production of furfural and levoglucosan via aquathermolysis – pyrolysis of biomass compared to the product selectivities in a direct pyrolysis approach

	Furfural			Levoglucosan		
	Aqua-thermolysis	Subsequent pyrolysis	Direct pyrolysis	Aqua-thermolysis	Subsequent pyrolysis	Direct pyrolysis
Beech	29	1	1	0	43	4
Poplar	21	1	1	0	39	1
Spruce	12	1	1	0	39	7
Straw	26	1	1	3	20	0

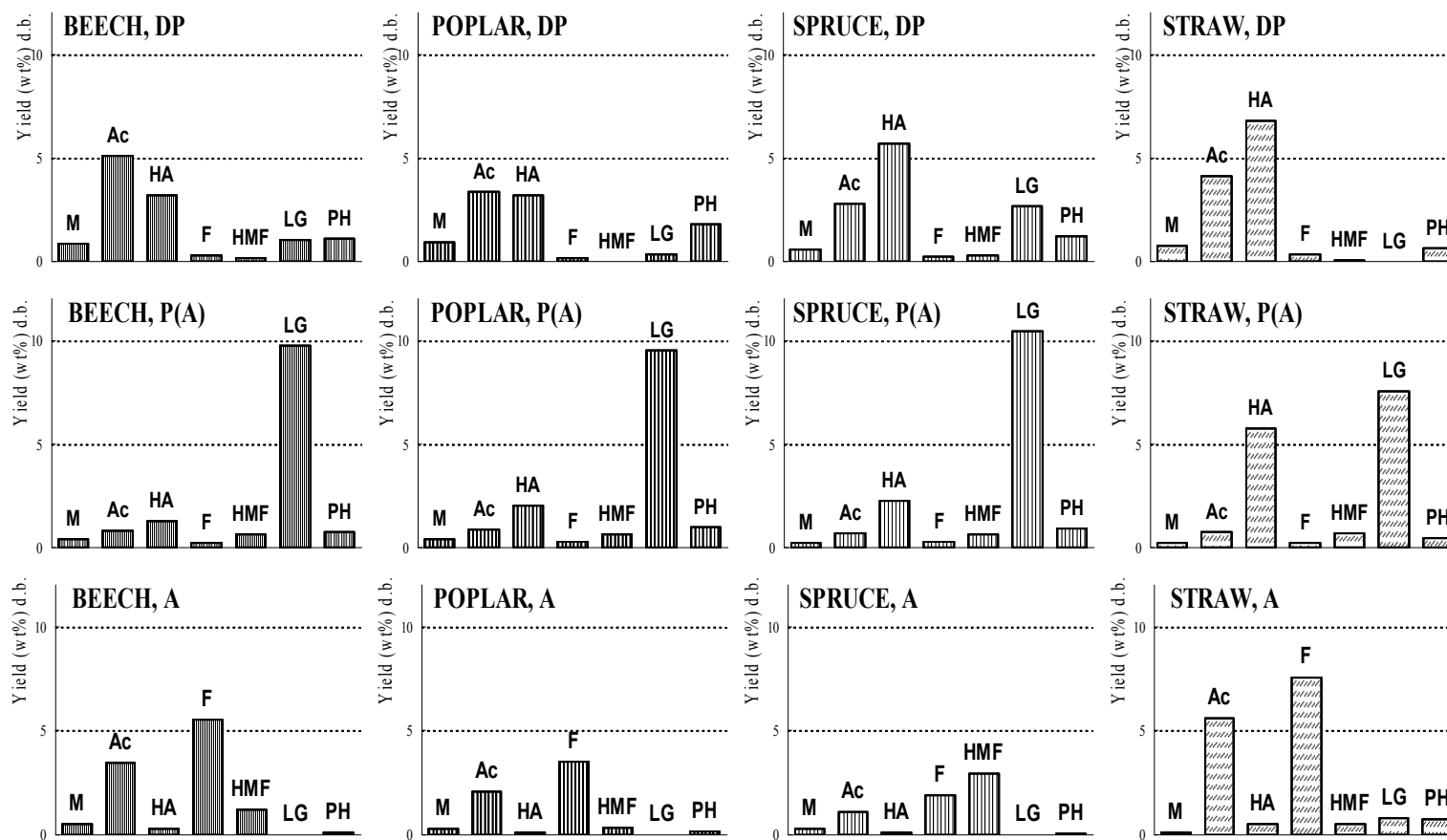


Figure 7 – Product yields from the aquathermolysis (A) – pyrolysis (P) concept compared with direct pyrolysis (DP) ($P(A)$ = pyrolysis of the aquathermolysed residue, M = methanol, Ac = acetic acid + formic acid, HA = hydroxyacetaldehyde + acetol, F = furfural, HMF = hydroxymethylfurfural, LG = levoglucosan, PH = sum of phenolic compounds (see Table 3).

^{13}C CP/MAS NMR STRUCTURAL CHARACTERISATION

The effects of the aquathermolysis and pyrolysis on the (chemical) structure of beech, spruce and poplar were studied using ^{13}C , cross-polarization, magic-angle-spinning (CP/MAS) NMR methods. With solid-state ^{13}C -NMR heat-induced structural changes in the wood samples can be non-destructively investigated on a molecular level by measuring (changes in) magnetic characteristics of the carbon-13 isotope (natural abundance approx. 1%).

For poplar and spruce, four different pretreated samples were measured: dried wood (sawdust, <0.25 mm diameter) (sample 0W), the product after aquathermolysis at 200 °C (sample 1H), the product after pyrolysis of the wood at 350 °C (sample 2P) and the product of pyrolysis of the aquathermolysed sample (sample 3HP). Figure 8 presents an overview of the samples and their treatment. The sawdust particles were sufficiently small to be tightly packed in the NMR rotor, the other samples were ground before they were measured.

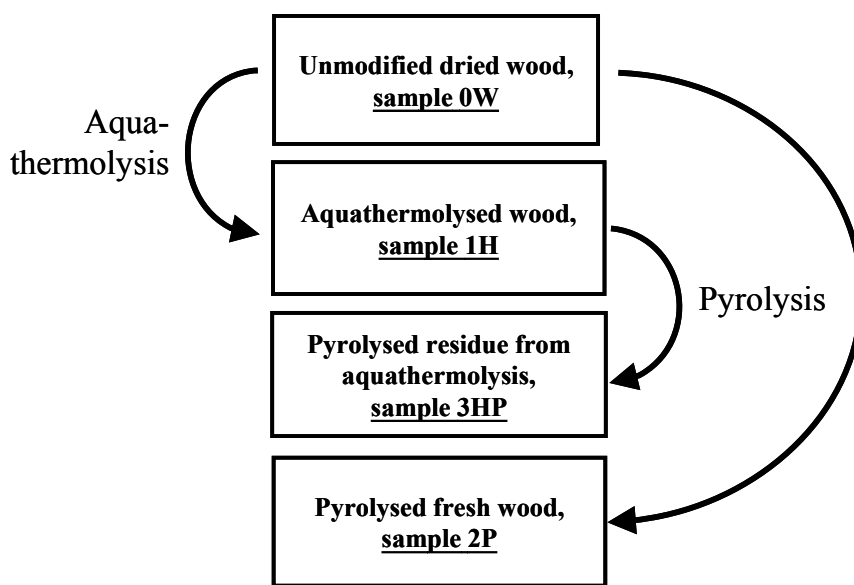


Figure 8 – NMR characterised wood samples.

An overview of chemical shifts of cellulose, hemicellulose and lignin groups can be found in Table 5 (Fengel and Wegener, 2003; Gilardi et al., 1995; Bardet et al., 2002). Figure 9 shows which carbon in cellulose, hemicellulose and lignin are represented by which numbers and Greek letters.

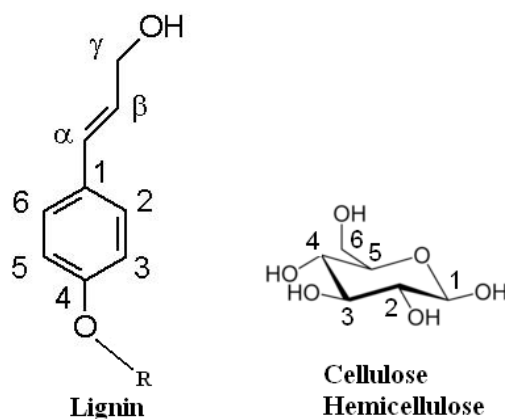


Figure 9 – Representation of carbons by numbers.

Table 5 – Peak assignment in ^{13}C CP/MAS spectra of wood.

Peak location (ppm)	code in spectrum	Assignment
21	H1	hemicellulose acetyl methyl
56	L1	lignin methoxyl carbon (OCH_3)
62	L2	lignin C_γ
63	C1	cellulose C-6 (amorphous)
63-66	H2	hemicellulose C-6
66	C2	cellulose C-6 (crystalline)
70-80	H3	hemicellulose C-2/3/5
72	C3	cellulose C-2/3/5
75	C4; L3	cellulose C-2/3/5, lignin C_α
84	C5; L4	cellulose C-4 (amorphous), lignin C_β
84-89	H4	hemicellulose C-4
89	C6	cellulose C-4 (crystalline)
103	H5	hemicellulose C-1
105	C7	cellulose C-1
106-140	L5	lignin aromatic C
147	L6	lignin C-4 unetherified
153	L7	lignin C-4 etherified
173	H6	hemicellulose acetyl carboxyl

Comparison of NMR spectra of all samples for poplar

In Figure 10, ^{13}C CP/MAS spectra of all poplar samples are shown. The spectra of unmodified wood (0W) and aquathermolysed wood (1H) are very similar, with a higher resolution for 1H. The δ 21 ppm signal of the CH_3 -acetyl carbons of hemicellulose is not observed in the spectrum of 1H.

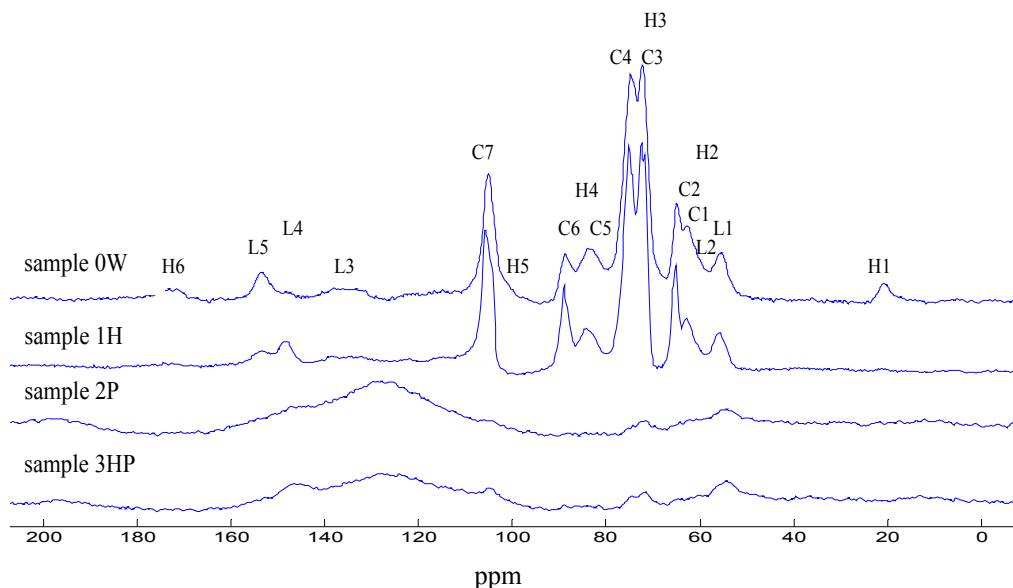


Figure 10 - ^{13}C NMR CP/MAS spectra of all poplar samples. Sample 0W = unmodified dried wood, sample 1H = aquathermolysed wood, sample 2P = pyrolysed fresh wood, sample 3HP = pyrolysed residue from the aquathermolysis.

H1	hemicellulose acetyl methyl
L1	lignin methoxyl carbon (OCH_3)
L2	lignin C_γ
C1	cellulose C-6 (amorphous)
H2	hemicellulose C-6
C2	cellulose C-6 (crystalline)
H3	hemicellulose C-2/3/5
C3	cellulose C-2/3/5
C4; L3	cellulose C-2/3/5, lignin C_α
C5; L4	cellulose C-4 (amorphous), lignin C_β
H4	hemicellulose C-4
C6	cellulose C-4 (crystalline)
H5	hemicellulose C-1
C7	cellulose C-1
L5	lignin aromatic C
L6	lignin C-4 unetherified
L7	lignin C-4 etherified
H6	hemicellulose acetyl carboxyl

This means that hemicellulose is either absent in sample 1H or present in a deacetylated form. The disappearance of the weak $\text{C}=\text{O}$ signal at δ 174 ppm also indicates a lower acetylated hemicellulose content.

Because of its amorphous character, hemicellulose gives rise to broad signals that are very close to the sharper cellulose signals due to the strong similarities of the cellulose and hemicellulose structures. So hemicellulose merely causes a broadening of the cellulose signals. The higher resolution of the spectrum of 1H with respect to 0W thus suggests that the hemicellulose content is actually lower and that hemicellulose is not just deacetylated.

The peaks of crystalline cellulose are shifted with respect to the peaks of amorphous cellulose (e.g. δ 89-84 ppm, δ 72-75 ppm and δ 65-63 ppm). Because the crystalline form is more ordered, this form gives rise to narrower peaks. The relative increase in intensity of the narrow peaks could be caused by the relative increase of crystalline cellulose compared to amorphous cellulose.

According to these results, aquathermolysis might increase the crystallinity of cellulose. In the spectrum of 1H, δ 72 ppm and δ 75 ppm signals are split in two.

Another difference between the spectra of 0W and 1H is the lower δ 153 ppm signal and the emergence of a δ 147 ppm signal in sample 1H when compared to 0W. This indicates the cleavage of lignin ether bonds. The δ 153 ppm signal originates from lignin units interconnected via (β -O-4) ether bonds, while the δ 147 ppm peak is attributed to the same carbons in unetherified lignin. From the intensity of the signals in both spectra, it can be concluded that aquathermolysis cleaves at least a part of the ether linkages between lignin units. The most striking features of the spectrum of sample 2P are the lack of resolution and a broad signal between δ 100 ppm and δ 160 ppm. This peak indicates the presence of lignin-derived aromatics. There is a small shoulder at about δ 145 ppm, which was assigned to furan (a degradation product of (hemi)cellulose) (Wooten et al., 2001) but might also be a signal from unetherified lignin.

The disappearance of distinct peaks between δ 60 ppm and δ 105 ppm indicates that most cellulose has been converted, but some of it is still intact. Comparing the spectra of samples 2P and 3HP, it is clear that the latter shows more different signals. The cellulose signals at δ 70-75 ppm and δ 105 ppm are stronger in sample 3HP than in sample 2P. This suggests that cellulose is stabilized by the hot pressurised water treatment prior to pyrolysis. Also, the δ 145 ppm signal has a higher intensity in sample 3HP than in sample 2P. If this signal is caused by unetherified lignin, this means that more lignin has stayed intact during pyrolysis, which suggests that lignin is largely stabilized by aquathermolysis treatment. If furan gives rise to this signal, it indicates that more of the degraded cellulose formed furan. A very small, broad signal appears between δ 20 ppm and δ 50 ppm. This indicates the presence of aliphatic carbons, which could be fragments of cellulose or lignin.

Comparison of NMR spectra of all samples for spruce

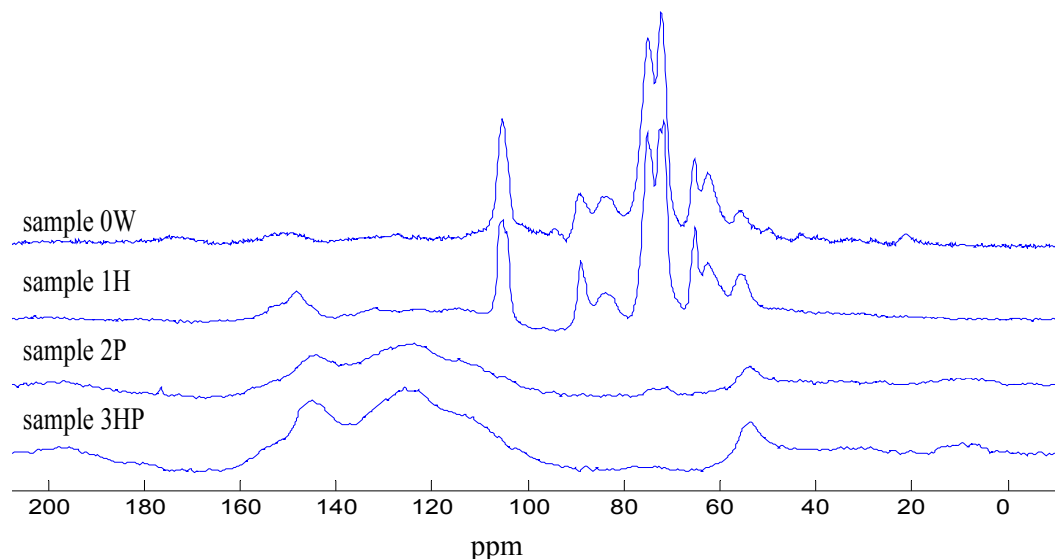


Figure 11 - ^{13}C NMR CP/MAS spectra of all spruce samples. Sample 0W = unmodified dried wood, sample 1H = aquathermolysed wood, sample 2P = pyrolysed fresh wood, sample 3HP = pyrolysed residue from the aquathermolysis.

CP/MAS spectra of samples of spruce are shown in Figure 11. The hemicellulose acetyl signals at δ 21 and δ 174 ppm, present in the spectrum of sample 0W, are absent in the spectrum of sample 1H, indicating that aquathermolysis breaks down the acetyl bonds in hemicellulose or the hemicellulose itself. The peaks of crystalline cellulose (δ 66 and δ 89 ppm) become higher in intensity compared to the amorphous cellulose signals (δ 63 and δ 84 ppm) when the wood has undergone treatment in hot pressurised water. The δ 72 and δ 75 ppm signals are weakly split in two. The signal of unetherified lignin at δ 147 ppm is more prominent in the spectrum of sample 1H than it is in sample 0W. The spectrum of sample 3HP contains more different signals than that of sample 2P. All signals present originate from lignin. The broad signal at δ 100-160 ppm in both spectra is caused by aromatic carbons in lignin. The peak at δ 56 ppm is caused by lignin methoxy carbons, the peak at δ 145 ppm by unetherified lignin or furan.

Results for beech wood

A NMR study with fresh beech wood, aquathermolysed beech and its pyrolysed residue give similar results as found previously for poplar and spruce. After

aquathermolysis at 200°C most hemicellulose is dissolved, while cellulose and lignin are largely retained, despite the fact that a large portion of the β -O-4 linkages in the lignin was hydrolysed. The NMR results for the pyrolysed material show that cellulose and the remaining hemicellulose had been completely converted, whereas part of the lignin appeared to be intact.

CONCLUDING REMARKS

Experimental studies with beech, poplar and spruce wood and wheat straw have indicated the potential of a hybrid thermolysis option to valorise lignocellulosic biomass. Aquathermolysis (treatment with hot pressurised water) in an autoclave at 200°C predominantly yields furfural and/or hydroxymethylfurfural, mainly from the hemicellulose fraction of the biomass. In a subsequent bubbling fluidised bed pyrolysis of the aquathermolysed residue at 350°C, the cellulose fraction is selectively depolymerised to levoglucosan, a promising chemical building block for a variety of products. Up to 8 wt% (d.b.) of furfural, 3 wt% (d.b.) of hydroxymethylfurfural and 11 wt% (d.b.) of levoglucosan were obtained in the hybrid thermolysis concept that demonstrates its potential as a selective route to achieve good yields of a limited number of chemicals.

To investigate the relations between the chemical changes in the biomass during the course of the hybrid process and the chemical products that are formed, a ^{13}C -solid state NMR studies was conducted. It was shown that aquathermolysis of beech, poplar and spruce wood causes hemicellulose to degrade and disappear from the wood samples. Although lignin ether bonds are broken, the lignin structure appears hardly affected by the pressurised hot water treatment. Cellulose is also retained and seems to become more crystalline, probably due to ordering of amorphous cellulose as the samples are cooled down after the treatment with hot pressurised water. This NMR results are in agreement with results from thermogravimetric analyses.

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