COST Action FP 0901
“Analytical techniques for biorefineries”
March 27 – 28, 2013

University of Natural Resources and Life Sciences, Vienna

UFT Tulln, Konrad-Lorenz-Str. 24 - 3430 Tulln – Austria

COST Action FP 0901
“Analytical techniques for biorefineries”
Program

UFT Tulln, Konrad-Lorenz-Str. 24 - 3430 Tulln - Austria

Tuesday, March 27th, 2013

08:30-9:00	• Registration • Adoption of the agenda • Local information	**Chair: S. Willför** **Host: A. Potthast**
Session 1		
09:00-12:00	• **S. Willför**: General items • **M.Tenkanen**: Novel specific antibody for glucopyranosyl uronic acid side groups in xylans • **V. Žepič**: Influence of drying conditions on thermal and morphological behavior of microfibrilated and nanofibrilated cellulose • **F. Bouxin**: Organosolv pretreatment of Sitka Spruce Sawdust	**Chair: S. Willför**
12:00-13:30	*LUNCH and Posters*	
Session 2 – STSM Reports		
13:30-15:00	• **J. Milanović**: Determination of functional groups in selective oxidized cellulose fibers by combining group-selective fluorescence labeling with GPC • **V. Vek**: Extractives of wound-associated wood in beech (*Fagus sylvatica*) • **B. Stefanović**: The role of fatty acids in the wrinkle reduction in cellulosic fabrics	**Chair: M. Tenkanen**
15:00-15:30	*COFFEE BREAK and Posters*	

Session 3		
15:30-16:30	- **F. Melone**: Selective oxidative functionalization of lignins - **A. Vig**: Comparative study of differently treated (cooked and bleached) industrial grass and straw fibres respectively by raman and energy-dispersive x-ray spectroscopy	**Chair: P. Oven**
16:30-16:45	*COFFEE BREAK*	
16:45-17:30	**WGs 1, 2 and 3 meetings in parallel, chaired by WG leaders**	
19:30	*JOINT DINNER at Heurigen "Zur Reblaus"*	

Wednesday, March 28th, 2013

Session 4		
9:00-11:30	- **B. Sithole**: Evidence for the occurrence of polymerized wood resin in pulp and paper samples from various analytical techniques - **I. Tumen**: Chemical constituents of naturally decayed beech (*Fagus orientalis Lipsky*) - **M. Orlandi**: GPC Monitoring of molecular weight distributions and LCCs of lignocellulosic materials during steam-explosion pretreatment - **A. Heigenmoser**: Investigation of biopolymers by means of multifunctional PYROLYSIS-GC/MS	**Chair: C. Crestini**
11:30-12:30	*LUNCH*	
12:30-14:15	Final Discussion Distribution of Round Robin samples Visit to UFT-Laboratories	**Chair: A. Potthast**
14:15-17:00	Visit of LOISIUM in Langenlois	

ORAL PRESENTATIONS

NOVEL SPECIFIC ANTIBODY FOR GLUCOPYRANOSYL URONIC ACID SIDE GROUPS IN XYLANS

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ABSTRACT

The main hemicelluloses in monocots and in the secondary cell walls of dicots are xylans which are composed of β-(1→4) linked D-xylopyranosyl (Xyl*p*) residues. Xylans can have different substituents depending on the origin. In monocots the backbone is mostly substituted with L-arabinofuranosyl (Ara*f*) residues through α-(1→2) and/or α(1→3) linkages. Ara*f* substituents can be further esterified with *p*-coumaric or ferulic acids at 5-*O* position. In addition, vegetative tissues in monocots contain α-(1→2)-linked D-glucopyranosyl uronic acid (GlcA), which is partly methylated at 4-*O* position (meGlcA) (Aspinall 1959). In dicots xylan is substituted with α-(1→2)-linked GlcA and/or meGlcA. The most abundant substituents, however, are acetyl groups, since 50-70% of Xyl*p* residues are acetylated at 2-*O* and/or 3-*O* positions (Aspinall 1959, Timell 1967). Acetyl groups are present in both monocot and dicot xylans, especially in the lignified parts of the plant. In contrast, xylan in gymnosperms is not acetylated but carries α-(1→3)-linked Ara*f* and α-(1→2)-linked meGlcA (Timell 1967).

An *in situ* visualisation of the localisation of cell wall components can be obtained using antibodies or carbohydrate binding modules as probes. A collection of monoclonal antibodies against xylans exist (McCartney et al. 2005, Guillon et al. 2004; Pattathil et al. 2010). However, they all recognize xylan backbone. The more detailed structural information would require side-group specific antibodies. We have recently succeeded in producing a novel monoclonal antibody which specifically recognizes meGlcA / GlcA substituents in xylan and has no cross-reactivity with linear or Ara*f*-substituted xylans. This required that the structure used for immunization had, in addition to meGlcA, only a single β-(1→4)-linked xylopyranosyl residue. The antibody labelled plant cell walls, but in most tissues an alkaline pretreatment was needed for antibody binding. The need for removed of acetyl groups from xylan indicated that the vicinity of meGlcA substituents is acetylated. The novel labelling patterns were observed in the xylem of tree species suggested that differences within the cell wall exist both in acetylation degree and in glucopyranosyl uronic acid content. The antibody characterisation as well as labelling of various plant tissues will be presented in the current paper.

ACKNOWLEDGEMENTS

This work was funded by the Academy of Finland (grant number 124281) and INRA, France, through EU ERA-Net programme WoodWisdom-Net2. Henriette L Petersen and William GT Willats from Copenhagen University, Denmark are thanked for help in the antibody characterization by glycan microarrays.

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INFLUENCE OF DRYING CONDITIONS ON THERMAL AND MORPHOLOGICAL BEHAVIOR OF MICROFIBRILATED AND NANOFIBRILATED CELLULOSE

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ABSTRACT

INTRODUCTION

Micro or nanocellulose fibrils initially are in the form of a water-based suspension. If the material is subjected to dehydration process, irreversible agglomeration can occur accompanied with decrease in mechanical properties of dry cellulose fibrils (Eyholzer 2010, Peng et al. 2011, Kalia et al. 2011). In order to maintain the micro and nanoscale dimensions, the effects of various drying techniques on the thermal and morphological behaviour of the microfibrillated (MFC) and nanofibrillated (NFC) cellulose were investigated.

MATERIAL AND METHODS

Cellulose suspension was subjected to air drying, oven drying, freeze drying and spray drying. Dried material was characterized by field emission scanning electron microscopy (FE-SEM), thermogravimetrical analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction analysis (XRD) and Fourier transform infrared spectroscopy (FTIR).

RESULTS AND DISCUSSION

Air and oven drying resulted in formation of continuous fiber network and a relatively solid bulk material, while coarse and fine powder formed upon freeze and spray drying. FE-SEM revealed dense textured film of randomly arranged fibrils in air and oven dried samples. Freeze drying of MFC and NFC suspension resulted in formation of irregularly shaped agglomerates with dimensions up to 80 μm and spray drying in spherical and rod-like structures of the size up to 20 μm.

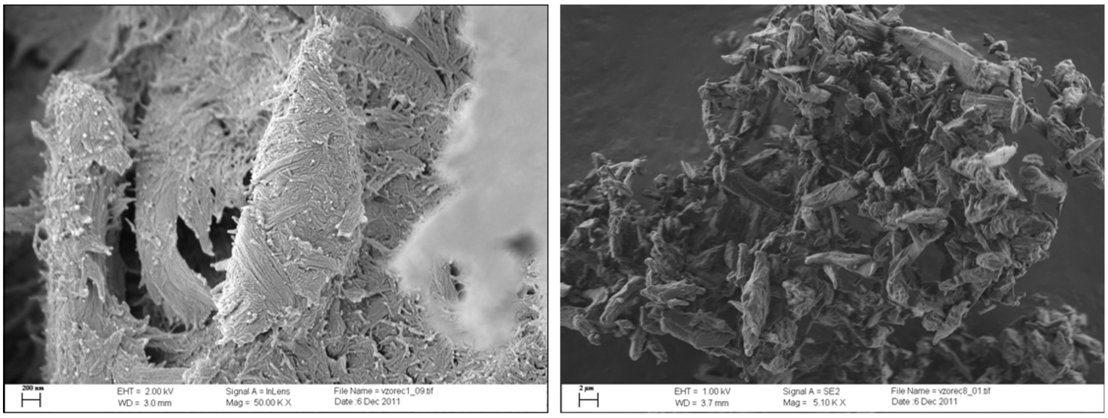

Figure 1. Morphology of air dried (left) and spray dried (right) cellulose microfibrils (MFC). FE-SEM.

Examination of dried samples by TGA and DSC showed better thermal stability of dried NFC compared to dried MFC, irrespective of drying method. Different percentage of crystalline versus amorphous phase was evaluated as a result of different drying processes applied to various type of starting material. The index of crystallinity observed by TG and DSC was compared by other analytical method such as X-Ray diffraction and FTIR spectroscopy. We assume that optimization of freeze and spray drying process would enable a potential route in generating cellulose micro and nanofibrils in powder form with targeted properties as an attractive alternative to conventional cellulose suspensions for the synthesis of bio nanocomposite materials (*cf.* Eichhorn et al. 2010, Siqueira et al. 2010).

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Organosolv pretreatment of Sitka Spruce Sawdust: Analysis of the cooking liquor

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ABSTRACT

Softwoods are not the ideal choice as starting material for biofuel production. The main reason comes from its recalcitrance toward bioconversion. However, softwoods, especially Sitka spruce, are very abundant in UK (1.5 Mha, 6 % of UK land). In 2010, the British coniferous fibre production was about 10 Mt. Timber industries generate high amount of sawdusts which can be used as starting material for the production of biofuel and high value co-products. Biorefinery of lignocellulosic materials is made up of three steps, pretreatment, saccharification/fermentation and recovery. The pretreatment, key step of the process, permits to increase the accessibility of the cellulose. Organosolv pretreatment has already been successfully employed on hardwood (Pan et al., 2006), grasses (Brosse et al., 2009; Huijgen et al., 2011) and softwood (Arato et al., 2005; Pan et al., 2005).

In our study, best organosolv cooking conditions led to a saccharification mass loss close to 90 %. As illustrated in figure 1, the pretreatment step solubilised 43 to 53 % of the starting material.

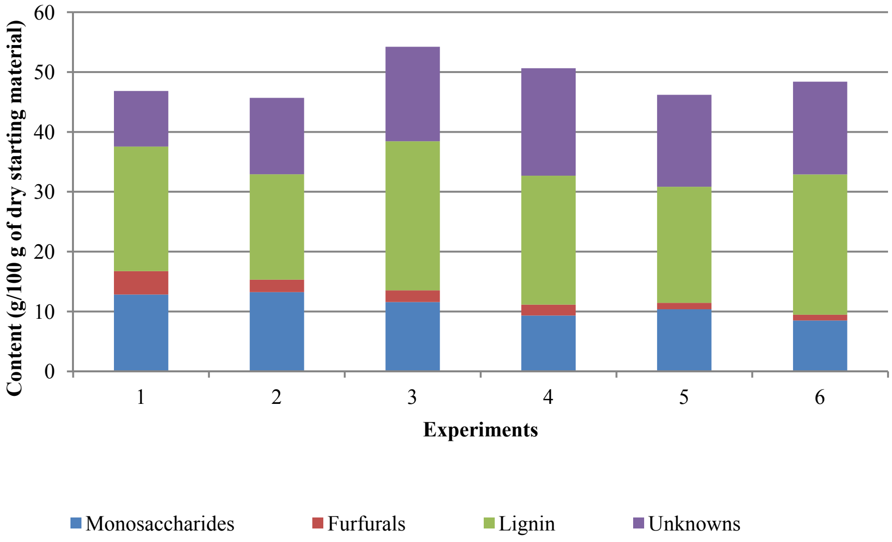

Figure 1 : Identification of the cooking mass loss content

Even if up to 50 % of the cooking mass loss is attributed to the extracted lignin, the remaining was supposed to be sugars. As illustrated in the figure 1, the preliminary analysis of the cooking liquor shown that 9 to 18% of the starting material mass loss couldn't be identified. A closer analysis of the cooking liquor has shown that high amount of ethylglycosides were produced during the cooking step.

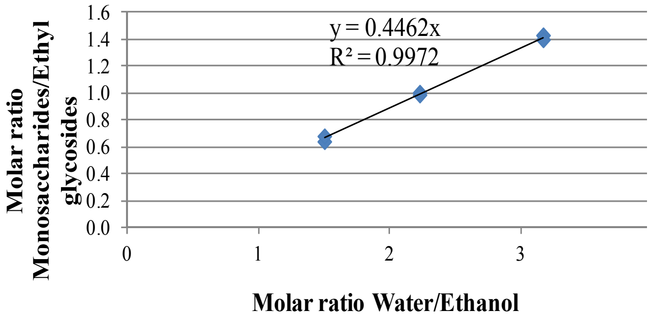

Figure2 : Correlation of the molar ratio of monosaccharides and ethylglycosides with the solvent molar ratio

As illustrated in figure 2, the molar ratio of monosaccharide/ethylglycoside is highly correlated to the molar ratio of water/ethanol. For a solvent molar ratio of 1, ethylglycosides are twice more present in the cooking liquor than monosaccharides. This could be explained by the higher stability of the ethylglycosides toward post degradation reaction.

Indeed, the furfural content slightly decrease (see figure 1, exp. 2 to 4) with the increase of the ethanol content. The furfural and HMF, generated by post-degradation of pentoses and hexoses respectively, are known to inhibit the fermentation step (Gurram et al., 2011). Exacerbate the production of ethylglycosides, which should limit the generation of furfurals, could be an interesting way to fermentate the sugars released during the organosolv pretreatment step.

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STSM

DETERMINATION OF FUNCTIONAL GROUPS IN SELECTIVE OXIDIZED CELLULOSE FIBERS BY COMBINING GROUP-SELECTIVE FLUORESCENCE LABELING WITH GPC

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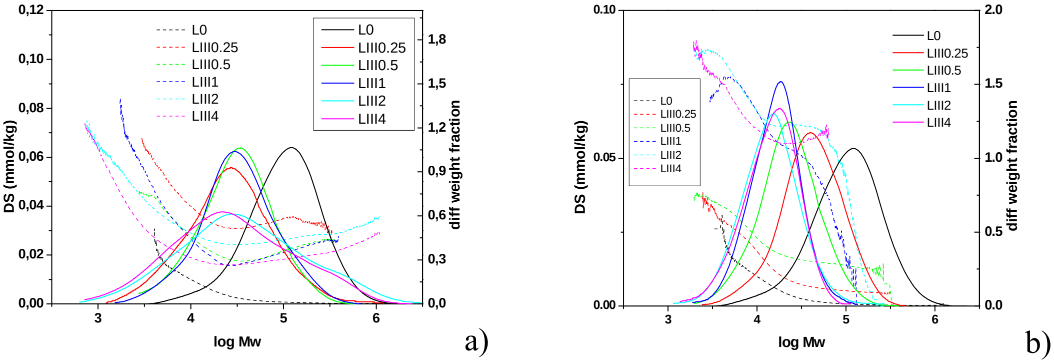
ABSTRACT

INTRODUCTION: The catalytic oxidation using nitroxyl radical 2,2′,6,6′-tetramethylpiperidine-1-oxyl (TEMPO) under aqueous conditions has become very interesting way for introduction of functional groups at C-6 positions of the anhydroglucose units of cellulose (de Nooy, et al. 1994, Saito et al. 2005). The introduced functionalities in cellulose fibers present one of the prime factors determining macroscopic properties and chemical behaviour of modified fibers, such as: water retention, wettability, strength properties, cross-linking, aging, yellowing, etc. According to the literature (Saito et al. 2005; 2006), the amount of introduced functional groups in TEMPO-oxidized cellulose samples were widely determined as a sum parameter, while a group profile in relation to the molecular weight of the oxidized cellulose has been investigated in considerable smaller scope (Potthast et al. 2007).
In the present paper, in order to get some deeper insight into the influence of TEMPO-mediated oxidation on distribution of introduced carbonyl and carboxyl functional groups, the nonmodified and oxidized lyocell fibers were analyzed by means of gel permeation chromatography (GPC) using multiple detection and group-selective fluorescence labeling.

MATERIALS AND METHODS: The oxidation procedure was based on the literature methodology (Saito et al. 2005). Carbazole-9-carbonyloxyamine (CCOA) labelling of carbonyl groups was performed as described by Röhrling et al. (2002). Fluorenyl diazomethane (FDAM) labelling of carboxyl groups followed the protocol of Bohrn et al. (2006).

RESULTS: Obtained results showed the increase of both carbonyl and carboxyl group content under all applied oxidative conditions (30.3 and 23.7 times higher than unmodified lyocell, for CO and COOH groups, respectively). With the lowest amount of NaClO (0.30 mmol/g cell), the increase of the carbonyl group content is obtained for oxidized samples and pronounced introduction of carbonyl group content is detected in the molecular weight region below 10.000 g/mol, corresponding to a DP below 100. Modification with 4.84 mmol NaClO/g cellulose causes shift of MWD curve in the left and for the first time the broad curve of molecular weight distribution was obtained, especially for the samples modified 2 and 4 hours. (Fig. 1a). Significant

amounts of COOH groups in the high molecular weight factions can be introduction by performing the oxidation using higher concentrations of NaClO at the time of modification of one hour and longer (Fig. 1b).



a) b)

Figure 1: Carbonyl (a) and carboxyl (b) profile DS – (dotted lines) and molecular weight distribution (MWD) – (solid lines) for unmodified and TEMPO-oxidized lyocell fibers where 4.84 mmol NaClO (per gram of cellulose) was applied to the cellulose slurry, during 0.25 - 4 h, at room temperature and pH 10.5.

CONCLUSION: When the carbonyl groups should be introduced into high molecular fraction, the better effect can be achieved by increasing the concentration of NaClO, than with the prolonged oxidation time. Introduction of significant amounts of COOH groups in the high molecular weight factions can be achieved by performing the oxidation using higher concentrations of NaClO (2.42-9.67 mmol NaClO/g cellulose) at the time of modification of one hour and longer.

Acknowledgements: This study has been supported by the Ministry of Education and Science of the Republic of Serbia (Project OI 172029) and COST action FP 0901.

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STSM

EXTRACTIVES OF WOUND-ASSOCIATED WOOD IN BEECH (*FAGUS SYLVATICA*)

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ABSTRACT

INTRODUCTION

Beech (*Fagus sylvatica L.*) is one of the prevalent and economically important tree species in Slovenia. Beech-wood is regularly depreciated by alteration of material triggered by mechanical wounding to trees. Wounding results in a series of complex events that lead to development of wood discolorations and formation of protective and defensive tissues (Shigo and Marx 1977). Compartmentalizing function of these tissues has been variously ascribed to anatomical and/or biochemical alterations (Pearce 1996). As opposed to structural research, characterization of extractives in wound-associated wood of beech received only little attention. The objectives of this preliminary report were to examine prevalent lipophilic and hydrophilic extractives and to quantitatively estimate the occurrence of catechin in different types of wound-associated wood and knots in beech.

MATERIAL AND METHODS

Samples of intact sapwood, wound-wood, reaction zone, red heart and live and dead knot of selected trees were included in the investigation. Lipophilic and hydrophilic compounds were extracted successively by cyclohexane and mixture of methanol/water (95:5, v/v) in a Büchi speed extractor E-916. After evaporation of the solvent extractives were silylated with mixture of BSTFA, TMCS and pyridine afterwards. Qualitative and quantitative analysis was then performed by gas chromatography, applying GC-FID and GC-MS. For quantification, heneicosanoic acid (C21:0) and betulinol were used as internal standards. Peak assignment and processing of chromatograms was done by Agilent's ChemStation software.

RESULTS AND DISCUSSION

The lipophilic fraction of wounded beech wood consisted of saturated and unsaturated fatty acids, fatty alcohols, some monoglycerides and sterols. The predominant unsaturated fatty acid was palmitic acid (C16:0) and various C18:n acids. On the other hand, the most important sterol was β-sitosterol, which was represented as most abundant peak on chromatograms of cyclohexane extracts.

The polar fraction (Figure 1) contained a large number of monomeric (*MS*) and oligomeric sugars (*OS*). Besides these, phenolic and sugar acids (*PA* and *SA*), inositols (*In*), sugar alcohols and a monolignol sinapyl alcohol (*ML*) were also characteristic for methanolic extracts. As expected, catechin was the predominant phenolic

compound. Our results are in agreement with studies which were done on beech wood of various origin (Zule and Može 2003, Koch et al. 2003, Kubel et al. 1988).

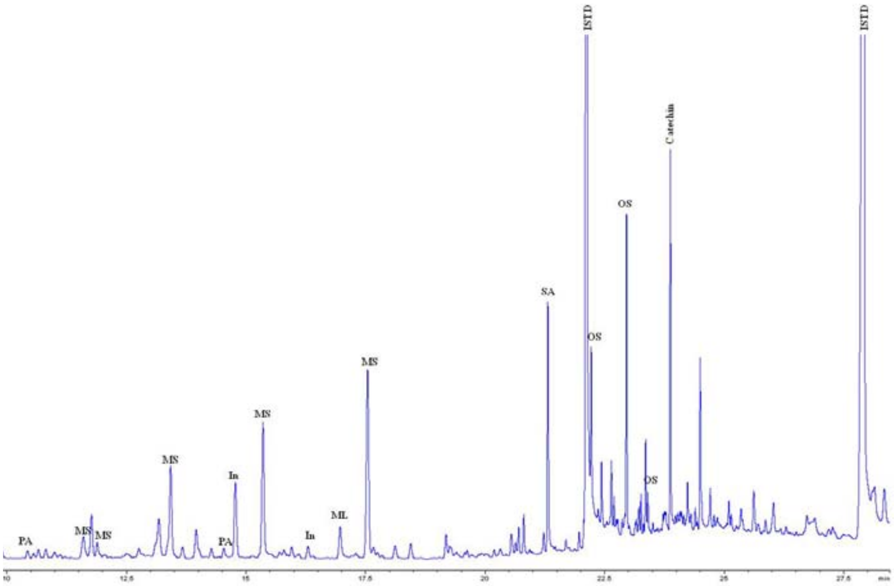

Figure 1: GC chromatogram of methanolic extract of the reaction zone of beech. ISTD's represents internal standards.

Quantitative GC analysis revealed that high concentrations of catechin were characteristic for wound-wood, sapwood and knots extracts. The highest amount of catechin was determined for methanolic extract of dead knot and the lowest for extracts of red heart. High amounts of catechin in beech knots are in accordance to results reported by Pietarinen et al. (2006). We assume that occurrence of high concentrations of catechin in particular wound-associated tissues reflect their protective function in living trees.

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STSM

THE ROLE OF FATTY ACIDS IN THE WRINKLE REDUCTION IN CELLULOSIC FABRICS

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ABSTRACT

A novel approach for improving wrinkle recovery of cotton fabrics by application of oil aqueous emulsion was studied. Cotton consists of practically pure cellulose and may be described as a polymer of β-(1→4) linked anhydroglucose units with some impurities. Beside numerous well know advantages of cotton, one of the main disadvantage is that wrinkles are easily formed eventually influencing the garments aesthetical appearance.

Since formaldehyde has been identified as potential human carcinogen in addition to its negative dermatological effects, many efforts have been made to develop textile finishing agents which are formaldehyde free. Treatment with a non-toxic aqueous oil emulsion in spray form is a treatment according to a “green chemistry concept” and it may serve as an addition to conventional finishing processes.

The obtained results revealed that the treatment performed results in remarkable improvement of wrinkle recovery (expressed as dry crease recovery angle and wrinkle factor) without affecting the whiteness index and tensile properties of cotton fabrics. Relaxation characteristics of the cotton fabrics and a dry crease recovery angle of about 270 ° within a few seconds after application proved the lubrication of textile fibres and the efficiency of the textile finishing agent.

The wrinkle recovery angle was measured for emulsions containing fatty acids from different sources. The fatty acids were characterized by HPLC and NMR. The influence of double bonds equivalents was compared between the formulations. Traditional methods like the German standard DIN 53890 are often not very suitable to characterize finishing agents applied in the spray form which show a comparably fast response towards wrinkling. Hence, we have developed a novel technique to measure wrinkle kinetics on textile surfaces. This method allows a detailed evaluation of the textile surface and for the first time gives access to kinetic profiles of textile relaxation after treatments. A time dependent response is very important for comparison and evaluation of textile finishing sprays.

SELECTIVE OXIDATIVE FUNCTIONALIZATION OF LIGNINS

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ABSTRACT

The goal of our research is the selective oxidation of lignin. Our intent is not the depolymerization, with the subsequent degradation, of its structure but is the introduction of oxidized functional groups.

Indeed, ketones and, above all, aldehydes and catechols represent an excellent "connection site" for several functionalizations that make lignin a versatile material, a starting matrix for the synthesis of new copolymers.

Several methodologies have been studied with the aim of introducing oxidized functional groups on the aromatic ring and on the side chains. In particular, *o*-quinonic and catecholic functions have been introduced on the guaiacylic units of lignin; the aldehydic and ketonic ones have been obtained from OH groups of the side chains by means of selective oxidizing agents.

We studied the oxidation of Pine kraft lignin with three different oxidizing agents: 2-Iodoxybenzoic acid (IBX), Pyridinium Chloro Cromate (PCC) and Dess-Martin Periodinane (DMP). 2-iodobenzoic acid gave rise to quinonic functionalities on guaiacylic units. A subsequent in situ reduction allowed to obtain catechols (**Fig. 1**) with a selectivity comparable to a demethylating enzyme. Catechols are potential groups that allow further functionalizations of the lignin structure or cross linking reactions.

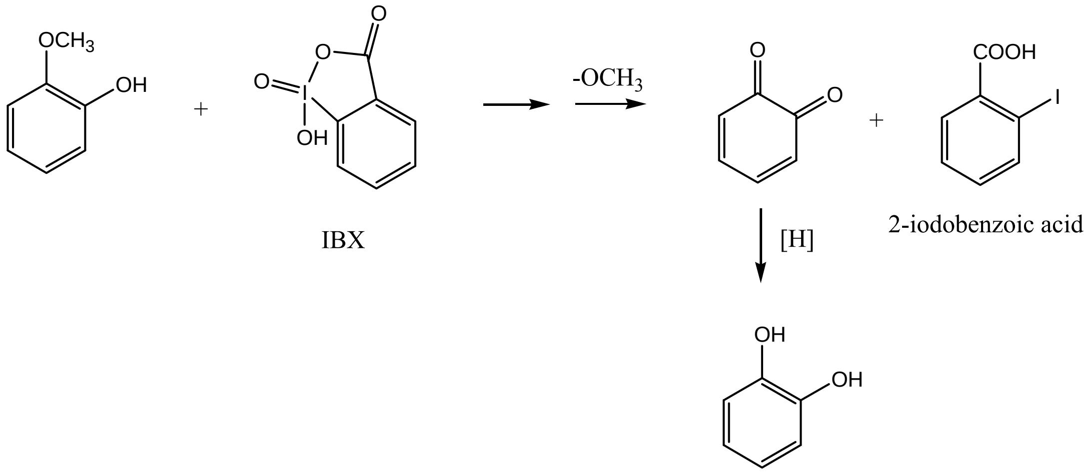

Figure 1: **Reaction of IBX with guaiacylic compounds.**

Oxidation of Pine kraft lignin with PCC and DMP allowed to obtain aldehydic and ketonic functions from aliphatic groups. These selective oxidative agents converted primary aliphatic groups into aldehydes and the secondary ones into ketons (Fig. 2).

Aldehydic functions in particular are excellent connection sites for further functionalization of lignin.

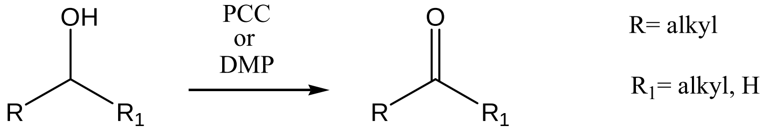

Figure 2: **Selective oxidation of alcohols.**

The oxidized products were characterized by means of FTIR and ^{31}P-NMR and ^{19}F-NMR spectroscopy.
FTIR allowed to clarify the conversion of functional groups.
The magnetic resonance of ^{31}P elucidated lignin structure labeling the labile protons of OH groups, distinguishing and quantifying aliphatic, phenolic and acidic hydroxyls.
Also the magnetic resonance of ^{19}F allowed to recognize catecholic groups, aldehydic and ketonic ones.
Magnetic resonance of ^{31}P and ^{19}F proved to be excellent analytical tools for elucidating modifications of lignin structure after selective oxidative functionalization.

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COMPARATIVE STUDY OF DIFFERENTLY TREATED (COOKED AND BLEACHED) INDUSTRIAL GRASS AND STRAW FIBRES RESPECTIVELY BY RAMAN AND ENERGY-DISPERSIVE X-RAY SPECTROSCOPY)

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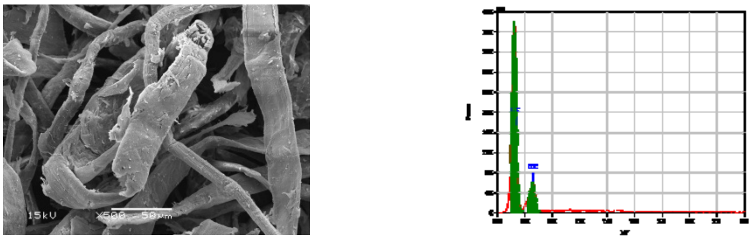
ABSTRACT

For the elemental analyses of the samples at a given surface places has been used an Energy-Dispersive X-ray Spectroscope connected to the scanning electron microscope.

Raman spectra has been determined on a Raman micro-spectroscope type of Jobin Yvon Labram with Olympus BX41 microscope.

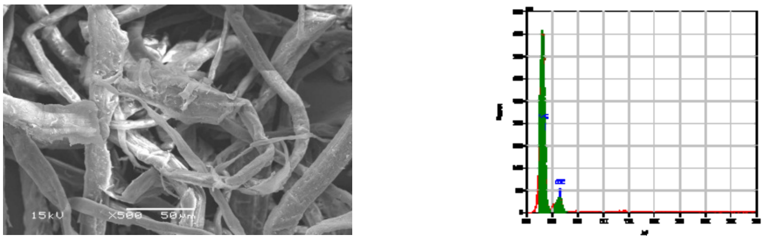
Element	Place of the signal keV	Amount	
		%, mass	%, atom
C	0.277	90.62 ± 3.2	93.25 ± 1.6
O	0.525	7.73 ± 1.3	5.97 ± 0.9



500× enlargement *EDS-spectrum*

Figure 1: EDS results of industrial grass cellulose.

Element	Place of the signal keV	Amount	
		%, mass	%, atom
C	0.277	90.38 ± 3.6	92.58 ± 2.8
O	0.525	9.62 ± 3.6	7.42 ± 2.8



500× enlargement *EDS-spectrum*

Figure 2: EDS results of industrial grass cellulose.

It could be established from the EDS elemental analyses data (Figure 1, Figure 2.) that the ratio of the carbon and oxygen on the surface is different from that of in the cellulose. It could be assumed that different contaminating compounds and modified cellulose molecules should be present on the surface.

Spectra [Eichhorn H. (2001), Mishra S. P. (1999), Stuart B. H. (1995)] elucidated supermolecular structural information for selection of most suitable processing for pulp and paper making.

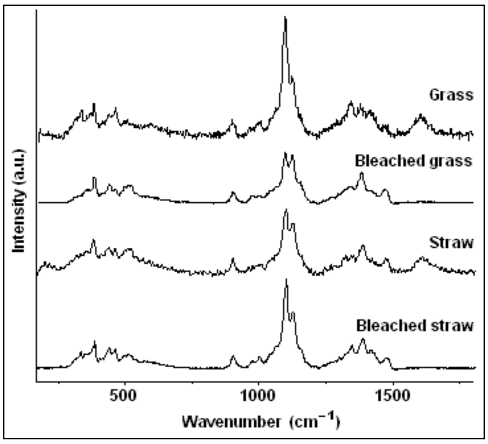


Figure 3: EDS results of industrial grass cellulose.

No essential differences could be observed between the Raman spectra of grass and straw cellulose fibres (Figure 3.).

The amount of contaminating compounds (lignin, hemicellulose) of cellulose easily can be followed by Raman spectra.

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EVIDENCE FOR THE OCCURRENCE OF POLYMERIZED WOOD RESIN IN PULP AND PAPER SAMPLES FROM VARIOUS ANALYTICAL TECHNIQUES

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ABSTRACT

Detailed characterization and analysis of wood resin is often a prerequisite to solving pitch deposition problems. However, such analyses by conventional gas chromatographic (GC) techniques can only identify less than 40% of the soluble wood resin components. The rest of the unidentified matter is assumed to be high molecular weight and/or polymerized wood resin components that are not volatile enough to be analyzed by GC. The impact of this polymerized material on pitch deposition is not well understood. This report demonstrates the occurrence of polymerized wood resin in pulp and paper samples as gleaned from literature reports and from work conducted in our laboratory. A number of techniques can be used to characterize polymerized wood resin. Size exclusion chromatography (SEC) gives some information about the molecular size of the polymeric matter, but no detailed information on its chemical composition. In addition, the SEC chromatograms are difficult to interpret in many instances. SEC considers only solvent-soluble polymeric material and hence misses the high MW fraction, which in many cases may be most of the polymerized extractives. FTIR can also be used to detect the presence of polymerized wood resin but the absorption bands tend to be broad with low intensities. GC-FID and GC-MS techniques offer opportunities for indirect quantification of polymeric matter in extracts. However, the techniques suffer from interferences from other compounds in the extracts that may not be polymerized wood resin. Pyrolysis-GC/MS is an ideal technique for characterization of polymeric compounds and gives some indication on the composition of the polymerized resin. Unfortunately, it does not give information on the structure of the original polymerized matter. The ultimate methods may be LC/MS (liquid chromatography with mass spectrometry detection) and/or MALDI-TOF-MS (matrix assisted laser desorption ionization – time-of-flight- mass spectrometry). Hypotheses to explain the formation of polymerized wood resin are discussed. The report sets the stage for future work that could be undertaken to better understand the implications of the occurrence of polymerized wood resin in pulp and paper production.

CHEMICAL CONSTITUENTS OF NATURALLY DECAYED BEECH (*Fagus orientalis* Lipsky.)

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ABSTRACT

Beech is a major tree species with a wide distribution throughout Europe covers roughly 14 million hectares of forest land, yields a utility timber that is widely used for furniture framing, flooring like parquet, engineering purposes, in plywood and in household items. Despite the useful properties it is susceptible to the white rot fungi particularly in freshly fallen wood. Early stage of white rot in the beech is also termed as spalted wood with the distinctive characteristics.

The first priority of a decay fungus is to reach to the nutrient resources that are stored within woody cell walls. This may be accomplished the act of entering into the wood itself, followed by movement in the wood (Rayner and Boddy 1988). The fungi hyphae grow in length along the surface, after penetrating in to the wood act from cell to cell through pit pairs or through bore holes created in the cell wall which is degraded progressively eventually (Bowyer et al. 2003). When the decay is detectable, but not obvious the early stage of decay occurs depending on the development of decay in the wood with the some characteristics such as slight changes in color, wood texture and appearing of fiber brashness (Zabel and Morrell 1992). White-rot fungi having a complete cellulose complex and ability to degrade lignin, decompose all structural components of wood becomes bleached or white black zone lines, occur mainly on hardwoods but can be found on softwoods as well. The degraded wood keeps outward dimensions but feels spongy on the other hand, strength properties decrease gradually as decay progresses, except toughness (Ibach, 2005).

In this study, main compounds of wood (Table 1), extractives values (Table 2), Monosaccharides, other extractives, hemicellulose and pectins (Table 3,4,5) were determined. Wood samples were freez-dried for 48 hours and subjected to analysis. Dried wood was extracted in Soxhlet apparatus with acetone:water (9:1) for 6 hours. The composition of hemicelluloses and pectin was analysed after methanolysis of wood with 2M HCl in anhydrous methanol for 5 hours at 105°C. TMS-derivatives of methanolysis products (methyl glucosides of corresponding sugar units) were then analysed by GC. The amounts of monomeric sugars after methanolysis related to original hemicelluloses and pectin and the unit is milligram per gram. The results were calculated as average of 3 analysis for each beech sample.

Table 1: Chemical constituents mean values (%).

	Material	
Chemical constituents	Beech-Control	Beech-Infected
Extractives	2.51	2.74
Holocellulose	78.22	77.67
α-Cellulose	51.28	48.42
Lignin	19.78	14.05
Cold water solubility	2.00	2.89
Hot water solubility	2.07	3.22

Table 2: Extractives values (gravimetric).

Material	Extractives (mg/g wood)
Beech -control	15.21
Beech -infected	15.25

Table 3: Monosaccharides (µg/g wood).

Material	Xylose	Glycose	Fructose	Sucrose	Total
Beech - control	7.2	244.7	158.5	20.1	430.5
Beech - infected	11.7	14.9	6.2	1.7	34.5

Table 4: Other extractives (µg/g wood).

	Material	
Extractives	Beech -control	Beech -infected
Glycerol	35.7	942.7
Malic acid	134.8	6.1
Erythritol	1.2	2056.9
Sugar alcohol 1	0.7	6125.6
Sugar alcohol 2	6.6	1780.5
Sucrose	88.1	5.8
Catechin	686.7	1.7
Sitosterol	63.4	50.8
Total	1017.1	10970.0

Table 5. Hemicellulose and Pectins (mg/g wood)

	Material	
Hemicellulose and Pectins	Beech -control	Beech -infected
Arabinose	4.6	4.5
Rhamnose	5.1	4.9
Xylose	185.7	184.7
Mannose	14.9	14.7
Galactose	9.7	9.3
Glc	24.8	15.3
4OMeGlcA	24.1	23.7
GlcA	1.3	1.2
GalA	19.3	19.1
Total	289.5	277.4

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GPC Monitoring of Molecular Weight Distributions and LCCs of Lignocellulosic Materials during Steam-Explosion Pretreatment

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ABSTRACT

In recent years, lignocellulosic biomasses from agricultural residues and herbaceous energy crops have been under intense investigation due to their annual renewability and large annual stock. Lignocellulose is an extremely structured natural material made up of three main biopolymers: cellulose, hemicellulose, and lignin.

Lignocellulose biorefinery generally includes three fundamental steps: firstly, a pretreatment to fractionate the recalcitrant lignocellulose structure; secondly, the enzymatic hydrolysis of the isolated cellulose moiety to obtain fermentable sugars; and thirdly, the fermentation to produce cellulosic ethanol or other bio-based chemicals.

Because of the resistant structure of crystalline cellulose and natural composite structure of lignocellulose, efficient pretreatment technologies are needed prior to the enzymatic hydrolysis. The recalcitrance of lignocellulosic materials to enzymatic hydrolysis is substantially attributed to the low accessibility of crystalline cellulose fibers, which restricts cellulase activity. Moreover the presence of lignin and hemicellulose on the surface of cellulose prevents cellulase from accessing the substrate. It is recognized that enzymes' performance is reduced during lignocellulose hydrolysis by interaction with lignin and, especially, lignin-carbohydrate complexes (LCCs).

The steam-explosion technology seems to be actually the best pretreatment method in order to maximize the enzymatic hydrolysis.

Using the method recently developed based on differential derivatization of lignocellulosic materials in homogeneous media (by ionic liquids for complete dissolution) and GPC analyses with UV detection, the change in molecular weight distributions and the fate of lignin carbohydrate complexes during steam-explosion pretreatment has been investigated.

The untreated material, the sample after steam explosion and the remaining material after fermentation of *Arundo donax* and Wheat Straw have been characterized by means of Gel Permeation Chromatography after benzoylation and acetylation. Using a UV detector setup at different wavelengths, it was possible to study the molecular weight distribution of the different materials and the change in the connection between lignin and polysaccharides. The analytical methodology could be useful in order to optimize the steam-explosion pretreatment.

INVESTIGATION OF BIOPOLYMERS BY MEANS OF MULTIFUNCTIONAL PYROLYSIS-GC/MS

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ABSTRACT

Conventional pyrolysis-GC/MS presents a reliable and rapid technique for the characterisation of biopolymers. A multifunctional pyrolysis-GC/MS system combining different pyrolytical methods opens up new possibilities for the investigation of biopolymers and allows advanced implementations in addition to conventional pyrolysis. By means of evolved gas analysis (EGA), for example, which provides results similar to thermogravimetric analysis, the arising gases formed by defined heating intervals can be used for characterizing the thermal behaviour of a sample. For this technique a stainless steel tube instead of a separation column has to be installed. EGA affords a fixed or a four-step temperature programme including adjustment of different heating rates and the option of holding final temperatures for each level. Application of selected ion monitoring (SIM) during EGA offers further options to determine the pyrolytic behaviour of specific components like hemicelluloses or cellulose. Previous investigations show that EGA presents a useful tool to characterise biopolymers and specify the conditions for analytical pyrolytic techniques (Fuchs et al. 2010, Heigenmoser et al. 2011). A so called heart-cut analysis (HCA) can adopt the heating conditions of the EGA programme and allows the identification of compounds contained in evolved gases for specified temperature ranges. For investigations of the gas formation at high temperature levels, HCA is supported by a selective sampler, which discards gases of subjacent temperature ranges from the system.

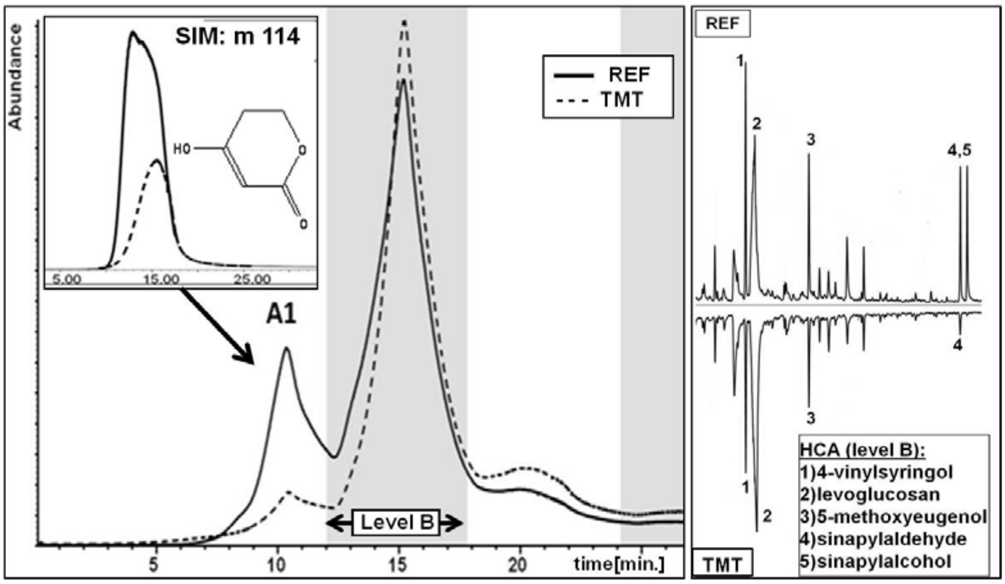

Figure 1: EGA profiles (left), EGA profiles in SIM mode (top left) and a section of the pyrogram of HCA of level B (right) for thermally treated beech (TMT) and the reference (REF), respectively

Figure 1 shows the potentials of EGA and HCA by analyses of thermally treated beech (TMT) and the corresponding reference material. With the EGA profiles it was possible to determine the pyrolytic behaviour of the samples. Maximum A1 shows a lower curve progression for TMT compared to the reference, which can be attributed to the decomposition of hemicelluloses and lignin as a result of thermal treatment. In a further step the difference in the hemicelluloses content was specified by EGA in the SIM mode at a molecular mass of 114 (Fig. 1, top left). The molecular mass 114 arises during the pyrolysis of wooden materials, especially for the compound 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one, a typical xylan degradation product (Ohnishi 1977, Bremer 1991). In this way it was possible to show characteristic degradation patterns of TMT.

Furthermore, the gas formation of temperature level B (290-360°C) was qualitatively analysed by HCA (Fig. 1, right). Compared to the reference TMT shows e. g. a lower content of specific lignin moieties (1,3,4,5) and a higher content of levoglucosan (2) as a result of decomposition mechanisms during thermal modification. These results are also expressed in the EGA profiles of level B by the different curve progression for TMT and the reference. This example of use emphasises that EGA in combination with HCA represents a powerful tool for the investigation of polymers exposed to defined heating conditions.

By comparison, qualitative investigations via HCA and conventional pyrolysis reveal deviations in some pyrolysis products caused by methodical differences. Due to the lower heating rate and the longer heating exposure of the samples during HCA considerably more secondary products were formed compared to SSA. In general, multifunctional Pyrolysis-GC/MS is a useful tool to investigate biopolymers in a rapid way. The technique of HCA includes potentials like simulation approaches of thermally treatment procedures of wood but also the examination of pyrolytical reaction mechanisms.

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POSTER PRESENTATIONS

SORPTION PROPERTIES AND ELECTRICAL RESISTANCE OF COTTON YARN TREATED WITH H_2O_2

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ABSTRACT

Introduction. Chemical oxidation is frequently used procedure for structural modification of cellulose fibers. Oxidation of cellulose fibers with various oxidation agents leads to introduction of different functional groups, i.e. carbonyl and carboxyl groups. Hydrogen peroxide is nonselective oxidation agent, therefore by changing treatment parameters, various functional groups in different quantity can be introduced into cellulose material. These functional groups have ability to react with various compounds, molecules, ions etc. thus obtaining multifunctional properties of cellulose (Kostic, et al. 2007a). Deposition of Ag^+ ions onto cellulose can provide both excellent antimicrobial effect (Praskalo-Milanovic, et al. 2010) and lower electrical resistance. Electrical resistance analysis of textile materials can provide good anticipation of material behavior during manufacturing process and exploitation, because textile materials are prone to generation of static electricity on their surface due to their poor electrical conductance (Morton and Hearle 1975).

Materials and methods. In this work, the effect of oxidation with H_2O_2 on sorption properties and electrical resistance of cotton yarn was investigated. Hydrogen peroxide of different concentration (3% and 6%) was used under various conditions (pH value of solution 7, 9, 11 and time of the treatment 10, 20, 30 min at room temperature). Carbonyl and carboxyl group content, sorption properties i.e. water retention value, iodine sorption value (ISV) and sorption of Ag^+ ions, before and after oxidation were investigated. Sorption of Ag^+ ions was done from aqueous $AgNO_3$ solution under previously optimized conditions (Kostic, et al. 2007b). Electrical resistance was measured using device developed at Department of Textile engineering of Faculty of Technology and Metallurgy (Asanovic 2003). Given that electrical resistance of textile materials strongly depends on relative humidity of ambient air, i.e. the ability of material to bind molecules of water from environment and therefore become more conductive (Asanovic 2003), resistance was measured under different humidity conditions. Relationship between introduced polar functional groups during oxidation, quantity of sorbed Ag^+ ions and electrical resistance was studied.

Experimental results. It was found that increase of peroxide concentration, pH value of solution and time of treatment leads to increase of carbonyl group content in samples. Water retention value decreased with increased time of treatment and it was observed that this effect is more pronounced when 3% H_2O_2 was used. ISV value increased in case of oxidation with 3% H_2O_2, while significantly decreased by oxidation with 6% H_2O_2. Samples oxidized with 6% H_2O_2 sorbed more Ag^+ ions than samples oxidized with 3% H_2O_2 and maximum content of silver was obtained for 6% H_2O_2, pH 7, during 20 and 30 minutes of the treatment. As expected, samples with silver exhibited lower electrical resistance compared to control and oxidized samples. Strong correlation between amount of Ag^+ ions presented in samples and electrical

resistance was found. Further, sorption of silver ions on cellulose fibers decreases resistance dependency on relative humidity as it is shown in Fig. 1.

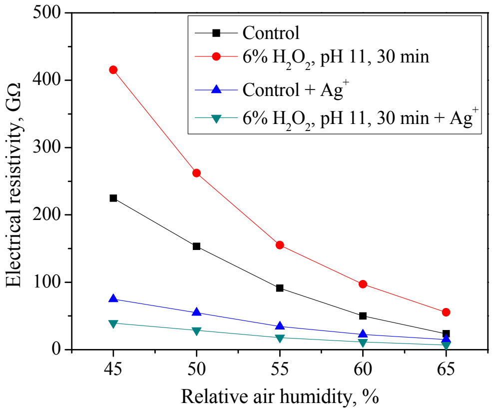

Figure 1: Dependency of electrical resistance on relative air humidity for control and modified samples

Conclusion. Oxidation of cellulose fibers with H_2O_2, under previously mentioned conditions, leads to introduction of mostly carbonyl groups, while only small increase in carboxyl group content was found. This influences not only sorption properties, but also electrical resistance of material which increased after oxidation, while, as expected, was significantly lower after sorption of silver ions. Furthermore, natural material like cellulose and non-toxic oxidizing agent like hydrogen peroxide are a good combination for chemically green process which provides satisfying utterly modification effect.

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PARTICLE SIZE ANALYSIS OF SOME LIGNINS MODIFIED UNDER COLD PLASMA CONDITIONS

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ABSTRACT

Alcell lignin was modified with different organic acids and butyrolactone in cold plasma conditions. Plasma technology is an efficient and suitable way to modify the properties of the polymeric substrates. Plasma modification approaches have a number of benefits as it requires small quantities of starting materials and the plasma processes are environmentally friendly because the organic solvents are avoided. The modified lignins were characterized by ^{1}H-NMR, ATR FT-IR spectroscopy, SEM, particle size analysis and zeta potential measurements. It has been established that by modification the structure, morphology and solution properties are specific for each kind of product obtained.

Experimental

Reagents used for the lignin modification were: carboxylic acids: *butyric acid* (BA) (Merck, purity 99%); *oleic acid* (OA) (Aldrich, 90 % purity); *lactic acid* (2-hydroxypropionic acid) (LA) (Aldrich, 90 % purity) and *4-butyrolactone* (4-hydroxybutiric acid lactone) (BL) (Merck, purity > 99%).

Plasma treatment procedure

The modification of lignin has been carried out in a R. F. cold plasma reactor specially designed for treatments on powdery materials under atmospheric pressure. The experimental set-up is presented in (Figure 1)

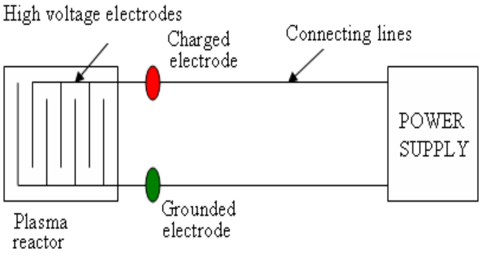

Figure 1. Laboratory experimental set-up for R.F. plasma treatment of the powdery materials.

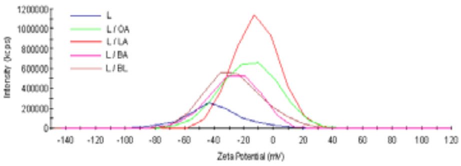

Figure 13. Zeta potential distribution for L and cold plasma modified lignins at pH 10.6

Particle size analysis of polymeric samples was done by using a *dynamic light scattering technique* (Zetasizer model Nano ZS (Malvern Instruments, UK)) with red laser wavelength of 633 nm (He/Ne). The system uses non-invasive back scatter (NIBS) technology wherein the optics are not in contact with the sample, back scattered light being detected. The use of NIBS technology reduces multiple scattering effects and consequently size distributions in higher concentrations of sample can be measured. This is the system for which the Mie method is applied over the whole measuring range from 0.6 nm to 6 μm. Determinations have been done on dilute solutions of copolymers at different pHs in the concentration interval of 1.25 – 8 mg/mL.

Results and Discussion

Studies on particle size distribution, conductivity and zeta potential were done in water and in NaOH solutions as it is known specific behaviour of lignin in both media (Dalimova, 2006)

In aqueous solutions, the distribution curves for particle size and zeta potential results present clear differentiation between unmodified and modified lignin. Particle size distribution curves are bimodal in all cases but the main peak of unmodified lignin is narrower than those of modified lignin. The Z-values of 150-400 nm are characteristic for the first peak are average while those for the second one ranges from 800 to 6500 nm. Both Z-average and zeta potential depend on pH of solution –Figure 2 -4.

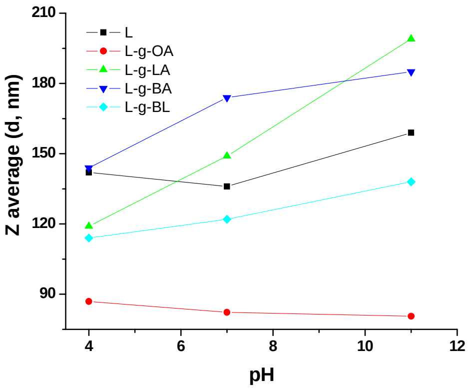

Figure 3. Z-average *vs* pH of solutions of L and cold plasma modified lignin.

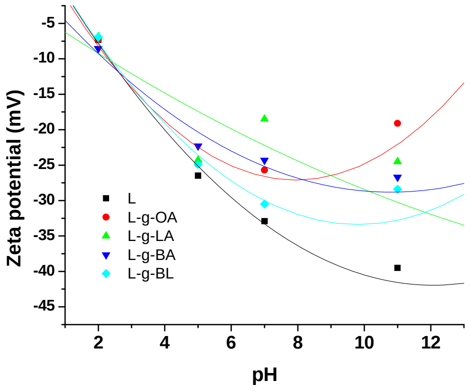

Figure 4. Zeta potential *vs* pH of solutions of L and cold plasma modified lignin

At a pH > 5.5 zeta potential of the modified lignins are superior to that of unmodified lignin (Fig. 13) but they decreased in respect with that of solution with low pH, a certain fraction of particles having zeta potential situated outside limits of stability of dispersion especially for unmodified lignin. However the average zeta potentials of modified lignins do not exceeds the stability limits (+30 - -30mV). (Mohanraj, and Chen, 2006) Zeta potential decreases with increasing pH up to pH 10 than levels. The lowest Zeta potential values are characteristic to unmodified lignin sample and the highest to L/LA sample. It can conclude that the cold plasma modified samples show a better stability than unmodified lignin sample. PDI values increase with increasing pH, dispersion being much heterogeneous. The conductivity decreased with increasing pH up to pH ~6 than remains constant.

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ISOTHERM AND KINETIC STUDIES OF THE BIOSORPTION OF Zn^{2+} IONS FROM WASTE WATER BY CHEMICALLY MODIFIED SHORT HEMP FIBERS

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ABSTRACT

Hemp fibers are traditionally used for production of textiles. From the economic aspect hemp presents a high-productive culture. Nowadays, there is an increasing interest in total exploitation of the plant, with the intention of using seeds, fiber and shive as raw materials. The increased production of hemp fibers brought about an increase in the amount of waste, namely shives, short and entangled fibers. Short and entangled fibers are very convenient for filter production, either from ecological and economical aspects, or because of their properties. Furthermore, in the recent years attention has been devoted to the development of adsorbents from agricultural products, also called bio sorbents as alternative for activated carbon. The application of bio sorbent for purification of waste water is a very cost-effective method, with advantage that one waste is used for cleaning up of another (Bailey et al. 1999, Volesky 2007). Our preliminary investigations have shown that short hemp fibers have a high potential of heavy metal ions uptake from aqueous solutions (Pejic et al. 2009).

In this work, unmodified and chemically modified short hemp fibers, that are waste material from textile industry, were used as a bio sorbent for removal of zinc ions from polluted water. Hemp fibers were modified with 17.5 % NaOH and 0.7 % $NaClO_2$ at different conditions, in order to obtain the material with better sorption properties. Chemical composition of unmodified and each of modified samples of hemp fibers was determined according to the scheme of Soutar and Bryden (Garner 1967) by successively removal of water solubles, fats and waxes, pectin, lignin and hemicelluloses. Sorption of zinc was performed from aqueous solutions of $Zn(CH_3COO)_2 \times 2H_2O$, concentration in the range of 0.1 – 0.5 mmol/L. All the experiments were carried out in batch process for 2 h, at room temperature with constant shaking. The decrease of ion concentration in solution during the sorption process was measured by atomic absorption spectrometry using Atomic Absorption Spectrometer—Pye Unicam SP9 (Pye Unicam, Ltd., UK). Biosorption of zinc ions by unmodified and modified short hemp fibers were evaluated through the total uptake capacity. The equilibrium and kinetic data were analyzed with Langmuir and Freundlich isotherms and pseudo-first and pseudo-second order kinetic models in order to understand the mechanism of adsorption process.

Obtained experimental results, showed that used chemical treatments leads to structural and morphological changes of hemp fibers, and improvement of fibers sorption properties. The sorption capacity of zinc ions for all modified hemp fibers is better than for unmodified sample. Equilibrium data obtained for all hemp fiber samples mainly fitted better with the Langmuir model, suggesting homogeneous distribution of active sites for adsorption on the surface of hemp fibers, with maximal

adsorption capacity of zinc ions from 7.07 to 8.33 mg/g. The suitability of the kinetic models was also discussed and it was found that adsorption of zinc ions on all tested hemp fiber samples obey the pseudo-second order adsorption kinetics. Intraparticle diffusion analysis demonstrates that zinc ions diffuse quickly at the beginning of the adsorption, intraparticle diffusion became active after 5 minutes and then the diffusion slows down and stabilizes.

Good sorption properties of modified hemp fibers and their low cost in comparison with other commercial sorbents enable successful use of these fibers in the production of filters for wastewater treatment.

***Acknowledgements*:** This study has been supported by the Ministry of Education and Science of the Republic of Serbia (Project OI 172029 and OI 172007).

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PYROLYSIS BEHAVIOUR OF VARIOUS KINDS OF BIOMASS

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Introduction

Pyrolysis utilizes biomass to produce a product that is used both as an energy source and a feedstock for chemical production. Considerable efforts have been made to convert wood biomass to liquid fuels and chemicals since the oil crisis in mid-1970s. Virtually any form of biomass can be considered for fast pyrolysis. Most work has been performed on wood, because of its consistency and comparability between tests. However, nearly 100 types of biomass have been tested, ranging from agricultural wastes such as straw, olive pits, and nut shells to energy crops such as miscanthus and sorghum. Forestry wastes such as bark and thinnings and other solid wastes, including sewage sludge and leather wastes, have also been studied [Dinesh et al. 2006]. It is well known that the very fast and very slow pyrolyses of biomass produce markedly different products, the variety of heating rates, temperatures, residence times, and feedstock varieties. Good agreement was obtained between structural changes inferred from size-exclusion chromatography and U.V. fluorescence and U.V. absorption spectroscopies. The characterization of liquid products by ^{1}H NMR. was found to be less informative than expected, due to the multiplicity of structural assignments in relatively narrow bands [Pindoria et al. 1997].

This paper deals with pyrolysis behaviour of two groups of biomass, less studied until now namely woody biomass and biomass from annual plants.

Experimental

Some characteristics of biomass samples are given in table 1.

Table 1. Characteristics of biomass samples

Samples	Moisture	Extractives	Carbohydrates	Lignin	Ash
Eucalyptus chips	7.03	1.06 – 2.98	57.1 – 70.6	24.5 – 27.6	0.53
Eucalyptus BSP	5.9	0.14 – 2.16	88.7 – 99.2	1.0 – 1.7	1.32
Norway spruce TMP	6.64	1.02 – 2.40	60.60 – 69.00	27.60 – 29.40	0.35
Pine Cones		4.8	Hemicellulose 37.6 Cellulose 32.7	24.9	0.9
Energy grass	5.72		44.36	Klason: 241.5mg/g	
Brassica Rape seed	6.55		40.32	Klason 179 mg/g	
Grape seeds	8.1				2.9

Pyrolysis procedure

Amounts of 0.5 g of biomass samples, PP or PE and PE or PP/biomass composites were thermally degraded by semi-batch procedure inside of a glass reactor at 500 °C and self-generated atmosphere. The pyrolysis products consisted of gases, aqueous phase, organic phase (oil), and a dark brown tar laid on the walls of reactor and solid residue remained at the bottom of reactor. The condensable degradation products (aqueous and organic phase) were collected in a trap cooled at –25°C and analyzed by gas chromatography coupled with mass spectrometry (GC-MSD) after dissolution in diethylether.

Pyrolysis products analysis was done by GC-MS, FT-IR and ^{1}H-NMR

Results and Discussion

Pyrolysis of biomass gave about 15-25 wt % gases, 15-30 wt% aqueous phase, 6-28 wt% oil, 1.5-7 wt% tar and 30-40 wt% residue (excepting BSP and Pine Cones with extreme values of 18 and 50 wt% residue respectively, probably due to lowest, respectively highest lignin amount), strongly depending on the biomass sample. Oil and tar were the fractions with greatest variation among studied samples. Unextracted Grape seeds gave lowest amount of oils and Brassica Rape gave lowest amount of tar. BSP gave highest amount of oils, this sample being the richest one in carbohydrates.

Pyrolysis of biomass gives polar oxygenated compounds coming from its lignocellulosic components and these compounds were partitioned between oil and aqueous phase. The distribution of compounds in oils strongly depends on biomass source and pretreatment – Figure 2.

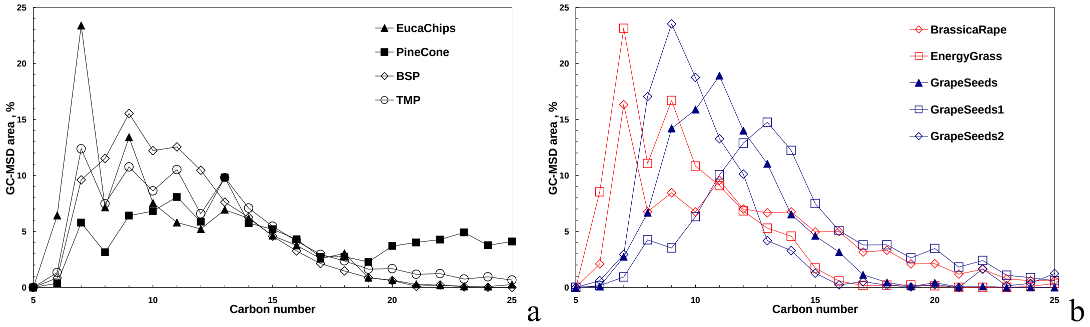

Figure 2. The distribution of various compounds in the pyrolysis oil obtained by biomass versus the carbon number

It is seems that the second groups of samples give a higher quantity of light compounds. The difference between samples is also evident in spectral data.

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Analysis of Oligosaccharides in Ionic Liquid Containing Solutions

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ABSTRACT

The controlled breakdown of lignocellulosic biomass to saccharides for further transformation to biofuels and chemicals is currently a very active research topic. Untreated biomass is however very recalcitrant towards enzymatic hydrolysis of the polysaccharide constituents and pretreaments are needed to render the biomass more susceptible for hydrolysis. A number of ionic liquids (ILs, salts with melting points < 100 °C) have the ability to dissolve biomass and thus also potential to serve as a powerful pretreatment method. Two different routes have been described for the use of ILs to promote biomass hydrolysis: 1. Dissolution in IL and regeneration of the biomass by adding a counter-solvent, whereby an easily hydrolysable substrate is obtained (Dadi et al. 2007) and 2. "*In-situ*" hydrolysis of biomass in a solution containing significant amounts of IL (Kamiya et al. 2008). Though the literature is seeing a growing amount of papers dealing with this topic, very little has been published about the difficulty of analysing soluble carbohydrates in IL containing matrices, such as hydrolysates from "*in-situ*" saccharification or mixtures obtained in the regeneration of biomass.

According to our experience significant contents (> 5 – 10 %) of ILs in a sample matrix will have deteriorating effects on any common method used in carbohydrate analytics, these including *e .g* DNS assay, several chromatography modes and capillary electrophoresis (CE) of underivatized saccharides in both direct and indirect detection modes. The derivatization of saccharides with UV active compounds at their reducing end was found to be a beneficial method to increase the detectability and by employing this strategy very low concentrations of mono- and oligosaccharides could be analysed by CE both qualitatively and quantitatively in the presence of high levels of ILs. It was found that the choice of derivatization reagent needs to be carried out based on the matrix IL and the different ILs influenced the CE analysis to very different degrees. In our work, we examined the influence of several hydrophilic, cellulose dissolving ILs. UV active labelling compounds used in our work include 4-aminobenzonitrile (ABN), 4-aminobenzoic acid ethyl ester (ABEE) and 6-aminoquinoline (6-AQ).

The CE method with pre-column derivatization was optimized and further developed based on an existing method (Sartori et al. 2003). Based on this optimized method, we assessed the separation of different wood-derived monosaccharides and oligosaccharides in four different matrices: pure water, 20 and 40 % (v/v) 1,3-dimethylimidazolium dimethylphosphate [DMIM]DMP and 20 % (v/v) 1-ethyl-3-methylimidazolium acetate [EMIM]AcO. Cellooligomers ranging from glucose to cellohexaose were calibrated against galactose as internal standard in all four matrices and a great number of IL containing hydrolysis samples was analysed employing the calibrated method (Fig 1). Interestingly, it was found that the presence of certain ILs in quite high concentrations could improve the separation of monosaccharides and the ILs cannot thus directly be said to deteriorate the analysis results in all cases. The separation of cello-, manno- and xylooligomers was studied employing this method in

aqueous sample matrices, though mannooligomers could not be separated from each other by this CE mode.

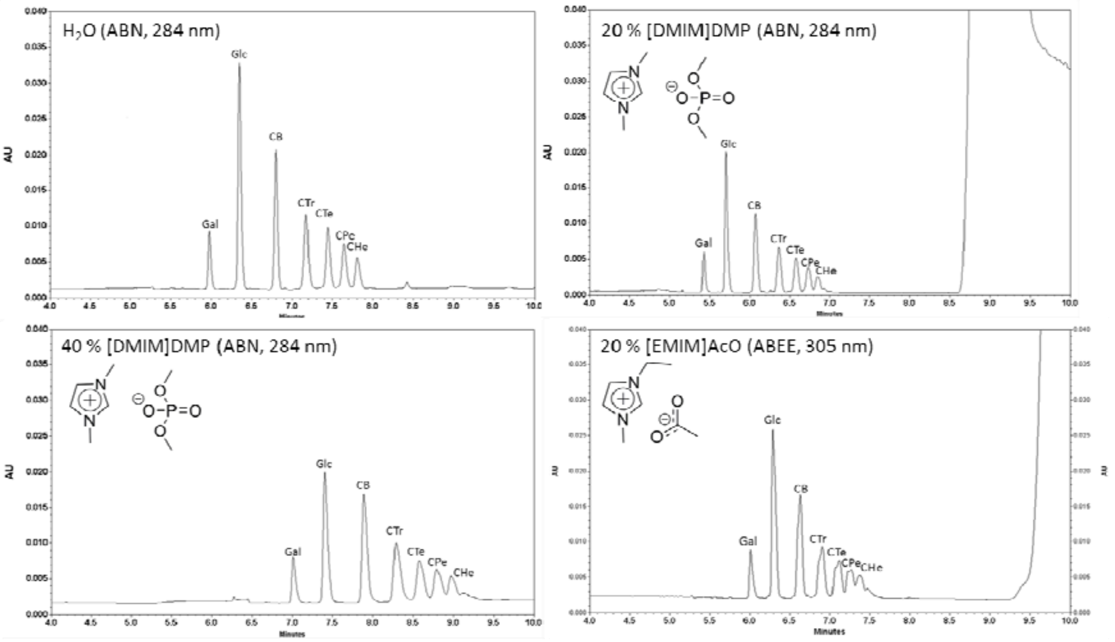

Figure 1: Analysis of derivatized cellooligomers in four different matrices. Gal – galactose (20 mg/L), Glc – glucose (100 mg/L), CB – cellobiose (100 mg/L), CTr – cellotriose (100 mg/L), CTe - cellotetraose (100 mg/L), CPe – cellopentaose (100 mg/L), CHe – cellohexaose (100 mg/L).

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FROM ORGANOSOLV OLIVE TREE PRUNING LIGNIN TO CHEMICALS: SCREENING CATALYST

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ABSTRACT

Phenolic compounds are needed in different fields e.g.: polymers formulation, drugs production, cosmetics, paints... Most of the phenolic compounds come from petroleum after cracking and refining it. As it is well known, petroleum reserves are decreasing and the push of the environmental policies make a good idea to diversify these chemicals origin. Lignocellulosic biomass could be used as a raw material for energy production but also for chemicals production. In these sense, lignin represents the major phenolic compounds source in nature. Lignin revalorization as a phenolic compounds source also could be a key economical factor for the second generation bioethanol plants.

In the present work, organosolv lignin was obtained from olive tree pruning using optimized conditions (200 ºC, 70% ethanol concentration 1:6 solid:liquid ratio, 90 minutes). Lignin was subjected to hydrothermal depolymerization catalyzed by bases. The used bases were: sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide and potassium carbonate. An experiment without catalyst was carried out as a reference.

In Table 1 the obtained oil yield referred to the initial lignin for each catalyst is presented. As it could be observed, the highest yield was obtained when sodium hydroxide was the catalyst and the lowest when no catalyst was added to the reaction mixture. Oil yield was also high for the experiment where potassium carbonate was the base. Calcium hydroxide catalyst gave the lowest oil yield. It was observed that the action of a base as a catalyst improved in all cases the oil yield gave by the no-catalyst experiment meaning that high hydroxyl ion or carbonate concentration favoured lignin hydrothermal depolymerisation. Depolymerization reaction also produced another non-desirable product, coke. Coke formation was enhanced by hydrolysis mechanism. The results in Table 1 suggested that the bases strength affected coke formation since the lowest values were given by sodium and potassium hydroxides. Residual lignin results seemed to be confusing but it has to be taken into account the coke formation. In these sense, low residual lignin content does not involve high oil content. For instance, the reference experiment looked as if it gave the best conversion since it has the lowest residual lignin content but it should be noticed that its coke yield is much higher than its oil yield. These data suggested that lignin alkali depolymerization could be improved.

	H_2O	NaOH	KOH	LiOH	K_2CO_3	$Ca(OH)_2$
Oil yield (%)	6.85	19.74	12.78	13.48	16.81	10.71
Coke (%)	35.58	5.33	3.48	13.61	9.38	10.23
Residual lignin (%)	15.61	43.61	43.46	42.88	34.65	39

Table 1. Base Catalyzed lignin Depolymerization yields.

Table 2 illustrates oil composition, the compounds percentages are referred to oil weight. When no catalyst was added, a wide variety of products were obtained. Among them, it has to be stress the high guaiacol and syringol content and the absence of cresols. Potassium carbonate experiment yielded the widest monomeric compounds diversity. Catechol and 4-methylcatechol were the main products and cresols obtaining was not clearly favoured. Hydroxide catalysts yielded as main compounds: phenol, cresols, catechol and 4-methylcatecol. This was not the case of calcium hydroxide. Calcium hydroxide was not strong enough to enhance phenol, cresol and catechol production. These results suggested that the reaction took place via different mechanisms for the hydroxide catalysts, in the case of the calcium hydroxide depolymerization mechanism seemed to be more similar to the hydrolysis experiment where no cresols where obtained and syringol was produced.

Compound	H_2O	NaOH	KOH	LiOH	K_2CO_3	$Ca(OH)_2$
phenol	0.37	1.01	1.07	0.91	0.49	0.27
o-cresol	-	0.16	0.15	0.14	-	-
p-cresol	-	0.23	0.22	0.23	0.08	-
m-cresol	-	0.25	0.24	0.25	-	-
guaiacol	13.86	1.24	1.58	0.45	2.14	5.15
catechol	0.76	10.22	15.13	7.86	13.58	0.65
4-methylcatechol	-	5.16	3.11	7.00	5.56	0.48
Syringol	20.40	-	-	-	0.14	0.27
Acetovanillone	0.17	-	-	-	0.08	-
Syringaldehyde	-	-	-	-	0.07	-
3,5-dimetoxy-4-hydroxyacetophenone	0.24	-	-	-	0.05	-
4-hydroxy-3-methoxy-phenylacetone	0.36	-	-	-	-	-

Table 2: Compounds present in the obtained oil Compounds yields (%) are referred to oil weight (w/w).

Concerning the obtained phenolic compounds, it seemed that guaiacol and syringol were produced easily when no catalyst was added to the reaction mixture but the yields of both products decreased as the employed base was stronger, above all, syringol content that disappeared for sodium, potassium and lithium hydroxides experiments. The reaction takes place via carbenium ions meaning that syringylic carbenium is more stable than guaiacylic carbenium since it has more methoxy substituent to disperse the positive charge. Then, syringylic products are produced easier as the reaction intermediate is more stable. Demethoxylation reactions of guaiacol and syringol took place to produce cresols and catechols, these reactions only occurred when the strongest bases were added to the reaction mixture.

CHEMICAL CHARACTERIZATION OF GRASS FOR UTILIZATION IN A BIOREFINERY PROCESS

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ABSTRACT

The chemical composition of a Hungarian grass sample, provided by Professor Andras Vig of Budapest University of Technology and Economics, was characterized by means of various wet chemical and instrumental analytical techniques.

The ash content determined at 525 °C as well as at 850 °C varies only slightly between 5.2 and 5.0 %, respectively. EDX analyses were performed for the elemental composition of the ashes. The content of elements, which were found (e.g. C, O, F, Na, Mg, Si, P, S, Cl, K, Ca, Mn) varies depending on the temperatures applied.

Extractions were carried out with different solvents by means of conventional Soxhlet and ASE equipment. A successive extraction with organic solvents was performed with petroleum ether, acetone and methanol. The amounts of the extractions vary between 0.4 and 5.1 % depending on the polarities of the solvents. This more time consuming extraction with three different solvents shows better separation of the substance classes and facilitates subsequent analyses of the constituents of the respective extracts. In addition, water extractions at room temperature and under reflux were carried out. The resulting extract contents vary between 6.7 and 14.0 %.

Qualitative comparison of the extracts was carried out by means of UV and FTIR spectroscopy as well as GC/MS analyses. For the GC/MS, the organic extracts were measured after derivatisation. The main constituents, such as fatty acids and sugar components were identified.

For the determination of the polysaccharide content and composition, hydrolyses with trifluoroacetic acid at 100 and 107 °C were undertaken, because besides glucose the more labile xylose was determined as the main sugar component.

A lignin content of 21 % was determined with a mixture of sulphuric acid and hydrobromic acid (“Runkel lignin”). A so called milled wood lignin (MWL) was obtained by ball milling the extracted sample for 72 h in toluene, followed by extraction in a mixture of dioxane-water under ultrasonic treatment and several further purification steps.

For further characterization, a multifunctional Py-GC/MS system, which combines different pyrolytical methods for the investigation of polymers, will be applied to examine the straw sample and the MWL. This equipment allows new implementations for the investigation of biopolymers: e.g., by means of evolved gas analysis (EGA), which provides results similar to thermogravimetric analysis, the arising gases formed by defined heating intervals can be used for characterizing the thermal behaviour of a sample. The application of selected ion monitoring (SIM) during EGA offers further options to determine specific components like volatile organic compounds. A so called heart-cut analysis (HCA) can adopt the heating conditions of the EGA programme and allows the analysis of the evolved gases for specified temperature ranges, whereas gases of subjacent temperature ranges can be discarded from the system. Moreover the conventional pyrolysis technique via single-shot analysis (SSA) will be carried out.

NEW ASPECTS IN THE ANALYSIS OF EXTRACTIVES OF SOME COMMERCIALLY TRADED TROPICAL TIMBERS

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ABSTRACT

The use of tropical wood species is appreciated due to the attractive coloring of the wood and the durability against wood destroying fungi and bacteria. They are used as flooring for a special classy look or as weatherproof faces of buildings. To understand the variations in durability against fungi, discoloring of surfaces and other difficulties in performance between the species, the chemistry of the extractives needs to be known. The extractives of these species consist of a great variety of components, of which only some are known. For example, the ingredients of lapacho (*Tabebuia spp.*) are known to be bioactive and have been used as medicine by indigenous people in various ways for a long time (Schmeda-Hirschmanna et al. 2003). Tectoquinone in teak (*Tectona grandis*) is known to be one of the major components responsible for its natural durability (Schwager et al. 1998).

With conventional analytical methods, such as GCMS, first identifications are made. Many different fatty acids as well as different steroids like sitosterol and stigmasterol were found. Quinones like lapachol and flavonoides like taxifolin were also identified. However, there are still difficulties in analyzing high molecular compounds, e.g. the ones which are present as glycosides. Besides classic methods like GCMS for characterization and identification, evolved gas analysis (EGA) and so called bubble separation were used for characterization and separation of these extract compounds for the first time. Biologically active compounds can be enriched and separated using foam fractionation, a separation method belonging to the adsorptive bubble separation (ABS). For the enrichment of surface-active substances, gases (e.g. nitrogen) are introduced, whereupon the substances tend to adsorb on the hydrophobic surface of gas bubbles and, therefore, enrich in the formed foam (Backleh-Sohrt et al. 2005).

Examination of the wood surface by means of FTIR/ATR shows the changes due to extraction with water (which simulates leaching in outdoor utilization in a first attempt). Bringing the information together the wood species can be divided into groups with similar ingredients and similar behavior to derive first maintenance instructions leading to a better preservation of the wood.

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CHEMICALS PRODUCTION BY THERMAL CONVERSION OF BIOMASS

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ABSTRACT

Nowadays, lignocellulosic agricultural wastes are regarded as alternative source of renewable raw materials. By different processes, chemicals with high added value such as biofuels, organic acids or biopolymers, could be obtained from these alternative materials components (Perego and Bianchi 2010, Bhatnagar and Sillanpää 2010).

In this work two methods have been studied to convert corn cobs into different organic acids and furfural.

In a first method, corn cobs were treated under high temperature and pressure in the presence of alkaline catalyst in a batch reactor. The optimal reaction conditions were determined to produce the maximum content in lactic acid. For this purpose, under the same conditions (275 ºC and 30 min) different concentrations of $Ca(OH)_2$ as alkaline catalyst were used (from 0.32 M to 1M). The maximum content of lactic acid (6.72 g/L) was obtained with 0.7 M of $Ca(OH)_2$. With this catalyst concentration, different reaction conditions were carried out varying the temperature 250, 275 and 300 ºC and reaction time 15, 30 and 45 min. The optimal conditions to produce the highest yield of lactic acid from corn cobs in alkaline conditions were determined at 300 ºC and 30 min, achieving 44.76 % (7.38 g/L of lactic acid) respect to the total cellulose and hemicellulose contained in the initial raw material (Fig. 1). The achieved conversion yield is higher than reported results by other authors (Kishida et al. 2006, Yan et al. 2009, Yan et al. 2010).

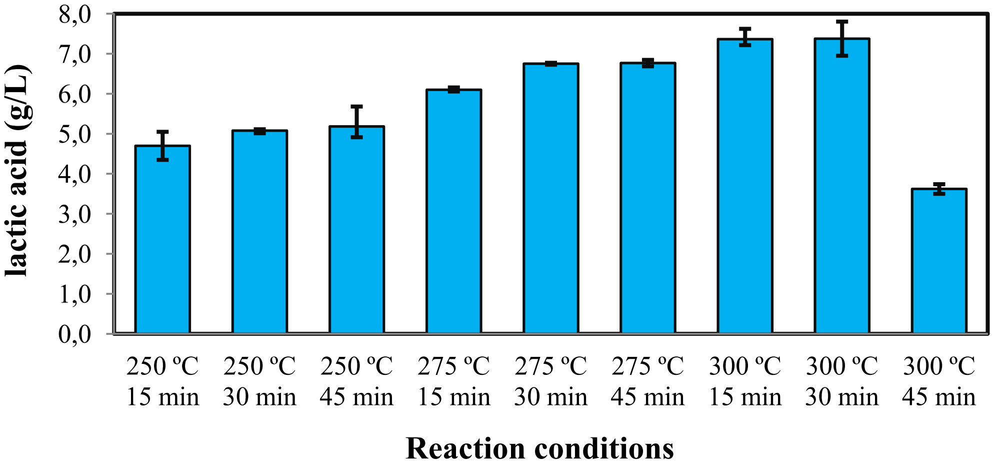

Figure 1: Lactic acid concentrations at different reaction conditions.

In the second method, furfural production from corn cobs was studied by using microwave technology. Corn cobs were subjected to autohydrolysis process to obtain a liquor rich in xylans. The liquor was treated in a microwave at different contiditions in presence of HCl and H_2SO_4 as acid catalysts to improve the furfural production. To determine the optimal conversion conditions, the reaction conditions were varied:

catalysts concentration (from 0 to 4%), the time (from 1 to 5 min) and temperature of reaction (from 160 to 200 ºC). Under the studied conditions, a maximum furfural yield of 37.47 % respect to the raw material total hemicelluloses (13.9 g/L) was obtained at 180 ºC and 5 min, using 2 % of HCl as catalyst. Other reported studies achieved 8.67 and 13.7 g/L of furfural, using other raw materials and methods (Riansa-ngawong and Prasertsan 2011, Vazquez et al. 2007). Further experiments are ongoing to determine the optimal conditions which maximise the furfural production.

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APPLICATION OF CAPILLARY ELECTROPHORESIS FOR MONITORING OF HEMICELLULOSE PROCESSING

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ABSTRACT

Necessity to find renewable alternatives for current oil based production of motor fuels and commodity products has led to a resurgence of the research of biomass processing. Analysis of sugars from the samples of biomass processing is demanding for both separation and detection. Techniques used for separation of saccharides include gas chromatography, high-performance liquid chromatography and capillary electrophoresis (CE). Novel methods facilitating the monitoring of hemicellulose processing are therefore demanded. Here we demonstrate the suitability of capillary electrophoresis in the analysis of hydrothermal pre-treatment and enzymatic hydrolysis of pre-treated willow. We found an excellent agreement between the results from CE and HPLC that has been conventionally used for the monitoring of hemicellulose processing. An advantage of CE was that it enabled simultaneous separation of different saccharides and pre-treatment by-products of lignocellulose, furfural and 5-hydroxymethylfurfural (Fig.1).

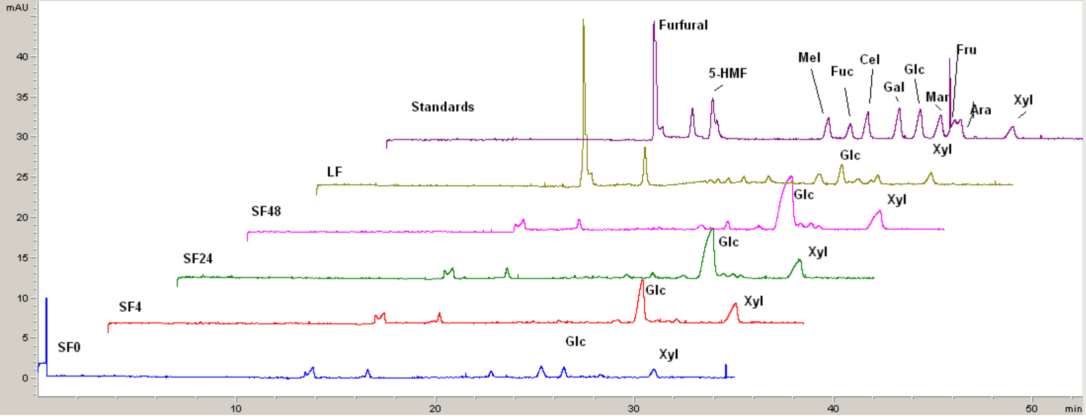

Figure 1: CE separation of liquid fraction (LF) from the HPW pre-treatment of willow and sugars released upon enzymatic hydrolysis of solid fraction (SF).

CE was also found to be suitable for the monitoring of cellulose degradation in ionic liquid (IL), 1-butyl-3-methylimidazoliumchloride (Fig.2).

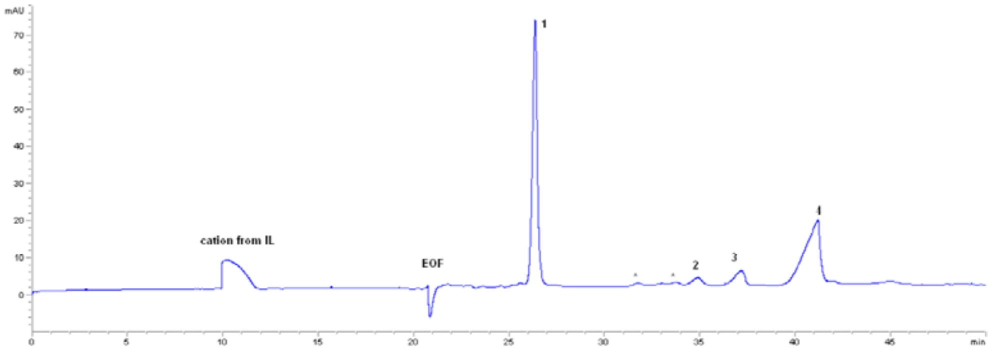

Figure 2: The electropherogram of the monitoring of the formation of di- and monosaccharides during hydrolysis of cellulose in IL. The peaks identified: 1 – 5--hydroxymethylfurfural, 2 – fucose, 3 – cellobiose, 4 – glucose.

COMPARATIVE STUDY OF DIFFERENTLY TREATED (COOKED AND BLEACHED) INDUSTRIAL GRASS AND STRAW FIBRES RESPECTIVELY BY SCANNING ELECTRON MICROSCOPY AND ATOMIC FORCE MICROSCOPY

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ABSTRACT

The offered fibres have been analysed for getting sufficient information about appropriate supermolecular and surface characteristics.

SEM (Scanning Electron Microscopy, Jeol-JSM LV) [Fratzl P. 2003] and AFM (Atomic Force Microscopy µTA 2990, tapping mode) [Gustafsson I. (Polymer) 2003, Gustafsson I. (Colloids and Surfaces) 2003, Paessler H. 1996] mapping have been used for the measurement.

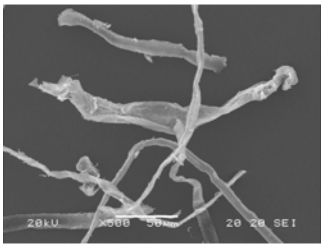
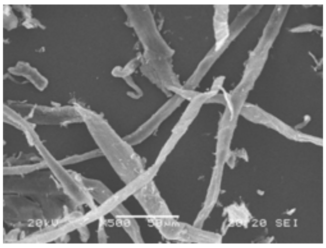
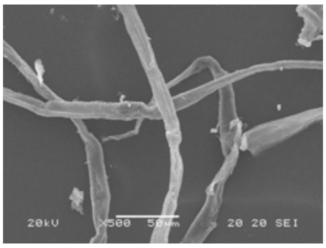
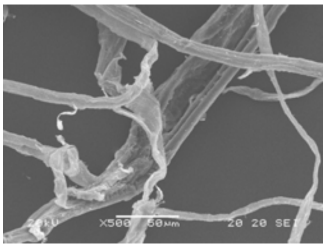
Scanning Electron Microscopy (SEM) measurements		
Straw fibres	 **without bleaching**	 **with bleaching**
Industrial grass fibres	 **without bleaching**	 **with bleaching**

Figure 1: SEM pictures of straw fibres without and with bleaching, respectively.

According to the SEM pictures (Figure 1.) surface of the fibres have been rougher after bleaching. This statement could be proved also with Atomic Force Microscopic data (Figure 2.)

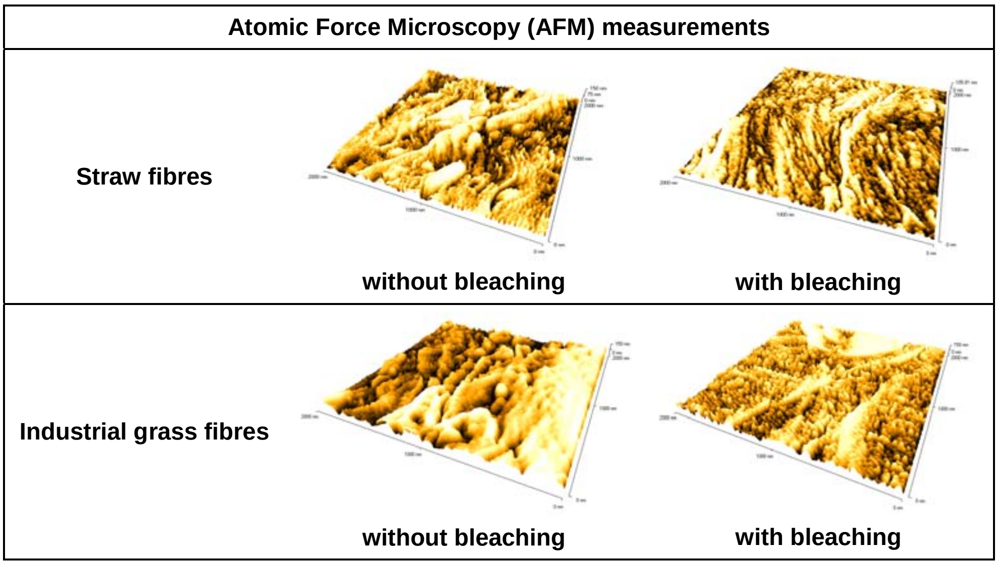


Figure 2: AFM pictures of straw fibres without and with bleaching, respectively.

The gained surface characteristics elucidated the differences between the two studied fibres and enabled the optimisation of fibre-fibre interaction during the sheet making process.

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MONOMERIC PHENOLIC COMPOUNDS FROM WASTE HYDROLYZED LIGNOCELLULOSIC MATERIALS

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ABSTRACT

The chemical treatment of wood to cellulose and monosaccharides is connected with the conversion of approx. one third of its mass into a lignin component as a residue. The bioethanol production from raw materials increases and hence the lignin utilization starts to attract significant interest.

The investigations on bioethanol production from agriculture lignocellulosic raw materials (wheat straw and maize stalks) were carried out. Steam explosion and dilute acid hydrolysis are used as pre-treatment methods. Their application was followed by enzyme hydrolysis with cellulase enzyme complex combined with β-glucosidase (Tsekova et al. 2011). The solid lignin-cellulosic mass which is in fact a waste product in this process is a suitable source of monomer phenolic compounds of well known inhibiting effect towards hydrocarbons oxidation (Nenkova et al. 2011).

The aim is to investigate the nature of the low-molecular products which are left in the liquid phase after the alkaline treatment from waste hydrolyzed lignocellulosic materials.

The alkaline treatment was performed in stirring autoclaves made of stainless steel, heated in a bath of polyethylene glycol at 180°C for 4 hours. A 5 % water solution of NaOH was used as a depolymerisation agent at biomass/ solution NaOH ratios - 1:8. The process conditions were determined based on the results of our earlier investigations (Nenkova et al. 2008, Vasileva et al. 2007, Radoykova et al.2010). The liquid fraction is subjected to triple extraction with toluene at organic/aqueous phase ratio 1:5 (Vasileva et al. 2007). The liquid phase separated after the extraction with toluene is subjected to double extraction with ethyl acetate at an organic-liquid phase ratio of 1:5. By means of GC/MS analysis, the following compounds have been identified in both extracts, but in different quantities: 2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone, etc. (Fig.1). The amounts of obtained extracts, insoluble residue and precipitated and non-precipitated lignin were determined.

The highest yield of low molecular weight compounds, extracted with toluene and ethyl acetate were obtained by alkaline treatment of the waste of steam explosion enzyme hydrolyzed straw (Fig.2). Possibly, the acid pre-treatment leads to some condensation of lignin in the lignocelluloses material, whereas explosive steam treatment (190°C for 10 min.) contributes to the destruction of lignin. It was found that the quality of dissolved and then precipitated lignin is highest in this processing.

That investigation has shown the type and yield of the monomeric phenolic compounds obtained from waste hydrolyzed lignocellulosic materials, which can be used for practical application.

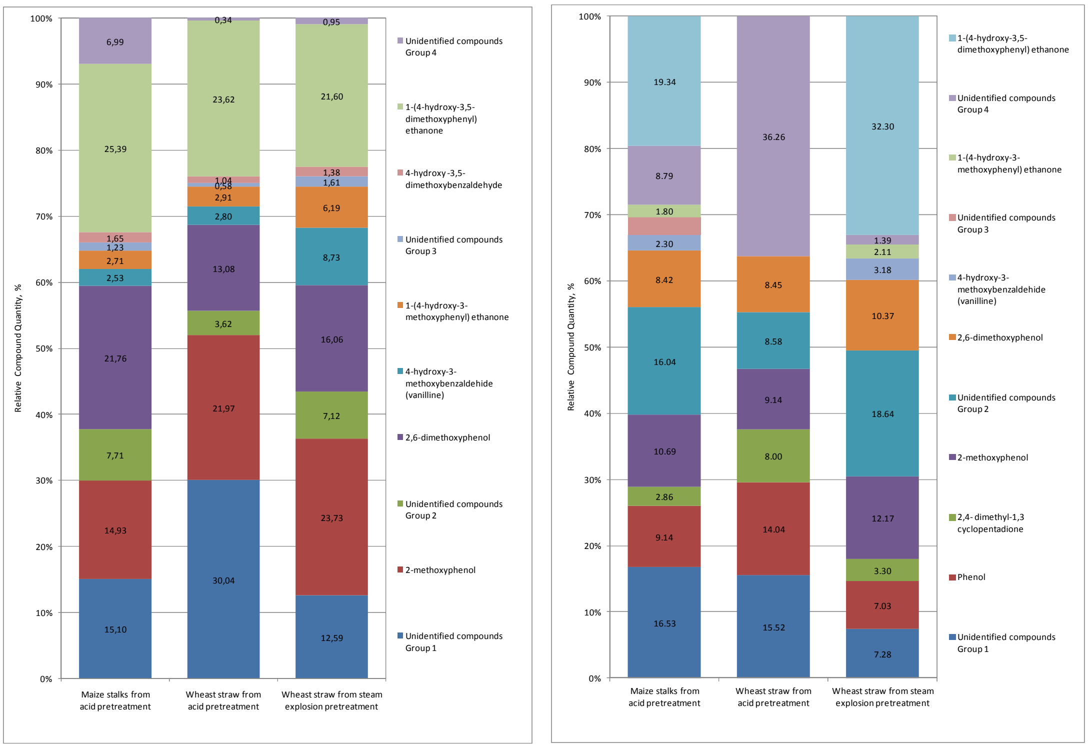

Figure 1: Compounds identified in toluene extract (left) and in ethyl acetate extract (right).

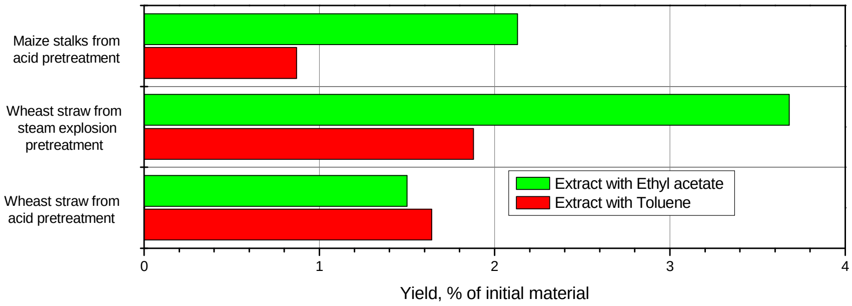

Figure 2: Yield of extracts.

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ADVANCED DEPICTING TECHNIQUES AND ANALYSIS TOOLS FOR CHARACTERIZATION AND QUANTIFICATION OF BIOMASS STRUCTURES

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ABSTRACT

The adequate utilization of lignocellulose material, wood pulp fibres and their nanofibrillated materials requires a comprehensive understanding of their structural and chemical properties. In this respect, microscopy techniques play an essential role. Novel microscopy techniques open for new opportunities to explore structures, provided that their limitations and complementary capabilities are considered and utilized adequately.

PFI has experience and expertise with methods covering a wide range of structure sizes, from the macro to the sub-nano level (Chinga-Carrasco and Syverud 2011, Chinga-Carrasco et al. 2011a and b). The methods are based on e.g. optical microscopy, laser profilometry, advanced electron microscopy, X-ray micro-tomography and computerized image analysis.

Multiscale analysis, using different depicting techniques, is essential in PFIs research on the production, characterization and utilization of micro fibrillated cellulose (MFC), see Figure 1. Such analysis covers several techniques, from optical microscopy to field-emission SEM, which offers the opportunity to study the size distributions of MFC, as shown for a MFC film in Figure 2. MFC and films thereof may be characterized by complementary techniques such as contact angle measurements, XPS, FTIR, carboxylate concentration and intrinsic viscosity (Syverud et al. 2010).

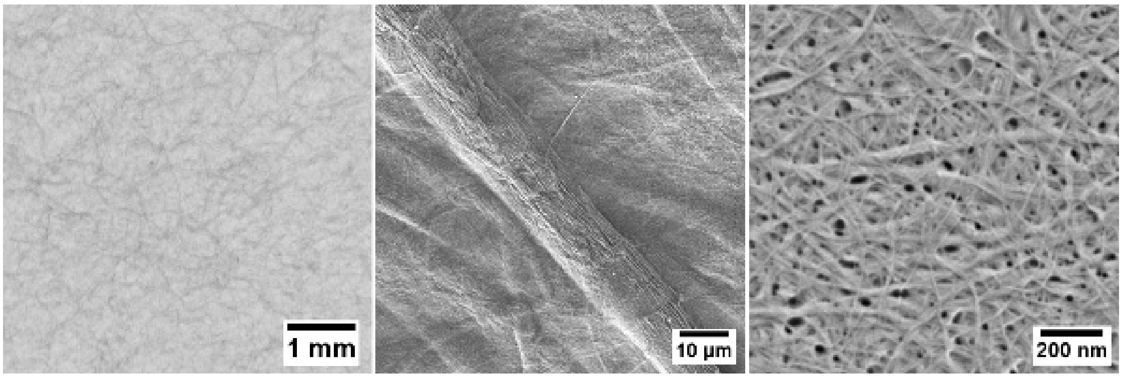

Fig. 1. Multiscale analysis of micro fibrillated cellulose Left: Optical image showing poorly fibrillated fibres as dark threadlike structures. Middle: The surface of a fibre surrounded by smooth areas composed of cellulose nanofibrils. Right: Image of cellulose nanofibrils, acquired with a field-emission SEM.

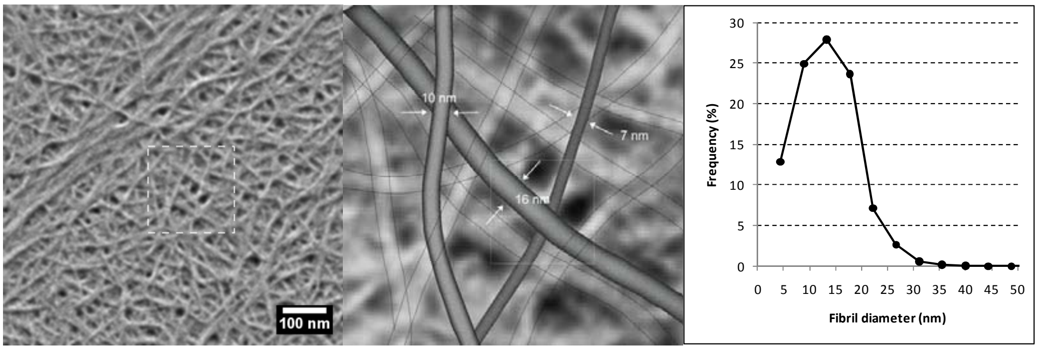

Fig. 2 Left: FE-SEM surface image of an area of a MFC-film. Middle: Schematic representation of some fibrils indicated in the area marked with a dashed rectangle in the left-image. Right: Diameter distribution of cellulose fibrils (Syverud et al. 2010).

Norway spruce is an important resource in biorefineries in Scandinavian countries. Wood biomass is highly recalcitrant to deconstruction and offers major challenges to pre-treatment prior to further processing (e.g. enzymatic hydrolysis). Microscopy techniques, such as SEM and FE-SEM, also offer valuable tools for evaluation of the effects of pre-treatment processes in biorefinery concepts (chemical, biochemical or thermochemical). This is exemplified in Figure 3, which shows the delamination and opening of the cell wall structure as an effect of the pre-treatment of spruce wood chips.

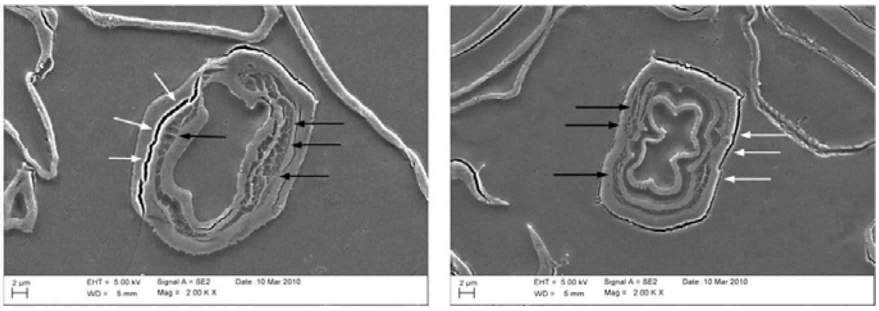

Fig 3. FE- SEM images of fibre cross sections of pre-treated Norway spruce. Black arrows indicate delamination of the fibre wall. White arrows indicate artefacts caused by sample preparation.

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SODA LIGNIN FROM WHEAT STRAW; ISOLATION AND CHARACTERISATION

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ABSTRACT

Future biorefineries might use abundantly available biomass as feedstock for the production of energy carriers, chemicals and materials from its composing elements: cellulose, hemicellulose and lignin. Obtaining fermentable sugars from lignocellulosic biomass usually requires two steps: firstly a pretreatment in which the cellulose fraction is isolated by hydrolysis of hemicellulose and delignification of the wheat straw, followed by enzymatic hydrolysis of the cellulose fraction to monomeric sugars. In addition, pretreatment can serve to isolate higher quality lignin fractions that can be upgraded for various purposes like binders and aromatic chemicals.

In this study lignin from wheat straw was isolated from a side stream of the pretreatment process, i.e. the alkaline black liquor. After pretreatment, the carbohydrate and lignin fractions were separated and characterised by various techniques (i.e. HPAEC-PAD, FT-IR, SEC, and NMR) on their composition and properties. Depending on the pretreatment method different types of lignins were obtained. Also the scale of work (lab scale or semi-technical scale) and the isolation method had a large influence on the lignin obtained.

Alkaline pretreatment of wheat straw resulted in an efficient fractionation under mild conditions. The pretreatment method provided a polymeric sugar fraction with good enzymatic degradability and lignin of reasonable quality. These results show potential for development of a wheat straw based biorefinery concept using alkaline pretreatment.

Soda lignin from wheat straw is one of the 5 lignins that are included in the Round Robins. First results will be presented on characterisation of the lignins by methods used in the Round Robins, i.e. thermal analysis and lignin content.

This work has been performed in the framework of the European FP6 Integrated Project Biosynergy (038994-SES6, www.biosynergy.eu) The support of the European Commission is gratefully acknowledged.

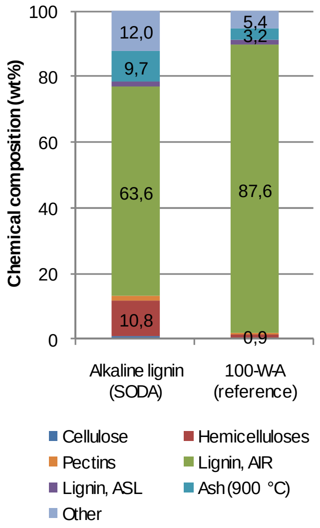

Figure 1: Chemical composition of soda wheat straw lignins

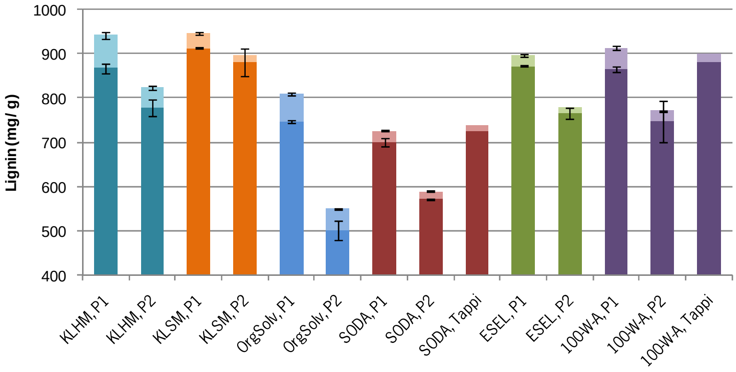

Figure 2: Comparison lignin content determined by Tappi method and FP0901 recommended methods

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FRACTIONATION AND CHARACTERIZATION OF LIGNOBOOST KRAFT LIGNIN WITH EMPHASIS ON ITS ANTIOXIDANT ACTIVITY

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ABSTRACT

The antioxidant properties of lignins open variety of fields for their topical application in industry, healthcare and agriculture (Pouteau et. al. 2005; Ugartondo et al. 2008). Lignin is characterized by higher stability and slower degradation rate than compounds with low molecular weight and could be applied in those fields in which the employment of a single molecule with antioxidant activity is inefficient. However, the well-known polydispersity and chemical heterogeneity along MMD ask for the detailed characterization of the lignins composition and structure, necessary for determination of their applicability as antioxidants in targeted systems. Despite the efforts made to increase the homogeneity of kraft lignin, it is significantly heterogeneous in terms of composition, structure and MMD. Sequential extraction of lignin with organic solvents seems to be attractive due to opportunity to decrease lignin heterogeneity (Ropponen et al. 2011).

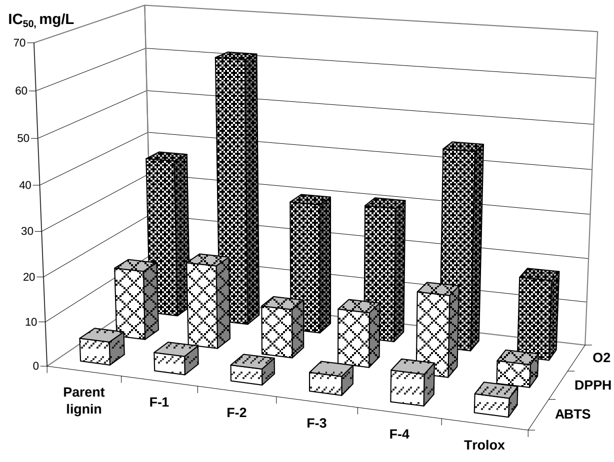
In the present study, hardwood kraft lignin, isolated from the original black liquors by Innventia AB according to the LignoBoost process, was fractionated by sequential extraction with organic solvents of increasing hydrogen-bonding capability: dichloromethane, n-propanol and methanol. Using physico-chemical methods (SEC, Py-GC/MS, EPR–and UV/VIS spectroscopy) and wet chemical analysis, the characteristics of each fraction in terms of functionality, MMD and composition of lignin substructures were determined and considered together with the results of DPPH$^{\bullet}$, ABTS$^{\bullet+}$ and $O_2^{\bullet-}$ antioxidant assays with the aim to understand the relationships governing antioxidant properties of lignin. Besides, the biological activity of the lignin and its fractions was assessed in 2-days tests on summer wheat (*Triticum v.*) sproutings.

The fractionation procedure solubilized in total 80% of the lignin. Three soluble and one insoluble fractions, containing 23.2% (dichloromethane-soluble fraction), 48.3% (propanol-soluble fraction), 9.2% (methanol-soluble fraction,) and 19.3% (insoluble residue after sequential extraction) of the parent hardwood lignin, were obtained. The SEC analysis (Agilent 1100 system, UV-DAD/RI detectors, 60°C, column AGI_PLgel 5µm MIXED-D 300x7.5 mm, eluent DMSO) showed that the fractionation yielded fractions of increasing molecular weight (Table 1). All fractions have much more narrow MMD in comparison with the parent lignin.

The radical scavenging capacities in ABTS$^{\bullet+}$, DPPH$^{\bullet+}$ and $O_2^{\bullet-}$ tests of the fractions soluble in n-propanol and methanol were significantly higher than those for parent lignin and two other fractions (Fig, 1) and were only slightly lower in comparison with the widely used reference standard Trolox (water soluble analogue of E vitamin).

Table 1: MMD of hardwood Lignoboost kraft lignin and its fractions.

Fraction	Average M_n, Da	Average M_w , Da	M_w/M_n
F-1 - CH_2Cl_2-soluble	184	799	4,3
F-2 - C_3H_7OH-soluble	392	1996	5,1
F-3 - CH_3OH-soluble	2137	4488	2,1
F-4 –insoluble residue	4959	18396	3,7



Parent lignin	421	4786	11.4

Figure 1: Radical scavenging capacity of hardwood Lignoboost lignin and its fractions determined in the tests with ABTS$^{\bullet+}$, DPPH$^{\bullet}$ and $O_2^{\bullet-}$ radicals. IC_{50} – a concentration of lignin sample needed for 50% inhibition of the test radicals. The fractions are denoted as in the Table 1.

The results of Py-GC/MS, EPR and chemical analysis showed distinctions existing between the fractions obtained in terms of carbohydrates and lipophillic extractives admixtures, OH_{phen} and OCH_3 groups contents, the ratio between syringyl and guaiacyl substructures, the portion of the side chains containing C=O groups and C=C bonds, and the extent of conjugation of lignin macromolecule. The characterization of lignin fractions brought the opportunity to estimate the contribution of different lignin features on its antioxidant properties. The molecular weight and extent of conjugation of lignin macromolecules were found to be the main parameters that establish lignin antioxidant activity. The antioxidant capacity linearly increases with increasing extent of conjugation, whereas the relationship between IC_{50} and average M_w passes through the point of extremum at $M_w \sim 2000$ Da. Phenolic and methoxyl functional groups contents are also influential features. The polydispersity and heterogeneity (the presence of carbohydrates and lipophillic extractive substances) have negative impact on the lignin radical scavenging capacity.

In the test on inhibition of oil oxidation by O_2 (a substrate - rapeseed oil), it was shown that the dichloromethane-soluble fraction, in spite of the lowest radical scavenging capacity, has a good potential as antioxidant for non-polar systems. Solvent fractionation can be considered as prospective tool for obtaining efficient antioxidants from LignoBoost kraft lignin.

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