# ReWoBioRef - Mobilisation and utilisation of recycled wood for lignocellulosic biorefinery processes

## FINAL REPORT

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| **Title of the research project** | Mobilisation and utilisation of recycled wood for lignocellulosic biorefinery processes |
| **Coordinator of the project** | Dr. Guido Hora |

## BASIC PROJECT DATA

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| **Project period** | 01.07.2014-30.06.2017 |
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| **URL of the project** | http://www.rewobioref.eu |

## FUNDING

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|---|---|
| **Total budget in EUR** | 1,636,737 |
| **Public funding from WoodWisdom-Net Research Programme:** | Total funding granted in EUR by source: |
| Finland<br>Tekes – the Finnish Funding Agency for Innovation | 359,000 |
| Germany<br>Agency for Renewable Resources (FNR) | 550,217 |
| Slovenia<br>Ministry of Education, Science and Sport (MIZS) | 210,000 |

| | |
|---|---|
| United Kingdom | |
| The Forestry Commissioners (FC) | 128,020 |

**Other funding:**

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|---|---|
| Enerkem Company, Canada | 43,500 – in-kind contribution |
| VTT, Finland | 180,900 |
| St1 Biofuels Oy, Finland | 30,000 |
| Roal Oy, Finland | 30,000 |

**PROJECT TEAM (main participants)**

| Name, degree, job title | Sex (M/F) | Organization | Country |
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**DEGREES** (if relevant)
Degrees earned or to be earned within this project.

| Year | Degree | Sex (M/F) | Name, year of birth and year of earning M.Sc., D.Sc., etc. Degree | University | Supervisor of thesis, supervisor’s organization |
|---|---|---|---|---|---|
| 2015 | M. Sc. | M | Kim-Fabian Reimer, 1989<br>2015, M.Sc. | T. U. Braunschweig | Dr. Guido Hora (WKI)<br>Stefan Andrews (T.U BS) |
| 2016 | B. Sc. | M | Philipp Hachmeister, 1983<br>2016, B.Sc. | T. U. Braunschweig | Dr. Guido Hora (WKI)<br>Felipe Cerdas (T.U BS) |

## PROJECT SUMMARY REPORT

With overall higher use of wood and wooden materials in the future, the importance of recycled wood will increase. Currently, Recycled wood (RW) is mainly used for the production of wood-based composites and for combustion. In the future, use of recycled wood can also be important as feedstock for biorefineries for the production of biobased chemicals and biofuels. Feasibility of recycled wood (A I & A II/A III mix according to German classification) for bioethanol production was explored using steam explosion, two-stage alkaline oxidation (AlkOx) and organosolv (OS) pretreatment processes. The presence of inorganic pollutants and non-wooden material in recycled wood material was investigated. The effect of recycled wood heterogeneity (e.g., variable wood species and wide particle size distribution) on performance of wood pretreatment and subsequent enzymatic hydrolysis was evaluated. In addition, valorisation of side-stream lignin and hemicellulose/sugar fractions were studied to further improve the process economy. Microeconomic analysis of lignocellulosic feedstock for a biorefinery using organosolv cooking and a gasification process was calculated in detail with various price scenarios and various proportions of recycled wood instead of currently used biobased feedstocks and municipal solid wastes for the gasification technology. The results show that the concentration of inorganic pollutants in A I is higher than in fresh wood but below the limit values for polluted wood. Results also support that recycled wood of A I and A II / A III mix may be a potential future raw material for biorefinery, and can significantly improve the economics of investment and operation in an industrial scale biorefinery.

The projects main achievements:

- RW deriving from larger annual process capacity plants with proper sorting systems contains fewer contaminations and provides cleaner secondary recycling wood feedstock.
- RW is a potential low-cost raw material for bioethanol production after efficient sorting. Especially, two-stage alkaline oxidation (AlkOx) pretreatment generated well hydrolysable pulp from AI and AII/AIII grades of RW, and ethanol yields were comparable with fresh spruce. Somewhat lower yields were obtained after steam explosion and ethanol based organosolv cooking.
- However, also organosolv pulping of AI recycling wood was successfully carried out and acid catalysed ethanol/water OS-treatment increased the yield of lignin. Process parameters affected functional groups in OS-lignin. No toxic contaminations were detected.
- Lignin is a potential tackifier in hot melt adhesives (HMA) and novel sustainable HMA formulations using on cellulose-based polymer were developed. The best formulations provided comparable or better performance compared to commercial HMA.
- Side-stream sugars offer a cost-efficient source of hydrophilic components for biobased surfactants. A sustainable method for the production of sugar-based surfactants with controlled architectures was established using click chemistry.
- Economics improve with lower feedstock prices of RW and stable multi-product revenues. LCA model within a “gate to gate” concept indicates trends for Carbon footprints and five other major impact factors.

- Efficient dissemination measures including business related prospects between industrial partners within the consortium were demonstrated.

## 1.1 Introduction

### 1.1.1 Background

According to studies by STAR-COLIBRI “Joint European Biorefinery Vision 2030”, bio-refineries processing a range of lignocellulosic (LC) biomass will be well established within the next 20 years. When considering an investment into lignocellulosic feedstock (LCF) biorefinery today often bioethanol is the product of interest. However, growing research and development work to utilize these feedstocks in the manufacture of other, more value-added chemicals e.g. from sugars derived from lignocelluloses can be noticed. As a by-product, substantial amount of lignin is also produced, and possibilities for lignin valorisation are presently explored to improve the cost-efficiency of lignocellulosic biorefineries producing sugars. Different sources of LC biomass must be used as feedstock, such as dry agricultural residues (straw, peelings, husks), woody biomass, and organic waste (waste paper, residues from waste paper pulping) to ensure a sustainable and reliable supply. Hence, an enormous not yet explored feedstock potential for LCF bio-refineries is in the utilisation of recycled waste wood. However, there is a critical lack of relevant detailed compositional information regarding this feedstock type to be processed in a LCF biorefinery, which should be explored. Pre-treatment technologies, such as the ethanol based organosolv cooking, two-stage alkaline oxidation (AlkOx) and steam explosion, which have been demonstrated for sugar production from lignocellulosics, should also be studied in more detail for recycled waste wood. The production economics of biomass-derived fuels and bio-based chemicals is a major challenge. Thus, state-of-the-art economic models should be created incorporating technological and quality factors of recycled waste wood feedstock for LCF biorefineries. Microeconomic modelling, described here, focuses mainly on the wood recycling sector and shall analyse major cost factors such as procurement, processing and minimal sales proceeds to estimate the profitability for an additional utilisation stream for recycled waste wood in a biorefinery process based on ethanol organosolv cooking.

The **ReWoBioRef** project addresses only recycled waste wood already gone through one utilisation step and therefore is considered as secondary raw material that has reached the end-of-waste criteria according to the EC waste directive. The recycling of this type of waste wood is increasing continuously. However, wood waste recycling in the different EU 28 countries is not yet harmonized.

### 1.1.2 Objectives

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The main objective was to explore the techno-economic feasibility, scientific requirements and material specifications to utilize recycled waste wood in lignocellulosic biorefinery processes as an alternative feedstock source. The secondary aim was to valorize the recycled waste wood components (cellulose, hemicelluloses and lignin), for more sustainable biobased fuels, chemicals and materials. The ReWoBioRef project addressed only recycled waste wood that has already gone through one utilisation stream and therefore is considered as secondary raw material having reached the end-of-waste criteria according to the EC waste directive.

The project had *four* main technical scopes:

1. A predominant focus was on the characterization of recycled waste wood materials by determining the chemical and physical composition of recycled wood mixtures and identifying the selection criteria through defining the technical specifications for processing the recycled waste wood as feedstock in a biorefinery process.
2. Optimal pre-treatment technologies for deconstruction of recycled wood mixtures from different sources and grades have been developed. Ethanol based organosolv (OS) cooking, two-stage alkaline oxidation (AlkOx) and steam explosion (SE) were studied as potential pre-treatment methods for maximal utilisation of cellulose, lignin and hemicellulose fractions originating from the recycled waste wood. Proof-of-concept of patented syngas technology for heavily contaminated waste wood classes was also carried out.
3. The primary aim of the pre-treatment methods was to produce well hydrolysable cellulosic pulp for production of chemicals from renewable sources by fermentation route. In addition, the polymeric and oligomeric lignin and hemicellulose fractions derived from recycled wood mixtures were valorised to improve the economic feasibility along the value chain. The target products were lignin based hot-melt adhesives and hemicellulose based surfactants.
4. Microeconomic and environmental assessments of recycled waste wood as secondary raw material in LC biorefinery processes were performed. Included are cost evaluation and analysis comprising procurement, processing and revenues for waste wood prior and after recycling and an LCA analysis comparing state-of-the-art with new utilisation streams for recycled wood.

## 1.2 Results and discussion

### ***WP 1 Characterization of recycled waste wood materials and selection criteria for pre-treatment steps***

Different types of recycling wood were collected from recycling companies in Germany (G), UK (E), Finland (F), Slovenia (S1) and a public utility company from Slovenia (S2) (Table 1.1). The collection of recycling wood was performed by recycling companies as part of their usual selection of recycled wood material. For sampling, recycled wood material was taken at all sites from at least five different parts of large piles of wood chips. The material was then mixed and a representative sample of 5 L was collected from this mix and sent for analysis. Softwood and hardwood chips from a Slovenian company (S1) were taken as control.

Specimens were visually assessed. Wood species, soft/hardwood and the presence of non-wood materials were determined. The samples were then oven dried at 103±2 °C for 24 h. Each sample was weighed and the mass of non-wood material was determined and expressed as a percentage of the total mass.

*Table 1.1: Samples used in the research*

| Mark | Country of origin | Type of company | Annual process capacity (t) | Quality* | Sampling schedule | Starting date | End date |
|---|---|---|---|---|---|---|---|
| GA | Germany | recycling | 100,000 | A I | 2 w | July 2014 | Oct. 2015 |
| GB | Germany | recycling | | A I - A III mix | 2 w | Oct. 2014 | Oct. 2015 |
| **S1A** | Slovenia | recycling | 30,000 | A I | 2 w - 4 w | Sep. 2014 | Oct. 2015 |
| **S1BS** | Slovenia | recycling | | A I - A III mix S | 2 w - 4 w | Sep.2014 | Oct. 2015 |
| **S1BB** | Slovenia | recycling | | A I - A III mix B | 2 w - 4 w | Sep. 2014 | Oct. 2015 |
| **S1CS** | Slovenia | recycling | | Softwood chips | 8 w | Sep. 2014 | Oct. 2015 |
| **S1CH** | Slovenia | recycling | | Hardwood chips | 8 w | Sep. 2014 | Oct. 2015 |
| **S2B** | Slovenia | public utility | 10,000 | A I - A III mix | 2 w - 4 w | Sep. 2014 | Oct. 2015 |
| **EA** | UK | recycling | ~ 300,000 | A I | - | Oct. 2014 | Oct. 2014 |
| **EB** | UK | recycling | | A I - A III mix | - | Oct. 2014 | Oct. 2014 |
| **FA** | Finland | recycling | 40,000 – 60,000 | AII | - | May 2015 | May 2015 |
| **FB** | Finland | recycling | | AIII | - | May 2015 | May 2015 |

## Fraction analysis

For fraction analysis, 20 kg of A II –A III mix recycled wood from German and Slovenian recycling companies was used. At both sites, sampling was performed in June 2015 in 10 different parts of a large pile. A second sampling of A II –A III mix recycled wood for fraction analysis was only performed between 11th June and 24th July 2015 in the German company. During this period, approximately 20 kg of sample was taken from large piles each working day. All of the selected material was mixed and homogenized at the end. Twenty kg of recycled wood chips was taken from this small pile for analysis. In the laboratory tests, samples were oven dried (103 °C) for 24 h. Half of the sample (10 kg) was visually assessed and the presence of non-wooden materials was determined and they were eliminated from samples. Half of the sample (10 kg) was used for fraction analysis as such. Fraction analysis was performed on a PAL sieve with nine sieves. Each sieving was completed on 200 g of recycled wood for 10 min. Sieving was repeated 10 times, after which the same fractions were merged together and homogenized. There were nine fractions prepared from recycled wood without non-wooden materials and nine fractions from recycled wood with non-wooden materials. The size of the different fractions can be seen from Tables 7 and 8. Pellets for XRF measurements were prepared from such samples.

## XRF measurements

After drying, samples were crushed with a laboratory mill Retsch SM 200 with a mesh size of 1 mm and homogenized. Three (3) parallel pallets ($r = 16$ mm; $d = 5$ mm) were prepared from each milled sample, using a Chemplex press. Calibration curves were prepared for the chosen elements (Cl, Cu, Cr, Fe, Zn, Br and Pb) (Hladnik, 2009). Measurements were performed with an XRF device TwinX, Oxford Instruments, England. Most of the elements (Cu, Cr, Fe, Zn, Br, and Pb) were measured on a PIN detector ($U = 26$ kV, $I = 115$ µA, $t = 300$ s). The concentration of chlorine was determined with a proportional detector under similar conditions in a helium atmosphere. All spectra were subsequently examined for the presence of any other undesirable chemical element. The content of F, PCP and PCB was not observed due to the technical limitations of the equipment.

### Soluble part and Klason lignin

The soluble part (extractive content) was determined on 5 g of dry (103±2°C, 24 h) sample for each of the nine fractions from fraction analysis (sampling for fraction analysis was performed in June 2015). Nine fractions were prepared from recycled wood without non-wooden materials and nine fractions from recycled wood with non-wooden materials. Three-stage continuous extraction was performed on a Büchi Extraction System B-811. The first samples were extracted with cyclohexane:ethanol (98%) = 2:1, the second with ethanol and finally with water. Each extraction cycle was performed for 20 h. Then, samples were dried at 103±2°C for 24 h, weighed and the soluble parts were calculated.

For determination of Klasson lignin, 1 g of extracted sample was used. The sample was added to a 50 mL cup and mixed with 72% H2SO4. After two hours, the mixture was diluted with distilled water to achieve a 3% H2SO4 aqueous solution and heated for an additional 4 h. The next day, the solution was filtered through filter paper. The filter paper with lignin was dried for 24 h at 103±2°C and weighed. The lignin content was then calculated.

### Visual assessment of samples and portion of non-wooden materials

Samples of hardwood and softwood chips were collected from a Slovenian company (S1). Softwood chips were mainly composed of Norway spruce (*Picea abies*) wood. Hardwood chip samples consisted of around 90% beech wood (*Fagus sylvatica*) and other hardwood species such as oak (*Quercus sp.*). There was no evidence of non-wood material in either wood chip mixture. A I recycled wood samples consisted mainly of softwoods (Norway spruce, Scots pine and silver fir) and smaller proportions of hardwoods such as poplar. The composition in smaller quantities varied between different countries and companies. This was expected, since A I recycled wood mainly originates from packaging material (Altholzverordnung, 2002). On the other hand, the composition of A I-A III mixtures varied more between companies and sampling dates. A I-A III mixtures consisted of wood based composites (65% - 80%) (particleboards, MDF, HDF), softwoods (Norway spruce, pine species and silver fir) (20% - 30%) and hardwoods (beech, oak, black locust) (5% - 10 %).

In addition to wood species, the authors focused on the presence and amounts of non-wooden materials in the samples, since the presence of non-wooden materials limits the further processing of wood to the highest extent. In recycled wood and wood chips samples, the occurrence was observed of glass, metals, plastic, fabric, paper, stones and other non-wooden material that cannot be specified into one of these categories. Similar pollutants of non-wooden materials in recycled wood fuels over an extended time scale was also reported in Sweden by Edo et al., 2015. Softwood and hardwood chips were clean of non-wooden materials. A slightly higher content of non-wooden materials was present in A I recycled wood samples. On average, the total content of non-wooden materials varied between 0.22% (GA) and 0.87% (S1A). The highest total average values for A I-A III mix samples varied from 1.00% (EB) up to 2.96% (S2B). The maximum content of non-wooden materials in A I-A III mix samples was between 1.00% (EB) and 6.51% (S2B) (Table 1.2). These results were expected. Samples from companies with less sophisticated sorting systems for waste wood before the recycling process had the highest content of non-wooden materials. Technically, it is extremely costly to avoid all non-wooden materials in recycled wood because sophisticated techniques are needed for proper separation from the wooden elements. Recycling companies sort wood and separate non-wooden materials but on an industrial sorting scale, so a small proportion of such material is always present. The Slovenian public utility company (S2) without any sorting system had the highest content of all detected materials. Recycled wood chips with such a high content of non-wooden material can only be used for energy production. On the other hand, A I recycled wood chips with a low content of non-wooden material can be used for particleboard production or for processing in bio-refineries. In particleboard plants, recycled wood is additionally sorted before being used in production (Lykidis and Grigoriou, 2008).

*Table 1.2: Presence of non-wooden materials in recycled wood samples. Legend of the sample origin and sampling schedule is the same as for Table 1.1.*

| Sample | Glass (%) | Metal (%) | Plastic (%) | Fabric (%) | Paper (%) | Stone (%) | Other (%) | Average of total (%) | Max of total (%) | Min of total (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| **GA** | 0.00 | 0.00 | 0.10 | 0.00 | 0.09 | 0.02 | 0.03 | 0.22 | 1.53 | 0.00 |
| **GB** | 0.06 | 0.17 | 0.35 | 0.03 | 0.31 | 0.03 | 0.19 | 1.04 | 5.58 | 0.00 |
| **S1A** | 0.00 | 0.56 | 0.01 | 0.00 | 0.03 | 0.02 | 0.00 | 0.87 | 4.27 | 0.00 |
| **S1BS** | 0.00 | 0.16 | 0.36 | 0.00 | 0.37 | 0.00 | 0.49 | 1.67 | 3.60 | 0.07 |
| **S1BB** | 0.08 | 0.06 | 0.16 | 0.00 | 0.10 | 0.78 | 0.03 | 1.83 | 3.43 | 0.19 |
| **S1CS** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **S1CH** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **S2B** | 0.16 | 1.16 | 0.45 | 0.44 | 0.14 | 0.08 | 0.21 | 2.96 | 6.51 | 0.85 |
| **EA** | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.32 | 0.33 | 0.33 | 0.00 |
| **EB** | 0.00 | 0.39 | 0.43 | 0.00 | 0.11 | 0.02 | 0.04 | 1.00 | 1.00 | 0.00 |

*Figure 1.1: Different fractions after fraction analysis of sample without non-wooden materials*

### Concentrations of inorganic elements in recycled wood

In Table 1.3, various parameters (minimum, maximum, average, number and proportion of samples above limits) for A I class recycled wood samples are presented. In this table, the average concentration of all measurements per group of samples are highlighted. The choice of monitored elements was based on previous analysis of recycled wood collected in a large pile at a public utility company (Hladnik, 2009). Concentrations of inorganic chemicals in wood chip samples S1CH and S1CS were comparable with concentrations in fresh wood presented in the CEN/TS 14961 (2005) standard (Table 3). None of the analysed samples from groups S1CH and S1CS exceeded the limit concentrations set in Altholzverordnung (2002) or EPF standard (2002). This result is logical and expected, since samples S1CH and S1CS were derived from “clean” wood, which had only been mechanically processed.

Concentrations of pollutants in the recycled wood A I/A III mixture were much higher. Altholzverordnung (2002) prescribes limit values only for A I and A II recycled wood intended for use for panel board production. None of the recycling companies included in this research separates A II and A III recycled wood. In the future, it will be necessary to increase utilization of recycled wood for material production. Because of this, better classification and cleaning systems will be needed (A III recycled wood should be removed).  The authors of the present research used Altholzverordnung and EPF limits also for A I /A III recycled wood mixture, which offers large possibilities of using more recycled wood for material production. The most critical inorganic elements in A I /A III recycled wood mixture were chlorine (Cl), chromium (Cr), copper (Cu) and lead (Pb).

*Table 1.3: Concentrations of inorganic elements in wood chips and A I recycled wood from German and Slovenian recycling companies. The legend for sample origin and sampling schedule is the same as in Table*

| **Group of Samples** | **Quality** | **Concentration/Number/ Percentage** | **Chemical elements in recycled wood samples (ppm)** | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Cl | Cr | Cu | Fe | Zn | Br | Pb |
| GA | A I | MIN | 66 | 0 | 0 | 58 | 5 | 0 | 1 |
| | | MAX | 708 | 39 | 30 | 322 | 168 | 4 | 10 |
| | | AVERAGE | 314 | 3 | 3 | 157 | 15 | 0 | 3 |
| | | STDEV | 120 | 6 | 5 | 67 | 20 | 0 | 2 |
| | | No. of samples | 64 | 64 | 64 | 64 | 64 | 64 | 64 |
| | | No. above AltholzV limit | 2 | 1 | 0 | - | - | - | 0 |
| | | No. above EPF limit | 0 | 2 | 0 | - | - | - | 0 |
| | | % above AltholzV limit | 3 | 2 | 0 | - | - | - | 0 |
| | | % above EPF limit | 0 | 3 | 0 | - | - | - | 0 |
| S1A | A I | MIN | 6 | 0 | 0 | 156 | 13 | 0 | 2 |
| | | MAX | 534 | 63 | 25 | 734 | 61 | 1 | 15 |
| | | AVERAGE | 261 | 13 | 7 | 376 | 22 | 0 | 5 |
| | | STDEV | 153 | 20 | 9 | 198 | 17 | 0 | 4 |
| | | No. of samples | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| | | No. above AltholzV limit | 0 | 1 | 0 | - | - | - | 0 |
| | | No. above EPF limit | 0 | 1 | 0 | - | - | - | 0 |
| | | % above AltholzV limit | 0 | 2 | 0 | - | - | - | 0 |
| | | % above EPF limit | 0 | 2 | 0 | - | - | - | 0 |
| S1CS | Softwood chips | MIN | 12 | 0 | 0 | 28 | 3 | 0 | 0 |
| | | MAX | 279 | 15 | 4 | 196 | 25 | 0 | 4 |
| | | AVERAGE | 109 | 5 | 1 | 80 | 11 | 0 | 1 |
| | | STDEV | 71 | 4 | 1 | 54 | 7 | 0 | 1 |
| | | No. of samples | 18 | 18 | 18 | 18 | 18 | 18 | 18 |
| | | No. above AltholzV limit | 0 | 0 | 0 | - | - | - | 0 |
| | | No. above EPF limit | 0 | 0 | 0 | - | - | - | 3 |
| | | % above AltholzV limit | 0 | 0 | 0 | - | - | - | 0 |
| | | % above EPF limit | 0 | 0 | 0 | - | - | - | 0 |
| S1CH | Hardwood chips | MIN | 53 | 0 | 0 | 49 | 0 | 0 | 0 |
| | | MAX | 153 | 6 | 2 | 99 | 8 | 0 | 2 |
| | | AVERAGE | 97 | 3 | 1 | 69 | 2 | 0 | 1 |
| | | STDEV | 39 | 2 | 1 | 16 | 3 | 0 | 1 |
| | | No. of samples | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| | | No. above AltholzV limit | 0 | 0 | 0 | - | - | - | 0 |
| | | No. above EPF limit | 0 | 0 | 0 | - | - | - | 2 |
| | | % above AltholzV limit | 0 | 0 | 0 | - | - | - | 0 |
| | | % above EPF limit | 0 | 0 | 0 | - | - | - | 0 |

One of the aims was to elucidate whether concentrations of inorganic elements varied within the year, and whether there is any possible seasonal influence. The concentration of inorganic pollutants was therefore monitored for one year in Germany and Slovenia only. The variation of concentrations of target inorganic pollutants in A I/A III recycled wood mixture was addressed. Results show that variations in inorganic content are not greatly influenced by the collecting season. The concentration varied mainly because of various origins of incoming recycled wood.

Fraction analysis was performed on an A I/A III recycled wood mixture from the German recycling company. The sample batch was divided into two parts. The first half of the sample batch was used for fraction analysis as such. The second half of the sample batch was checked and all non-wooden material was eliminated from the sample. In total, 0.44% of non-wooden materials were monitored. The highest share of this was plastic and other materials that cannot be further specified.

After fraction analysis, 9 fractions were separated. In the samples from the German recycling company after fraction analysis of the first three fractions, 86% (GB) (without non-wooden materials) remained in the first fractions, compared to 95% from samples in long term sampling (Table 1.4). This indicates that most non-wooden materials remained in the first fractions with the biggest particles. About 2% to 6% of the total mass was in fraction 4, while other smaller fractions represented only around 2% of total mass. In the next step, separate fractions were individually analysed. With extraction, the soluble parts (extractives and other soluble components – resins, coatings etc.) of individual fractions were determined. The soluble part in recycled wood samples varied between 7% and 14.5%. These values are considerably higher than reported in the literature (Fengel and Wegener, 1989). The main reason for the increased proportion of the soluble fraction of wood is that old wood is partially photodegraded or degraded by fungi, which results in an increased portion of water soluble fractions. With decreasing fraction size, the soluble part increases with both types of samples (with and without non-wooden materials). An increased soluble part with decreased fraction size was expected, since in smaller fractions all components are easily accessible for chemicals and so they can be easily leached from wood. The smaller fraction contains higher amounts of elusive residues of surface coatings, glues and other sources. Similarly, as reported for soluble parts, the Klason lignin content also increased with decreasing fraction size. This was predominantly visible with the smallest fractions, from which the amount of lignin was higher than reported in the literature (Fengel and Wegener, 1989). For all sampling dates and both sampling sites, there were no statistically significant differences between samples with and without non-wooden materials in the concentrations of analysed inorganic materials. With all samples, the concentrations of Cl, Fe, Zn, Pb, Cr and Cu increased with decreasing particle size. The highest concentrations of elements were in fractions from 0.00 mm - 0.237 mm (bottom fraction).

*Table 1.4 Average concentrations of chemical elements, soluble part and lignin content in recycled wood after fraction analysis; the first sample was taken on 22th June 2015 and the second sample between 11th June and 24th July from the German recycling company. The legend of sample origin and sampling schedule is the same as in Table 1.*

| | | | **Cl** | **Cr** | **Cu** | **Fe** | **Zn** | **Pb** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **Fractions (mm)** | **Sieve no.** | **Concentration of respective elements (%)** | | | | | | **Mass share of fraction (%)** | **Soluble part (%)** | **Lignin (%)** |
| GB without non-wooden materials sampling 22nd June | >6.14 | 1 | 734 | 48 | 28 | 179 | 62 | 26 | 49 | 8.9 | 28.5 |
| | 4.0 - 6.14 | 2 | 880 | 38 | 25 | 212 | 104 | 22 | 20 | 7.0 | 28.4 |
| | 2.0 - 4.0 | 3 | 1098 | 29 | 15 | 269 | 93 | 34 | 17 | 8.0 | 29.0 |
| | 1.5 -2.0 | 4 | 1124 | 25 | 12 | 329 | 91 | 28 | 6 | 8.3 | 28.0 |
| | 1.27 -1.5 | 5 | 1287 | 35 | 11 | 411 | 117 | 37 | 2 | 7.8 | 28.7 |
| | 1.0 - 1.27 | 6 | 1361 | 28 | 10 | 474 | 117 | 41 | 2 | 8.0 | 29.8 |
| | 0.60 - 1.0 | 7 | 1410 | 43 | 12 | 586 | 164 | 56 | 3 | 11.1 | 30.9 |
| | 0.237 - 0.6 | 8 | 1727 | 51 | 17 | 992 | 306 | 91 | 2 | 11.7 | 31.3 |
| | 0.0 - 0.237 | 9 | 2560 | 92 | 36 | 3986 | 672 | 219 | 2 | 12.8 | 35.6 |
| GB with non-wooden materials sampling 22nd June | >6.14 | 1 | 755 | 36 | 24 | 207 | 51 | 21 | 52 | 8.5 | 29.1 |
| | 4.0 - 6.14 | 2 | 879 | 42 | 23 | 225 | 67 | 34 | 20 | 9.0 | 25.8 |
| | 2.0 - 4.0 | 3 | 1173 | 34 | 20 | 266 | 95 | 54 | 16 | 7.0 | 25.8 |
| | 1.5 -2.0 | 4 | 1220 | 26 | 13 | 332 | 100 | 30 | 5 | 7.5 | 28.0 |
| | 1.27 -1.5 | 5 | 1429 | 33 | 11 | 428 | 98 | 41 | 2 | 9.3 | 28.3 |
| | 1.0 - 1.27 | 6 | 1326 | 35 | 12 | 445 | 122 | 44 | 2 | 8.4 | 29.5 |
| | 0.60 - 1.0 | 7 | 1453 | 32 | 9 | 564 | 153 | 42 | 2 | 9.5 | 30.5 |
| | 0.237 - 0.6 | 8 | 1723 | 46 | 16 | 956 | 296 | 86 | 2 | 10.3 | 32.3 |
| | 0.0 - 0.237 | 9 | 2552 | 91 | 37 | 3922 | 658 | 215 | 2 | 14.5 | 36.0 |
| GB without non-wooden materials sampling 11th June to 24th July | >6.14 | 1 | 611 | 18 | 14 | 245 | 47 | 11 | 57 | - | - |
| | 4.0 - 6.14 | 2 | 628 | 10 | 8 | 187 | 29 | 7 | 25 | - | - |
| | 2.0 - 4.0 | 3 | 843 | 15 | 10 | 257 | 46 | 20 | 13 | - | - |
| | 1.5 -2.0 | 4 | 1135 | 16 | 10 | 310 | 51 | 22 | 2 | - | - |
| | 1.27 -1.5 | 5 | 1089 | 19 | 6 | 403 | 71 | 20 | 1 | - | - |
| | 1.0 - 1.27 | 6 | 1290 | 21 | 6 | 496 | 90 | 29 | 1 | - | - |
| | 0.60 - 1.0 | 7 | 1354 | 28 | 13 | 754 | 89 | 20 | 1 | - | - |
| | 0.237 - 0.6 | 8 | 1360 | 24 | 7 | 889 | 109 | 23 | 0 | - | - |
| | 0.0 - 0.237 | 9 | 1927 | 70 | 29 | 5239 | 417 | 114 | 1 | - | - |
| GB with non-wooden materials sampling 11th June to 24th July | >6.14 | 1 | 637 | 15 | 9 | 163 | 53 | 42 | 57 | - | - |
| | 4.0 - 6.14 | 2 | 779 | 18 | 10 | 192 | 36 | 11 | 25 | - | - |
| | 2.0 - 4.0 | 3 | 891 | 16 | 9 | 241 | 47 | 18 | 13 | - | - |
| | 1.5 -2.0 | 4 | 1347 | 22 | 10 | 342 | 57 | 19 | 2 | - | - |
| | 1.27 -1.5 | 5 | 1281 | 17 | 8 | 436 | 102 | 37 | 1 | - | - |
| | 1.0 - 1.27 | 6 | 1358 | 16 | 11 | 496 | 89 | 30 | 1 | - | - |
| | 0.60 - 1.0 | 7 | 1427 | 23 | 9 | 703 | 82 | 29 | 1 | - | - |
| | 0.237 - 0.6 | 8 | 1475 | 26 | 11 | 1036 | 158 | 37 | 1 | - | - |
| | 0.0 - 0.237 | 9 | 2144 | 75 | 32 | 5354 | 477 | 140 | 1 | - | - |

### Composition of recycled wood class A I and A II/A III mixture (German classification system)

For all pre-treatments for **WP 2**, 30 kg recycled wood class A I and A II/A III mixture from a German recycling company (German classification) was collected. Both A I and A II/A III grades (as such and milled) were used for AlkOx and SE pretreatments, and the performance was compared with fresh spruce. Only milled A1 grade was used in ethanol based organosolv cooking. The AI was milled in a cutting mill and graded into particle fractions of <3.15; 3.15-5.6 and > 5.6 mm with additional sieves (Figure 2). The composition of the recycled wood samples and the spruce reference is summarized in Table 1.5.

*Table 1.5: Composition of dry recycled wood class A I and A II/A III according to the German classification system and reference spruce wood.*

| **Composition:** | **% of d.m.** | | |
|---|---|---|---|
| | **Waste wood A I class** | **Waste wood A II/A III class** | **Spruce** |
| **Lignin, total** | **28,3** | **28,0** | **27,5** |
| Klason | 27,5 | 26,8 | 27,4 |
| soluble | 0,8 | 1,1 | 0,2 |
| **Carbohydrates** | **69,9** | **64,5** | **71,3** |
| Cellulose | 44,9 | 40,8 | 44,7 |
| GGM | 13,5 | 12,8 | 18,0 |
| "xylan" | 8,9 | 8,1 | 5,8 |
| "arabinan + galactan" | 2,4 | 2,6 | 2,6 |
| other (from Rha) | 0,2 | 0,2 | 0,2 |
| **Extractives** | **1,3** | **1,3** | **0,9** |
| **Ash** | **0,5** | **2,0** | **0,3** |
| **Plastics, glass and metal** | **0** | **0,7** | **0** |
| **"Bic particles"** | | **3,5** | |

## ***<u>WP 2 Pre-Treatment methods for recycled wood mixtures</u>***

### Auto-catalysed Ethanol-water-organosolv pulping of recycled wood

The ethanol-water organosolv process was adapted for converting recycled wood class AI from a German company (German classification system, *mixture of softwood and hardwood*) into organosolv lignin, cellulosic fibre and hemicellulose/sugar fractions. The effect of process conditions (temperature, ethanol concentration and reaction time, with and without a catalyst) on product yields was investigated using an experimental matrix designed with response surface methodology (RSM).

The conditions of the Box-Behnken-model ranged from 160 – 220 °C, 120 – 240 min and 35−75% ethanol concentration ($w_{EtOH}$) without catalytic amounts of sulfuric acid (auto-catalysed organosolv pulping). In the case of acid catalysed Ethanol/water-organosolv pulping following process parameters were combined temperature from 160 to 190°C, 120min-240min and ethanol concentration from 35 to 75%. The results indicate that temperature, time and ethanol concentration and their interaction have a significant effect on the yield of lignin, delignification degree, yield of fibre, cellulose purity, enzymatic accessibility to cellulose fibres and on the structural features of the generated lignin fraction.

Figure 2.1 illustrates the trend of the process parameter effects (temperature and time) on the yields of unmilled fibre and lignin at constant $w_{EtOH}$ (65%) in pulping liquor. The grey dots in Figure 2.1 illustrate the amount of cellulose and lignin in extract free recycled wood class A I.

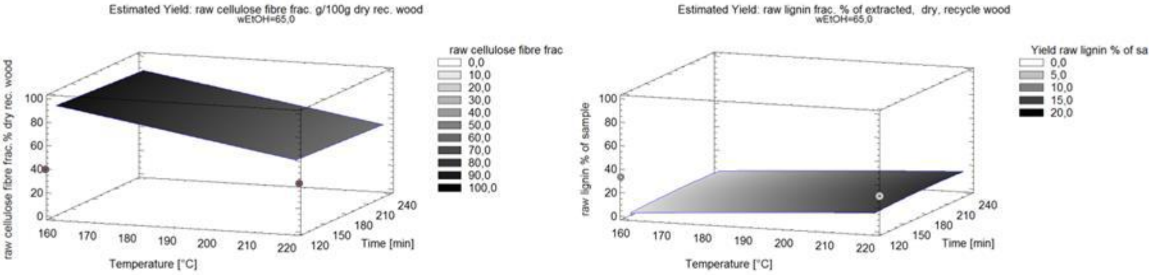


*Figure 2.1: Estimated yield of unmilled cellulose fibre fraction (left) and unmilled lignin fraction (Lignin PL& WL, right) depending on process parameters (temperature [°C] & pulping time [min]) at const. $w_{EtOH}$ of 65% in pulping liquor of auto-catalysed organosolv cooking. Black dots illustrate the amounts of cellulose (left cube: ~44%) and of lignin (right cube: ~34%) in the used pre-extracted recycled wood class A I particle size 3.15-5.6mm A I (German classification system), software supported by Statgraphics centurion XV.*

Figure 2.2 shows the degree of delignification as a function of the process parameters (temperature and time) and the Pareto-plot illustrating the main effects of the above-mentioned process parameters on the delignification degree. From the Pareto-plot in Figure 4, it can be deduced that the optimal process time of 196min and optimal ethanol concentration of 65% are at an optimal temperature of 220 °C in order to maximize the degree of delignification/yield of lignin by auto-catalysed ethanol-water-organosolv-pulping without sulfuric acid (catalyst) on pre-extracted recycled wood A I. The extrapolation results in a maximal lignin yield of 17.3 g/100 g of extract free, dry recycled wood (approx. 51% of lignin content) by auto-catalysed ethanol-water-organosolv pulping without catalytic amounts of sulfuric acid. The equation describing the yield of lignin as a function of the above-mentioned process parameter is as follows:

$$Y\,L\,[\%] = -117.347 + 0.362588 \times [T] + 0.310622 \times [t] + 1.18225 \times [w_{EtOH}] - 0.00153981 \times [T^2] - 0.0000152778 \times [T] \times [t] + 0.0126667 \times [T] \times w_{EtOH} - 0.00101204 \times [t^2] + 0.00141875 \times [t] \times [w_{EtOH}] - 0.0324021 \times [w_{EtOH}{}^2].$$

The coefficient of determination ($R^2$) is 96.49%. This result does not include the soluble lignin present in the hemicellulose/ hydrolysate solution.

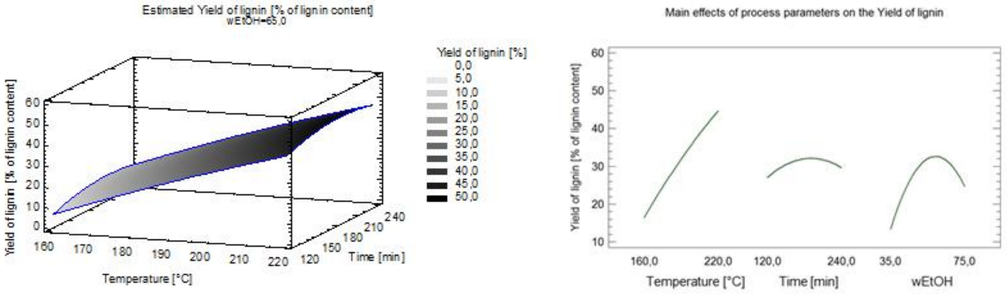


*Figure 2.2: Degree of lignin extraction (left) depending on process parameters (temperature [°C], pulping time [min], const. $w_{EtOH}$: 65%), as well as the effect of the main parameters (Pareto-plot, right) on the lignin extraction degree during ethanol-water-organosolv-pulping of pre-extracted recycled wood class A I (German classification system), software supported by Statgraphics enturion XV. Optimal parameter combination for auto-catalysed organosolv treatment without an additional catalyst (sulfuric acid): t: 196min, T:220°C, $w_{EtOH}$: 65%.*

Figure 2.3 illustrates the main effects of pulping conditions mentioned above on selected structural features ($M_N$, $M_W$) of organosolv lignin generated by auto-catalysed ethanol-water-organosolv pulping without catalytic amounts of sulfuric acid. The process temperature has the strongest effect on the number average molecular weight ($M_N$) and on the weight average molecular weight ($M_W$) of organosolv lignin. Increasing the process temperature from 160 to 220 °C significantly decreased the values of both $M_N$ and $M_W$. The effects of pulping time (120-240 min) and $w_{EtOH}$ (35-75%) on the structural features of the generated lignin are more complex. With increasing time, the values of $M_N$ decreased whereas the values of $M_W$ passed through a plateau and later decreased. The content of ethanol in the pulping liquor used, described as $w_{EtOH}$, had different effects on the values of $M_N$ and $M_W$ of organosolv lignin samples. Generally, with increasing $w_{EtOH}$ of the pulping liquor the value of $M_W$ increased, whereas the value of $M_N$ increased at first, passed through a plateau and decreased again slightly.

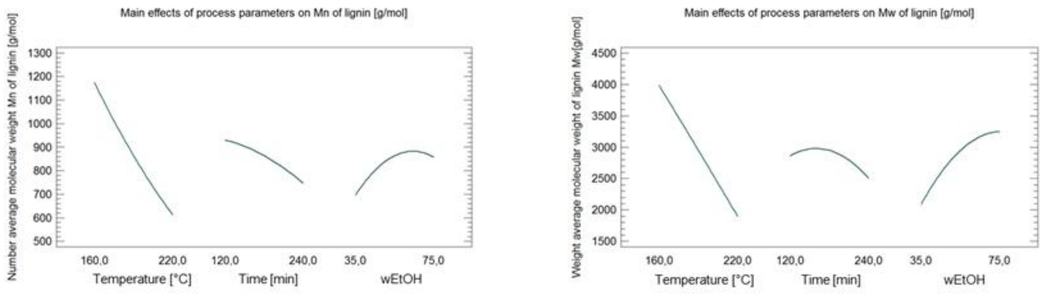


*Figure 2.3: Main effects of process parameters (temperature [°C], pulping time [min]) and $w_{EtOH}$ in pulping liquor on structural features ($M_N$ (left) and $M_W$ (right) [g/mol]) of organosolv lignin, generated by ethanol-water-organosolv pulping of pre-extracted recycled wood class A I. Pareto-plots are software supported by Statgraphics centurion XV.*

Figure 2.4 illustrates the main effects of cooking conditions mentioned above on selected structural features (number of phenolic OH- and aliphatic OH-groups) of organosolv lignin generated by auto-catalysed ethanol-water-organosolv pulping. The process temperature has the strongest effect on the number of phenolic OH groups and on the number of aliphatic OH-groups of organosolv lignin. Increasing the process temperature from 160 to 220 °C decreases the values of the aliphatic OH-groups significantly and increases the number of phenolic OH-groups. The aliphatic and phenolic OH numbers of all lignin samples were determined by $^{31}$P-NMR-technique.

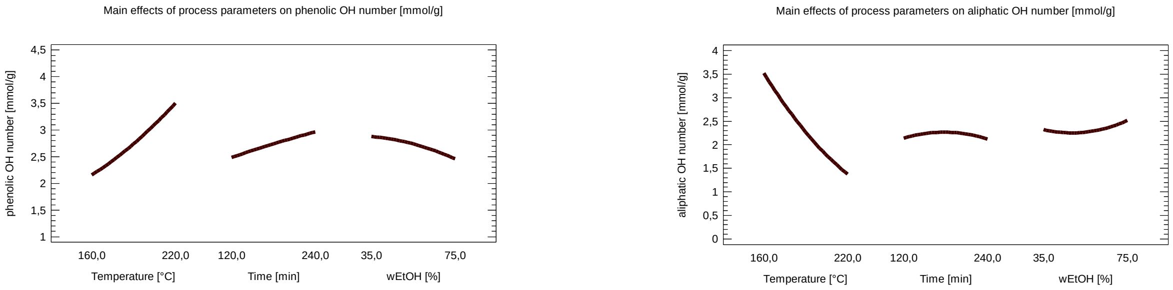


*Figure 2.4: Main effects of process parameters (temperature [°C], pulping time [min]) and $w_{EtOH}$ in pulping liquor on structural features (phenolic OH groups (left) and aliphatic OH groups (right) [mmol/g]) of organosolv lignin, generated by auto-catalysed ethanol-water-organosolv pulping of pre-extracted recycled wood class A I. Pareto-plots are software supported by Statgraphics centurion XV.*

### Results of acid -catalysed ethanol-water-organosolv pulping

Additional 15 experiments were realized by acid-catalysed ethanol-water organosolv pulping on the same recycled wood class A I sample. The investigation was supported again by statistical design of experiments (Box-Behnlen-model). However, the conditions of the Box-Behnken-model ranged now from 160 – 190 °C, 120 – 240 min and 35−75% ethanol concentration ($w_{EtOH}$) and with a constant catalytic amount of sulfuric acid of 0.5% of dry wood weight (acid-catalysed organosolv pulping). The temperature range was reduced.

Figure 2.5 illustrates the trend of the process parameter effects (temperature and time) on the yields of unmilled fibre and lignin at constant $w_{EtOH}$ (75%) in pulping liquor. The red dots in Figure 5 illustrate the amount of cellulose and lignin in extract free recycled wood class A I.

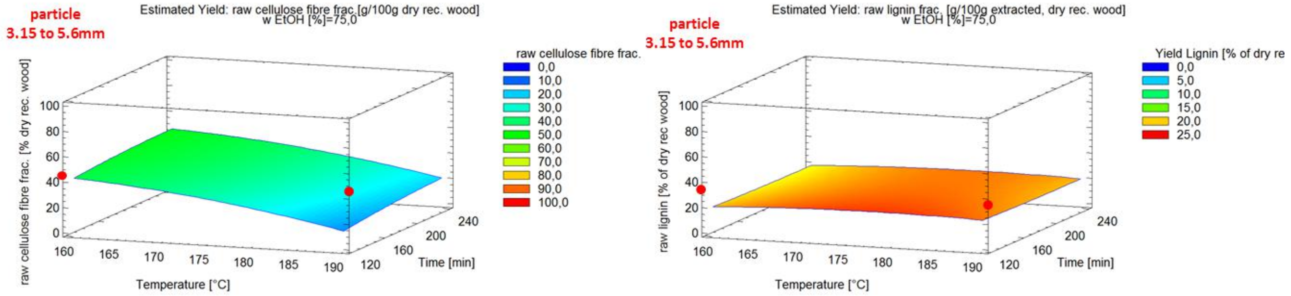


*Figure 2.5: Estimated yield of unmilled cellulose fibre fraction (left) and unmilled lignin fraction (Lignin PL& WL, right) depending on process parameters (temperature [°C] & pulping time [min]) at const.* $w_{EtOH}$ *of 75% in pulping liquor of acid-catalysed organosolv cooking. Red dots illustrate the amounts of cellulose (left cube: ~44%) and of lignin (right cube: ~34%) in the used pre-extracted recycled wood class A I particle size 3.15-5.6mm A1 (German classification system), software supported by Statgraphics centurion XV.*

Figure 2.6 shows the degree of delignification as a function of the process parameters (temperature and time) and the Pareto-plot illustrating the main effects of the above-mentioned process parameters on the delignification degree. From the Pareto-plot in Figure 2.6, it can be deduced that the optimal process time, ethanol concentration and temperature are 120 min, 75% and 177°C, respectively in order to maximize the degree of delignification/yield of lignin by ethanol-water-organosolv-pulping without sulfuric acid (catalyst) on pre-extracted recycled wood A I. The extrapolation results in a maximal lignin yield of 20 to 24g/100 g of extract free, dry recycled wood (approx. 73.9% of lignin content) by auto-catalysed ethanol-water-organosolv pulping. The equation describing the yield of lignin as a function of the above-mentioned process parameter is as follows:

Y Lignin = -997,725 + 11,3226*Temperature [°C] - 0,158021*Time [min] + 1,20995*$w_{EtOH}$ [%] - 0,0326648*Temperature [°C]^2 + 0,000116667*Temperature [°C]*Time [min] + 0,003775*Temperature [°C]*$w_{EtOH}$ [%] + 0,000453588*Time [min]^2 - 0,0009125*Time [min]*$w_{EtOH}$ [%] - 0,00566146*$w_{EtOH}$ [%]^2.

The coefficient of determination ($R^2$) is 98.51%. This result does not include the soluble lignin present in the hemicellulose/ hydrolysate solution.

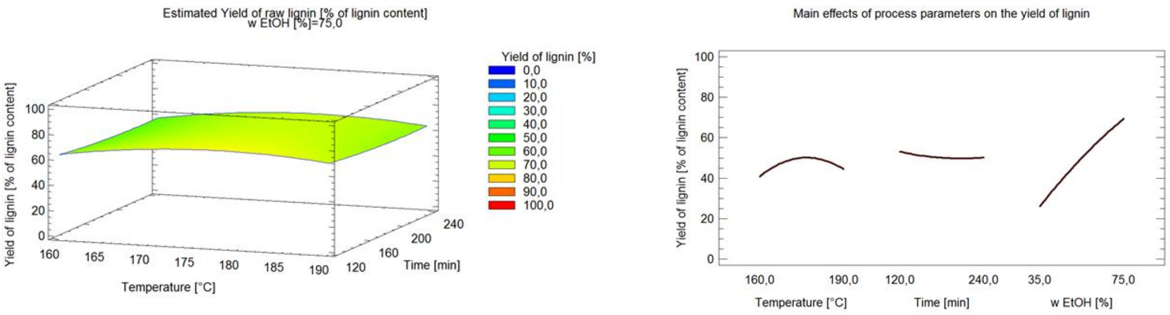


*Figure 6: Degree of lignin extraction (left) depending on process parameters (temperature [°C], pulping time [min], const. $w_{EtOH}$: 75%), as well as the effect of the main parameters (Pareto-plot, right) on the lignin extraction degree during acid-catalysed ethanol-water-organosolv-pulping of pre-extracted recycled wood class A I (German classification system), software supported by Statgraphics enturion XV. Optimal parameter combination for acid-catalyzed organosolv treatment: t:120min, T:177°C, $w_{EtOH}$: 75%.*

Compared to auto-catalysed ethanol-water-organosolv cooking the lignin yield will be increased at lower process temperature and higher ethanol content using catalytically amounts of sulfuric acid during the cooking process.

Figure 2.7 illustrates the main effects of pulping conditions mentioned above on selected structural features ($M_N$, $M_W$) of organosolv lignin generated by acid-catalysed ethanol-water-organosolv pulping. The process temperature has the strongest effect on the number average molecular weight ($M_N$) and on the weight average molecular weight ($M_W$) of this organosolv lignin. Increasing the process temperature from 160 to 190 °C significantly decreased the values of both $M_N$ and $M_W$. The effects of pulping time (120-240 min) and $w_{EtOH}$ (35-75%) on the structural features of the generated lignin are more complex. With increasing time, the values of $M_N$ decreased whereas the values of $M_W$ passed through a plateau and later decreased. The content of ethanol in the pulping liquor used, described as $w_{EtOH}$, had different effects on the values of $M_N$ and $M_W$ of organosolv lignin samples. Generally, with increasing $w_{EtOH}$ of the pulping liquor the value of $M_W$ decreased first, passed through a plateau and increased again slightly, whereas the value of $M_N$ increased.

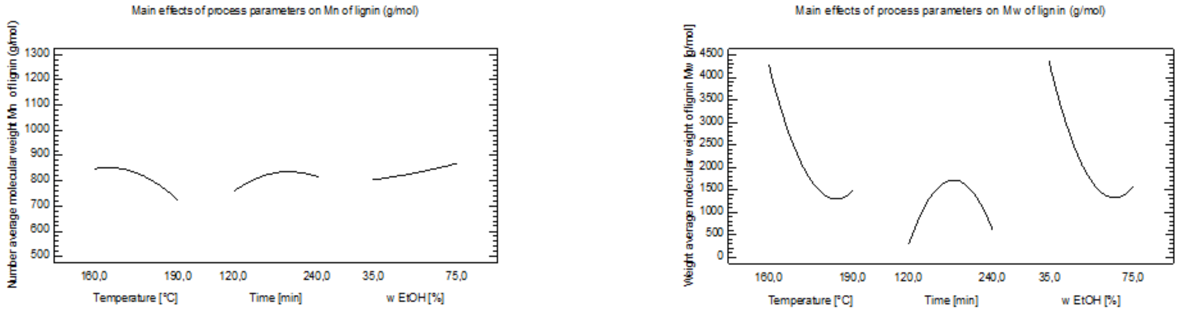


*Figure 2.7: Main effects of process parameters (temperature [°C], pulping time [min]) and $w_{EtOH}$ in pulping liquor on structural features ($M_N$ (left) and $M_W$ (right) [g/mol]) of organosolv lignin, generated by acid-catalysed ethanol-water-organosolv pulping of pre-extracted recycled wood class A I. Pareto-plots are software supported by Statgraphics centurion XV.*

Figure 2.8 illustrates the main effects of cooking conditions mentioned above on selected structural features (number of phenolic OH- and aliphatic OH-groups) of organosolv lignin generated by acid-catalysed ethanol-water-organosolv pulping. The process temperature has the strongest effect on the number of phenolic OH groups and on the number of aliphatic OH-groups of organosolv lignin. Increasing the process temperature from 160 to 190 °C significantly increases the number of phenolic OH-groups, whereas the number of aliphatic OH-groups is always low. The aliphatic and phenolic OH numbers of all lignin samples were determined by $^{31}$P-NMR-technique.

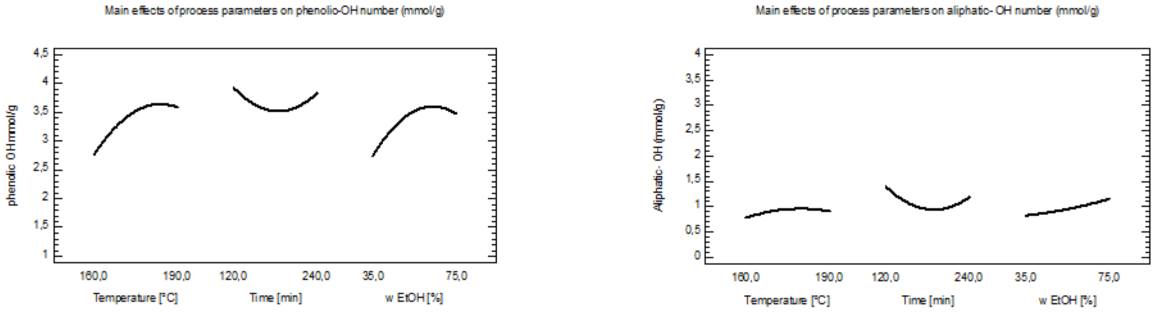


*Figure 2.8: Main effects of process parameters (temperature [°C], pulping time [min]) and $w_{EtOH}$ in pulping liquor on structural features (phenolic OH groups (left) and aliphatic OH groups (right) [mmol/g]) of organosolv lignin, generated by acid-catalysed ethanol-water-organosolv pulping of pre-extracted recycled wood class A I. Pareto-plots are software supported by Statgraphics centurion XV.*

## Fractionation of recycled wood by alkaline oxidation

Fractionation of recycled wood was also investigated using alkaline oxidation (AlkOx) technology, which has been studied as a potential pre-treatment for bioethanol production (Kallioinen et al., 2013). AlkOx is based on the treatment by $Na_2CO_3$ in the presence of molecular oxygen. Here a two-stage procedure with inter-stage refining, developed for coarse woody materials (e.g. wood chips) was used. The method produces partially delignified cellulosic fibre fraction, well suitable e.g. for ethanol production and a liquid fraction containing mainly soluble oxidized lignin.

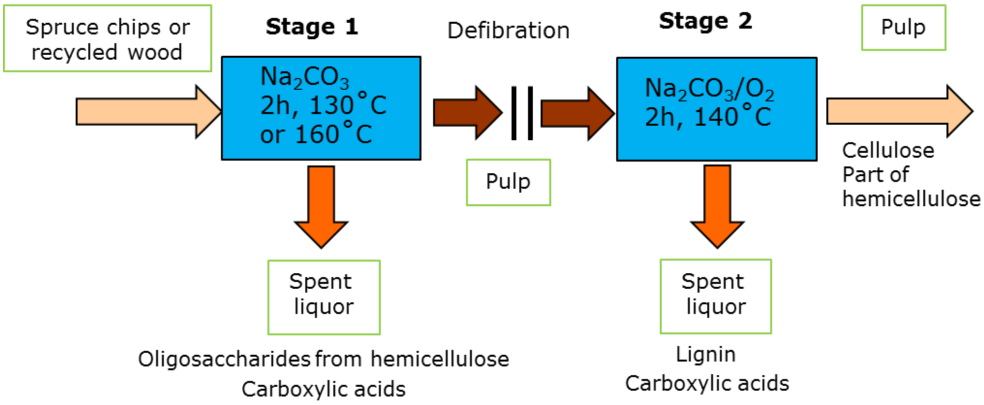


*Figure 2.4: Alkaline oxidation process used for fractionation of recycled wood.*

Recycled wood class A I (as such and milled), and a mixture of A II and A III qualities (after manual removal of contaminating materials) were cooked, and compared with fresh spruce chips. Mild (130 °C, 2h) and severe (160 °C, 2h) cooking conditions were used in the Stage 1. In the following Stage 2, the conditions (140 °C, 2h, 10 bar $O_2$) were similar in both cases.

In general, recycled wood of A I and A II /A III grades showed typical behavior of softwood material in AlkOx processing. However, the A II/A III grade required manual sorting with removal of contaminating material (ca. 4 % of the sample). Based on pulp yields and chemical compositions, there was no significant difference between A I and A II/A III qualities in AlkOx. There was no need for using essentially different reaction conditions compared to softwood in general. Milling was not necessary either, and crushed recycled wood is suitable as such for the AlkOx process. The yield of recycled wood samples was only slightly lower than of the spruce reference which may reflect the presence of a small amount of hardwood material in recycled wood. Hardwood is known to be processed more efficiently by AlkOx. Composition of cellulosic (fibre) fractions from AlkOx was mainly dependent on the severity of the treatment. The harsher conditions resulted in higher degree of delignification and higher release of hemicelluloses, especially galactoglucomannan, to the cooking liquors. The somewhat higher galactoglucomannan and lower xylan content of spruce reference was also reflected in the fibre fractions.

*Table 2.1: Composition of cellulosic fractions from alkaline oxidation*.

| | Sample | Yield | Extractives | Lignin | | | Ash | Carbohydrates |
|---|---|---|---|---|---|---|---|---|
| | | | | Klason | Soluble | **Total** | | |
| | | % | % | % | % | % | % | % |
| **Mild conditions** | **Spruce chips** | 59,4 | 0,06 | 13,4 | 0,6 | 14,0 | 1,7 | 84,2 |
| | **Grade A I** | 56,7 | 0,003 | 13,3 | 0,8 | 14,1 | 1,9 | 84,0 |
| | **Grade A I - milled** | 56,6 | 0,09 | 13,2 | 0,7 | 13,9 | 1,8 | 84,3 |
| | **Grade A II/A III** | 55,9 | 0,05 | 13,5 | 1,2 | 14,6 | 2,2 | 83,1 |
| **Severe conditions** | **Spruce chips** | 50,5 | 0,60 | 6,4 | 0,5 | 6,9 | 1,4 | 91,1 |
| | **Grade A I** | 47,8 | 0,10 | 4,5 | 0,7 | 5,2 | 1,2 | 93,5 |
| | **Grade A I - milled** | 47,9 | 0,25 | 5,0 | 0,5 | 5,5 | 1,2 | 93,1 |
| | **Grade A II/A III** | 46,5 | 0,11 | 4,4 | 0,6 | 5,1 | 1,7 | 93,1 |

### Steam explosion pre-treatment of recycled wood

Steam explosion is a state-of art pretreatment method and was used as refrence technology in the project. It is so far best established pre-treatment technology for the 2nd generation bioethanol production from different lignocellulosic feedstocks. In steam explosion studies, the same recycled wood samples of A I quality (milled, non-milled), A II/A III mixture, and spruce reference were used. Typical conditions of softwood were used for recycled wood containing mainly softwood (impregnated with 0.5% sulfuric acid, followed by steam pre-treatment at 205 °C for 15 min or 30 min). The conditions used are somewhat milder than typically reported to be optimal for softwood due to the temperature limitations of the used reactor. At the end of the pre-treatment, pressure was released explosively from the reactor. However, since the material was held in the basket, no direct mechanical effect occurred on discharge.

As shown in Table 2.2, the yield of steam exploded materials varied between 80-88% before washing, and between 74-82% after washing of the fibre fraction. During SE treatment, mainly hemicelluloses were dissolved, whereas lignin was enriched in the fibre fraction. Based on yield and composition, the treatment was slightly more efficient for spruce than for unmilled recycled wood. One explanation for this may be the freshwood nature of spruce, compared to the dry recycled wood. The milling clearly intensified the steam explosion effect of recycled wood, which could be seen as increased solubilisation of hemicelluloses and reduced yield. In this respect, the effect of steam explosion on milled A I quality was comparable or even greater than for the reference spruce. This may be due to the presence of hardwood material in recycled wood sample. Hardwood is known to be more sensitive than softwood for more severe steam explosion conditions.

*Table 2.2: Yield and chemical composition of fibre fractions of steam exploded materials (205 °C, 15 min).*

| | A I RW as such | | A I RW milled | A II/A III RW as such | | Spruce reference | |
|---|---|---|---|---|---|---|---|
| | **15 min** | **30 min** | **15 min** | **15 min** | **30min** | **15 min** | **30 min** |
| Yield (unwashed) [%] | 87.8 | 79.2 | 80.2 | - | 84.0 | 83.2 | |
| Yield (washed) [%] | 82.2 | 76.8 | 74.3 | 95.6 | 87.1 | 77.5 | |
| Total lignin [%] | 35.8 | 42.3 | 36.5 | 39.3 | 41.1 | 37.9 | 44.3 |
| Total polysaccharides [%] | 54.5 | 57.0 | 57.1 | 59.8 | 57.9 | 61.2 | 54.8 |
| Cellulose [%] | 44.7 | 54.8 | 50.2 | 51.2 | 54.3 | 53.0 | 50.9 |
| Hemicelluloses (*)[%] | 9.7 | 1.6 | 6.9 | 8.6 | 3.6 | 8.1 | 3.8 |
| Extractives [%] | 1.0 | 0.7 | 0.9 | 0.9 | 1.0 | 0.9 | 0.9 |

(*) The amount of hemicelluloses includes the amount of galactoglucomannan, calculated from the amount of mannose, and assuming ratios of Man:Glu:Gal to be 3:1:0.2.

## WP 3 Valorisation of waste wood fractions into high-value products

In WP3 the valorisation of recycled wood fractions into high-value products were studied for different recycling wood qualities and particle sizes and partially compared with results for fresh spruce. The bioethanol production potential of produced cellulosic fibre fraction by fermentation was evaluated, and lignin based hot-melt adhesives and hemicellulose based surfactants were developed.

### Enzymatic hydrolysability of unmilled A I recycled wood after steam explosion and different organosolv cooking processes

The enzymatic hydrolysability of the pre-treated fibre fractions was evaluated based on the amount of sugars released in enzymatic hydrolysis. As shown in Table 5, after steam explosion no major differences in hydrolysability were observed between recycled wood and spruce. Steam explosion pre-treatment of recycled wood was performed at slightly sub-optimal conditions due to the temperature limitations of the reactor and it resulted in a fibre fraction that was relatively hard to hydrolyse, and only 62 - 65% of theoretical sugar yield was released in the 48 hour test from pre-treated waste wood. Relatively low hydrolysability is typical of softwoods, and comparable yields were also detected for the spruce reference. Based on the hydrolysis results, milling was not necessary prior to the recycled wood processing through steam explosion. Due to enhanced hemicellulose dissolution during steam explosion, a slightly lower sugar yield from the insoluble (fibre) fraction was detected for the milled recycled wood. Organosolv treatment in optimal cooking conditions produced slightly better hydrolysable material than steam explosion. However, very drastic cooking conditions at 220 °C were required without any acid catalyst. When lower cooking temperatures were used, the hydrolysability was significantly lower. The hydrolysability of organosolv pulps, out of auto-catalysed organosolv cooking, correlated with the removal of hemicelluloses rather than with the degree of delignification (figure 3.1 and figure 3.2).

However, the enzymatically hydrolysability of organosolv pulps, out of acid-catalysed organosolv cooking, correlated with the content of lignin and with the content of glucose (figure 3.3). Hemicellulose was not present in organosolv pulps out of acid-catalysed organosolv cooking.

Organosolv-pulps generated at temperatures above 177°C under acid-catalysed conditions are over cooked. These samples are anymore pulps, these samples are more and more so called hydrolysis lignin.

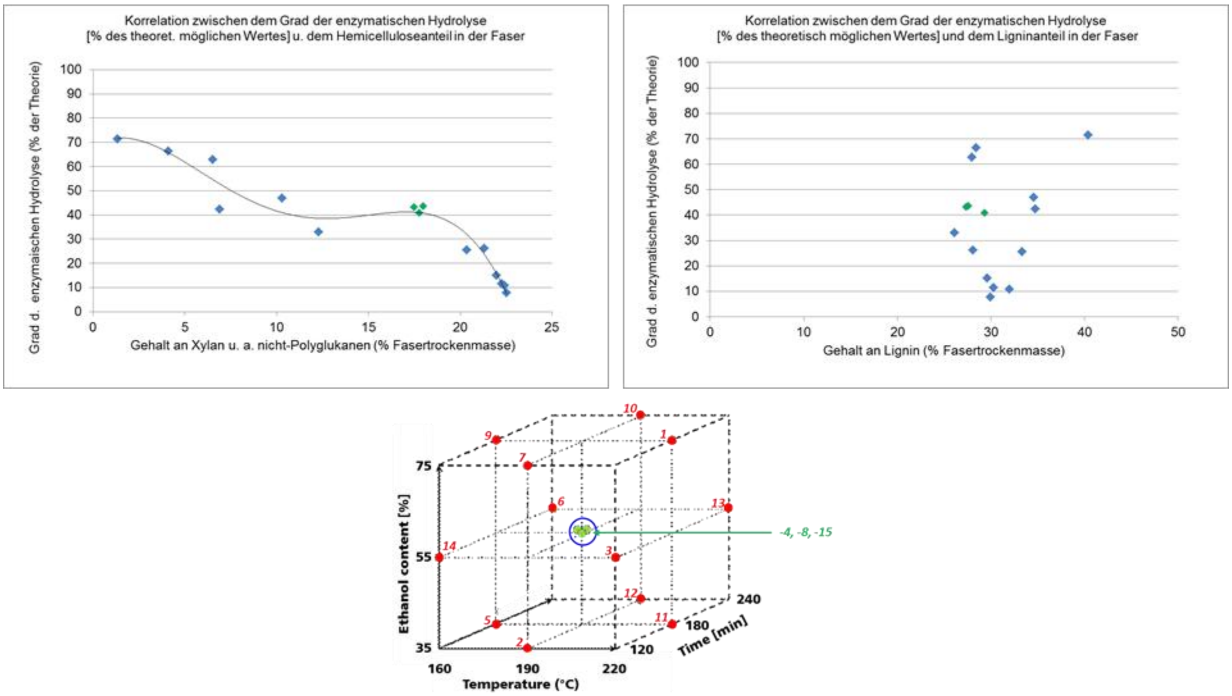


*Figure 3.1: Correlation between the degree of enzymatically hydrolysis of organosolv pulp (% of theoretically value) and the content of hemicellulose (left) as well as the content of lignin in the fibre (right) (in % of dry matter). Fibre samples were generated by auto-catalysed ethanol-water organosolv pulping, according to the conditions of the Box-Behnken-model ranged from 160 – 220 °C, 120 – 240 min and 35−75% ethanol concentration ($w_{EtOH}$).Green points correlate to fibres generated by experiments of the dice centre.*

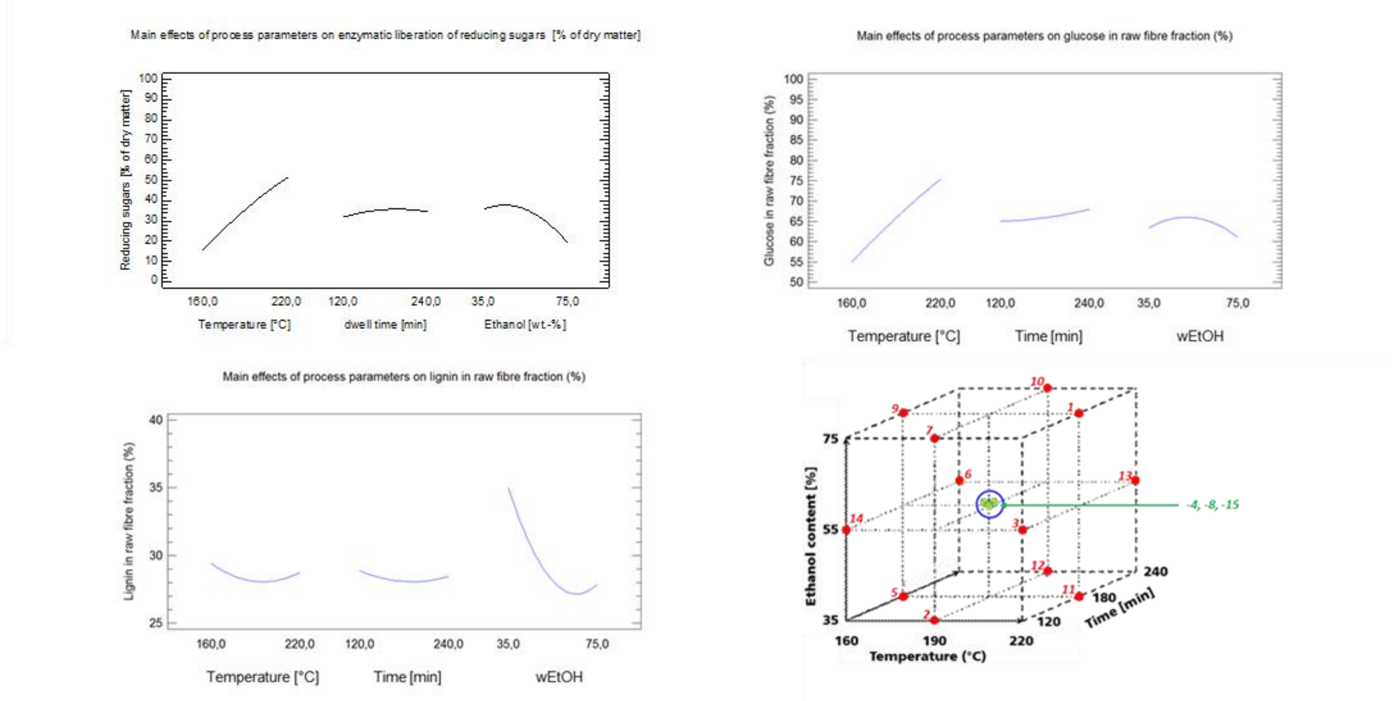


*Figure 3.2: Release of reducing sugars by enzymatically hydrolysis of organosolv pulp (% of dry matter, left, above). Content of glucose in the organosolv pulp (% of dry matter) depending on the cooking conditions of the auto-catalysed ethanol-water organosolv cooking process (right, above) as well as content of lignin in fibres (% of dry matter) (left, below) depending on the cooking conditions of the organosolv process. Fibre samples were generated by auto-catalysed ethanol-water organosolv pulping according to the conditions of the Box-Behnken-model ranged from 160 – 220 °C, 120 – 240min and 35−75% ethanol concentration ($w_{EtOH}$).*

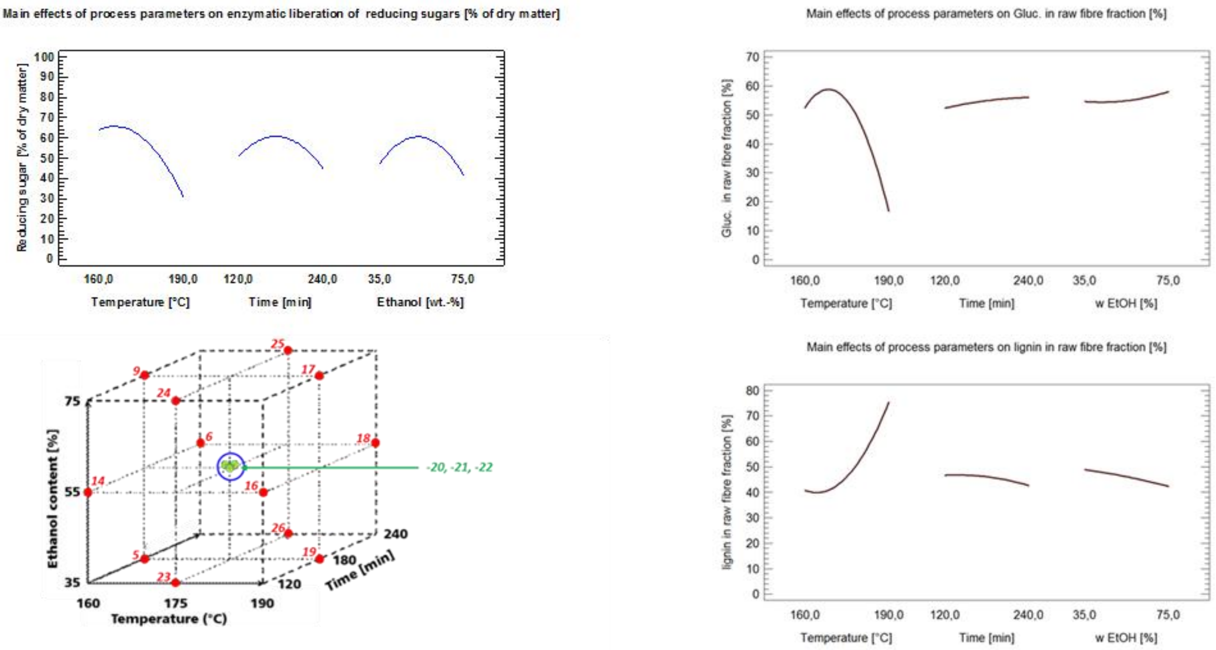


*Figure 3.3: Release of reducing sugars by enzymatically hydrolysis of raw fibres (% of dry matter; left, above). Content of glucose in the raw fibres (% of dry matter) depending on the cooking conditions of the acid-catalysed ethanol-water organosolv cooking process (right, above) as well as content of lignin in fibres (% of dry matter) (right, below) depending on the cooking conditions of the acid-catalysed organosolv process. Fibre samples were generated by acid-catalysed ethanol-water organosolv pulping according to the conditions of the Box-Behnken-model ranged from 160 – 190°C, 120 – 240min and 35−75% ethanol concentration ($w_{EtOH}$).*

### Enzymatic hydrolysis of fibre fractions from milled and crushed A I and A II / A III recycled wood in comparison with fresh spruce

The sugar production potential after different pre-treatment and fractionation procedures was evaluated using enzymatic hydrolysis in standard conditions (Table 3.1). The materials from steam explosion were milled (Wiley mill, 2 mm sieve) but the other materials from AlkOx and organosolv pulping (provided by Fraunhofer ICT) were used as such.

Recycled wood of A I and A II/A III grades showed typical behaviour of softwood material in steam explosion and AlkOx pretreatments, as evaluated based on hydrolysability of the fibre fractions. No significant difference between A I and A II/A III qualities was seen, especially concerning AlkOx. However, manual check and removal of contaminants from A II/A III quality was required. Based on the results, extra milling of recycled wood was not necessary prior to AlkOx or steam explosion.

Alkaline oxidation resulted in highly hydrolysable fibre fraction and the milder conditions resulted in higher overall sugar yields. The sugar yields were clearly higher than with steam explosion and obtainable with clearly lower enzyme dosage (results not shown). Organosolv treatments, selected on basis of highest sugar yields, produced materials with lower hydrolysability than AlkOx but higher than steam explosion. This is possibly because recycled wood was mainly softwood, which is regarded as challenging raw material for organosolv type of processes. More harsh organosolv cooking conditions were required for higher hydrolysability without acid catalyst (220°C, 2-4h), whereas in the presence of 0.5% acid catalyst the highest sugar yields in respect of the original wood were obtained at lower cooking temperature (160-175°C, 2-3h). In both cases, the conversion of A I recycled wood polysaccharides to sugars was lower compared to the steam explosion and AlkOx because of the lower pre-treatment yield.

Steam explosion pre-treatment of recycled wood was performed at slightly sub-optimal conditions due to the temperature limitations of the reactor and it resulted in a fibre fraction that was relatively hard to hydrolyse. Relatively low hydrolysability is typical for softwoods, and comparable yields were detected for the spruce reference. Processing of the reference fresh spruce material proved to be somewhat more efficient than that of (dry) recycled wood samples by steam explosion. Due to enhanced hemicellulose dissolution during steam explosion, a slightly lower sugar yield from the insoluble (fibre) fraction was detected for the milled recycled wood.

*Table 3.1: Sugar production potential from the raw materials after pretreatment and hydrolysis calculated as sugars obtainable from 1 kg of dry raw material. Hydrolysability result is given as hydrolysis yield from pretreated material. Sugar yield from 1 kg of wood is calculated considering both the yields from pre-treatment and hydrolysis.*

| **Raw material** | **Treatment** | **Pre-treatment yield** | **Hydrolysis yield** | **Sugars yield from 1 kg d.m. wood** |
|---|---|---|---|---|
| | | **%** | **% sugars of d.m.** | **g** |
| **Spruce chips** | **Steam explosion - 15 min** | 77,5 | 50,4 | **390** |
| | **AlkOx - mild conditions** | 59,4 | 90,8 | **539** |
| | **AlkOx - severe conditions** | 50,5 | 96,3 | **486** |
| **A I milled RW** | **Organosolv** - no catalyst - 220˚C/120 min/55% EtOH | 55,0 | 52,0 | **286** |
| | **Organosolv** - no catalyst - 220˚C/180 min/35% EtOH | 54,2 | 48,9 | **265** |
| | **Organosolv** - no catalyst - 220˚C/240 min/55% EtOH | 51,4 | 55,8 | **287** |
| | **Organosolv** - + catalyst - 160˚C/180 min/75% EtOH | 44,7 | 62,0 | **277** |
| | **Organosolv** - + catalyst - 160˚C/120 min/55% EtOH | 50,2 | 58,5 | **293** |
| | **Organosolv** - + catalyst - 175˚C/180 min/55% EtOH | 45,2 | 61,7 | **279** |
| | **Organosolv** - + catalyst - 175˚C/180 min/55% EtOH | 45,1 | 59,6 | **269** |
| **A I crushed RW** | **Steam explosion - 15 min** | 82,2 | 41,4 | **340** |
| | **AlkOx - mild conditions** | 56,7 | 88,3 | **501** |
| | **AlkOx - severe conditions** | 47,8 | 88,9 | **425** |
| **A II/A III crushed RW** | **Steam explosion - 15 min (*)** | *95,7* | 36,1 | ***345*** |
| | **Steam explosion - 30 min** | 87,2 | 37,0 | **322** |
| | **AlkOx - mild conditions** | 55,9 | 91,7 | **513** |
| | **AlkOx - severe conditions** | 46,5 | 99,1 | **461** |

(*) The measured treatment yield erroneously too high, result not reliable. In all cases, enzymatic hydrolysis was carried out in 1% consistency at pH 5 and 45 °C with magnetic stirring for 48 hours, using a commercial cellulase mixture (Celluclast 1.5 FP, Novozymes) at a dosage of 10 FPU/g dry weight and β-glucosidase (Novozym 188, Novozymes) at a dosage of 200 nkat/g dry weight.

### Ethanol production potential of pre-treated and fractionated recycled wood

The ethanol production potential was evaluated after different pre-treatment processes by simple fermentation experiments. Also pretreatment yields were taken into account when the ethanol production per raw material usage was calculated.

Ethanol production per dry matter from recycled wood (A I, A II/III grades) was highest for AlkOx fibre fraction (ca. 160 – 180 g/kg), and relatively good also for the organosolv fraction produced with acid catalyst (ca. 120 g/kg). Organosolv without catalyst and steam explosion pretreatments were comparable with ca 90 g/kg ethanol yields. Slow hydrolysis and release of sugars was the major limiting factor for ethanol production in the high dry matter conditions used. In actual process conditions higher ethanol yields and clearly more rapid process can be expected in reactors with essentially better mixing conditions.

Fibre fractions from alkaline oxidation showed almost complete utilization of C-6 sugars to ethanol also in higher dry matter conditions, and ethanol yields from A I and A II/A III grades were nearly comparable with spruce reference. With milder AlkOx treatment the overall ethanol yield was slightly higher on spruce than on the recycled wood grades. With severe conditions the yields were practically same. No inhibitory effects on yeast were seen with any of the samples studies.

Samples from organosolv pretreatment of A I recycled wood having highest sugar production in small scale hydrolysis experiments were selected for fermentations. Of these, the samples pretreated without catalyst resembled the samples from steam explosion in their behavior, having deficient hydrolysis especially becoming apparent in high dry matter conditions. On the contrary, the samples pretreated with catalyst performed slightly better in fermentation than could be expected based on hydrolysis results.

Regarding materials from steam explosion, the reference spruce performed slightly better than the samples from recycled wood, although A I was slightly better compared to A II/A III and not far from the reference spruce. The recycled wood samples had ethanol yield of about or below 50 % of theoretical maximum. In high dry matter conditions the yeast performance was also deficient, evidently due to the higher concentration of inhibitors.

*Table 3.2. Ethanol production potential from the raw materials after pretreatment and fermentation calculated as ethanol produced from 1 kg of dry raw material. Ethanol concentration measured by HPLC. Ethanol production from 1 kg of wood was calculated considering both the yields from pre-treatment and fermentation.*

| **Raw material** | **Treatment** | **Pre-treatment yield** | **Ethanol yield in fermentation** | **Ethanol from 1 kg d.m. wood** | |
|---|---|---|---|---|---|
| | | **%** | **g EtOH per g d.m.** | **g** | **L** |
| **Spruce chips** | Steam explosion - 15 min | 77,5 | 0,130 | **101** | 128 |
| | AlkOx - severe conditions | 50,5 | 0,341 | **172** | 218 |
| | AlkOx - mild conditions | 59,4 | 0,303 | **180** | 228 |
| **A I crushed RW** | Steam explosion - 15 min | 82,2 | 0,110 | **90** | 115 |
| | AlkOx - severe conditions | 47,8 | 0,361 | **173** | 219 |
| | AlkOx - mild conditions | 56,7 | 0,292 | **166** | 210 |
| **A I milled RW** | Organosolv - no catalyst A-OPT 3-F | 55,0 | 0,150 | **83** | 105 |
| | Organosolv - no catalyst A-OPT 13-F | 51,4 | 0,177 | **91** | 115 |
| | Organosolv - catalyst A-OPT_Kat_9-F | 44,7 | 0,258 | **115** | 146 |
| | Organosolv - catalyst A-OPT_Kat_21-F | 45,2 | 0,264 | **119** | 151 |
| | Organosolv - catalyst A-OPT_Kat_22-F | 45,1 | 0,279 | **126** | 159 |
| **A II/A III crushed RW** | Steam explosion - 15 min (*) | *95,7* | 0,091 | ***87*** | *110* |
| | AlkOx - severe conditions | 46,5 | 0,354 | **165** | 209 |
| | AlkOx - mild conditions | 55,9 | 0,268 | **150** | 190 |

(*) The measured treatment yield erroneously too high, result not reliable. In all cases, ethanol fermentation procedure consisted of a pre-hydrolysis (12 % dry matter, pH 5, 50 ºC, 6 h using a 20 mg/g dry matter commercial enzyme mixture Flashzyme Plus/Roal Oy) with dosage and fermentation stages (10% dry matter content, 35 ºC, 7 days, 1 g/l Red Star yeast).

## Lignin based hot melt adhesives

Side-stream lignins produced by recycled wood fractionation were tested as tackifiers in hot melt adhesives (HMA). HMAs are thermoplastic adhesives that are applied as liquid when hot, forming the glue seam by solidification when cooled down. In many applications, *e.g.* in packaging and bookbinding, the HMAs have replaced the solvent-based adhesives to avoid the release of volatile compounds. The main constituents of HMAs typically comprise a cohesive polymer providing the strength properties and a tackifier providing adhesion and compatibility. Optionally waxes and plasticizers can be used to adjust the melt flow properties. Lignin as a non-linear biopolymer with rather low molar mass is not likely for strength providing cohesive polymer. However, the crosslinked resin-like structure could serve as a tackifier, replacing current higher-price or partly synthetic products (*e.g* rosin and terpene-phenol resins).

Novel biobased hot melt adhesive formulations were developed using lignin as a tackifier (as such or after chemical modification) with oxidised cellulose acetate (CAOx). Also, ethylene-vinyl acetate (EVA) was tested but best results were obtained with CAOx. Lignins originating from different processes (Organosolv, AlkOx, SE) and having distinct structural features (Tg, Mw, functionalities, purity) were testes as such and compared with commercial kraft lignin reference. Esterification (acetylation, TOFA) was performed for kraft lignin reference to improve the thermoplastic properties, enabling lower processing temperatures and formulations free of plasticizers. Variable proportions of lignin tackifier, cohesive polymer and plasticizers were tested.

All studied lignins are potential tackifiers for hot melt adhesives (HMA) and pressure sensitive adhesives (PSA). The best lignin formulations showed equal or better bond strength compared to a commercial HMA reference. Lignin modification was not necessary but provided further possibilities to adjust the properties for different products (reversible PSA vs. irreversible HMAs). Unmodified and acetylated lignin needed additional plasticizer and the properties could be adjusted by the proportion of plasticizer. Rather high content (30-50%) of plasticizers is needed with all unmodified lignins. 100% biobased HMAs without external plasticizer were demonstrated for TOFA lignin.

With unmodified lignins, the melting point of the formulations increased and the gluing performance decreased with lignin molar mass and Tg. The lower the Tg, the better the gluing performance. The acid washing to remove ash was not necessary for AlkOx lignin. Compared to other unmodified lignins, the hydrolysis lignin had somewhat lower performance. TOFA-lignin formulations with lowest Tg provided best gluing performance. With the unmodified lignin tackifiers, the CAOx provided better performance as cohesive polymer than commercial EVA. This provides good possibilities to produce 100% biobased HMAs.

## Hemicellulose based surfactants

Possibilities to utilise the side-stream hemicelluloses/sugars produced in recycled wood fractionation were studied as low-cost hydrophilic components for preparation of bio-based surfactants. Surfactants are amphiphilic molecules that lower the surface tension of the liquid at the liquid-air interface, the interfacial tension between two liquids or the interfacial tension between a liquid and a solid. Due to their amphiphilic character, surfactants carry both hydrophilic and hydrophobic parts within one structure. Surfactants can act as detergents, wetting agents, emulsifiers, foaming agents or dispersants in a large number of applications

Click chemistry method based on copper catalysed azide-alkyne cycloaddition (CuAAC) was developed to link selectively functional moieties with each other. Click reactions are modular, quick and quantitative at mild conditions, and generate inoffensive or no byproducts. This offers a sustainable tool to construct variable molecular architectures for surfactants. Click method was developed using glucose and Pluronic copolymers as model compounds. Pluronics with variable properties are commercially available, having controlled structures and well-defined surface-active properties. The developed click method was further tested for the preparation of amphiphilic click compounds based on sugar fraction originating from organosolv filtrates (OSS) and Pluronic precursors. In addition, the etherified derivative obtained by butoxyhydroxypropylation of OSS fraction was synthesised as a reference compound for the click products.

Click products based on glucose and Pluronic precursors with different architectures were successfully prepared. The click method was demonstrated successfully also for coupling of impure organosolv sugar (OSS) fractions. The click model compounds showed lower critical micelle concentrations (CMC) compared to the Pluronics as such. In addition, the click products based on organosolv sugar fraction and Pluronic precursors showed lower or comparable CMC compared to the Pluronics as such. However, based on application testing, the initially good foaming and emulsifying performance of pluronics could not be improved in most cases by Click of glucose monomer or OSS for the studied structures and architectures. Interestingly, the 3-Butoxyhydroxy propylate OSS showed comparable foaming and emulsification performance with the commercial Tween 20, although the stability was at lower level. All samples emulsified with formation of a foam-like layer on the top. In addition to the butoxyhydroxy propylated OSS, the Click model compound with PE10400 pluronics (Click-3) showed comparable emulsification properties with Tween 20 reference. In many cases, the foam and emulsion stability was better with the Click products.

*Table 3.3: Surface active properties of sugar based surfactants prepare and used pluronic precursors compared to commercial references..*

| **Sample code** | **Click product/Precursor/Reference** | **Molar ratio** | **CMC in water, (wt%)** | **Foaming capacity, FC (%)** | **Emulsifying activity index, EAI ($m^2/g$)** |
|---|---|---|---|---|---|
| Tween 20 | Commercial reference | - | ~ 0.002 | 210 | 12 |
| **Model compound systems using glucose and pluronics** | | | | | |
| PE6800 | Precursor | - | ~ 0.006 | 180 | 16 |
| Click-1 | 4-Propargyl glucose : $N_3$-PE6800-$N_3$ | 1:2.5 | ~ 0.002 | 75 | 10 |
| Click-7 | 4-Propargyl glucose : $N_3$-PE6800-$N_3$ | 1:4.5 | ~ 0.0025 | - | - |
| F108 | Precursor | - | ~ 0.003 | 200 | 18 |
| Click-2 | 4-Propargyl glucose : $N_3$-F108-$N_3$ | 1:2.5 | ~ 0.002 | 25 | 8 |
| Click-8 | 4-Propargyl glucose : $N_3$-F108-$N_3$ | 1:4.5 | ~ 0.0022 | - | 4 |
| PE10400 | Precursor | - | ~ 0.01 | 250 | 31 |
| Click-3 | 4-Propargyl glucose : $N_3$-PE10400-$N_3$ | 1:2.5 | ~ 0.0015 | 180 | 15 |
| Click-4 | 4-Propargyl glucose : $N_3$-PE10400-$N_3$ | 1:4:5 | ~ 0.0038 | 50 | 10 |
| **Modified sugar fraction (originating from organosolv cooking)** | | | | | |
| Click-9 | Propargylated organosolv sugar : $N_3$-PE10400-$N_3$ | 1:2.5 | + | 40 | 6 |
| Click-10 | Propargylated organosolv sugar : $N_3$-F108-$N_3$ | 1:2.5 | + | 50 | 5 |
| OSS-BHP | 3-Butoxyhydrohypropylated OSS | - | + | 200 | 15 |

## ***WP 4 Microeconomic and environmental assessments for the waste wood recycling industry***

### *Techno-economic modelling of bio refinery processes*

In the first approach, basic economic models of the two biorefinery processes Organosolv Pretreatment and EnerkemProcess© were sketched out and the effects of the use of recycled wood compared to fresh and residual wood and other lignocellulosic sources were calculated.

### Organosolv process

The used financial models include different price scenarios and different proportions of recycled wood as a substitute for fresh beech chips. Pure "cost models" for two technologically relevant processes were used as the basis for the profitability analysis. The economic model considerations for the organosolv process were derived from the main OS-lignin output product, as well as the by-product products glucose, hydrolysis lignin and xylose, and are based on profit-cost comparisons. In particular, glucose is used as the main secondary product in the model, for which an annual production of approximately 150 Tt was initially accepted at a sugar market price of 400 € / t. The underlying cost-effectiveness of raw materials and excipients, sources of energy, operation, maintenance, revenues for by-products and investments were mainly included in OS-Lignin's production costs. The used cost factors and the associated data for cost-effectiveness modeling are shown in Table 4.1. The necessary sorting and cleaning measures for the further processing of A I recycled wood in a lignocellulose biorefinery were taken into account with a 10% CAPEX surcharge and the respective revenues reduced by 5%.

*Table 4.1: Main parameters and associated data or data for the economic modeling of an OS decomposition process using A I recycled wood with adapted data basis according to current price scenarios and CAPEX assumptions*

| Parameter | Data |
|---|---|
| Process | Organsolv-pre-treatment with and without sulforic acid |
| Main output after drying | Organosolv-Lignin |
| Processing capacity in t/a PC | 400.000 |
| Operating hours in h OH | 8.000 |
| PC/OH in t/h | 50 |
| Production capacity per h | 7.5 |
| Production capacity per a | 60.000,00 |
| By-products | Glucose<br>Hydrolysis Lignin<br>Xylose |
| Feedstock infeed assumptions | 100% Beech wood chips<br>75% Beech / 25 % A I recycling wood<br>50% Beech / 50 % A I recycling wood<br>100% A I Recycling wood |
| Feedstock price assumptions in € per dry t | Beech wood chips: 70 (best)<br>: 80 (basic)<br>:100 (worst case)<br>A I Recycling Wood: 20 (best)<br>: 26 (basic)<br>: 33 (worst case) |
| Investment costs in Mio. € | 100.00 (without sulfonic acid)<br>92.00 (with sulfonic acid) |

### *Implication of the utilisation of recycled waste wood in an economic model for a Lignocellulosic biorefinery*

The efficiency of the organosolv-process was improved by replacing beech wood chips with A I recycled wood. For example, assuming an average price level of € 26 / t for recycled wood and no additional processing costs as well as a process control without sulfuric acid, production costs of approx. € 235 / t can be calculated for the production of the lignin (see Figure 8, above). Using beech wood chips with a price of 100 € / t, production costs of approx. 595 € / t were derived. If an OS model process using sulfuric acid is used, production costs for the OS lignin are calculated in the amount of approx. 170 € / t with 100% use of A I recycled wood and approx. 530 € / t of beech wood chips.

In these model calculations, the duration of the repayment could be reduced by approximately 70%, even if, as here, approx. 5% lower yields and 10% higher investment costs for the use of A I recycled wood are assumed (see Figure 4.3). Considering the possible current revenues of approximately € 500 / t of OS-lignin and the scale effect of the Organosolv process is mainly due to the high operating costs and the actual low revenues for the other revenue-generating output products hardly economical, fresh beech woodchips are processed as feedstock.

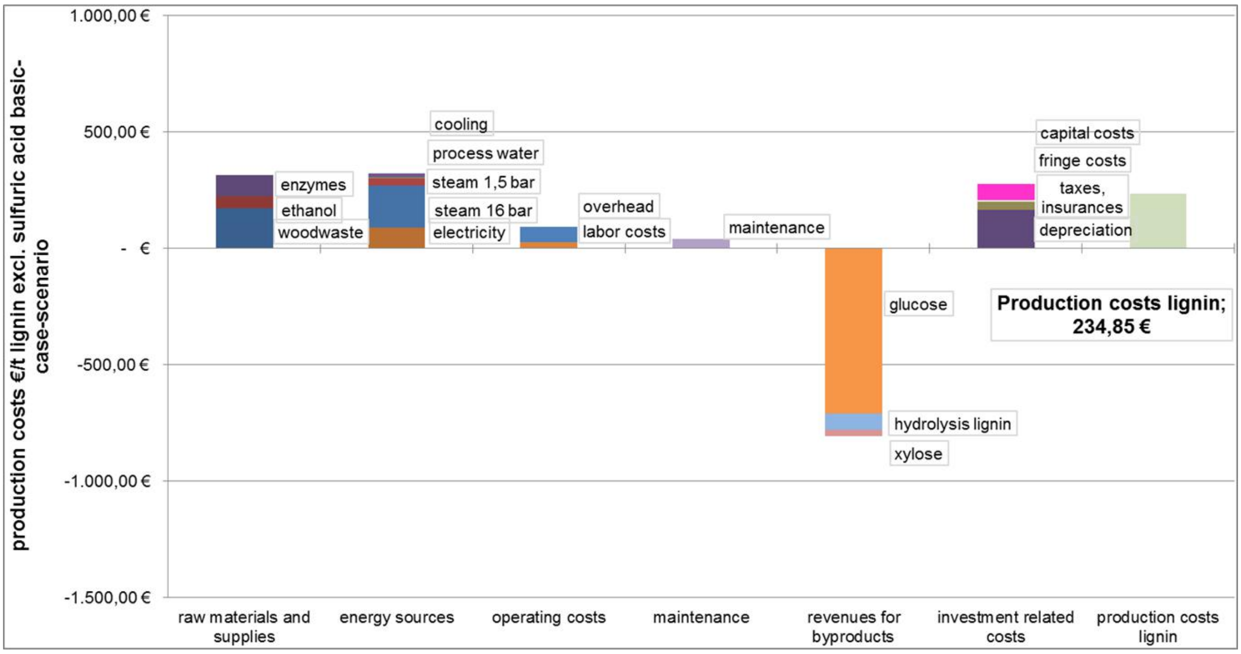


*Figure 4.1: Results of a modeled cost-effectiveness analysis to determine the manufacturing costs of lignin using A I recycled wood with organosolv digestion without sulfuric acid and updated market prices of May 2016.*

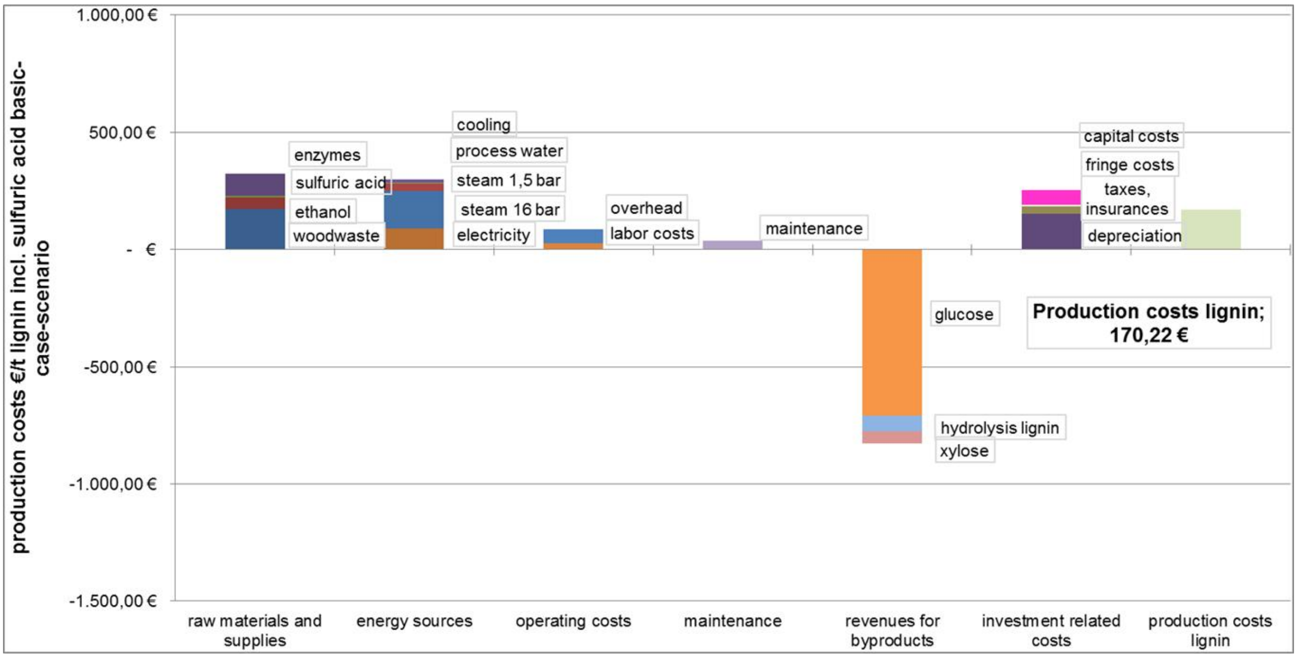


*Figure 4.2: Results of a modeled cost-effectiveness analysis to determine the manufacturing costs of lignin using A I recycled wood with organosolv digestion with sulfuric acid (bottom) and updated market prices of May 2016.*

| | | 100% Beechwood | 100% A I Recyclingwood | 100% Beechwood | 100% A I Recyclingwood |
|---|---|---|---|---|---|
| | **Quantity t/y** | **Price EUR/t** | | **m EUR/a** | |
| **Income / Revenues** | | | | | |
| Glucose | 152.000 | 280 | 280 | 43 | 40 |
| Xylose | 17.000 | 200 | 200 | 3 | 3 |
| Hydrolysis Lignin | 42.000 | 125 | 125 | 7 | 7 |
| Organosolv Lignin | 60.000 | 502 | 502 | 30 | 28 |
| **Total** | | | | **83** | **79** |
| | | | | | |
| **Costs / Expenditures** | | | | | |
| Raw materials | 400.000 | 80 | 26 | 32 | 10 |
| Utilities | | | | 28 | 29 |
| Labour incl. overheads | | | | 4 | 5 |
| Maintenance | | | | 2 | 2 |
| Other | | | | 10 | 11 |
| **Total** | | | | **76** | **57** |
| | | | | | |
| | | | | | |
| **Capital investment (in mio. EUR)** | | | | **101** | **111** |
| **Payback period (a)** | | | | **14** | **5** |
| Production costs OS-Lignin | | 728 | 235 | | |

*Figure 4.3: Comparative economic model calculations based on an organosolv process (without sulfuric acid) for beechwood and A I Recycled wood for the production of lignin and by-products for estimating the repayment periods (updated and extended basic data from the literature list as of May 2016)*

### Enerkem Process©

On the other hand, the economic parameters of a novel gasification process were modeled. This was mainly derived from publicly available and partially published data from the Canadian company Enerkem with the only output product ethanol. Missing data pairs were supplemented with appropriate literature data. The assumption of the boundary data was initially based on general literature data and was then based on their real process in trustful communication with Enerkem. Due to strict confidentiality and the lack of disclosure of the figures, especially in the case of capital-intensive cost blocks, the profitability models drawn up are based on “close to reality” estimates. These were, however matched with Enerkem to ensure an approximate orientation aid and basic validation of the developed figures from the models. Thus, at least the main cost factors on the revenue and expenditure side are taken into account. The repayment time and ethanol and methanol production costs are not to be understood as absolute values, but merely as a general orientation and as a comparison with alternative routes.

The economic modeling for pure A IV recycled wood to the organic settling waste ratios of 20% and 50%, based on the Enerkem process©, provides an ethanol cost between 0.28 and 0.31 €/L, respectively. The addition of A IV recycled wood fractions to organic municipal solid waste (MSW) leads to higher production costs for ethanol. These processes remain economically interesting with repayment periods of approx. 10 years if the ethanol price remains at a stable price level of approx.> 500 € / t (0.39 € / L).

In 2016, however, this price was significantly lower than € 400 / t (€ 0.30 / l), so that an A IV recycling mix for the production of bioethanol would have been less economical with this technology, as the repayment periods of the investment would be approx. 20 years. The investment costs of this model were assumed to be € 75 million. Though, the ethanol price in 2017 has recovered significantly, so the process is again interesting. However, this volatile price trend in ethanol shows the high risks and uncertainties of investing in pure bioethanol production.

Regardless of the original scope of ReWoBioRef, Enerkem has changed its company strategy at the end of 2014, which was mainly related to the unpredictable price fluctuations of ethanol. Instead of ethanol, the focus was turned towards the production of methanol as the final product. Market prices for methanol were and still are significantly more stable in North America and Europe, so that investment risks are minimized in the longer term. There was also an industrial interest in the technology in the Netherlands, see:

https://www.akzonobel.com/fc/news_center/news/news_and_press_releases/2014/akzonobel_and_partners_to_explore_use_of_waste_as_chemicals_feedstock.aspx)

Comparing the two approaches, if the Enerkem process produces methanol instead of ethanol, higher and more secure profitability can be calculated (see Figure 4.4). Despite higher CAPEX costs, a better and less risky profitability is due to the higher production volume and the higher and more stable price of methanol can be derived. However, since methanol is an organic basic chemical and a large-scale alcohol produced by large quantities, direct material and energy use is limited. Rather, methanol predominantly serves as a starting material for many other basic chemicals and secondary products. For this reason, only large-scale chemicals as a direct purchaser can be considered.

| | | 0% A IV Recycling | 20% A IV Recycling | 50% A IV Recycling | 0% A IV Recycling | 20% A IV Recycling | 50% A IV Recycling |
|---|---|---|---|---|---|---|---|
| | **Quantity l/y** | | **Price EUR/t** | | | **m EUR/a** | |
| **Income / Revenues** | | | | | | | |
| Methanol | 52.500.000 | 0,32 | 0,32 | 0,32 | 17 | 16 | 16 |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| **Total** | | | | | **17** | **16** | **16** |
| | | | | | | | |
| **Costs / Expenditures** | | | | | | | |
| Wastewood [0%/20% / 50%] | 0/23.000/57.500 | - 50 | - 50 | - 40 | - | - 1 | - 2 |
| MSW [0%/80% / 50%] | 115000 / 92.000 / 57.500 | - 110 | - 110 | - 110 | - 13 | - 10 | - 6 |
| Labour incl. overhead | | | | | 12 | 12 | 13 |
| Maintenance | | | | | 4 | 4 | 4 |
| Other | | | | | 2 | 2 | 2 |
| **Total** | | | | | **4** | **6** | **9** |
| | | | | | | | |
| | | | | | | | |
| **Capital investment (in mio. EUR)** | | | | | **93** | **98** | **98** |
| **Payback period (a)** | | | | | **5,0** | **6,0** | **7,6** |
| Production costs Methanol | | 0,21 | 0,26 | 0,28 | | | |

*Figure 4.4: Economic model calculations of the amortization period based on the ENERKEM process © for A IV Recycling wood and other organic wastes for the production of biomethanol (for basic data see: Michels et al., Methanol price, A IV Recycling price and urban waste: December 2016)*

### *Environmental Assessments by LCA modelling*

The ecological assessment was initially intended to compare various pre-treatment processes of recycled wood with regard to their environmental effects. Primarily, the processing to produce recycled wood was tested in recycling facilities designed for this purpose. Furthermore, other various pretreatment methods for enzymatic hydrolysis followed by fermentation and ethanol distillation were considered as alternative utilization streams for recycled wood as secondary feedstock. The two pretreatment procedures are, analogously to WP 2, the steam explosion and the organosolv method. The LCA modelling carried out was set to a screening eco-balance, which should first localize and estimate the critical parameters. The data sets for LCA modelling for Organosolv and Steam Explosion Pretreatments are based on literature and database figures.

> *Important Note: Due to the "screening" character of the ecological and material balances developed in the project and the lack of methodological recommendations for carrying out eco- or material balances for recycled wood and products, fully tangible conclusions cannot be drawn from the results obtained here. Furthermore, these eco- and material balances are observed as a scientific approach to the complex methodology of the eco-balancing of recycled wood and the possible material use of it by low-TRL technologies. Nevertheless, the implementation was supported in accordance with the existing standards DIN EN ISO 14040 and DIN EN ISO 14044.*

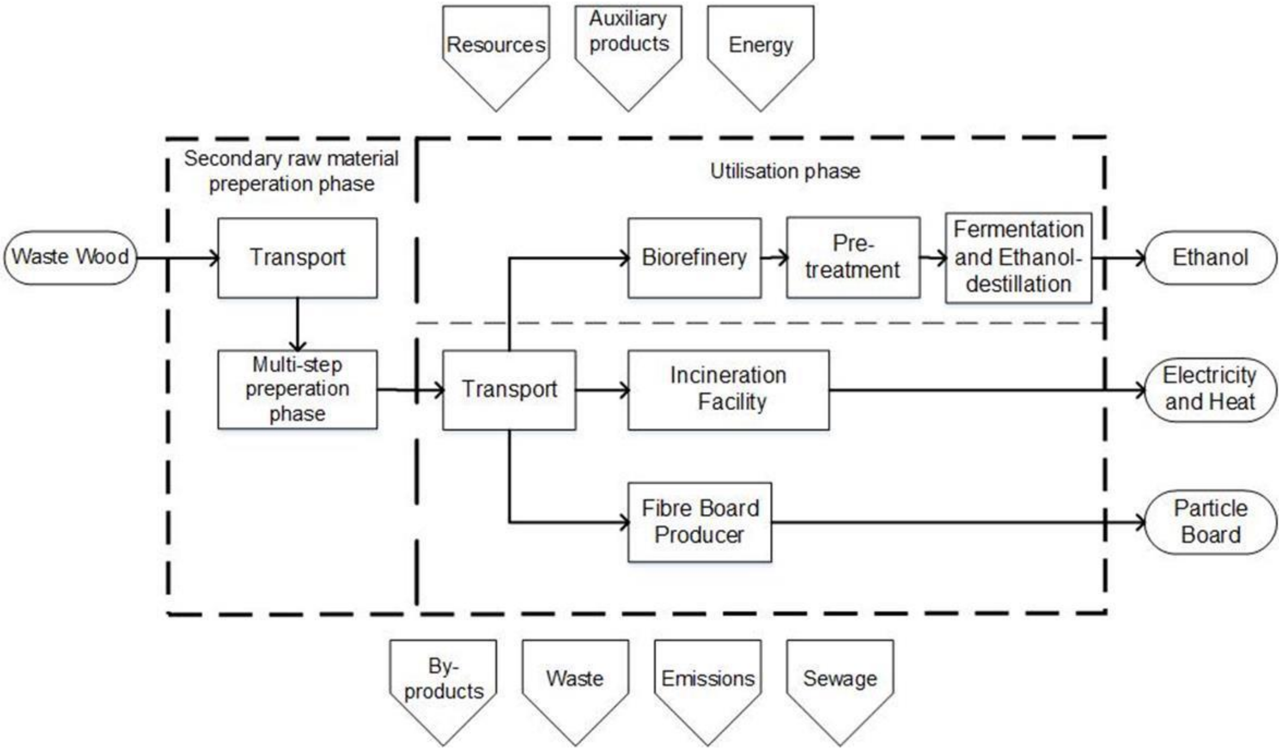


*Figure 4.5: General LCA boundary system for Waste Wood Recycling Process used in ReWoBioRef*

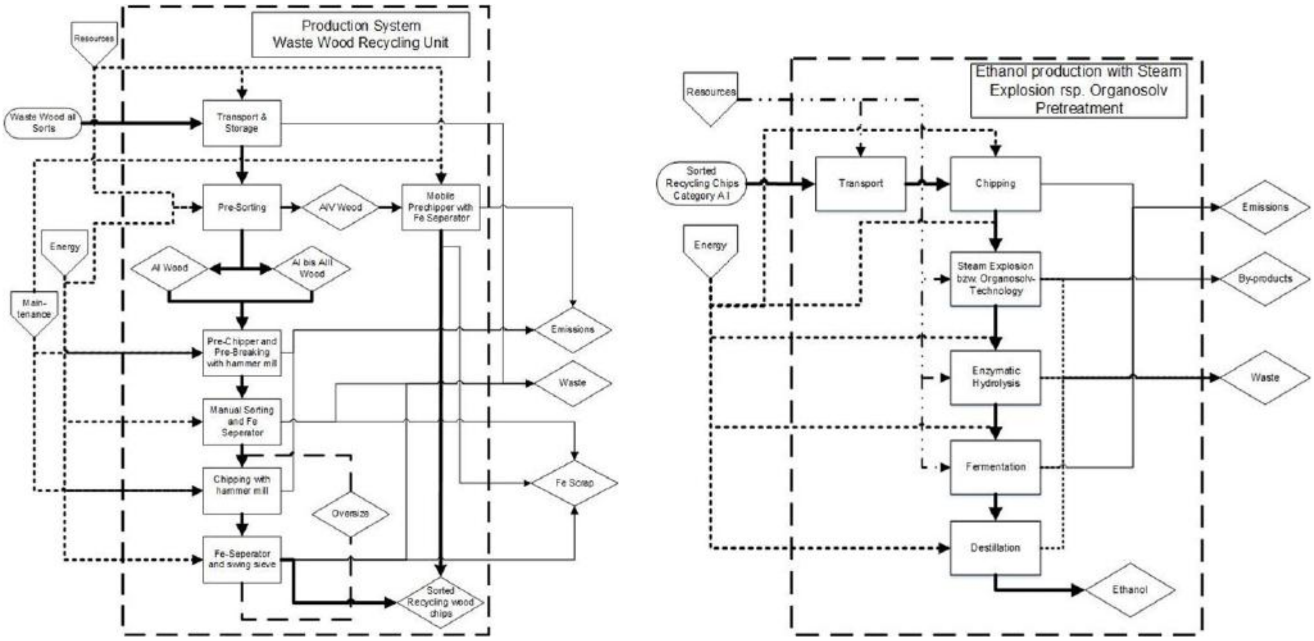


*Figure 4.6: Detailed LCA system boundaries analysis of cradle to gate type for the production system waste wood recycling (left) and ethanol production with OS- and steam explosion pretreatment (right) with system inner and outer processes and parameters.*

The recycling process of 100,000 tonnes of A I quality in chips produces a total of about 5,000 tonnes of CO2 equivalents. At the same time, about 500 tonnes of oil equivalents are needed. The acidification process contributes to acidification with 8.7 tonnes of SO2 equivalents. The contribution to the fine dust load is 4.3 tonnes PM10 equivalents. The formation of photosmog can be calculated 12.3 tons NMVOC equivalents. The results for the entire processing process in the wood recycling operation considered are shown in Figure 4.7, the orange bar.

Figure 4.7 shows the greenhouse effect of the various recycling paths on the left, using the emitted carbon dioxide equivalents. The use of the steam explosion method has the highest emissions (56,281 tonnes of CO2 equivalents). The energetic utilization causes the least influence on the greenhouse effect under the assumed boundary conditions. However, this result should be considered very critically in the context since the recycled wood is consumed to produce electricity and heat, and thus it is permanently removed from the material cycle immediately after recycling. The organosolv process and chipboard production roughly vary from 35,000 to 40,000 tonnes of CO2 equivalents with regard to the contribution to the greenhouse effect. Since the production of ethanol is directly linked to the formation of carbon dioxide and the distillation is energy-intensive, the emission of 60,000 tonnes of CO2 equivalents in the steam explosion process can be well understood. The significantly lower value in the Organosolv process can be attributed to the lower ethanol output compared to the steam explosion method, since less carbon dioxide is released as well. In the case of the steam explosion processes, not only power and heat (coupling products of ethanol production) but also higher-quality products, such as ethanol or chipboards.

In both cases, the wood is kept at least in a further cascade, which in the end involves the possibility of energetic utilization but not necessarily. Further cascade stages are possible. From these considerations, it is therefore appropriate to attribute the values of the energy recovery to the other methods as credit. In this work, this approach was not followed up, but rather the uncorrected evaluation results of the impact categories were presented. The direct comparison is carried out in the following section to illustrate the differences.

The resource depletion in kilograms of oil equivalents is illustrated in Figure 4.7, middle left. The consumption of about 16,000 tonnes of oil equivalents is striking large for the chipboard production. Resource consumption also reflects the energy requirements of a process. Chipboard production is a mature process in which the consumption is well known. Moreover, no coupling products are produced in the form of heat or electricity. The other methods provide these coupling products, whereby the energetic utilization is assumed especially for the production of electricity and heat. This process saves primary raw materials (oil). This explains the low value of 2,482 tonnes of oil equivalents. In both processes, ethanol production generates coupling products, which compensate for the crude oil. The steam explosion process requires 6,279 tonnes of oil equivalents, whereas the Organosolv process requires 3,990 tonnes of oil equivalents. However, the energy requirement was calculated on the basis of the values of a pilot experiment on the pilot scale and was additionally interpolated to the input quantity of 100,000 tonnes. These rough estimates are very likely to result in greater inaccuracies, which can only be reduced by more detailed investigations or more detailed data collection and processing. In order to determine general trends, the assumptions and estimates made are sufficient for a first approximation.

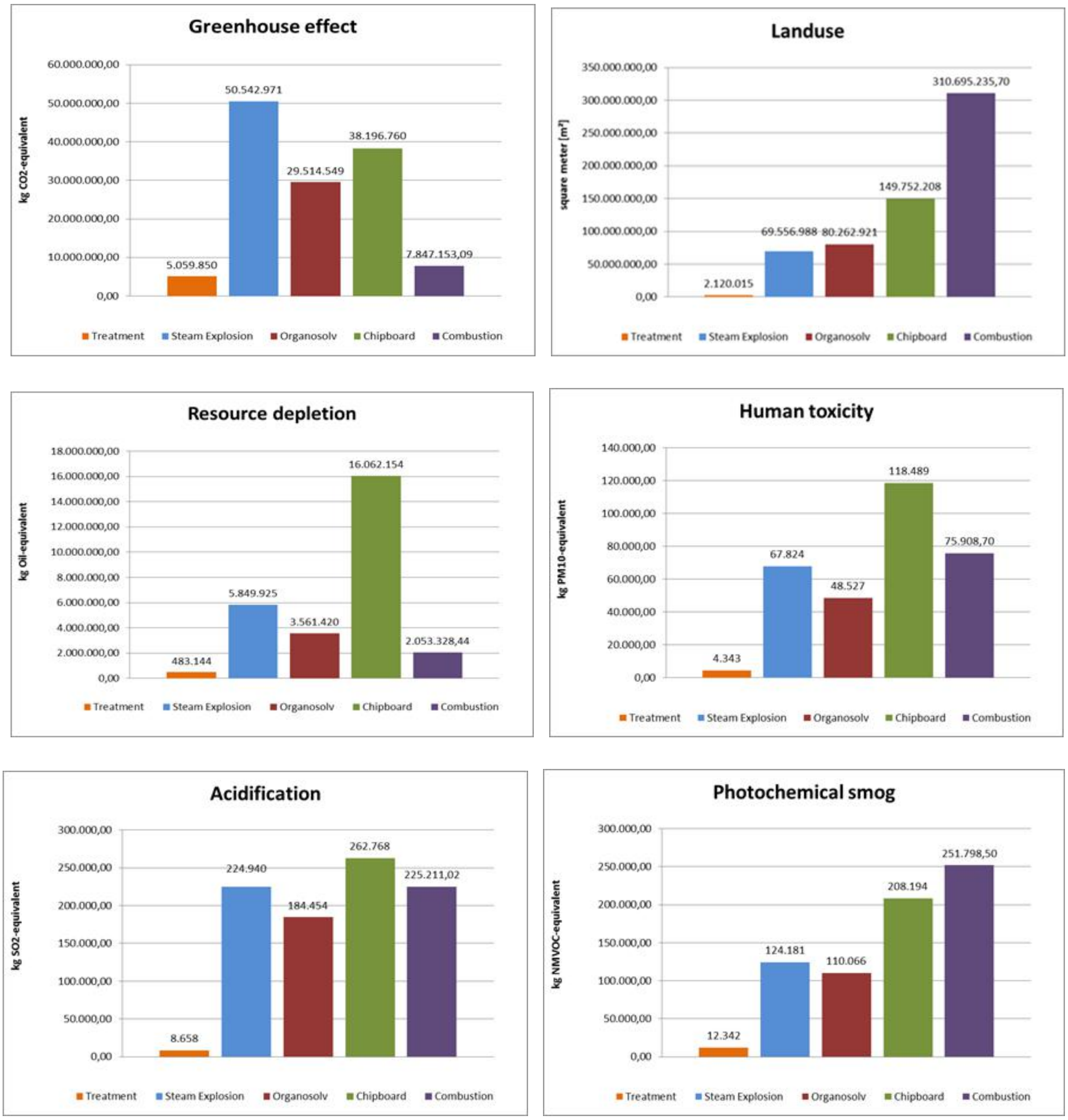


*Figure 4.7: Results of the LCA modelling following ISO 14044 principles for the utilisation of A I Recycling wood for energy generation, particleboard production and biorefinery processes (**not for general public use**)*

Figure 4.7 also shows the results for human toxicity in the middle right, which is illustrated by kilograms of PM10 equivalents and will be briefly explained, since this category of activity is in contrast to the other active categories. The production of chipboard is the top value with around 120 tonnes. The detail depth of the module used for chipboard production from fresh wood is used to record a large part of the resulting dusts. The dusts arise mainly during crushing or transport. Since no data on the emitted dust and fine dust particles were taken into account during the ethanol processes and the processing phase, it is to be assumed that these values would have an adverse effect on the process. In this sense, only the detected fine dust from the respective system expansions (for example, electricity generation from wood chips) are taken into account. The energy utilization with about 80 tonnes of PM10 equivalents takes into account the system-specific emissions of this type. A further upward correction can nevertheless be carried out even if the dust emissions are also included in the wood treatment. Thus, compared to the full use of A I recycled wood, this effect category is clearly more negative in one of the two adopted ethanol production processes, in contrast to direct energy use.

### ***WP 5 Transnational dissemination activities***

See 1.4 and 1.6

### ***WP 6  Project Management***

In October 2014, a consortium agreement was signed by all partners and sent to the FNR. The committee accompanying the project was also set up. The kick-off meeting took place on April 10, 2015 at the BMEL. During the reporting period a total of six project meetings were planned, implemented and recorded. The invitations, agenda and minutes were regularly sent to the FNR. The project meetings and places are summarized in the following table.

| **Date** | **Place and Hosts** |
|---|---|
| 2./3. **July 2014** | Fraunhofer WKI, Braunschweig, Germany |
| 21./22. **January 2015** | Universität Ljubljana, Ljubljana, Slovenia |
| 27./28. **August 2015** | VTT und St 1 Biofuels, Espoo/Helsinki, Finland |
| 4./5. **February 2016** | Fraunhofer ICT, Karlsruhe/Pfinztal, Germany |
| 1./2. **September 2016** | Brunel Universität, Uxbridge, United Kingdom |
| 9./10. **March 2017** | Reiling Unternehmensgruppe, Marienfeld, Germany |

An important component of the project management was the planning and coordination of the sampling for WP 1 in close consultation with the project partners and directly with the responsible personnel. Likewise, coordination was needed between the project partners to ensure a smooth project process. These includes: guaranteeing the continuous supply of material for WP 2 and WP 3, material supply and monitoring of analytical monitoring for WP 2.5 at the Canadian partner Enerkem, coordination of the work in WP 5.

In **September 2015**, ReWoBioRef was presented to the experts audience in Dübendorf (CH) as part of a short presentation on the occasion of the "ANNUAL SEMINAR OF THE 4TH JOINT CALL OF WOODWISDOM-NET RESEARCH PROGRAMS". In **April 2017,** the preliminary final results were presented and discussed in the "FINAL SEMINAR OF THE 4TH JOINT CALL OF WOODWISDOM-NET RESEARCH PROGRAMS" in Edinburgh (UK).

The first two German scientific advisory board meetings of ReWoBioRef and CareWood, who took place at the BMEL in Berlin on 10 April 2015 and at the Fraunhofer WKI on 10 May 2016 for his second meeting, informed the dedicated members mainly from industrial stakeholder associations and institutions regularly, mainly via email or in part, personally about the progress. The intermediate results of techno-economic and LCA modelling were critically reviewed and occasionally altered. The last meeting was scheduled for 20 June 2017 at the BMEL in Bonn. The agenda and minutes of the meetings were prepared by Prof. Klaus Richter (CaReWood), who has coordinated the committee meetings.

## 1.3 Conclusions

The main conclusions are summarised as bullet points deriving from the individual WP.

For WP 1 on the ***Characterization of recycled waste wood materials and selection criteria for pre-treatment steps*** the main conclusions were derived

- AI recycled wood has low portions of non-wooden material in average 0,2% on dry mass
- AII-AIII recycled wood has 6 times higher portions of non-wooden material than AI wood in average 1,2%
- Samples from companies with sophisticated sorting systems have lower portions of non-wooden materials.
- Only 3% of analyzed AI recycled wood samples exceeds limit values according to *Altholz*
- The most critical inorganic elements (exceeding limit values according to *Altholz* and EPF) are Cl, Cr, Cu and Pb
- 63 % of samples exceed Altholz limits values for Cl and 31 % for Cr, and even more samples exceed limit values for Cr according EPF 42 %
- Limit values for utilization of recycled wood in different pre-treatments are not well known
- Results of fraction analysis show that in the first three fractions (mesh sizes > 2 mm) more than 85 % of the total sample mass were captured
- Concentration of all analyzed inorganic pollutants increase with lower mesh size (more fine material)
- Values of each inorganic pollutants for samples with and without non wooden material are comparable, non-wooden material does not influence on concentration of inorganic elements
- Lignin content and soluble part (extractives) slightly increase with lower mesh size, this is also a reason for higher concentrations of inorganic pollutants, because they are mostly bound to lignin

For WP 2 on the ***Pre-Treatment methods for recycled wood mixtures*** the main conclusions were derived:

- Recycled wood of A I and A II/A III grades showed typical behaviour of softwood material in steam explosion and AlkOx pre-treatments, and are suitable for lignocellulosic biorefinery.
    - ✓ Milling of recycled wood was not necessary for AlkOx or SE
    - ✓ No significant difference between A I and A II/A III qualities, especially in AlkOx. However, manual check and removal of contaminants from A II/A III quality is essential.
    - ✓ No need for using more drastic reaction conditions compared to softwood in general
    - ✓ Processing of the reference fresh spruce material proved to be somewhat more efficient than (dry) recycled wood samples by steam explosion
- Pulping of matured wood class A I by ethanol/water-organosolv process is also possible, after removing of extractives and pre-swelling and increasing the moisture content
    - ✓ Acid-catalysed ethanol/water organosolv pulping increases yield of lignin, and lower temperature and process time can be used.
    - ✓ Process parameters affect also the functional groups in organosolv lignin: phenolic OH groups increase and aliphatic OH groups decrease with increasing temperature and time
- Toxic contaminations were not found
- Alkaline oxidation resulted in highly hydrolysable fibre fraction for bioethanol production
    - ✓ Performance for reference material (fresh spruce) and recycled wood material was practically similar. In addition, A II/A III grade was readily processable after manual removal of contaminants.
    - ✓ Milder conditions resulted in higher overall sugar yields
    - ✓ Sugar yields were higher than using steam explosion and obtainable also with clearly lower enzyme dosage
- Organosolv treatment was less efficient than AlkOx pre-treatment method for recycled wood
    - ✓ More harsh organosolv cooking conditions were required without acid catalyst (220°C, 2-4h), whereas in the presence of 0.5% acid catalyst the highest sugar yields in respect of the original wood were obtained at lower cooking temperature (160-175°C, 2-3h).
    - ✓ In both cases, the conversion of A I recycled wood polysaccharides to sugars was lower compared to the steam explosion and AlkOx pre-treatments.
    - ✓ Hydrolysability seemed to correlate with removal of hemicellulose (samples without catalyst) – in that respect results resemble those of samples from steam explosion

For WP 3 on the ***Valorisation of waste wood fractions into high-value products*** the derived main conclusions were:

- Recycled wood is a potential lower cost raw material for bioethanol production after efficient sorting to ensure removal of metal, plastic or stone particles.
    - ✓ The two-stage alkaline oxidation (AlkOx) pre-treatment produced well hydrolysable pulp from recycled wood.
    - ✓ Ethanol yields from A I and A II/A III grades were nearly comparable with fresh spruce. Lower yields were obtained after steam explosion and ethanol based organosolv cooking.
    - ✓ Ethanol production yields after acid-catalysed organosolv pretreament were higher compared the non-catalysed organosolv or steam explosion.
- Lignin can be used as a tackifier in hot melt adhesives, and novel sustainable HMA formulations were developed with cellulose-based cohesive polymer.
    - ✓ Best formulations provided comparable or higher bond strength compared to commercial HMA reference.
    - ✓ Lignin could be used as such without any chemical modification, but the properties could be further adjusted e.g. by TOFA-esterification.
- Side-stream sugars of biorefineries offer cost-efficient source of hydrophilic components for biobased surfactants.
    - ✓ Sustainable method for production of sugar based surfactants with controlled architectures was developed using click chemistry, which was applicable also to impure sugar fractions originating from biorefineries.
    - ✓ Butoxyhydroxy propylated crude sugar fraction originating from organosolv cooking showed comparable foaming and emulsification performance compared to the commercial reference.

For WP 4.1 on the ***Microeconomic assessments for the waste wood recycling industry*** the derived main conclusions were:

- Multitude of biorefinery concepts for LC feedstock are available with varying industrial scale readiness level
- Technical plant specifications including feedstock type and main products(s) impact on CAPEX and OPEX
    - ✓ + plus proper feedstock supply agreements
    - ✓ + plus proper product sales contracts to form a sound basis for economic modeling
- Economics are moderately feedstock and highly output product price sensitive & improve significantly with lower feedstock prices and stable product revenues
- Long term supply contracts and a higher number of output products ***can*** secure economics and attract investors

For WP 4.2 on the ***Ecological assessments for the waste wood recycling industry by means of LCA*** the derived main conclusions were:

- An LCA model within a "gate to gate" concept for a waste wood recycling process reveals the environmental impact on GWP 100 and five other major impact factors
- Data sets taken from the Ecoinvent data base 3.2 indicate lower impact on GWP 100 of a direct incineration process vs. material usage of recycling wood
- Sensitivity on data sets have shown that GWP 100 calculations vary by up to 300%, if alternative Ecoinvent data sets are taken
- Incineration processes for energy utilizing wood pellets instead of wood chips also have about up to 250% higher GWP 100
- Transport routes and means play a minor role on GWP 100 calculations; the energy source for OS and SE-pretreatments are of significantly higher impact

## 1.4a Capabilities generated by the project

The following types of patents are still conceivable, but were not announced in the reporting period:

- Process engineering patents for the generation of new material flows from recycled recycled materials for the production of a novel secondary raw material.
- Material patents for the production and characterization of a novel secondary raw material from recycled recycling after sorting and sorting

One patent application was filed on lignin use in hot melt adhesives:

- Laine, C., Willberg-Keyriläinen, P., Talja R., Ropponen, J., Liitiä, T. Biobased hot-melt ad hesive including lignin as component, FI20175001.

The foreseeable effects of this project for the European economy are:

1) Generation of an additional material flow for wood recycling plants by obtaining an economically interesting secondary raw material flow for use in biorefinery processes (recycling industry).
2) Expansion of the raw material base for investors and owners of lignocellulosic biorefining plants for the production of different biobased chemicals from cellulose, hemicellulose and lignin (bio-based industries)
3) Application and further development of chemical pretreatment processes for the production of well hydrolysable pulp for the production of bio-based chemicals via fermentation routes (mechanical engineering and process engineering).
4) Preparation of lignin-based hot adhesives and hemicellulose-based surfactants for the chemical industry from the polymer and oligomeric lignin and hemicellulose fractions not only from recycled wood but also more generally (chemistry).

The technical success prospects for generating additional material flows in waste wood recycling plants, especially from the current A I to A III mixing fractions, would be high. By means of a suitable combination of modern detection techniques, it seems technically feasible to increase the amount of recycled material used from currently about 20% to significantly more than 50% and thus to achieve similar exploitation rates as in other European countries. However, to this end, the legal framework conditions, in particular the German recycling ordinance, must be adapted in accordance with the provisions of the European Waste Directive and the industrial recycling and pre-treatment processing steps must be adapted.

On the part of the German companies and associations involved so far, there is still significant interest in a targeted up-scaling of the technologies, for example within the framework of a national demonstration project with national funding organizations or investment programmes together with the Fraunhofer CBP in Leuna. Fraunhofer CBP was not officially involved in ReWoBioREf, but owns an OS-demonstration plant for up-scaling trials. The Chief Executive Officer of the Federal Association of Secondary Raw Materials and Disposal bvse e.V., Mr. Eric Rehbock and the Managing Director of Global Bioenergies GmbH Mr. Ales Bulc, have issued written declarations of intent already in February 2015.

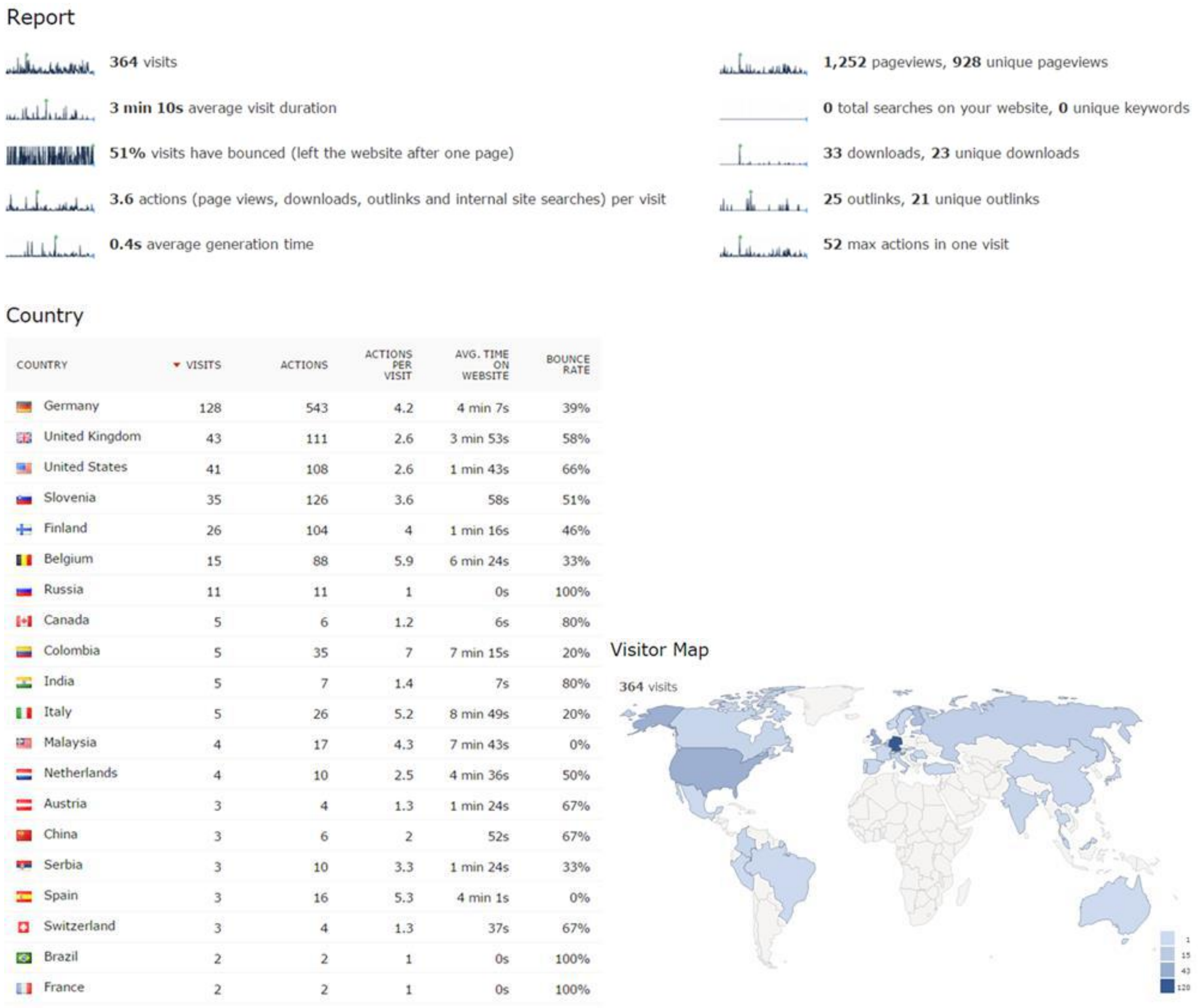
In the autumn of 2016, St1 Biofuels signed an agreement with Alholmens Kraft and UPM, which includes a sawmill and recycled ethanol plant in the Alholma industrial area in Pietarsaari. The planned production capacity of the plant is 50 million liters of 2-G bioethanol per year.

Enerkem and a substantial consortium led by Akzo Nobel BV has been developing a project in Rotterdam in the Netherlands since late 2015. There are two lines in Rotterdam. This industrial plant will be twice as large as the current industrial plants in Canada and concentrate exclusively on methanol. Since the middle of 2016, Enerkem has been in close contact with Reiling Holzrecycling GmbH and other German and European companies. To ensure a reliable and sustainable supply of raw materials to Rotterdam.

## 1.4b Utilisation of results

This brief description summarizes the scope of WP 5 of the project.

**Fraunhofer WKI** has set up a website at **www.rewobioref.eu** for the entire project as an administrator, which has been updated frequently and should inform interested parties outside the consortium about the latest developments in the project. During the reporting period, the website was regularly optimized and adapted to include the latest developments. The aim was to achieve a higher visibility of the project content among international experts and stakeholders. A secure statistical tool on the number of visitors was set up and evaluated in the last project year. For example, there were 364 visits between 01.02.2016 and 31.12.2016 on the website with an average dwell time of about 3 min. The website visitors were of global origin, however, with a focus from Europe and the participating countries (see Figure 5.1).



Report

**364** visits

**3 min 10s** average visit duration

**51%** visits have bounced (left the website after one page)

**3.6** actions (page views, downloads, outlinks and internal site searches) per visit

**0.4s** average generation time

**1,252** pageviews, **928** unique pageviews

**0** total searches on your website, **0** unique keywords

**33** downloads, **23** unique downloads

**25** outlinks, **21** unique outlinks

**52** max actions in one visit

Country

| COUNTRY | ▾ VISITS | ACTIONS | ACTIONS PER VISIT | AVG. TIME ON WEBSITE | BOUNCE RATE |
|---|---|---|---|---|---|
| Germany | 128 | 543 | 4.2 | 4 min 7s | 39% |
| United Kingdom | 43 | 111 | 2.6 | 3 min 53s | 58% |
| United States | 41 | 108 | 2.6 | 1 min 43s | 66% |
| Slovenia | 35 | 126 | 3.6 | 58s | 51% |
| Finland | 26 | 104 | 4 | 1 min 16s | 46% |
| Belgium | 15 | 88 | 5.9 | 6 min 24s | 33% |
| Russia | 11 | 11 | 1 | 0s | 100% |
| Canada | 5 | 6 | 1.2 | 6s | 80% |
| Colombia | 5 | 35 | 7 | 7 min 15s | 20% |
| India | 5 | 7 | 1.4 | 7s | 80% |
| Italy | 5 | 26 | 5.2 | 8 min 49s | 20% |
| Malaysia | 4 | 17 | 4.3 | 7 min 43s | 0% |
| Netherlands | 4 | 10 | 2.5 | 4 min 36s | 50% |
| Austria | 3 | 4 | 1.3 | 1 min 24s | 67% |
| China | 3 | 6 | 2 | 52s | 67% |
| Serbia | 3 | 10 | 3.3 | 1 min 24s | 33% |
| Spain | 3 | 16 | 5.3 | 4 min 1s | 0% |
| Switzerland | 3 | 4 | 1.3 | 37s | 67% |
| Brazil | 2 | 2 | 1 | 0s | 100% |
| France | 2 | 2 | 1 | 0s | 100% |

Visitor Map

364 visits

*Figure 5.1: Statistical analyzes of clicks, dwellings, visited pages and countries of origin on www.rewobioref.eu in the period from February 2016 to December 2016*

In addition, the Fraunhofer-Gesellschaft (Fraunhofer IGB, CBP, WKI, ICT and others) will utilize the results obtained after completion of the project to strengthen and further develop the competence in the economic utilization of waste wood as a secondary raw material for bio-refinery processes and the material Use of alternative lignocellulose sources. In the summer of 2016 pilot-oriented pilot experiments were conducted at Fraunhofer CBP, which were to provide essential technical insights for a subsequent research and development project. The long-term project objective of a national R & D project should be to promote the development of an economic process for obtaining high-quality basic chemicals from low-grade recycled wood.

## 1.5 Publications and communication

a) Scientific publications

### 1. Articles in international scientific journals with peer review

B. Lesar, et al: Utilization of recycled wood in biorefineries - preliminary results of steam explosion and ethanol/water organosolv pulping without a catalyst, *European Journal of Wood and Wood Products*, (2016) 74:5, 711-723.

### 2. Articles in international scientific compilation works and international scientific conference proceedings with peer review

B. Lesar; M. Humar, G. Hora: Contamination of recycled wood from selected recycling companies in Europe, The International Research Group on Wood Protection, Proceedings IRG Annual Meeting in Lisbon/Portugal, (2016), IRG/WP 16-50322, 20 pages, ISSN 2000-8953

### 3. Articles in national scientific journals with peer review

None

### 4. Articles in national scientific compilation works and national scientific conference proceedings with peer review

None

### 5. Scientific monographs

None

**6. Other scientific publications, such as articles in scientific non-refereed journals and publications in university and institute series**

- An invited oral presentation: M. Siika-aho, "Approaches to improve enzymatic hydrolysis of cell wall polysaccharides“, *Lignobiotech III, in Concepcion, Chile, October 26-29, 2014 .*
- M. Siika-aho: Sugars from Biomass – High Cellulose Hydrolysability of Oxygen Alkali Treated Spruce, Beech and Wheat Straw, *6th Nordic Wood Biorefinery Conference 20 – 22 October, 2015, Helsinki, Finland*
- Siika-aho, et al: Fractionation of recycled wood for biorefineries by 2-stage alkaline oxidation, *7th Nordic Wood Biorefinery Conference, 27-30 March, 2017, Stockholm, Sweden.*
- Anghelescu-Hakala, A., Laine, C., Liitiä, T. Novel bio-based surfactants from valorized waste wood fractions obtained through Click reaction, 6th International conference on bio-based polymers, *Taoyuan, Taiwan, May 14-17th 2017*
- Liitiä et al: Lignin as a functional component in thermoplastic products, to be presented in International Symposium on Wood, Fibre and Pulping Chemistry, to be presented in *Aug 30-Sept 2 2017, Porto Seguro, Brazil*.
- Hora, G.; Meinlschmidt, P.; Briesemeister, R.: Nutzungspotentiale von Recyclingholz zur Herstellung von Plattformchemikalien in Bioraffinerien in: Rohstoffeffizienz und Rohstoffinnovationen, Teipel; U. und Reller; A. (Hrsg.); S. 371- 388; *2014*
- Hora, G.; Hachmeister, P.; Lesar, B.; Humar, M.; Schmiedl, D.; Pindel, E.; Siika-aho, M.; Liitiä, T.: Technische und ökonomische Untersuchungen zur wirtschaftlichen Nutzung von Recyclingholz in Bioraffinerien nach Aufschluss mittels Steam-Explosion oder dem Organosolv-Verfahren, 4. Symposium Rohstoffeffizienz und Rohstoffinnovationen 2016, Teipel; U. und Reller; A. (Hrsg.); S. 137- 152, *2016*
- Detlef Schmiedl, Jürgen Graf, Beatrice Tübke, Tiina Liitiä, Anna-Stiina Jääskeläinen, Matti Sika-aho (2017) Potential deconstruction of recycled wood, structural features of isolated lignin and ways to activate it for material applications. 5th. International Conference on Green Chemistry and Technology, Rome, Italy, *July 24-26. 2017*:

a) Other dissemination

- *VTT webinar ' Cellulose in a circular economy - When will trash become cash?‘ on December 1st, 2015*, including recycled wood fermentation results after AlkOx pretreatment
- 37th Webinar of Fraunhofer WKI, *Wirtschaftliche Nutzung von Recyclingholz in Bioraffinerien* (in German), *June 2016*
- VTT’s ForestTech newsletter on main results of ReWoBioRef project, *May 2017*.

## 1.6 National and international cooperation

Collaboration between main research partners (Fraunhofer-WKI, Fraunhofer-ICT, University of Ljubljana, Brunel) was working well, and a joint manuscript has been published. VTT collaborated especially with Fh-ICT analysing and testing their samples. Additionally, Finnish recycled wood samples (provided by Lassila & Tikanoja) were analysed in Uni of Ljubljana, even though L&T

was not a project partner. Finnish industrial partners were actively following the project, and some recycled wood was also tested by St1.

A 3-month scientific exchange between the Slovenian project partner and Fraunhofer WKI was carried out between April and June 2015. The main objective was the preparation and submission of a scientific and technical publication in a specialist journal or a specialist magazine. An article titled "Utilization of recycled wood in biorefineries - preliminary results of steam explosion and ethanol / water organosolv-pulping without a catalyst" was filed in June 2015 (revised in December 2015) in the European Journal of Wood and Wood Products. The paper was published in May 2016. Toward the end of the project period in late 2016, a young guest scientist from Colombia has been interested in the content and objectives of the project through the BMBF-funded Green Talent Awards program.  On June 1, 2017, he started a 3-month research stay at the Fraunhofer WKI to generate flanking project approaches and international follow-up projects based on ReWoBioRef. In May 2017, a contribution was made to the LCA workshop 2017, which will be held in September 2017 at the T.U. Braunschweig, and was accepted as a lecture on 15.06.2017. The LCA workshop is an event for young scientists who carry out research in the field of life cycle assessment (LCA), life cycle assessment, or lifecycle analysis for applied questions. It is planned to publish the lectures in the Springer series "Sustainable Production, Life Cycle Engineering and Management" after the event. The publication will be available in English in 2018.