Controlled separation and conversion process for wood hemicelluloses (COSEPA)

FINAL REPORT

Title of the research project	**Controlled separation and conversion process for wood hemicelluloses**
Coordinator of the project	Eeva Jernström / Mika Mänttäri

BASIC PROJECT DATA

Project period	01.01.2014-30.06.2017
Contact information of the coordinator (institute/unit, address, telephone, fax, e-mail)	Lappeenranta University of Technology Skinnarilankatu 34 53850 Lappeenranta Tel. +358 405570918 E-mail: eeva.jernstrom@lut.fi
URL of the project	http://lut.fi

FUNDING

Total budget in EUR	**1 119 000 €**
Public funding from WoodWisdom-Net Research Programme:	Total funding granted in EUR by source:
Finland Tekes – the Finnish Funding Agency for Innovation	323 338 €
Germany Agency for Renewable Resources (FNR)	291,428.09 EUR

<u>Sweden</u> Swedish Governmental Agency for Innovation Systems (VINNOVA)	105 000 €
<u>United Kingdom</u> The Forestry Commissioners (FC)	168 000 €

Other public funding:

Other funding:

UPM Oyj, Finland	37 500 €
Cursor Oy, Finland	9 000
Xylophane, Sweden	50 000

PROJECT TEAM (main participants)

Name, degree, job title	Sex (M/F)	Organization	Country
Ulf Prüße, PD Dr., Scientific Director	Sex (M)	Thünen Institute	Germany
Anja Kuenz, Dr., Senior Scientist	Sex (F)	Thünen Institute	Germany
Malee Kallbach, MSc., PhD Student	Sex (F)	Thünen Institute	Germany
Cornelius Staude, MSc., PhD Student	Sex (M)	Thünen Institute	Germany
Mika Mänttäri, Dr. (tech), Project leader	Sex (M)	Lappeenranta University of Technology	Finland
Mari Kallioinen, Dr. (tech), WP2 leader	Sex (F)	Lappeenranta University of Technology	Finland
Eeva Jernström, Dr. (tech), coordinator	Sex (F)	Lappeenranta University of Technology	Finland
Harri Niemi, Dr. (tech), Senior Scientist	Sex (M)	Lappeenranta University of Technology	Finland

Oskari Salmenhaara, MSc., researcher	Sex (M)	Lappeenranta University of Technology	Finland
Timo Vornamo, MSc., researcher	Sex (M)	Lappeenranta University of Technology	Finland
Maria Sedin, PhD	Sex (F)	Innventia	Sweden
Sverker Danielsson, PhD	Sex (M)	Innventia	Sweden
Philip Turner, PhD, prof.	Sex (M)	Edinburg Napier University	United Kingdom
John Zhao, PhD	Sex (M)	Edinburg Napier University	United Kingdom
Maria Gröndahl	Sex (F)	Xylophane	Sweden

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
2014	BSc	F	Hannah Götze, born 1993, B.Sc. in 2015,	Ostfalia Wolfenbüttel	PD Dr. Ulf Prüße, Thünen Institute
2015	MSc	F	Sonja Horn, born 1990, MSc. in 2015	TU Braunschweig	PD Dr. Ulf Prüße, Thünen Institute
2016	MSc	M	Simon Drewes, born 1987, MSc. in 2016	TU Braunschweig	PD Dr. Ulf Prüße, Thünen Institute
2016	BSc	M	Arne Lüddecke, born 1992, BSc. in 2016	Hochschule Hannover	PD Dr. Ulf Prüße, Thünen Institute
2017/18	Dr. rer. nat.	F	Malee Kallbach, born 1985, Dr. in 2017/18	TU Braunschweig	PD Dr. Ulf Prüße, Thünen Institute
2017/18	Dr. rer. nat.	M	Cornelius Staude, born 1988, Dr. in 2017/18	TU Braunschweig	PD Dr. Ulf Prüße, Thünen Institute
2017	M.Sc..	M	Md Hujjatul Islam .	LUT	Prof. Dr. Tuomas Koiranen, Ass.prof. Dr Eeva Jernström

PROJECT SUMMARY REPORT

A summary of the project, preferably one page only

In this project the aim was to evaluate availability of wood raw material, especially underused wood raw material streams and the quantities of hemicelluloses from different species and from different material sources including sawdust, wood shavings and chips. A key element of the COSEPA research project is focused on the extraction of hemicelluloses (HC) from wood that is destined for fuel pellet manufacture. The purpose was also to develop novel alternative ways to separate and utilize hemicelluloses..

Membrane filtration was studied to purify and concentrate extraction liquid. At first it was assumed that high temperature would be beneficial in fractionation and purification of extracts due to less membrane fouling. However, membrane filtration at extraction temperature led to very low permeate flux and high fouling. The original hypothesis related to the filtration at high temperatures was discredited in this case. This is a significant finding, which affects the designing of the recovery processes for hemicelluloses in wood hydrolysates.

The extraction liquors were used as a raw material for films and platform chemicals. The xylose in the extraction liquor was biochemically and catalytically converted to 2,3-butanediol (2,3-BDO) and furfural respectively. Bacillus vallismortis has the broadest substrate spectrum to be used for 2,3-BDO production. Further on, *B. vallismortis* is less prone to common inhibiting compounds (20 g/L acetate led to a significant inhibition) in lignocellulosic extracts/hydrolysates. Hence, it is possible to convert hemicellulose extracts concentrated by ultrafiltration with *B. vallismortis* after enzymatic saccharification. After reduction of acetate concentration by extraction the xylose usage and 2,3-BDO production is basically the same as if pure xylose is used. A new furfural production process from xylose using HFIP as in-situ extracting agent was also developed which leads to outstanding up to > 99% furfural yield from pure xylose as well as from hemicellulose extracts. However, maleic acid production by oxidation of furfural using heteropolyacid-based catalysts systems lead to only moderate yields of less than 50% (no viable process option).

The saw dust after extraction of hemicelluloses was used in preparation of pellets and properties of pellets were compared with the pellet manufactured from unextracted saw dust. The extracted sawdust samples indicated an improvement in pellet formation in comparison with untreated biomass and also better heating values and energy densities. Combining the pelleting and hemicellulose extraction seems to be the most attractive concept to start production of hemicelluloses.

1.1 Introduction

1.1.1 Background

Describe the background of the project and the basic problem that it sought to address.

The EU forest-based sector is going through major structural changes, which are leading to its realignment as a key player in a newly emerging bio-based society. In supporting this change one of the essential research and innovation activities involves development of resource efficient bio-refining concepts for turning wood into high-value products. Such an approach raises a number of challenges, which need to be resolved. The first of these is to develop new technologies for breaking down the wood cell wall and/or extracting and separating different chemical components, e.g. carbohydrates in a cost-effective way. The second is to identify which products and processes are the most promising to target in the early stages of development of new biochemical and biomaterials markets. In this project availability of wood raw material, especially underused wood raw material streams and the quantities of hemicelluloses from different species and from different material sources including sawdust, wood shavings and chips is estimated. In addition, both extraction and purification processes to separate hemicelluloses from wood as well as downstream processes to refine new products from hemicelluloses are developed.

1.1.2 Objectives

Describe the project objectives.

The project objectives are

- to evaluate availability of wood raw material, especially underused wood raw material streams and the quantities of hemicelluloses from different species and from different material sources including sawdust, wood shavings and chips.
- to develop novel alternative ways to separate and utilize hemicelluloses.
- to use purified hemicelluloses to manufacture barrier films
- to biotechnically and catalytically convert carbohydrates to platform chemicals (2,3-butanediol, furfural and maleic acid).
- to evaluate the attractiveness of process concepts

1.2 Results and discussion

Main achievements of the project, quality, innovativeness, industrial relevance and contribution to competitiveness, environmental and societal impact.

WP1. Selection of potential raw materials

Evaluation of potential softwood and hardwood raw material streams for wood fuel pellet production was made. The study included an analysis of the scales of current and future availability of material used within wood pellet production processes, including sources such as thinning's, harvesting residues and chip screening residues destined for energy production. This was translated into potential scales of industrial production of HC as part of wood fuel pellet production, that could be considered in different regions, within the countries evaluated. In the UK (one of the main case studies) softwood (primarily Sitka spruce) represents the most likely first case scenario for the development of a HC extraction process from wood pellets destined for energy generation. This is based on the presence of existing operations for fuel pellet production and the large volumes of residuals from sawmills around the UK.There is a detailed report on the availability of raw material specifically in the UK and more generally in Europe: A report on Work package 1: "Controlled separation and conversion process for wood hemicellulose" (COSEPA), May 2106, John Zhao and Philip Turner

WP2 Development of combined extraction and purification process
Extraction of hemicelluloses from birch chips were made both in Innventia and LUT. Different temperatures (110-160 °C) and times (1-28 h) were used in the extraction aiming to recover hemicelluloses and lower molar mass carbohydrates. Hemicellulose were purified by membrane filtration and tested in film production (Xylophane in Sweden, WP4) and the hemicellulose concentrates were hydrolysed, purified and finally tested for fermentation processes by Thünen Institute (WP3). The effect of pressurised hot water extraction on the pellet properties were also studied.

At first it was assumed that high temperature would be beneficial in fractionation and purification of extracts due to less membrane fouling. Therefore, one aim was to find out, how long time the extract can be treated at high temperature without significant changes in its content, when the recovery and separation of hemicelluloses are both done at high temperature. The main conclusion of the results is, that no remarkable decomposition of hemicelluloses could be observed at 120 °C, while at 160 °C clear changes were seen. Therefore, processing the extract at high temperature would likely to be safe at 120 °C for several hours. However, membrane filtration at extraction temperature led to very low permeate flux and high fouling. The original hypothesis related to the filtration at high temperatures was discredited in this case. This is a significant finding, which affects the designing of the recovery processes for hemicelluloses in wood hydrolysates.

The extracted saw dust was used in preparation of pellets and properties of pellets were compared with the pellet manufactured from unextracted saw dust (WP2, WP5). The extracted sawdust samples indicated an improvement in pellet formation in comparison with untreated biomass and also better heating values and energy densities.

WP 3: Conversion of carbohydrates (biotechnological and catalytic)
The screening for new microbial strains for 2,3-BDO production resulted in several so far not recognized risk class 1 strains (see Kallbach et al. Appl. Microbiol. Biotechnol. (2017) 101: 1025-1033). It turned out that *Bacillus vallismortis* has the broadest substrate spectrum to be used for 2,3-BDO production (see Jurchescu et al. Appl Microbiol Biotechnol (2013) 97:6715–6723). Further on, *B. vallismortis* is less prone to common inhibiting compounds in lignocellulo-

sic extracts/hydrolysates. Hence, it is possible to convert hemicellulose extracts concentrated by ultrafiltration provided by the project partner LUT with *B. vallismortis* after enzymatic saccharification. Tests revealed that the potentially inhibiting compounds furfural, syringaldehyde and 5-HMF do not inhibit 2,3-BDO production, whereas the acetate concentration of nearly 20 g/l led to a significant inhibition. However, after reduction of its concentration by extraction the xylose usage and 2,3-BDO production is basically the same as if pure xylose is used (Fig. 1).

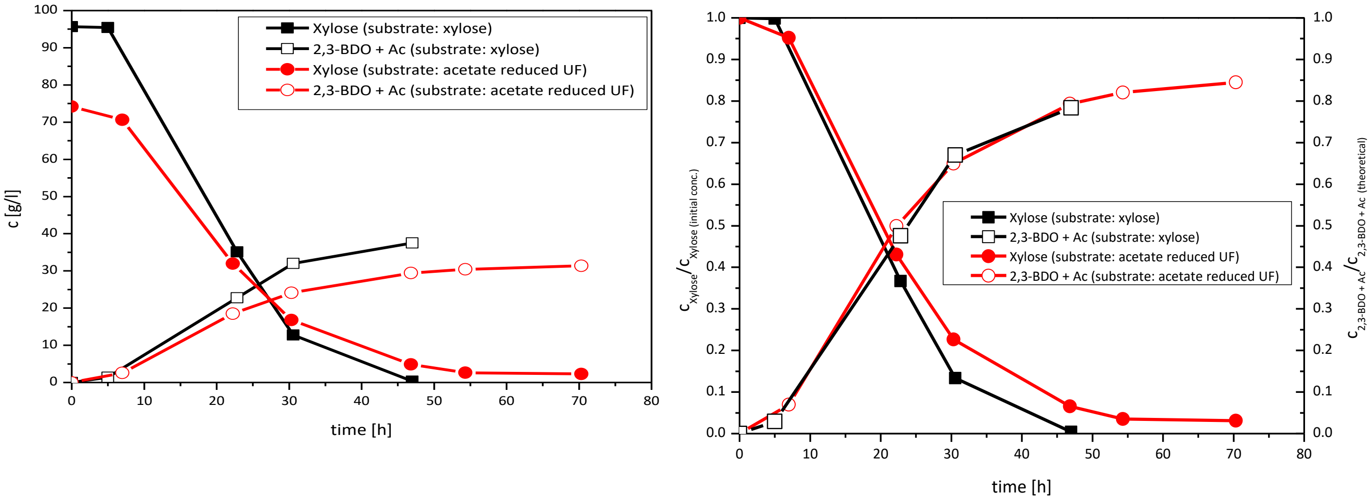

Fig. 1: Comparison of fermentation courses of pure xylose (black) and hydrolysed hemicellulose extract concentrated by ultrafiltration (UF) and reduced in acetate concentration (red) with *Bacillus vallismortis*. Left: Concentration-time courses of substrate xylose and products 2,3-BDO + acetoin (Ac). Right: Normalized substrate concentration and product formation (2,3-BDO + acetoin) in terms of % of the theory. Cultivation in a 250 mL reactor with a filling volume of 100 mL, 37 °C, aeration rate of 25 sL/h, 300 rpm, pH control at 5.8.

To study the chemocatalytic reaction of xylose to maleic acid via furfural as key intermediate first the two reactions xylose → furfural (dehydration reaction) and furfural → maleic acid (oxidation reaction) where studied separately. For the conversion of xylose to furfural a proprietary biphasic reaction system (patent application WO 2016/055608) using water and hexafluoroisopropanol (HFIP) which act under reaction conditions as in-situ extracting agent was studied in detail. Both 5% xylose solution (Fig. 2) and hemicellulose extract were converted to furfural with a yield > 99%.

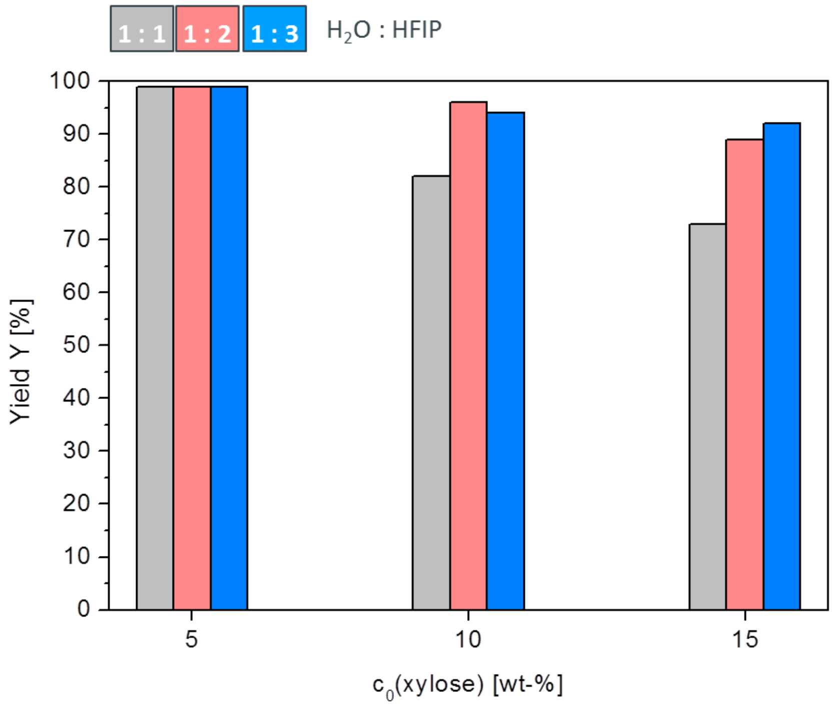

Fig. 2: Furfural yield in dependence of the initial xylose concentration (in water) and applied ratio of water and HFIP as extractant. Reaction conditions: T = 103 – 106 °C, 6 mol/L HCl, H_2O:HFIP = 1:1 – 1:3 (v/v).

These results are outstanding compared to the known literature and to the current industrial production process (furfural yield 30-55%, H_2SO_4 as catalyst, T = 150 – 200 °C). The developed process is ready to be transferred to a larger scale. Maleic acid production by oxidation of furfural using heteropolyacid-based catalysts systems lead to only moderate yields of up to 44% (no viable process option).

WP 4: Barrier film formulation and characterisation

Extraction liquor from birch chips was used for film production by Xylophane. The molar mass of hemicelluloses in extraction liquor was probably too low for high quality film production in this case.

WP5: Biorefinery concepts

This workpackage aimed at identification of the range of opportunities for exploitation of HC in different products to be considered alongside a techno-economic analysis of the technology developed within the project. The main conclusion is that techno-economically extraction alone would not be feasible but combined with pelleting operation could offer an opportunity to produce added value hemicellulose products in addition to better quality fuel pellets.

When considering markets, the most attractive application for wood based hemicelluloses in the short term, which requires the least additional development work would be in the sale of HC as additives for animal feedstock. In the short to medium term the potential for production of furfural is also an attractive proposition although it would be more attractive once the cost of HFIP has been reduced. The potential production of maleic acid considered in this project has not yet progressed to the point where it could be considered an efficient commercial process and more work on the technological development is still required. Finally, the development of the process to produce 2,3-butanediol has proved to be extremely successful from an academic perspective. However, when considering that the main end market for 2,3-butanediol: the solvent Methyl Ethyl Ketone (MEK) the overall process is not yet cost efficient enough to compete with established oil based processes without some form of government subsidy.

1.3 Conclusions

The most important contributions to the state-of-the-art, derived from the results and discussion.

- No remarkable decomposition of birch hemicelluloses at 120 °C, while at 160 °C it was clearly noticeable after more than 3 hours exposure time.
- Therefore, fractionation and purification of extract at high temperature might be possible
- However, the results showed that a high temperature (above 100 °C) is not beneficial in purification and concentration of hemicelluloses by membrane filtration.
- Novel 2,3-BDO producing microbial strains (risk class 1) have been characterized
- *Bacillus vallismortis* can be regarded as very promising strain for industrial 2,3-BDO production due to its outstanding properties (broad substrate spectrum, high final 2,3-BDO concentration, high yield, high productivity, high tolerance against common inhibiting compounds in lignocellulosic substrates)
- Conversion of a xylose-rich hydrolysed hemicellulose extract to 2,3-BDO was achieved with *Bacillus vallismortis* at the same yield and productivity as with pure xylose
- A new furfural production process from xylose using HFIP as in-situ extracting agent was developed which leads to outstanding up to > 99% furfural yield from pure xylose as well as from hemicellulose extracts
- Maleic acid production by oxidation of furfural using heteropolyacid-based catalysts systems lead to only moderate yields of less than 50% (no viable process option)
- Combining the HFIP-based furfural production with. gas-phase furfural oxidation process should lead to an overall yield of maleic acid from xylose of > 70% which can be regarded as viable bio-based alternative to the current petrochemical process
- Combining the pelleting and hemicellulose extraction seems to be the most attractive concept to start production of hemicelluloses

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1.4a Capabilities generated by the project

Knowledge generated in the project / outcomes of the project, such as unpublished doctoral theses, patents and patent applications, computer programs, prototypes, new processes and practices; established new businesses; potential to create new business opportunities in the sector.

- Novel potent 2,3-BDO producing strain (*Bacillus vallismortis*) with high potential to be used in industrial scale
- New furfural production process leading to outstanding high furfural yields (> 99%), protected by patent application WO 2016/055608
- Combination of the developed furfural production process with gas-phase furfural oxidation should lead to bio-based maleic acid from xylose at > 70% overall yield (potentially competitive with current petrochemical route)

- Malee Kallbach, doctoral thesis, Technical University Braunschweig (unpublished)
- Cornelius Staude, doctoral thesis, Technical University Braunschweig (unpublished)

1.4b Utilisation of results

Give a brief description of how the results of the research and development have been used and/or what is the exploitation plan or plans for transferring the results into practice.

Parts of the results already have been published as paper or conference contributions. Further paper publications are planned:

- Kallbach M, Jäger D, Niemi H, Kallioinen M, Mänttäri M, Kuenz A, Prüße U. Conversion of xylose from birch wood hemicellulose extract to 2,3-butanediol with *Bacillus vallismortis* (paper in preparation)
- Kallbach M, Kuenz A, Prüße U. Process optimization of 2,3-butanediol production with *Bacillus vallismortis* (paper in preparation)
- Staude C, Prüße U. Acid-catalyzed furfural production using HFIP as in-situ extraction agent (paper in preparation)

The project outcomes in terms of 2,3-BDO and furfural production shall be further exploited with interested industrial partners.

The results of WP1 and WP5 have been reported in two project internal reports which in turn can be used in making a presentation to the company partners or other potential users of the results:

- A report on Work package 1: Controlled separation and conversion process for wood hemicellulose (COSEPA), May 2106, John Zhao and Philip Turner
- A report on Work Package 5: Technical evaluation of the impact of hemicellulose extraction on the manufacture of wood fuel pellets, John Zhao and Philip Turner (ENU), Mari Kallioinen, Harri Niemi, Eeva Jernström, Mika Mänttäri (LUT), February 2017

1.5 Publications and communication

a) Scientific publications

For publications indicate a complete literature reference with all authors and for articles a complete name. Indicate the current stage of the publishing process when mentioning texts accepted for publication or in print. Abstracts are not reported. Indicate the five most important publications with an asterisk.

1. Articles in international scientific journals with peer review

Kallbach M, Horn S, Kuenz A, Prüße U (2017). Screening of novel bacteria for the 2,3-butanediol production. Appl. Microbiol. Biotechnol., 101: 1025-1033

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

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3. Articles in national scientific journals with peer review

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

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5. Scientific monographs

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

Md Hujjatul Islam, Techno-economic feasibility study of hemicellulose extraction from softwood saw dust, M.Sc. Thesis 2017, LUT

a) Other dissemination

Such as text books, manuals, user guidelines, newspaper articles, TV and radio programmes, meetings and contacts for users and results.
Dissemination of results to industrial partners and industrial partners dissemination within the company.

Contributions at Scientific Conferences

Kallbach M, Kuenz A, Hevekerl A, Prüße U (2015). Microorganism screening for the conversion of xylose to 2,3-butanediol, ECCE10+ECAB3+EPIC5, Nice, France

Niemi H, Kallioinen M, Puro L, Danielsson S, Sedin M, Mänttäri M (2015). Evaluation of degradation tendency of wood polymeric compounds in wood extract at high temperature, 18th International Symposium on Wood, Fibre and Pulping Chemistry (University of Natural Resources and Life Sciences (BOKU), Vienna, Austria.

Kallbach M, Kuenz A, Prüße U (2016). Conversion of xylose to 2,3-butanediol with a screened Bacillus ssp. strain, 12th International Conference on Renewable Resources & Biorefineries, Ghent, Belgium

Staude C, Prüße U (2016). HFIP as new powerful in-situ extractant for the synthesis of furfural from xylose, 8th Green Solvents Conference, Kiel, Germany

Staude C, Prüße U (2016). Chemical-catalytic conversion of xylose to furfural in an aqueous new organic solvent biphasic system, 12th International Conference on Renewable Resources & Biorefineries, Ghent, Belgium

Staude C, Prüße U (2016). HFIP als neues und effektives in-situ Extraktionsmittel für die Synthese von Furfural aus Xylose, ProcessNet-Jahrestagung und 32. DECHEMA-Jahrestagung der Biotechnologen, Aachen, Germany

Kallbach M, Kuenz A, Prüße U (2016). Neuer Stamm zur biotechnischen Umsetzung von Xylose zu 2,3-Butandiol, ProcessNet-Jahrestagung und 32. DECHEMA-Jahrestagung der Biotechnologen, Aachen, Germany

Staude C, Prüße U (2016). HFIP as new powerful in-situ extractant for the synthesis of furfural from xylose, 8th Green Solvents Conference, Kiel, Germany

Weingart E, Teevs L, Staude C, Prüße U (2017). Hexafluoroisopropanol as extraction solvent for HMF and furfural production with superior selectivity, 50. Jahrestreffen Deutscher Katalytiker, Weimar, Germany

Staude C, Prüße U (2017). Acid-catalyzed xylose dehydration to furfural and its further oxidation to maleic acid, 50. Jahrestreffen Deutscher Katalytiker, Weimar, Germany

Kallbach M, Drewes S, Niemi H, Kallioinen M, Mänttäri M, Kuenz A, Prüße U (2017). Conversion of xylose from birch hemicellulose hydrolysate to 2,3-butanediol with Bacillus vallismortis, 7th Nordic Wood Biorefinery Conference 2017, Stockholm, Schweden

Staude C, Prüße U (2017), The synthesis of furfural from xylose in a biphasic system comprising of water and a new organic solvent, 7th Nordic Wood Biorefinery Conference 2017, Stockholm, Schweden

Weingart E, Teevs L, Staude C, Prüße U (2017). Hexafluoroisopropanol as extraction solvent for HMF and furfural production with superior selectivity, International Symposium on Green Chemistry (ISGC-2017), La Rochelle, France

Kallbach M, Staude C, Prüße U (2017). Biotechnical and chemical conversion of xylose to 2,3-butanediol, furfural and maleic acid, International Symposium on Green Chemistry (ISGC-2017), La Rochelle, France

1.6 National and international cooperation

Give a brief description of the cooperation/ networking (partnership between the project participants and how this has developed; industrial involvement; synergies of industrial and research expertise; Has the project collaborated with similar projects in the WW-Net countries or other regions, or established new links with/ between local or international organisations involved in the respective research field? Describe how these partnerships have supported the project.
National vs. transnational aspects in the project; added value for the project and its impacts which result from transnational cooperation.

- Close collaboration between LUT and Thünen Institute concerning hemicellulose valorization in the project, shall be continued in further collaboration projects
- Synergy between LUT wood/pulp & paper and separation expertise with Thünen expertise in valorization of biomass streams into bio-based chemicals
- Dr. Ulf Pruße visit at LUT (project meeting, joint publications and lectures for students)
- Pelleting experiments in Latvia (new research partner, Latvian State Institute for Wood Chemistry (IWC)) Dr. Alexandr Arsanican)
- Close collaboration between LUT and Innventia in extraction and purification(reseach visits in Innventia (Harri Niemi), hemicellulose extraction and filtrations, equipment exchange, LUT membrane filter in Innventia)
- Research visit at LUT, Prof. Philip Turner
- Hemicellulose films have been made by Xylophane (industrial partner of the project)