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Program

April 28, Radisson Blu Latvia, Elizabetes Street 55	
9:00	Opening Ceremony
9:10	Tips on how to identify and avoid predatory publishers and conferences. Gita Rozenberga (The Library of the University of Latvia, OpenAIRE National Open Access Desk)
9:50	The research landscape of biorefinery: a scientometric overview. Arnis Kokorevics (Latvian State Institute of Wood Chemistry)
10:30	Coffee Break
10:50-12:30	Session 1A Chair Vladimirs Biziks
	Session 1B Chair Uģis Cābulis
10:50	Suberinic acids - from isolation to feedstock for bio-polyol synthesis. D.Godina, R.Makars, A.Abolins, A.Paze, M.Kirpluks, J. Rizikovs (Latvian State Institute of Wood Chemistry)
	Impact of arginine containing fertilizer on nitrogen isotope ratio and elemental content in young conifer stands. M.Bertins, L.Busa, D.Lazdina, K.Dumins, M.Klavins, A.Viksna (University of Latvia)
11:10	Novel bio-polyols for the polyurethane synthesis. O.Gotkiewicz, H.Beneš (Institute of Macromolecular Chemistry CAS)
	Effect of various fertilizers on stable isotope ratios and amino acid content in apple seeds. L.Buša, R.Kravceviča, J.Ruško, A.Viksna (University of Latvia)
11:30	Michael donor monomer synthesis for bio-based thermoset polymers using tall oil fatty acids. R.Pomilovskis, A.Fridrihsone, M.Kirpluks (Latvian State Institute of Wood Chemistry)
	Use of wood ash in the forest ecosystem and its effect on the rare earth element content in the forest soil and blueberries (<i>Vaccinium Myrtillus L.</i>). V.Lazarenko, V.Rudoviča, A.Viksna, M.Bērtiņš, J.Burlakovs, D.Lazdiņa (Faculty of Chemistry, Department of Analytical Chemistry, University of Latvia)
11:50	Michael donor monomer synthesis for polymeric materials using rapeseed oil. D.Eihe, A.Abolins, M.Kirpluks (Latvian State Institute of Wood Chemistry)
	Bio-fertilizers of spent coffee grounds and green algae <i>Chlorella sp.</i> biomass for enhancement of soil organic matter. D.Ragauskaitė, R.Šlinkšienė (Kaunas University of Technology)
12:10	Comparison between neat tall oil fatty acid and their methyl ester epoxidation in a rotating packed bed reactor. E.Kauliņa, R.Pomilovskis, M.Kirpluks (Latvian State Institute of Wood Chemistry)
	An insight into challenges of conducting an LCA study for a food waste biorefinery. K.Balina, E.Dace (University of Latvia)
12:30	Lunch
13:20-15:00	Session 2A Chair Agnė Kairytė
	Session 2B Chair Arturs Viksna
13:20	Development of an analytical method for the determination of tar in co-produced gases in the biomass pyrolysis process. S.Osipovs, A.Pučkins (Daugavpils University)
	Characterization and evaluation of water-based ecological paint for the protection of wood materials coated using dipping technique. E.Sansonetti, D.Cīrule, E.Kuka, B.Andersons, I.Andersone, M.Daniels (Latvian State Institute of Wood Chemistry)
13:40	Study of a novel bio-refining method for obtaining 2-furaldehyde, acetic acid and pulp from birch wood. M.Puke, D.Godina, P.Brazdausks, J.Rizikovs (Latvian State Institute of Wood Chemistry)
	The study of betulin particles containing hydrogels prepared by antisolvent precipitation. A.Pāže, S.Vītoliņa, R.Bērziņš, J.Rižikovs, R.Makars, D.Godina, A.Tereško (Latvian State Institute of Wood Chemistry)
14:00	New possibilities of using waste hemp biomass. J.Frankowski, D.Sieracka, W.Czeszak (Institute of Natural Fibres & Medicinal Plants – National Research Institute)
	Optimization of betulin colloidal aqueous suspension pretreatment for determination of particle characteristics. S.Vitolina, A.Paze, R.Berzins, J.Rizhikovs, R.Makars, D.Godina, A.Teresko (Latvian State Institute of Wood Chemistry)

14:20	Flammability studies of a pine sawdust coated with multicomponent suspension. N.Augaitis, S.Vaitkus, A.Kairyte, G.Balčiūnas, A.Kremensas, S.Vėjelis (Vilnius Gediminas Technical University)	Synthesis of novel C(3)-linked betulin azole conjugates. E.Jansons, J.Lugiņina, M.Turks (Institute of Organic Chemistry and Material science, Faculty of Materials Science and Applied Chemistry, Riga Technical University)
14:40	Potential of some Latvian industrial crops residuals for conversion to eco-friendly thermal insulation material. A.Berzins, R.Tupciauskas, M.Andzs, G.Pavlovichs (Latvian State Institute of Wood Chemistry)	Adaptation of the methylene blue adsorption method for specific surface area determination of betulin particles. R.Berzins, A.Paze, S.Vitolina, J.Rizhikovs, R.Makars, D.Godina, A.Teresko (Latvian State Institute of Wood Chemistry)
15:00	Coffee Break	
15:30-17:30	Session 3A Chair Kristīne Meile	Session 3B Francesco Romagnoli
15:30	Experimental design of cellobiose hydrolysis using activated biochar catalyst. D.Godina (Latvian State Institute of Wood Chemistry)	Water uptake and swelling of wood-plastic composites based on recycled polymer. A.Verovkins, J.Jaunslavietis, G.Shulga, B.Neiberte, S.Vitolina, T.Betkers, J.Brovkina, S.Livcha (Latvian State Institute of Wood Chemistry)
15:50	Partly unlocked macromolecule of technical lignins with vacuum, low temperature, microwave assisted pyrolysis. V.Biziks, J.Karthäuser, H.Frauendorf, H.Militz (Surfactor Germany GmbH)	Mycelium composites – an eco-friendly alternative to traditionally used synthetic packaging materials. G.D.Loris, I.Irbe, M.Škute, I.Filipova, L.Andže (Latvian State Institute of Wood Chemistry)
16:10	Study of catalysts for suberinic acid-based adhesive polymerization. R.Makars, J.Rizikovs, A.Paze (Latvian State Institute of Wood Chemistry)	PLA/lignin composites doped with Cu nanoparticles for food packaging applications. E.S. Esakkimuthu, I.Pylypchuk, D.DeVallance, M.H.Sipponen (InnoRenew CoE)
16:30	Optimization of solvent choice in resin desorption process after the separation of wood pyrolysis liquids. A.Jermolajeva, K.Meile, A.Zhurinsh (BaltTest)	Rheological, thermal and mechanical properties of wood plastic composites based on virgin and recycled polypropylenes and birch plywood waste. K.Kalnins, J.Kajaks, J.Matvejs (Institute of Polymer Materials, Faculty of Material Science and Applied Chemistry, Riga Technical University)
16:50	Properties of Kraft lignin substituted phenol formaldehyde resin for paper impregnation. M.Thébault, H.Lammer, A.R.Mahendran (Kompetenzzentrum Holz GmbH)	A study on waste paper reinforced recycled polypropylene biocomposite. J.Jaunslavietis, J.Ozolins, M.Kalnins, G.Shulga, B.Neiberte (Latvian State Institute of Wood Chemistry)
17:10	Analysis of gas-liquid interaction and constraint handling in stirred tank bioreactors. A.Buss, A.Suleiko, N.Jekabsons, J.Vanags, D.Loca (Rudolfs Cimdins Riga Biomaterials Innovations and Development Centre of RTU, Institute of General Chemical Engineering, Faculty of Materials Science and Applied Chemistry, Riga Technical University)	
19:30	Conference Dinner at Gutenbergs Rooftop Restaurant, Doma Square 1	

April 29, Radisson Blu Latvia, Elizabethes Street 55			
9:00-10:40	Session 4A Chair Inese Filipova	Session 4B Chair Jānis Rižikovs	Session 4C Chair Miķelis Kirplūks
9:00	Nanocellulose-coated paper dipsticks with visual response towards heavy metal ions. A.Frigola, R.Aguado, Q.Tarrés, P.Mutjé, M.Delgado-Aguilar (University of Girona)	Enabling circular bioeconomy via estimating the potentially valorisable food loss and waste in the Northern European region. R.Soloha, L.K.Lukasa, K.Balina, E.Dace (University of Latvia)	Bioeconomy based biorefining solutions for valorisation of food wastes to obtain bioactive and functional ingredients. L.Klavins (The Natural Resource Research Centre of the University of Latvia)
9:20	The protective coatings of the lignocellulose-based composite boards formed using the drying and semi-drying oils. D.Vasiliauskienė, G.Balčiūnas, R.Boris, A.Kairytė, A.Kremensas, J.Urbonavičius (Vilnius Gediminas technical university)	The resource potential of fermentation residues. A.Stikane, E.Dace, E.Stalidzans (Institute of Microbiology and Biotechnology, University of Latvia)	Vanillic and Meldrum's acid containing antioxidant. L. Bērziņa, I. Mieriņa (Riga Technical University)
9:40	Densified juniper wood for use in bone implants. L.Andze, M.Andzs, M.Skulte, V.Nefjodov, R.Tupciauskas (Latvian State Institute of Wood Chemistry)	Waste rapeseed cooking oil is perspective substrate for biosurfactant synthesis via yeast <i>Starmerella Bombicola</i>. I.Berzina, L.K.Lukasa, J.Liepins (Institute of Microbiology and Biotechnology, University of Latvia)	Determination of antioxidant activity in fractions of pyrolysis liquids. E.Volkova, K.Meile, A.Zhurinsh (Latvian State Institute of Wood Chemistry)
10:00	Cellulose Modification with maleic anhydride. V.Fridrihsone, J.Zoldners, M.Skute, L.Andze, I.Filipova (Latvian State Institute of Wood Chemistry)	Development of low-cost medium for <i>Bacillus Subtilis</i> spore obtainment. E.Didrihsone, O.Grīgs, E.Bolmanis (Latvian State Institute of Wood Chemistry)	Valorization of liquid by-products from hemp carbonization. M.Zouari, L.Marrot, K.Meile, R.Herrera Diaz (Innorennew CoE)
10:20	Homogeneous synthesis of cellulose palmitate derivatives in ionic liquid via transesterification. N.Savale, E.Tarasova, I.Krasnou, V.Gudkova, A.Krumme (Tallin University of Technology)	Medium formulation and fed-batch cultivation of <i>Methylosinus Trichosporium</i>. A.Suleiko, K.Dubencovs, A.Suleiko, J.Vanags, S.Glukhikh (Latvian State Institute of Wood Chemistry)	Torrefaction of pulp industry sludge: Experimental validation, opportunities and challenges. T.R.K.C Doddapapenei, L.Pärn, T.Kikas (Institute of Forestry and Engineering, Estonian University of Life Sciences)
10:40	Coffee Break		
11:00	The failure of success - are research assessments helping or hurting science? Noémie Aubert Bonn (Hasselt University and Amsterdam UMC)		
11:40	How to get in: the story of a young researcher reaching for the Horizon. Laura Andže (Latvian State Institute of Wood Chemistry)		
12:20	Closing Ceremony, Awards		
12:30	Lunch		

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THE RESEARCH LANDSCAPE OF BIOREFINERY: A SCIENTOMETRIC VIEWPOINT

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Scientometric analysis of a research field/subject allows to recognize the dynamic, stakeholders, cooperation, connected research disciplines, more cited authors and works, and other tendencies. The set of publications devoted to biorefinery was the object of this study. The previous scientometric review on biorefinery research was published ten years ago [1]. Search (21.01.2022) in Scopus (www.scopus.com) for publications with truncated terms “biorefin*” or “bio-refin*” in Title, Abstract and Keywords allowed to find 14808 records since 1981 (first publication with term “biorefining” indexed in Scopus) and 5427 records during the last years 2019-2021 (without Erratum and Retraction type publications). A permanent increase of publication number starts in 1999 and will be approximated by the power function

$$\text{publications} = 0.77 * (\text{year} - 1998)^{2.50} \quad \text{with} \quad R^2 = 0.996.$$

It also allows to predict a rapid increase of biorefinery publications for the coming years.

The geography of biorefinery research is very wide and includes output of 114 countries, 76 of them with 10 and more publications. Largest output by countries: USA, PR China, Brazil – 20.8%, 12.4%, 6.9% of all publications since 1981, respectively. Since 2019 output of PR China overtakes that of USA. At some time, part of output of countries of EU/EEA/Switzerland (including UK) form 43.9% during 2019-2021. The three most productive research centers since 1981: Chinese Academy of Sciences, Technical University of Denmark, State University of Campinas (Brazil) – 266, 255, 227 publications. Three most productive author since 1981: Ragauskas A.J. (The University of Tennessee, Knoxville, USA), Sun R.C. (Dalian Polytechnic University, China), Labidi J. (University of the Basque Country, Spain) – 75, 72, 70 publications.

The scientific co-operation at country level during 2019-2021 has been analyzed by scientometric tool VOSviewer (www.vosviewer.com). It allows to recognize 6 interconnected clusters of more strongly co-operated countries: PR China-USA-South Korea-Far East Asia countries...; Spain-Italy-France-European countries...; Brazil-Germany-Mexico-Latin America countries...; India-Netherlands-Belgium-Norway...; UK-Canada-Denmark-South Africa...; Vietnam-Pakistan-Turkey-United Arab Emirates.... Therefore, not in all cases the strongest co-operation has been offered by regional partners.

Biorefinery publications belong to 27 subject areas according to Scopus, most significant of them: Chemical engineering, Energy, Environmental science – 42.4%, 39.1%, 35.6% of all publications since 1981, respectively. 7.0% of all publications and 8.0% of them during 2019—2020 are attributed to subject areas of social sciences. The co-occurrence analysis of keywords during 2019-2021 by VOSviewer show 4 thematical interconnected clusters formed by 338 most popular keywords (with 50 occurrences at least): biorefinery-biomass-refining-biofuels... (including analysis of economic aspects and life cycle analysis); lignin-cellulose-lignocellulose-hydrolysis...; nonhuman-fermentation-metabolism-algae/microalgae...; different synonyms of ethanol-bagasse/sugarcane-saccharification-crop residues/straw....

References. [1] O. Konur, Energy Educ. Sci. Technol. Part A. Energy Sci. Res., **30** (2012) 347-358.



THE FAILURE OF SUCCESS – ARE RESEARCH ASSESSMENTS HELPING OR HURTING?

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Research assessments play a central role on the way research is conducted. Not only do they shape the practices and decisions of researchers, but they also define how we, as a broader community, perceive success in science. In the past few years, there has been growing concerns about the way researchers are assessed, and several initiatives have been put in place to understand how research assessments can promote better, more responsible science.

In this presentation, I will discuss research we conducted to understand how different stakeholders perceive research success and what impacts current research assessments have on researchers, research practices, and research integrity. Our work included interviews, focus groups, and surveys with a wide array of research stakeholders from the Flemish research scene, including funders, researchers, policy makers, institution leaders, researchers who left academia, and other stakeholders relevant to the research ecosystem. We found that there was an obvious misalignment between ‘career’ success and ‘research’ success. ‘Career’ success largely focus on quantity, outputs, individual achievements, and exceptional findings, but they disregard aspects which are essential in advancing science, such as transparency, quality, openness, and innovation. We also found that the career structures embedded in current academia adds to the problem, placing early career researchers in an hypercompetitive, unstable, and often unsupportive environment. Together, these issue have a profound impact on research cultures, researchers, and research outputs.

To conclude, I will look at a few advances which propose changes to research assessments, discussing how these require not only a realignment of the indicators used to assess researchers, but also a change in profound structural and cultural aspects of research.



SUBERINIC ACIDS – FROM ISOLATION TO FEEDSTOCK FOR BIO-POLYOL SYNTHESIS

D. Godina*, R. Makars, A. Abolins, A. Paze, M. Kirpluks, J. Rizikovs

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Depolymerized suberinic acids (SA) can be considered as an alternative material to obtain bio-polyols that can be further used in polymeric material production.

Isolated and fractionated birch outer bark from AS Latvijas Finieris plywood factory (Latvia) was used in these experiments. Prior to use the birch outer bark was extracted with ethanol to remove extractives (triterpenoids, phenolic compounds etc.). The main goal of this research was to evaluate the potential of birch outer bark SA as a raw material for pilot scale polyol synthesis with less oligomeric fractions, and the impact of process conditions on the resulting SA content and properties. To set preliminary parameters for the SA isolation process different depolymerisation solvents, acidification pH levels and SA drying temperatures were tested. In order to determine the chemical properties of obtained SA samples total phenolic content (TPC), total amount of hexoses, acid number, saponification number, epoxy groups and hydroxyl number were determined. Four instrumental methods were used – DSC, FTIR, GC-MS and SEC-RID. GC-MS analysis was performed with 2 separate sample preparation methods to characterise both monomeric fraction as well as polymeric fraction present in SA samples. After the obtained data the optimal SA isolation conditions were selected and with obtained SA sample bio-polyol synthesis was performed via esterification reaction with diethylene glycol (DEG). The obtained bio-polyol samples were characterised using previously described methods.

The increase in the pH value of SA acidification from pH1 to pH5 slightly decreased the saponification number in the obtained samples, whereas the hydroxyl number showed the opposite trend. In GC-MS analysis, it was concluded that after depolymerisation, all samples were dominated by hydroxy acids, which increases by increasing the drying temperature of SA at lower acidification pH. SEC-RID analysis showed that the most abundant detected fraction was the lower molecular weight fraction with <1300 Da. When comparing different acidification pH, it can be seen that as the pH increases, the lower molecular weight fraction (<1300 Da) slightly decreased. DSC analysis highlighted that elevated drying temperature had a higher impact on samples with lower acidification pH values – further SA depolymerisation occurred in the sample while drying. The synthesized SA bio-polyols had high hydroxyl values, which are typical and necessary for polyols to be used for rigid PU foam production. However, the apparent viscosity of bio-polyols was too high. Therefore, in future, further studies need to be conducted to achieve lower acid values and apparent viscosity.

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NOVEL BIO-POLYOLS FOR THE POLYURETHANE SYNTHESIS

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Recent sustainable chemistry concept has promoted investigations using various renewable resources for the synthesis of novel bio-based polyurethanes (PUs). Bio-based feedstocks for polyols have been intensively studied in the last decades. Vegetable oil-based polyols have been largely investigated and already commercialized [1, 2]. Contrary to that, bio-sourced acid polyols are much less explored despite the fact that they may provide large platforms for the synthesis of various low molar mass compounds, potentially applicable as versatile building blocks for the synthesis of fully bio-based PUs [3, 4].

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MICHAEL DONOR MONOMER SYNTHESIS FOR BIO-BASED THERMOSET POLYMERS USING TALL OIL FATTY ACIDS

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The European Commission has set up the “European Green Deal” to tackle climate and environmental challenges. It is a growth strategy that aims to transform the European Union into a prosperous society with a modern, resource-efficient and competitive economy, achieving climate neutrality, a balance of carbon emissions and removals by 2050 [1]. Bio-based polymer development is essential for this transition into a circular bioeconomy.

Tall oil is obtained as a side stream in pulp production, and distilled tall oil mainly contains oleic and linoleic acid [2]. Currently, its potential to produce high-added value bio-based substances and materials has been relatively little investigated. In this study, the tall oil fatty acids (TOFA) have been successfully used to synthesize Michael donor monomers. Moreover, polymeric materials have been obtained by carbon-Michael nucleophilic addition reaction.

The introduction of oxirane groups into the chemical structure of TOFA was the first stage in the bio-based thermoset synthesis process. TOFA was epoxidized in the presence of acidic ion exchange resin Amberlite IR-120 H using in-situ generated peroxyacetic acid from acetic acid and hydrogen peroxide. The precursors for Michael donor monomers were synthesized from epoxidized TOFA by oxirane ring-opening reaction with two different alcohols. The transesterification reaction of polyol -OH groups with t-butyl acetoacetate ester provided the functional groups required for the carbon-Michael addition process.

It is important to note that ion exchange resins are easily recyclable and reusable catalysts. Moreover, no solvent was used in any of the monomer and polymer syntheses steps, nor an excess of an intermediate product, such as tall oil methyl esters, was obtained. Mentioned points make the process “greener” following the Twelve Principles of Green Chemistry.

The obtained compounds were one component of a two-component room-temperature curing thermoset polymer system. Following properties of the developed polyols and their acetoacetates were analyzed: OH value, acid value, moisture content, viscosity. The chemical structure was determined using GPC/SEC, FTIR and MALDI-TOF spectra.

Developed acetoacetates of two tall oil-based and two commercial polyols were used to obtain thermoset polymers by a carbon-Michael nucleophilic addition reaction in the presence of 1,1,3,3-tetramethylguanidine as a catalyst. For polymerization reactions, three acrylates with different functionalities were used. Different chemical structures and functionality of developed bio-based monomers allowed developing polymer formulations with varied crosslink density. The obtained polymers were cured at room temperature, forming a rigid, transparent material.

The physical and thermal properties of the developed polymers were studied using DMA, DSC, TGA, TMA and universal strength testing machines.

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MICHAEL DONOR MONOMER SYNTHESIS FOR POLYMERIC MATERIALS USING RAPESEED OIL

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Plant oils are one of the most important renewable feedstocks of the chemical industry, pushing the search towards industrially applicable alternatives to nonrenewable resources [1]. By modifying plant oils, it is possible to obtain a large variety of monomers and polymers, including polyols. Bio-based polyols are an ideal raw material for nucleophilic Michael donor monomer synthesis, which can further be used to obtain polymeric materials via carbon-Michael nucleophilic addition reaction.

In this study the oxirane groups were introduced into the chemical structure of rapeseed oil (RO) [2]. Epoxidized RO can be easily converted to polyols with different hydroxyl group functionality. Methanol (MeOH), diethylene glycol (DEG), 1,4-butanediol (BD) and trimethylolpropane (TMP) were used as oxirane ring-opening reagents.

Further, an acetoacetate group was introduced into the epoxidized RO polyol structure via hydroxyl group transesterification with t-butyl acetoacetate, converting the bio-polyols into acetoacetate esters.

The chemical structure of raw material, each intermediate and acetoacetate esters was analyzed using size-exclusion chromatography (GPC/SEC), Fourier transform infrared (FTIR) spectra. Properties of these materials were determined by apparent viscosity measurement and titrimetric methods.

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COMPARISON BETWEEN NEAT TALL OIL FATTY ACID AND THEIR METHYL ESTER EPOXIDATION IN A ROTATING PACKED BED REACTOR

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Bio-polyols have been a widely discussed topic in recent years due to sustainability being among the main criteria in the production of materials. One of the raw materials used for the production of bio-polyols can be tall oil. Tall oils are a second-generation feedstock that does not compete with the food and feed chain. They have relatively low prices and wide availability, and their components are easy to functionalize. These factors make it possible to convert them into bio-polyols in a cost-effective and environmentally friendly process.

Distilled tall oil fatty acid (TOFA) fraction consists mainly of fatty acids such as oleic and linoleic acids, and a small percent of rosin acids and unsaponifiables. Unsaturated double bonds in the structure of present fatty acids can attach reactive functional groups suitable for polyol production. Our approach is, first, to epoxidize double bonds and, second, use alcohols for oxirane ring-opening to produce polyols. However, due to free acid groups, oligomerization and oxirane ring-opening are common side reactions. Acid group esterification could help to reduce the occurrence of these reactions.

In this study, we compared neat tall oil fatty acid epoxidation and their methyl ester (TOFAME) epoxidation in a rotating packed bed reactor. Tall oil fatty acid methylation was carried out with methanol in the presence of sulfuric acid. Epoxidation reaction was accomplished with *in-situ* generated peracetic acid in the presence of Amberlite IR120 H ion exchange resin. Further studies of both epoxidized TOFA and epoxidized TOFAME were carried out.

Results showed that methylation of tall oil fatty acids allows to obtain a product with higher relative conversion to oxirane and smaller viscosity. Using TOFAME promotes transesterification and reduces oligomerization in polyol synthesis. Furthermore, epoxidation in a rotating packed bed reactor facilitates the purification process thus saving time and money, and provides the opportunity of reusing the catalyst.

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**USE OF WOOD ASH IN THE FOREST ECOSYSTEM AND ITS EFFECT
ON THE RARE EARTH ELEMENT CONTENT IN THE FOREST SOIL
AND BLUEBERRIES (*VACCINIUM MYRTILLUS L.*)**

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One of the most crucial roles in the Latvian forest policy is to increase the development of the forest ecosystem. By performing forest management works (e.g., final felling) occur nutrient deficiency and reduces buffer capacity in the forest soil. These factors impair plant growth conditions and increase soil acidity, which increases the solubility of many toxic chemical compounds resulting leaching into the deepest soil layers and water reservoirs. Wood ash as fertilizer can be applied to restore the forest ecosystem by providing plants with necessary nutrients and reducing soil acidity.

Wood ash is biomass that is produced by the combustion processes of wood products and contains a high amount of macro- and micro- elements. Wood ash is divided into two main fractions: bottom ash and fly ash which differ in particle size and chemical composition. The use of wood ash for fertilization purposes can solve two important issues: improves forest ecosystem growth conditions and ensures efficient use and utilization of wood ash from factory areas.

In recent years, research about the content of rare earth elements in soil and plants has become more topic. Several studies have described that rare earth elements can improve plant growth conditions, while other studies dispute their importance. Studies on the content of rare earth elements in wood ash and their impact on the forest ecosystem are very small.

The aim of this research was to investigate the effect of wood ash on the content of rare earth elements in the forest soil and blueberries (*Vaccinium myrtillus L.*). For this research, two forest areas were selected, which were fertilized with fly and bottom wood ash. To evaluate the impact of wood ash on the rare earth element content, each forest area was divided into two sampling plots – fertilized and control.

The obtained results show that the forest with the dispersion of fly wood ash shows an increment of rare earth element content in forest soil and blueberry fine roots ~2-4 times (fertilized plots). Transfer factor values (forest soil/fine roots) and (fine roots/shoots) show a positive correlation regardless of the forest area and type of wood ash.

IMPACT OF ARGININE CONTAINING FERTILIZER ON NITROGEN ISOTOPE RATIO AND ELEMENTAL CONTENT IN YOUNG CONIFER STANDS

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Forests in Latvia cover more than half (52%) of territory - 3.4 million ha. Forest areas continue to increase both naturally and through the afforestation of abandoned agricultural land and other landuse fields, including former mining areas. Forest soil fertilization after regenerative felling is being used for the addition of lacking nutrient elements and improving tree growth conditions, as for increasing of competitiveness of planted seedling with forest environment vegetation.

One of the most important and quantifiable nutrients in a plant as a component of all plant and animal proteins is nitrogen (N). As fertilizer N is typically introduced to the soil in the form of nitrates or ammonia. Recent studies show that introducing N in a form of an organic compound – for example, amino acid arginine (arGrow® Granulat, Arevo AB, Umeå, Sweden) would benefit to improved growth and stress resistance with reduced environmental impact and simplified cultivation. The use of arginine also has a positive effect on reduced N leakage and therefore reduced use of fertilizers.

In total 4 research sites from different forest types (Vacciniosa mel. and Myrtillosa both dry and drained mineral soil) were chosen for the experiment. For the experiment samples of needles, branches, roots, and soil both from unfertilized control plots and fertilized plots were taken for isotope ratio and elemental analysis.

The light-stable isotope ratio mass spectrometry (IRMS) is a method used to determine the effect of a suitable soil improver on a plant and, thus, to assess the effectiveness of forest soil fertilization. IRMS (Elemental analyzer EA3000 coupled to Nu instruments mass spectrometer) was used for the determination of the N and C mass fraction and N and C isotope ratio. Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 8900 ICPMS QQQ) was used for the determination of Na, K, Mg, Ca, Al, Fe, Mn, P, B, Sr, Zn, Cu, Cd, Cr, Ni, and Pb in studied needles and plant parts. The Chemometric (Chemometric Agile Tool (CAT)) approach was used for the evaluation and statistical treatment of obtained data.

The aim of this study was to evaluate the impact of the applied arginine phosphate fertilizer on the N circulation and elemental content in Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* (L.) H.Karst) needles in established experimental plots.

First results show that after fertilization with an arginine phosphate-containing product, both an increase in the mass fraction of N in spruce needles and a decrease in the value of N isotope ratio are observed, which indicates arginine phosphate as the main source of N in spruce needles. In the case of pine seedlings, such a pronounced trend is not observed, which leads to the conclusion that arginine phosphate was not the main source of N in pine needles.

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EFFECT OF VARIOUS FERTILIZERS ON STABLE ISOTOPE RATIOS AND AMINO ACID CONTENT IN APPLE SEEDS

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Apples are widely cultivated edible fruits of the *Rosaceae* family. European Union is the second largest apple producer in World with $11.3 \cdot 10^6$ T in 2020 [1]. As other fruits and vegetables, apples are grown using both conventional and biological farming methods that differentiate not only in the use of plant protection products, but also fertilizers. The aim of this study was to evaluate effect of different fertilizers (both conventional and biological ones) on the stable isotope ratios and amino acid content in apple seeds.

Apple seeds ($n=90$) were collected at the Institute of Horticulture, Dobele, Latvia in 2018. The seeds were taken from five different apple tree varieties (*Aļesja*, *Antej*, *Gita*, *Ligol*, *Rubin*) that were fertilized with nitrogen containing fertilizer ($6 \text{ g} \cdot \text{m}^{-2}$), vermicompost or without additional fertilizer. The carbon and nitrogen isotope ratios were measured using continuous flow EA-IRMS system Nu-Horizon (*Nu Instruments*) and expressed relative to VPDB ($\delta^{13}\text{C}$) and atmosphere air ($\delta^{15}\text{N}$). The IRMS results were used to calculate total carbon and nitrogen content in apple seeds. The amino acid relative content in apple seeds was measured with GC-FID (*Agilent 6890*).

The results showed that $\delta^{13}\text{C}_{\text{VPDB}}$ values for apple seeds vary from -27 ‰ to -23.8 ‰ and are not dependent on the fertilizer used. These values correspond to the $\delta^{13}\text{C}_{\text{VPDB}}$ values described previously and are characteristic for C_3 plants. The $\delta^{15}\text{N}_{\text{AIR}}$ values on the other hand are from 0.2 ‰ to 2.4 ‰ for apple seeds from unfertilized apple trees, from 2.0 ‰ to 2.4 ‰ for apples from trees fertilized with nitrogen and 3.2 ‰ for apples from the apple tree fertilized with vermicompost. The smaller dispersion and higher values of $\delta^{15}\text{N}_{\text{AIR}}$ for apple seeds from trees fertilized with additional nitrogen or vermicompost can give information of the fertilizer used.

Relative content of 18 amino acids was determined in apple seeds ($n=15$). Seven of these amino acids showed relative content higher than 5%: Ala, Val, Leu, Ser, Met, Glu, Lys. When comparing the relative content of tryptophan and alanine to the respective sample $\delta^{15}\text{N}_{\text{AIR}}$ values, positive correlation can be observed. Therefore, additional preparative chromatography with following isotope ratio measurements should be carried out to evaluate to possibility to use amino acid relative content for determination of the fertilizer used.

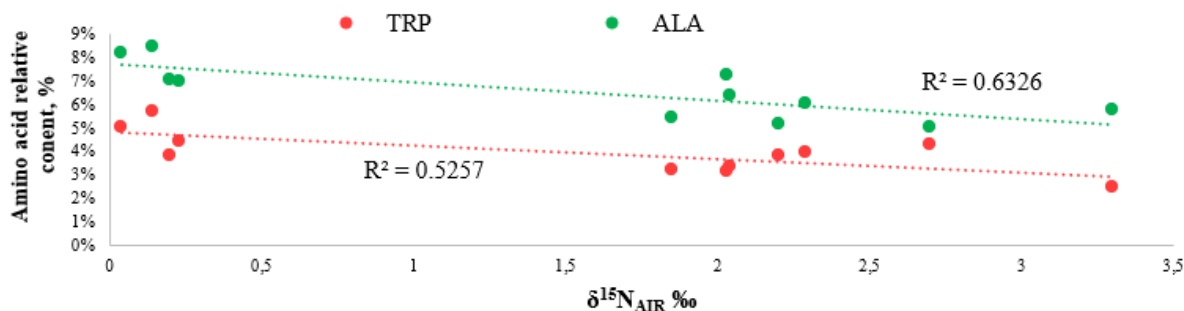


Fig. 1. Correlation between Trp and Ala relative content in apple seeds with $\delta^{15}\text{N}_{\text{AIR}}$ values

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BIO-FERTILIZERS OF SPENT COFFEE GROUNDS AND GREEN ALGAE *CHLORELLA* SP. BIOMASS FOR ENHANCEMENT OF SOIL ORGANIC MATTER

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Coffee is one of the most consumed beverages in the world. Moreover, demand for coffee increases every year [1]. It is a general knowledge that, to prepare double shot of an espresso, on average, 14 – 24 grams of ground coffee is being used. Thus, the number of grams varies and depends on the coffee roasting profile. Following that, coffee brewing generates large amount of waste material, which is called spent coffee grounds (SCG) [2]. Scientific article, presented by Simao et al., 2020, suggests that SCG could be used as an alternative source of fertilizing substance, which enhances biomass and the microbial activity of the soil [3]. On the other hand, this high in moisture biomass material, due to presence of caffeine and polyphenols is hazardous to the environment and has a negative impact to sustainability [4]. Moreover, during the decomposition in the landfill, wet SCG emits greenhouse gases, such as carbon dioxide and methane.

An alternative approach to the mentioned problem is to mix SCG with other organic materials in order to reduce the negative impact of the hazardous organic compounds. Our previous studies showed that, SCG cannot be granulated alone. Nevertheless, additional materials, such as buckwheat husk ashes, urea, molasses were not suitable enough for forming the granules. The aim of this study was to create granular organic fertilizer, composed of SCG and green algae *Chlorella* sp. biomass. This green approach was implemented with laboratory drum granulator-dryer. During the experiment, obtained granular fertilizers physical and chemical properties (loose bulk density, moisture content, strengths of granules, hygroscopicity, pH value) were measured according to the standard testing methods for fertilizers. In addition to that, to determine the nutrient content (N, P, K, C_{org.}) chemical analysis was performed.

Overall, it could be stated that during the experiment high value-added product with good physical and chemical properties was obtained.

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AN INSIGHT INTO CHALLENGES OF CONDUCTING AN LCA STUDY FOR A FOOD WASTE BIOREFINERY

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Biofuels, along with biomaterials and biochemicals can be produced from biomass instead of fossil resources using biotechnologies. A biomass biorefinery including biowaste is an upcoming strategy, and its growing popularity raises questions about its environmental impact [1]. Life Cycle Assessment (LCA) is the most common tool for the assessment of the environmental performance of a process or a product. Applications of LCA methods are very wide, but more often it is applied on technical manufacturing than biological processes like fermentation [2].

There is an ongoing study that develops biotechnology for producing a novel biosurfactant using waste cooking oil as the substrate and yeast as the producer (Waste2Surf project, No. 1.1.1.1/19/A/047). Aim of this abstract is to communicate the challenges identified while carrying comparative gate to gate LCA of biosurfactants with waste cooking oil and raw (refined but uncooked) vegetable oil as substrate alternatives. The application of the surfactant and clear niche in the market is not defined at this stage of the research. The production technology is characterized by low technological readiness level.

LCA is based on ISO 14040 series of standards, and they define main methodological phases, and the way results are processed [3]. The main challenges identified through the LCA study are organized that they follow those phases.

Goal and scope definition is the initial phase of LCA, in which the functional unit, scope and boundaries of the assessment are defined [3]. In our study, the main challenge in defining the functional unit is the lack of data and knowledge about the application of the end-product. Having that information would allow to compare the obtained waste-derived product with other bio-based or chemically synthesized alternatives. The selected solution is to define the functional unit based on the end-product's properties. Thus, the defined functional unit is defined as the concentration of the product that can reduce surface tension of relevant amount of the distilled water by 20%.

Life cycle inventory (LCI) analysis identifies and quantifies all physical input flows of materials, resources, products and output flows of emissions, waste, and the end-products of the system. The inventory analysis is supported by data collected on-site, from literature or in international databases [3]. For biorefinery and biotechnology studies, the availability of data is currently a problem in LCA. Incompletely described input flows of chemicals used in fermentation medium limits the accuracy and applicability of results. Most of the datasets are global scale therefore the results have high variation. Additionally, the commonly used databases lack quality data and well-described information of waste materials as substrates.

Life cycle impact assessment evaluates the potential environmental impacts by converting the LCI results into specific impact indicators [3]. The perception that bioproducts have a lower environmental impact can be misleading. Although the biomass itself has less negative environmental impacts than fossil-based resources, more energy, logistics and time are needed to convert it into a sustainable product. Therefore, impact categories must be selected, assigned, and calculated very carefully. The same principle applies also to **Life cycle interpretation** to avoid misconceptions and identify significant issues in the LCA results.

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CHARACTERIZATION AND EVALUATION OF WATER-BASED ECOLOGICAL PAINT FOR THE PROTECTION OF WOOD MATERIALS COATED USING DIPPING TECHNIQUE

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In this study, it has been investigated the performance of two wood species, pine (*Pinus sylvestris* L.) and spruce (*Picea abies*), coated with an ecological water based wood furniture paint for outdoor utilization and subjected to artificial weathering process. Dipping as an alternative to traditional brush or spraying application methods has been used, due to the interest of an outdoor furniture producer to optimize the production process. Dipping is a one-stage coating application method, with reduced treatment time, as wooden details can be grouped in stacks rather than painted individually, although the process needs to be adjusted for better results. The use of laboratory weathering devices, which combine the action of water, temperature and UV radiation, is acknowledged as a reliable technique in predicting the durability of coatings, reproducing in a shorter period of time the effects of outdoor [1-2]. Our samples have been prepared by dipping for 60, 90 and 120 sec. and then exposed to a two-stage artificial weathering test: 500 hours of UV lamps irradiation, followed by 500 hours of UV and H₂O combined action. CIELab color model has been used for the characterization of painted samples and for the measurements of color changes during artificial weathering. The obtained

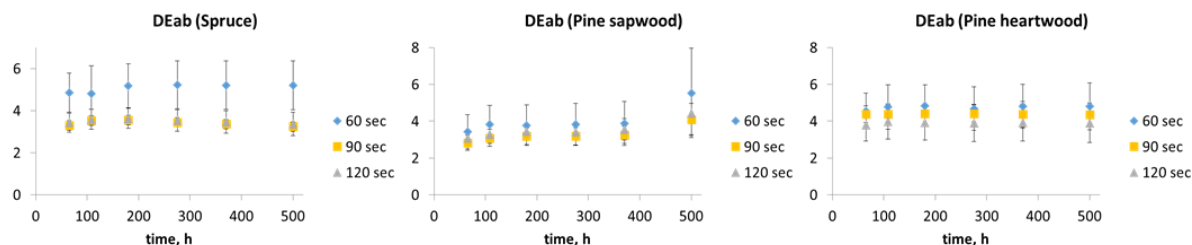


Fig. 1. Color changes of spruce, pine sapwood and pine heartwood during 500h of UV irradiation

results show that coated surfaces of pine wood have similar response to degrading factors despite different dipping times (Fig.1), with fast color changes occurring at the beginning of the experiment. In the case of spruce wood, the samples prepared by dipping for 60 sec. had higher color changes and the decrease in lightness L* was almost double compared to the samples dipped for 90 and 120 sec. The combined action of UV and H₂O after colour changes due to UV irradiation had reached equilibrium caused considerable discoloration of the coated wood surfaces of both species. The different pattern of three color parameters (L*, a*, b*) in the two stages of the artificial weathering suggests different degradation mechanisms of wood surface.

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THE STUDY OF BETULIN PARTICLES CONTAINING HYDROGELS PREPARED BY ANTISOLVENT PRECIPITATION

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The outer, white layer of the birch bark, which mostly burned for heat energy purposes, is an undervalued, renewable resource for the industrial production of sustainable, bio-based materials and chemical compounds [1]. Outer bark of silver birch (*Betula pendula* Roth.) should be highlighted because it has a unique chemical composition. Most of the extractives are composed of the two main lupane-type pentacyclic triterpenes – betulin (22.3 wt% from the oven dry birch outer bark (BOB)) and lupeol (2.2 wt%) [2]. Due to the chemical structure of triterpenes, they have not only biological activities useful for the treatment of human health, but also the ability to spontaneously self-assembling and to form a supramolecular gel from micro-, nano-sized particles in different liquid mediums [3]. Supramolecular gels have a great potential to be used in medicine, food, cosmetics, chemical sensors and nano-catalysis [4]. To obtain supramolecular gels from suspensions containing micro-, nano-particles of BOB betulin, it is advantageous to use an antisolvent precipitation method [5]. The aim of the study was to investigate the effect of process parameters on the production of hydrogels with antisolvent precipitation using unpurified (UB) and purified (PB) BOB betulin powder samples.

During the study the maximum solubility in ethanol at boiling point of PB (22 g/L) and UB (50 g/L) was determined. Similar weight of saturated ethanol solutions at boiling point were added to different volumes of water at room temperature. As a result, a suspension of the disperse systems – fine particles of sample (dispersed phase) in ethanol solutions (continuous phase) with different concentrations (from 63-66 vol% to 12-13 vol%) were obtained. The suspensions were filtered obtaining hydrogels. The hydrogels obtained from UB (betulin content 58 wt%) contained ethanol solution from 86.4 to 93.3 wt% and the yield of recovered sample dry matter in the hydrogels ranged from 89.7 to 97.2 wt% of the initial sample weight, while the obtained hydrogels from PB (betulin content 98 wt%) contained ethanol solution from 79.7 to 95.0 wt% and the recovered dry matter in the hydrogels ranged from 48.5 to 93.0 wt%. In the experiment with UB, at the highest ethanol dilution (12 vol%), a significant amount of sample particles (47.8 wt% from the highest hydrogel dry matter yield) was clearly observed to leach through the filter paper together with a solution in the filtrate to form a stable suspension against particle sedimentation by time or colloidal suspension. Particle leaching could be explained by a decrease in the stability of the hydrogel, which is most likely due to UB impurities, which account for 42 wt%, as well as possible changes in the average particle size and morphology obtained under certain conditions. A higher concentration of water in the continuous phase could interfere the formation of hydrogen bonds necessary for the successful self-assembling of the particles and the subsequent formation of a stable hydrogel structure. In contrast, in an experiment with PB under similar conditions, aforementioned leaching effect of the particles could not be observed, confirming the impact of betulin impurity factor on hydrogel stability.

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OPTIMIZATION OF BETULIN COLLOIDAL AQUEOUS SUSPENSION PRETREATMENT FOR DETERMINATION OF PARTICLE CHARACTERISTICS

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Outer bark of silver birch (*Betula pendula* Roth.) contains 36.5 wt% of extractives most of which - 61.1 wt% is betulin, a pentacyclic triterpene – bioactive compound with various pharmacological activities [1,2]. It has been shown that naturally occurring pentacyclic triterpenes can spontaneously self-assemble in liquids to form supramolecular structures, creating soft solid-like materials. Supramolecular hydrogels, where particles form a supramolecular 3D network in water via self-assembly, are of special significance due to their range of applications in pharmacology, cosmetics, removal of toxic chemicals, etc [3]. To obtain supramolecular hydrogels of betulin micro/nanoparticles, it is advantageous to use a liquid antisolvent precipitation process, which has proven to be a good technique for obtaining ultrafine particles [4]. The reduction in particle size increases the bioavailability of hydrophobic betulin and thus its activity and adsorption capacity. Therefore, accurate determination of the particle size and size distribution is essential to evaluate the effects of process parameters (the volume ratio of antisolvent to solution, stirring intensity, precipitation time, temperature) and various raw materials on the properties of obtained betulin particle hydrogels [4].

The aim of the study was to optimize the pretreatment of a colloidal aqueous suspension for the determination of the characteristics of the smallest supramolecular hydrogel particles using dynamic light scattering analysis with Zetasizer Nano-ZS (Malvern Instruments, UK). Target particles were obtained from purified and unpurified betulin samples by the liquid antisolvent precipitation method. Colloidal suspensions were prepared by dispersing betulin agglomerates of hydrogel in a pure aqueous medium using a two-step non-destructive dispersion technique, first forming a primary coarse suspension with a larger particle size in the micron range and then subjecting it to a high energy dispersion method to reduce the average particle size to the colloidal range. First stage suspensions after homogenization with Ultra-Turrax had very high polydispersity index and size measurements showed large agglomerates up to 2 µm. After ultrasonication the polydispersity index of suspensions was significantly reduced within the acceptable limit of analysis to obtain a good description of the particle size. Suspensions had mono-modal particle size distribution with mean particle size of 200-230 nm. It is concluded that after a rapid size reduction in the first minute of treatment, continued ultrasonication no longer contributes to the reduction in particle size. Analysis of the surface charge of betulin particles as a function of pH showed that the initial pH of the aqueous suspension (5.9-6.0) was optimal for the suspension to be stable and to prevent the particles from reagglomeration. The obtained results showed a good reproducibility of the sample preparation with two-step non-destructive dispersion technique. Intensity size distributions obtained from independently prepared suspensions overlap relatively well.

Acknowledgements. This study was supported by the European Regional Development Fund project No. 1.1.1.1/20/A/071 “Research of the production and application of high specific surface birch outer bark betulin particles in dispersed systems”.

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SYNTHESIS OF NOVEL C(3)-LINKED BETULIN AZOLE CONJUGATES

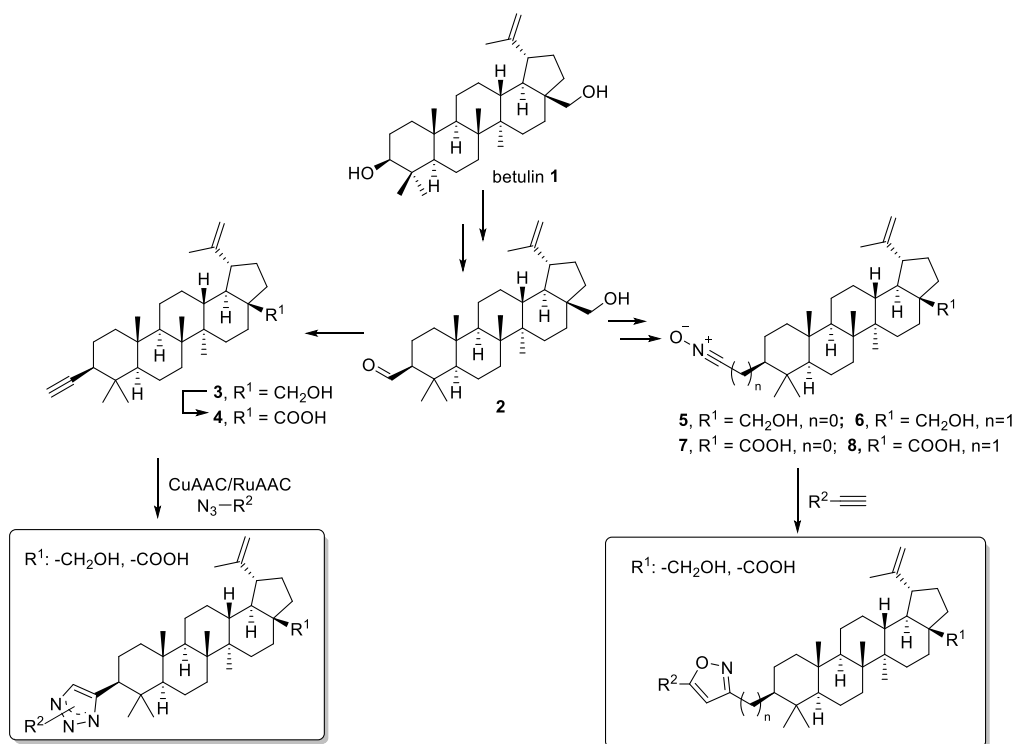
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Nowadays medicinal chemistry is focusing on novel drug synthesis based on naturally occurring biologically active compounds and their semi-synthetic analogs. Betulin and its natural analog betulinic acid are lupane type pentacyclic triterpenoids found in many plants, but mostly in outer layer of birch bark (*Betulaceae*, *Betula sp.*). Betulinic acid possesses wide range of antiviral and anticancer activities. Also *in vitro* and *in vivo* studies of synthetically modified triterpenoids showed considerable anticancer activity. Literature studies revealed that nitrogen containing triterpenoid-azole conjugates possesses greater therapeutical properties compared to betulinic acid [1,2]. First, betulin C(3) position was subjected to multistep homologation reaction to afford betulin homologous aldehyde **2**. Newly formed aldehyde group was transformed to corresponding alkyne, nitroethyl and nitrile oxide moieties. Latter ones were submitted to 1,3-dipolar cycloaddition reactions to afford novel betulin and betulinic acid-azole conjugates linked to triterpenoid A ring through C-C bond.

Synthesized triterpenoid-azole conjugates will be tested for their biological cytotoxicity.



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ADAPTATION OF THE METHYLENE BLUE ADSORPTION METHOD FOR SPECIFIC SURFACE AREA DETERMINATION OF BETULIN PARTICLES

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Birch wood is widely used in the pulp, paper and wood construction industries. Continuous processing of birch wood results in a significant amount of birch bark by-product, which accumulates in wood processing plants after the peeling process, and is burned to produce heat [1]. Birch bark contains about 27 wt% of birch outer bark, which is comprised of a wide range of biologically active extractives, mainly triterpenoid compounds such as betulin, lupeol and betulinic acid. Betulin is known to have antiviral, immunomodulatory and wound-healing effects [2], furthermore there is a growing interest in the ability of betulin particles to self-assemble to form stable hydrogels that have a potential to be used in pharmacological, food and cosmetic products [3]. The hydrogel micro-, nano-particle surface area accessible for interaction at the solid/liquid interface plays a significant role in biological activity. In this connection, most classical studies focus on particle size reduction to nano-scale, in turn, this also changes the specific surface area of the particles in a hydrogel. The surface activity and adsorption are changed according to the specific surface area [4].

The aim of the study was to adapt and apply the methylene blue adsorption method in determining specific surface area (S_{MB}) of betulin particles in hydrogels obtained from purified or unpurified betulin samples. In order to study and accurately determine the maximum adsorption of methylene blue (q_m) on betulin particles, initial concentration of methylene blue was varied. An analysis of the adsorption process with the Langmuir adsorption model was performed. For betulin particles suspension it is necessary to adjust pH and keep it at a value which the system is stable at, therefore a phosphate buffer was used.

Table 1. Specific surface area of studied betulin samples.

Betulin sample	Betulin content, %	Determination coefficient R^2	q_m , $mg \cdot g^{-1}$	S_{MB} , $m^2 \cdot g^{-1}$
Unpurified	60	0,9971	18,66	45,67
Purified	99	0,9929	16,92	41,42

The obtained results as seen in Table 1. indicate that the unpurified betulin particles have a larger S_{MB} than purified particles. The linearity of the results shows that the experimental data fits very well within the Langmuir adsorption model, which indicates that the surface of the studied betulin particles is energetically homogeneous and a monomolecular coverage was formed during adsorption. The methylene blue adsorption method adapted for different purity betulin particles in hydrogels is simple, with short processing time and requires less complex apparatus than other methods. It is not necessary to dry the sample for analysis, which leads to sample alteration, so it is possible to determine the specific surface area for varying purity betulin samples that can be used to characterize the surface properties of betulin particles in hydrogels.

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DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF TAR IN CO-PRODUCED GASES IN THE BIOMASS PYROLYSIS PROCESS

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Pyrolysis is a one of promising technique for the production of energy from biomass. Pyrolysis dissolves biomass and also produces useful by-products. In this case, gas, liquid and solid phases are formed. Gas mixture containing tar, among other components. Traditional methods for tar sampling are based on cold solvent-trapping coupled with solvent absorption in impingers.

The present work focuses on a solid-phase adsorption (SPA) method for determining the concentration of tar compounds. A modified sampling device consisting of 500 mg of amino-phase sorbent and 100 mg of activated coconut charcoal was chosen as optimal for sampling tar (including its volatile organic compounds) in gas produced in biomass pyrolysis [1-3]. For research in a real life context, the double-layered fixed-bed reactor situated in eastern Latvia (Daugavpils) was used. Varying volumes of pyrolytic gas were drawn through the adsorbents, and the total amount of tar was then compared to the number of its individual component compounds.

Tar was sampled at the pyrolytic gas temperature of 200°C. It was drawn through the adsorbent cartridges at the flow rate of 100 – 200 mL min⁻¹ for various periods of time, resulting in 200, 400, and 600 mL of the pyrolytic gas being drawn through the adsorbents respectively.

All heavy compounds of the tar are completely adsorbed on amino-phase adsorbent, and light compounds of the tar, such as benzene and toluene, are partially adsorbed on this amino-phase adsorbent, and partially on activated coconut charcoal. The total amounts of each compound were calculated, as well as the tar on both sorbents. The dependence of the concentration of the total tar and some of its compounds on both sorbents on the volume of the pyrolytic gas passed through them has been investigated. It was concluded that the volume of pyrolytic gas had little or no effect on the total amount of tar found on both adsorbents.

Testing the device in real life conditions, along with varying volumes of the pyrolytic gas drawn through the adsorbents, gave results that were comparable in the total amounts of both tar and its individual component compounds. However, with an increase of the volume of pyrolytic gas drawn through the adsorbents, greater amounts of benzene, toluene, and other light compounds pass through the amino-phase adsorbent and are collected on the activated coconut charcoal. An increased volume of pyrolytic gas leads to a growing number of compounds detected and identified on the amino-phase adsorbent. It appears reasonable to take into account the concentration of tar in the pyrolytic gas while selecting the volume of gas for sampling, as well as whether it is necessary to detect those individual tar compounds whose concentration is very small.

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STUDY OF A NOVEL BIO-REFINING METHOD FOR OBTAINING 2-FURALDEHYDE, ACETIC ACID AND PULP FROM BIRCH WOOD

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Latvia is one of the largest manufacturer of plywood in Eastern Europe, with an annual production of 250,000 m³. In Latvia's climatic conditions, birch (*Betula pendula*) is the main tree species that is mainly used for plywood production. A significant part (up to 30 %) of the processed wood is made of low value residues like veneer shorts, cores and cut-offs [1], which have a high potential for value-added product obtaining. The aim of this research was to comprehensively characterize lignocellulosic biomass that was obtained after 2-furaldehyde production, in terms of further valorization of this resource. The material can be used in the new biorefinery concept for production of 2-furaldehyde, acetic acid and subsequent cellulose pulp obtaining, using thermomechanical (TMP) and alkaline peroxide mechanical (APMP) pulping process. To achieve the objective several screening tests were performed, and further experimental plan was developed using DesignExpert11. Process yields were analyzed both in terms of total yield and at individual time increments. In addition, obtained lignocellulosic residue was also characterized. Unique bench-scale reactor system was used to obtain a lignocellulosic material without pentoses and with maximum preservation of cellulose fiber for further use. Studies on the deacetylation and dehydration of birch wood hemicelluloses of pentose monosaccharides to 2-furaldehyde and acetic acid using orthophosphoric acid as a catalyst were carried out. Results showed that depending on the used pre-treatment conditions the 2-furaldehyde yield was from 0.04 to 10.84 % o.d.m., the acetic acid yield was from 0.51 to 6.50 % o.d.m. and the lignocellulose residue yield was from 68.13 to 98.07 % o.d.m. with minimal content of admixtures. Process optimization using DesignExpert11 revealed that the main pre-treatment process parameters that influence the yield of 2-furaldehyde in the pretreatment process are process temperature (53.3 %) and process duration (29.8 %). In addition, experimentally develop best 2-furaldehyde production conditions to optimize purity and usability of cellulose in leftover of lignocellulosic material. Best results in terms of both 2-furaldehyde yield and purity of residual lignocellulose were obtained in experiment where catalyst concentration was 70%, catalyst amount 4 wt.%, reaction temperature 175 °C and treatment time 60 min.

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NEW POSSIBILITIES OF USING WASTE HEMP BIOMASS

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Hemp (*Cannabis sativa* L.) biomass is useful in many branches of the economy. The hemp cultivation to obtain seeds has been gaining importance recently. In this process shredded straw is a waste biomass. The possibilities of using ecological waste hemp biomass for solid biofuel production as well as a substrate for horticulture industry were described on the example of Henola variety [1].

Analyses of the chemical composition of the waste hemp biomass were performed at the Poznan University of Life Sciences, according to the PN-92/P-50092 standard. Experimental materials were ground in a Pulverisette 15 laboratory mill, with the analytical fraction of 0.1-0.4 mm being separated on sieves. In the hemp straw samples, the content of macro- and microelements was also determined, using the procedures compliant with the requirements of the following standards: PN-EN 15104: 2011 and PN-EN 15289: 2011 [2-3]. The obtained results of hemp biomass of Henola variety from an organic plantation were shown in Table 1, as the mean value of three analyzed samples.

Table 1. The basic results of ecological hemp biomass chemical composition analysis (% of dry mass).

Analyzed characteristics	Content (% of DM)
cellulose	32.56 ± 1.22
lignin	13.79 ± 0.14
hemicellulose	33.91 ± 1.76
holocellulose	66.47 ± 0.56
mineral substances	7.65 ± 0.05
nitrogen	0.52 ± 0.07
hydrogen	5.66 ± 0.02
humidity	8.5

± - standard deviation

The obtained results allowed to determine the suitability of ecological hemp waste biomass for various applications in the economy. Solid biofuels produced from straw had the heat of combustion and calorific value 18 300 kJ·kg⁻¹ and 17 100 kJ·kg⁻¹, respectively.

In addition, fiber from hemp waste biomass was the raw material for the preparation of specialized substrates for plant cultivation. The addition of various fractions of hemp biomass to peat resulted in better absorption of moisture and liquid fertilizers, and increased the content of organic matter attainable to plants.

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FLAMMABILITY STUDIES OF A PINE SAWDUST COATED WITH MULTICOMPONENT SUSPENSION

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This paper reports results of developed multicomponent suspension for pine sawdust, which improves physical properties, resistant to fire. Currently, wood and agricultural wastes are used for biofuel production thus providing short-term benefits. The use of these waste materials in the production of thermal insulating materials would bring long-term benefits and contribute to the current energy performance of buildings. The objective is to test if loose-fill thermal insulating materials from wood waste could be used as thermal insulating fire-resistant materials.

The aim is to take sawdust waste from large-scale wood processing facilities and convert them into eco-friendly fire-resistant thermal insulating materials for buildings, which should be non-polluting, eventually recycled, and locally available.

36 samples with different multicomponent suspension compositions for pine sawdust were prepared and analyzed (sawdust, liquid glass, tung oil, expandable graphite).

The reaction to fire properties of organic waste materials was evaluated by thermogravimetric measurements, combustion heat, continuous smoldering, and single-flame source methods.

The results of the combustion heat tests showed that liquid glass, depending on the amount in proportion, can decrease the combustion heat by up to 33% from 18,5 Mj/kg to 12,4 18 Mj/kg.

The results of the single flame source method showed that using only liquid glass does not guarantee the acceptable result of the tested specimens. The multicomponent suspension has to be added to sawdust to achieve better performance.

Continuous smoldering tests showed, that only a few of 36 multicomponent suspension compositions can pass the test. It was found that even 2 % of tung oil makes pine sawdust smolder, and that ratio between pine sawdust, liquid glass, expandable graphite 1:0,75:0,1 is acceptable-tested specimen passes the continuous smoldering test.

The thermal behavior of treated and untreated specimens in an air atmosphere was tested. The main decomposition occurred at the range 180 °C and 320 °C, leading to a mass reduction of 37.23 % at 280 °C. This weight loss was mainly ascribed to the release of combustible gases of the sawdust [1]. Weight loss slowed when the temperature was greater than 320 °C. When the temperature was 670 °C, the total weight loss of the sawdust was 52.25 %, while untreated sawdust had 90% of mass reduction at 490 °C. This indicated that the silicate inorganic components in the hybrid can endure higher temperatures and can hopefully improve the thermal stability of poplar wood.

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POTENTIAL OF SOME LATVIAN INDUSTRIAL CROPS RESIDUALS FOR CONVERSION TO ECO-FRIENDLY THERMAL INSULATION MATERIAL

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Nowadays building insulation generally is made from plastic-based fibres and foams and other non-renewable mineral materials with at least 90% on the global market share. Therefore, the shift to “green building” is urgently needed, because it includes not only nearly zero energy buildings but also the use of renewable biomaterials as biomass fibres. On 14 July 2021, the European Commission adopted a set of proposals to make the EU's climate, energy, transport and taxation policies fit for reducing net greenhouse gas emissions by at least 55% by 2030, compared to 1990 levels.

From the perspective of sustainable development, it is important to choose easily recyclable, renewable, locally available and environmentally friendly raw materials. Agricultural by-products like barley and wheat straw, corn cob, rice straw and husks, sunflowers, pineapple leaves, coconut fibres, bagasse, date palm fibres were recognized as potential raw materials for building insulation purposes. In Latvia crop residues such as wheat straw, buckwheat husks, corn and reed stems has a potential as new eco-friendly thermal insulation material. In Latvia, 2/3 of the annual cereal crop consists of wheat. After the grain harvesting the straw is the by-product with still limited application. More than 1 Mt of wheat straw is available in Latvia. Buckwheat crop cover of 27 900 ha with a potential husk part of 4 000 t/year, corn crop - 25 600 ha with its residual stalk biomass of 250 000 t/year, and reeds cover 13 200 ha of area in Latvia with harvestable area of about 10 000 ha.

The study demonstrates a steam explosion (SE) method as very effective technology for converting raw lignocellulosic material to fibrous making it suitable to be used as thermal insulation in buildings. The SE pre-treatment of lignocellulosics improves its thermal insulation properties, particularly increases the insulation area (Table 1). The benefits offered by the technology are simplicity, the advantage of using biomass residues, fast production process with relatively low energy content and water consumption, obtaining ecological zero-waste thermal insulation material with good properties. The preliminary data shows that selected crop residuals have a potential to be used as loose-fill thermal insulation even without SE pre-treatment.

Table 1. Effect of SE pre-treatment of some crop residuals on thermal insulation properties

Material	Before steam explosion			After steam explosion		
	Density (kg*m ⁻³)	Thermal conductivity (W*m ⁻¹ *K ⁻¹)	Insulated m ² from 1 t of raw material	Density (kg*m ⁻³)	Thermal conductivity (W*m ⁻¹ *K ⁻¹)	Insulated m ² from 1 t of raw material
Reeds (leaves)	71	0.040	81	48	0.048	100
Reeds (stems)	125	0.043	42	68	0.055	61
Corn stalks	99	0.051	46	83	0.050	56
Wheat straw	83	0.042	65	54	0.045	95
Buckwheat husks	127	0.054	34			

EXPERIMENTAL DESIGN OF CELLOBIOSE HYDROLYSIS USING ACTIVATED BIOCHAR CATALYST

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Lignocellulosic biomass is a type of renewable resources that can be used not only for energy, but also for production of carbon-containing chemicals and materials [1]. Biomass has great potential to be used as a sustainable resource to provide biofuels, biochemicals, and biomaterials [2]. Effectively converting the most abundant biopolymers into useful C5 sugars platform compounds, such as furfural (FF), 5-hydroxymethylfurfural (HMF), is a highly desirable endeavour [3]. The hydrolysis of biomass into monomeric sugars and their further conversion is one of the most important research topics in biomass upgrading [4,5]. Enzymes, mineral acids, and solid acids, have been employed in biomass hydrolysis [6,7]. The enzymatic hydrolysis of biomass is slow and costly, and the hydrolysis of biomass by mineral acids are corrosive and usually produces various environmental hazards [8,9]. Several studies reported that biochar-based solid acid is a promising alternative to mineral acid in biomass hydrolysis and dehydration due to its high reaction activity, recyclability, and low cost [10]. The aim of this work is to develop experimental model using DesignExpert11 of cellobiose hydrolysis as a model compound, using activated biochar catalyst to achieve maximum yield of glucose.

Biochar was obtained in fast pyrolysis process. Fast pyrolysis char and tar samples were prepared, using lignocellulose obtained from hydrolysed birch (*Betula pendula*) chips (0.40 – 0.63 mm). The by-product of fast pyrolysis was activated with concentrated sulfuric acid or nitric acid. The condensate (bio-oil) obtained in the fast pyrolysis process was hydrolysed at 121 °C with 0.2 M H₂SO₄ solution and the obtained solid non-hydrolysable residue, mainly consisting of phenolic type compounds, was used as sulfonated biocarbon catalyst. The tar obtained in the fast pyrolysis process was carbonized at 220 °C with 20% sulfuric acid solution. The obtained residue was used as sulfured biocarbon catalyst. For the determination of the catalytic activity, cellobiose (CB) hydrolysis was performed as a model reaction. The experiments to determine CB hydrolysis reaction kinetics and the optimal conditions were done at 3 different temperatures – 103, 110 and 120 °C. The reaction time was 1, 2, 3, 6, 7 and 24 h. In test experiments, the mass ratio of CB and catalyst were 1:5. In the optimal conditions (120 °C and 24 h) we tested also different CB and catalyst mass ratios – 1:0.5, 1:1, 1:2.5, 1:5; 1:10; 1:15; 1:20; 1:25. Using experimental data the process model was obtained with DesignExpert11.

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PARTLY UNLOCKED MACROMOLECULE OF TECHNICAL LIGNINS WITH VACUUM, LOW TEMPERATURE, MICROWAVE ASSISTED PYROLYSIS

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Different independent expert groups predicted the steadily annual growth on availability of well-known technical lignin such as kraft lignin, as well due to the production of cellulosic ethanol, the enormous pile of enzymatically hydrolyzed lignin will be available, too. The potential of lignin lies in its structure and via different conversation methods is recognized as a renewable resource of aromatics (mono-phenolic compounds) on Earth. However, the common thing for all type of technical lignins leis on their versatile, complex and locked structures which pose serious challenges for their efficient valorization. One of the most promising approach to unlock the lignin`s macromolecule is microwave assisted pyrolysis. Due to the more efficient energy consumption and purity of phenolic fraction in the pyrolytic bio-oil, our research, is based on the usage of vacuum, low temperature, microwave assisted pyrolysis to convert (decompose) the lignin into low-molecular weight phenolic compounds. Four technical lignins, such as pine wood kraft lignin, beech and spruce organosolv lignin and spruce lignosulfonate were pyrolyzed from room temperature until 280 °C. With the described method, a phenolic fraction can be obtained from all four technical lignins. However, the yield of the phenolic fraction is highly dependent on the origin of the lignin. As such, the phenolic fraction yield of pine kraft lignin was almost ten times higher than that of lignosulfonate. Pine kraft lignin and spruce organosolv lignin were the lignins with the highest phenolic fraction yield, followed by beech organosolv lignin and spruce lignosulfonate. Pine kraft lignin and spruce organosolv lignin had a clear maximum of condensate productions at 140 and 180 °C respectively. Additionally, the influence of lignin density and heating rates on the bio-oil yield and product distribution was investigated, too. Our findings clearly shows, that we were partly successful to unlock the macromolecule of several lignins and further work is necessary for development of success.



STUDY OF CATALYSTS FOR SUBERINIC ACID-BASED ADHESIVE POLYMERIZATION

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Birch outer bark (BOB) is rich in suberin polyester and can be used for obtaining suberinic acids (SA) by hydrolytic depolymerization. In a previous study we have demonstrated that birch outer bark SA-based adhesive can be used in the production of particleboards with optimal pressing temperature reaching 226 °C [1].

To further improve properties of SA-based particleboards we looked into utilization of catalysts (additives) for SA-binder polymerization. The suitability of catalyst was assessed by differential scanning calorimetry (DSC) by heating up the sample up to 220 °C and comparing the specific enthalpy of the peak in thermograms with onset values ranging from 168 to 184 °C. The catalysts studied are given in Table 1.

Table 1. Catalysts studied for SA binder polymerization

Group of catalysts	Catalysts
Protonic acids	Sulfanilic acid, p-toluenesulfonic acid, 5-sulfosalicylic acid, 2-naphthalenesulfonic acid
Lewis acids	Al ₂ (SO ₄) ₃
Tin-based	SnCl ₄ , SnCl ₄ /p-toluenesulfonic acid, dibutyltin oxide, dibutyltin dilaurate
Antimony-based	Sb ₂ O ₃
Amines	Hexamine
Peroxides	t-Butyl peroxybenzoate

Based on the results from DSC, six catalysts (sulfanilic acid, p-toluenesulfonic acid, SnCl₄, SnCl₄/p-toluenesulfonic acid, dibutyltin oxide, Al₂(SO₄)₃) were chosen for further studies on mechanical properties of particleboards.

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OPTIMIZATION OF SOLVENT CHOICE IN RESIN DESORPTION PROCESS AFTER THE SEPARATION OF WOOD PYROLYSIS LIQUIDS

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Pyrolysis of biomass is a promising route to produce valuable chemicals, also it is one of the options on how to replace fossil raw materials with renewable alternatives. It is important to investigate the chemical composition of pyrolysis liquids in order to separate and extract various chemical compounds. From a chemical point of view, pyrolysis liquid is a complex mixture of organic components¹.

Pyrolysis liquid, obtained from birch wood chips after pre-treatment with diluted sulphuric acid, was separated using preparative column chromatography. As the solid phase *Lewatit VPOC 1074* anion exchange resin was used. The aromatic constituents of the pyrolysis liquid were adsorbed on the resin, while the sugar derivative fraction was eluted with water. This paper focuses on analyzing the most favourable conditions for the extraction (desorption) of chemical compounds from the resin. In this study resin desorption is investigated by using different combinations of solvents (using room temperature H₂O and heated H₂O (at ~60°C), ultra-sonication, different organic solvents such as CH₃OH, CH₃COOH). Firstly, solvents were used separately, and it was investigated which components are better extracted in water and which in organic solvents; then the sequential desorption was reviewed and compared to each other. The main method for the analysis of the chemical composition of the desorbed fractions was reversed phase ultrahigh-performance liquid chromatography with UV spectrophotometry and mass spectrometry (Waters Acquity H-Class). The main findings were that heated water was a more effective desorbent than ultra-sonicated water. Furthermore, addition of acetic acid to methanol improved the overall desorption, at the same time comparing the phenol desorption with methanol or a methanol/acetic acid mixture, qualitative differences could be observed. Namely, the addition of acetic acid improved the desorption of syringic acid and vanillic acid. Therefore, consecutive desorption with different solvents could be a way to extract and concentrated individual chemicals of chemical compound groups with similar functionalities.

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PROPERTIES OF KRAFT LIGNIN SUBSTITUTED PHENOL FORMALDEHYDE RESIN FOR PAPER IMPREGNATION

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Phenol replacement in the phenolic resins using renewable lignin have been researched for a long time. However, because of its low reactivity, now a days method to improve reactivity before resin synthesis might be of interest. It includes alkylation, hydroxymethylation and phenolation. Phenolation (Fig.1) enhances lignin's reactivity by increasing the phenolic hydroxyl groups content by reacting with phenol in an acidic medium. This reaction splits the ether bonds, decreasing lignin's molecular weight [1]. In this work, phenol-formaldehyde resin were synthesized where either 30% or 50% (in weight) of the phenol monomer were substituted by phenolated kraft lignin. The lignin substituted phenol formaldehyde was characterized by Fourier Transform Infra-Red (FTIR) spectroscopy, Size Exclusion Chromatography (SEC), Differential Scanning Calorimetry (DSC), contact angle and surface measurement. The curing is relatively slow hence to accelerate the curing the additives zinc borate, potassium carbonate, and propylene carbonate were added to the resin and the cure kinetics was analyzed using model free kinetics.

The viscosities of the studied resins showed a rather complex behavior and depended strongly on the level of phenol substitution and whether a phenolation pretreatment was performed or not. With phenolation modification, LPF resins became generally much less viscous upon dilution with methanol although their average molecular weight was extensively higher. The molecular weight distribution of the phenolated lignins generally showed a reduction in average molecular weight and an increase in reactivity towards condensation with phenolic resin. It was found that the type of lignin, its content in the resin and the degree of its additional activation (phenolation), significantly influence the relative proportions of different molecular weight fractions present in the resulting oligomeric hybrid resin.

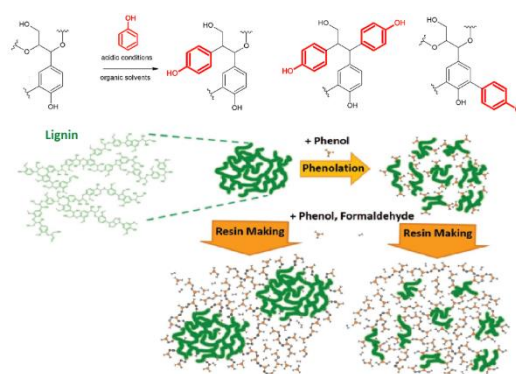


Fig. 1. Phenolation reaction on lignin's monomers and schematic representation of the phenolation effect on LPF resins morphology.

Among the cure accelerators potassium carbonate showed a beneficial effect on the curing behavior of the resin. While 4 wt.% K_2CO_3 reduced the curing time to about half of the cure time required by reference LPF resin. Based on dynamic DSC experiments, isoconversional kinetic analysis of resin curing was performed and it was found that both approaches using the advanced Vyazovkin method or the Kissinger–Akahira–Sunose method lead to similar results with the catalyst containing KLPF resin and both are suitable for predicting the curing kinetics of catalyzed LPF resin.

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ANALYSIS OF GAS-LIQUID INTERACTION AND CONSTRAINT HANDLING IN STIRRED TANK BIOREACTORS

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Large scale productions, based on microorganism fermentation, are the pillar of multiple industry branches stemming from the food to the cosmetic industry. Despite the myriad of adverse conditions needed for the optimal bacteria functionality, they are heavily used in in situ production of various polysaccharides. To obtain a high-throughput process, careful design and analysis of the fermentation operating conditions is highly encouraged. Bearing that in mind, the aim of this study was to perform an in-depth Computational Fluid Dynamics (CFD) simulation on a gas-liquid interaction in stirred tank bioreactors. The operating conditions were chosen on the account of settings used for production of xanthan gum via fermenting [1]. The focus was on determining the choice and position of the impellers influencing the mixing capacity characteristics (e.g., torques produced, velocity profiles, gas volume fraction, and bubble distribution). The best configuration was intended to provide the optimum values for average fluid velocity and gas distribution, as well as mixing speed with a continuous power input [2].

The mixing process of a non-Newtonian fluid, in a bioreactor with a working volume of 15m³, was assessed by using k-epsilon turbulence model, Multiple Reference Frame (MRF) and Population Balance Model (PBM) methodologies. Standard Rushton, Pitch-blade and Scaba® impellers were used for the current study. Research methods were designed in such a way to encompass a detailed bioreactor setup, CFD, as well as mesh generation and numerical technique.

As a result of the current study, Pitched-Rushton-Scaba and Scaba-Rushton-Pitched have shown to be suitable for generating the maximum production efficiency and at the same time they were considered to be cost efficient. The multi-methodology approach has proven to be indispensable in decision making prior to building the physical equipment for large scale production purposes.

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WATER UPTAKE AND SWELLING OF WOOD-PLASTIC COMPOSITES BASED ON RECYCLED POLYMER

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Wood-plastic composites (WPCs) are a young generation of (semi)biocomposites with rapidly growing usage within the plastics industry. They are characterized by a low cost, biodegradability, light mass, enhanced filling degree, etc. WPCs find wide application in building engineering, packaging, automotive industry, garden and outdoor goods, etc. The wetting properties of WPC depend on the interfacial adhesion between wood filler and polymer matrix that are defined by many factors such as lignocellulosic fiber, polymer matrix, compatibilizer, crosslinking, processing mode, etc. Moisture uptake irreversibly affects the morphology and properties of WPCs due to its negatively influence on the matrix-fiber interaction. That is why a knowledge of water uptake and swelling behaviour of WPCs is very important for prediction of the their exploitation properties. The aim of the work is to summarize our results on water uptake and swelling of the developed WPC samples with different functionalized hardwood fillers [1-3].

The amination of the birch wood sawdust microparticles was carried out with diethylepoxypropylamine. The water uptake and swelling degree of the WPC samples with the aminated birch sawdust were essentially lower than those for the sample with the initial sawdust. However, at the nitrogen content more than the optimal one, the excess of the negatively charged groups, which were formed as a side effect of the amination procedure, decreased hydrophobicity of the WPC samples. The ammoxidation of the aspen sawdust microparticles was performed by their treatment with a NH_4OH solution in the presence of persulfate ammonium as an oxidizing agent. The ammoxidized sawdust adsorbed water to a lesser extent than unmodified sawdust. The lower ability to uptake water was conditioned by the reduction of the content of hemicelluloses, as well as the formation of covalent amide bonds in the ammoxidized samples. The WPC samples filled the ammoxidized aspen sawdust additionally treated with the developed compatibilizer (Fig. 1.) had larger contact angles, lower adhesion energy, and remarkably lower water sorption and swelling compared with the WPC samples with unmodified sawdust particles.



Fig. 1. WPC samples for water uptake study

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MYCELIUM COMPOSITES – AN ECO-FRIENDLY ALTERNATIVE TO TRADITIONALLY USED SYNTHETIC PACKAGING MATERIALS

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As plastic waste persists to be a global issue with the problematic recycling [1], leakages into the ocean, its unsustainable production and consumption is unfortunately continued in an exponential manner [2, 3]. Moreover, approximately half of the produced plastic is for packaging purposes, discarded far earlier than the material resilience would allow [3] and contributes to the global plastic waste which exerts detrimental effects to ecosystems both directly and propagating the toxicity of other pollutants in the environment [4], therefore an eco-appropriate alternative requires urgent attention.

In our study we manufactured and investigated the properties of a biological composite material from hemp shives and the white-rot fungus *Trametes versicolor* mycelium, a material that we refer to as mycelium composite (MC). Shives were used as the lignocellulosic substrate that was subdivided into 3 variants – shives with added wheat bran, shives with added bran and silver birch bark, and solely shives. In two step cultivation process: first in jars, then in plastic moulds, we produced specimens, which were heat dried and formed with band saw for analyses. We obtained results for specimen water absorption properties, chemical composition, namely, lignin, cellulose, ash content and also fungal biomass content at various production stages to assess substrate destruction and fungal growth, mechanical properties, namely, compression at 10% deformation, resistance to mold growth and biodegradation by composting method.

Best mechanical properties were observed with substrate variant with added bran – 0.18 MPa in compression strength and 4.12 MPa in elastic modulus which are competitive values in comparison to synthetic expanded polystyrene (EPS). Water absorption was considerably high and the highest in the mentioned variant, up to 935%, and obviously lower in the variant with added birch bark – 723%. Resistance to mold growth was low and similar throughout the variants. All specimens showed complete biodegradability after 12 weeks of being immersed in natural compost soil. Chemical analyses showed decreased cellulose content and relatively increased lignin content in final MC specimens.

Our study brings novelty to the field with biodegradability and mold resistance data and also broadens the collective data range on chemical and physical properties. We conclude that the MC from hemp shives is ecologically compatible and its production is low-cost as it relies on agriculture waste products and biological growth. MC is readily comparable with EPS with regards to mechanical properties, nevertheless reducing its water absorption and resistance to mold growth is in need, therefore future research should focus on finding solutions to optimize these properties for more adequate MC usage as an effective alternative packaging material to synthetic ones.

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PLA/LIGNIN COMPOSITES DOPED WITH CU NANOPARTICLES FOR FOOD PACKAGING APPLICATIONS

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The polymers used in packaging increased from 5 million tons to 100 million tons in over the past 60 years. The polymers used in food packaging are noticeably high due to convenience over the traditional glass and metal packaging. The most used food packaging polymers are poly lactic acid, polyethylene, polypropylene, etc. Among them, polylactic acid (PLA) is a biopolymer produced from natural resources and widely used in plastic films, bottles, and biodegradable medical devices [1]. However, due to poor thermal stability, slow crystallization and high cost, PLA polymer is unsuitable to use in food storage applications requiring long shelf life.

Since lignin has good thermal and mechanical properties, limitations of PLA can be overcome through incorporation of biopolymers like lignin. Lignin can be obtained as a low-cost byproduct from agricultural and forest biorefineries and contains several different functional groups (hydroxyl, carbonyl, and carboxyl groups) [2]. Recent work [3] demonstrated that lignin nanoparticles with different polymers have potential for many applications. Lignin-based nanoparticles (LNP) are used to improve strength, toughness and stiffness over traditional fillers due to their higher dispersibility, lower agglomeration and higher surface area per mass.

Lignin nanoparticles were prepared from kraft lignin by dissolving in acetone:water mixture with a 3:1 ratio and stirred at room temperature for 1 hour. After, a 1000 g of water was poured into the lignin solvent mixture under vigorous stirring and continued for another 1 hour, then filtered to remove the undissolved solids and proceeded to solvent evaporation using rotavapor. Additionally, to improve the anti-microbial property of the packaging film, copper (Cu) nanoparticles could be incorporated into the composite through a solvent casting process. The morphology of produced composite films was examined using scanning electron microscopy. Similarly, the composites physical (mechanical- tensile, Young's modulus and thermal: glass transition temperature) and chemical (type of interaction and bonding between the lignin and PLA matrix) properties were examined. The weight percentage of lignin nanoparticles and in the composites was optimized based on the resulting properties and according to the European standard [4]. In the future studies the anti-bacterial performance of the composite film will be evaluated against foodborne bacteria such as *Escherichia coli* (gram-negative) and *Staphylococcus aureus* (gram-positive). The proposed work will provide significant advances to boost the utilization of PLA polymer at low costs for various food packaging applications.

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RHEOLOGICAL, THERMAL AND MECHANICAL PROPERTIES OF WOOD PLASTIC COMPOSITES BASED ON VIRGIN AND RECYCLED POLYPROPYLENES AND BIRCH PLYWOOD WASTE

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Wood plastic composites are perspective and widely used material in different branches of industry. One of them is the usage of WPCs as coating of plywood [1]. The use of recycled polypropylene allows to save up a fossil resources, successfully to solve ecological problems and to decrease of the price of WPC without essential diminishing of exploitation properties. To produce qualitative WPC sheets necessary to know the rheological properties of WPC melts [2]. At the same time the processing conditions can influence also exploitation properties of WPC sheets. As objects of investigations industrially prepared wood plastic composites (WPCs), based on virgin and recycled polypropylenes (vPP, rPP) and birch plywood production waste product- plywood sanding dust (PSD) were used. Investigated WPCs contain 40 and 50 wt. % PSD different another modifier, such as functional lubricant Struktol TWP-113, antioxidant 1010, thermal stabilizer 168, UV stabilizer 770 and different color pigments. According to our studies, we can conclude that rheological properties studied by capillary rheometry method depends on WPCs composition and experimental parameters: shear stress, shear deformation rate and temperature. The curves of the fluidity indicate to the character of typical pseudo-plasticity of all polymer melts of which viscosity not only depends on temperature, but also decreases with an increase of shear stress and shear deformation rate Pseudo-plastic properties confirm also the signed values of fluidity index (n) which for pseudo-plastic liquids always are smaller than one. TGA measurements showed that all systems have the high thermal stability and the weight losses after dynamic heating up to processing temperature 215oC are not more than 5.53 %, but during isothermal heating (1 h) at 215oC only 4.51%. Differential scanning calorimetry (DSC) showed a small changes of melting temperatures, but the beginning of thermal destruction temperature fluctuates between 256.96 and 188.5oC. Depending on the composition of WPC the density of all composites changes in limits 1.02-1.09 g/cm³, temperatures by Vika 154.4-158.7oC, microhardness 125.1-151.8 MPa and the impact strength 7.81-15.39 kJ/m².

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A STUDY ON WASTE PAPER REINFORCED RECYCLED POLYPROPYLENE BIOCOMPOSITE

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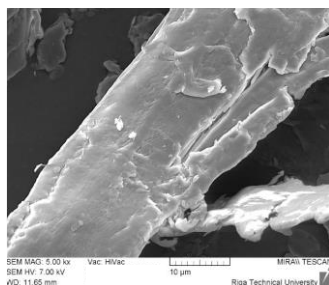
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Wastes and industrial side streams play a significant role as raw materials in the European bioeconomy. Nowadays, waste biomass research is focusing on its conversion into value-added products. Aside from being carbon neutral, the use of biomass for energy reduces dependency on the consumption of fossil fuel contributes to energy security and climate change mitigation.

The objective of this research is to obtain a new advanced material from waste paper and to use it as a filler in a bio-composite. Biocomposites and new materials based on lignocellulosic components offer a huge potential in a large variety of applications such as building engineering, packaging, medicine, etc. The extraction of recycled cellulose from the paper waste was carried out by its mechanical disintegration with the followed acid hydrolysis. In comparison with the known methods, the proposed one was realized under more energy-saving mode. The obtained recycled cellulose powder was characterized by chemical properties, XRD spectra, crystallinity index, particle size distribution as well as by its surface properties such as contact angle and surface free energy [1].

The obtained biocomposite samples contained recycled polypropylene as a matrix, the recycled cellulose powder as a filler, and maleic anhydride polypropylene (MAPP) as a compatibilizer were fabricated by extrusion and molding methods. The content of the waste cellulose in the composite varied from 10% to 50%. The obtained biocomposite samples with the recycled cellulose filler composite were characterised by mechanical and wetting properties as well as by a morphological study. It was found that the fabricated biocomposite samples showed the increase in both tensile and bending strength with increasing the filler content relatively the mechanical properties of the recycled polymer. For the biocomposite with a 50% content of the recycled cellulose, the flexural strength increased by 74%, reaching 36.1 MPa, compared to the flexural strength of the recycled PP. At the same time, the polar part of surface free energy increased for the biocomposite sample with a 50% content of the recycled paper due to the pronounced hydrophilic nature of cellulose.



SEM image of the recycled paper particle

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NANOCELLULOSE-COATED PAPER DIPSTICKS WITH VISUAL RESPONSE TOWARDS HEAVY METAL IONS

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Heavy metal pollution of water bodies and streams is a serious issue all around the world, but, more often than not, atomic absorption spectrophotometry or luminescent bacteria tests are not at our disposal. Undoubtedly, all communities in general, and developing countries in particular, would benefit by having disposable paper dipsticks that could display a visual response towards heavy metal ions.

This was achieved by means of a number of substances that are commercially available and readily responsive, be it selectively or not, to at least one transition metal ion. Such substances include aminofluorene, pyrrole, and tetramethylbenzidine (TMB). The three of them present a different response towards highly oxidizing transition metal ions, like Fe(III): the fluorescence of aminofluorene is turned off, pyrrole (light brown) is polymerized towards a dark blue—and, by the way, electrically conductive—polymer, and TMB goes from colorless to blue [1]. Dithizone turns reddish in presence of Hg(II).



Fig. 1. Luminescence quenching of Eu(III).

Other sensory substances, such as lanthanide ions, need to form coordination compounds with proper ligands to display enough luminescence under ultraviolet radiation [2]. For instance, Fig. 1 shows paper strips coated with europium(III) bound to a polymeric ligand (a Lewis base) and 1,10-phenanthroline. Certain metal ions (Lewis acids) switch off the fluorescence of the complex.

An even simpler approach lies in the colored nature of most transition metal complexes. Oxycellulose nanofibers, obtained by TEMPO-mediated oxidation and fibrillation, readily turn blue by adsorbing copper(II). Cellulose nanofibers, like virtually any glycan, can also be a reducing agent for silver nitrate, allowing for the vast possibilities of mercury detection based on the surface plasmon resonance of silver nanoparticles [3].

In this work, responsive coating solutions, nanocellulose/ responsive substance combined coating, and functionalized (oxidized or complexed) nanofibers were placed onto the surface of paper. The visual response of the resulting paper strips towards different heavy metal ions was assessed by advanced imaging software.

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THE PROTECTIVE COATINGS OF THE LIGNOCELLULOSE-BASED COMPOSITE BOARDS FORMED USING THE DRYING AND SEMI-DRYING OILS

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Modern eco-friendly thermal insulation materials are produced using lignocellulose containing materials. The boards made of such composites are susceptible to excess humidity that accelerates the biodegradation process. In this work, hydrophobic protective coatings on the lignocellulose-based composite boards (LCB) formed using drying oils such as a tung tree, linseed, and semi-drying hempseed oil were studied. The LCBs were made of hemp shives, corn starch binder and flame retardants such as expanded graphite or multifunctional aqueous mixture based on phosphorus and nitrogen organic compounds. The hydrophobic coatings were formed in the vacuum desiccator by covering boards with specific oil types. After this, LCBs covered with oil were maintained at 40°C, 90°C, or 120°C. The respective protective films were formed by the autooxidation and polycondensation mechanisms. The hydrophobic protective coatings were imaged by scanning electronic microscopy (SEM) to monitor (Fig.1) the hemp shivs with the respective film made of either hemp seed, linseed or tung tree oil.

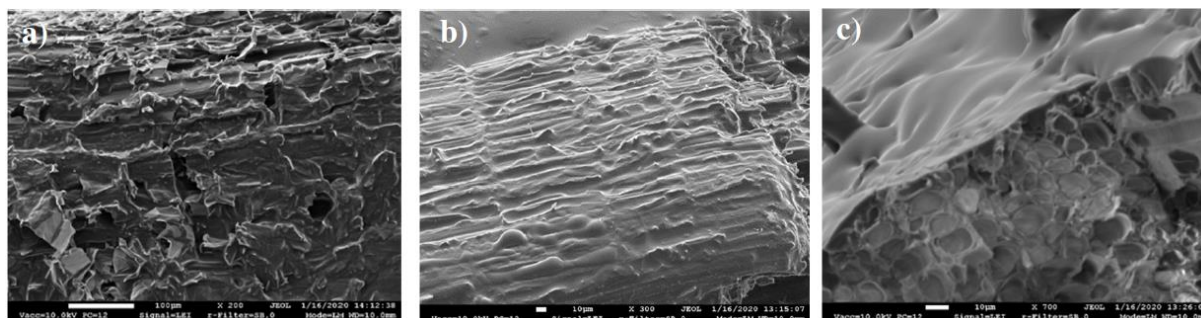


Fig.1. The microstructure analysis of the protective coating on the hemp shives
a) with hemp seed oil, b) with linseed oil, c) with tung oil

Also, it was demonstrated that the compressive strength (at 10% of relative deformation) of such composite boards with the oil protective coatings compared to the untreated boards increased up to 4.5 fold and could reach up to 14 MPa, the bending strength increased by 2.78 fold up to 19 MPa, the water absorption decreased around 4-fold (from 1.34 kg/m² to 0.37 kg/m²), swelling in thickness decreased from 7.51% to 4.59%, while the thermal conductivity remained unchanged and was around 0.085 W/(m·K). It was concluded that the most desired properties of such materials were obtained when the tung tree oil was used for coating.

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DENSIFIED JUNIPER WOOD FOR USE IN BONE IMPLANTS

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Bone implants have been extensively studied in both material and medicine science for decades. There are thousands of scientific articles on the bone implants. Demand for non-metallic implant materials is growing rapidly, not only because of metal implants damage bone over time due to loosening and biocorrosion, but also because of increased use of modern medical diagnostic systems, e.g., nuclear magnetic resonance (NMR) (1). Materials such as calcium phosphate, calcium carbonate and calcium sulphate are mainly studied as potential bone substitutes. Materials obtained directly from nature are also being studied, e.g., corals (2). At the same time, wood as a natural material for bone implants has been studied insufficiently.

The main advantage of wood as a bone implant biomaterial is its structural similarity to bone structure. Internal structural similarity also leads to similar properties, e.g. density, anisotropy and fluid transport in cells. Previous studies have shown that wood have a good biocompatibility and osteoconductivity with no toxicity has been observed (3; 4).

The idea of the study is based on two previous investigations - use of *Juniperus communis* in bone implants by prof. dr. hab. med. E. Ezerietis (5) and a study on the delignification and compaction of wood to produce high-performance materials (6).

The above studies indicate that wood can be used successfully as a bone implant material. However, there are still a number of problems that prevent wood from using in bone implants. The main ones - wood has a variable density and composition depending on age, species and growing conditions; the density of wood is less than that of bone.

These problems could be prevented by partial delignification and subsequent compression of wood leading to increased density and improved physical-mechanical properties.

Sulphate cooking of juniper wood has been used in the preliminary study for partial delignification at the temperature of 165°C for different residence time (0-40 min) following by thermal compression for densification under a pressure about 5 MPa at 100°C and different time (20-28 h).

The densified and natural juniper wood samples were characterized by chemical composition, mechanical properties and swelling in saline.

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CELLULOSE MODIFICATION WITH MALEIC ANHYDRIDE

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Cellulose is well known natural polymer. and has been broadly investigated for decades; furthermore, cellulose derivatives represent significant part of the extensive polysaccharide research. Commonly used methods of derivatisation are esterification, oxidation, and etherification [1-2]. Reactions are performed via cellulose's hydroxyl groups (-OH). Cellulose esters and ethers have found practical application various fields such as food industry, cosmetics, packaging etc. However, there are still gaps to fill – cellulose derivatives with dicarboxylic acid anhydrides and their influence on paper materials.

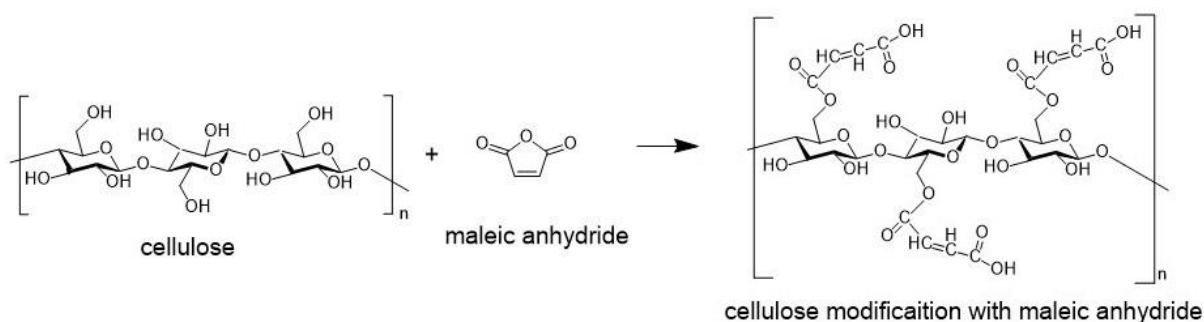


Figure 1. Scheme of cellulose modification with dicarboxylic anhydride (as example – maleic anhydride) suggested by Caldwell's patent – Polysaccharide derivatives of substituted dicarboxylic acids

In presented research new method was proposed and Cellulose esterification with maleic anhydride (Figure 1) was performed in an anhydrous environment to avoid side reactions with other substances containing free hydroxyl groups. Increased heating promotes anhydride ring opening.

Fourier Transmission Infrared spectroscopy of derivatized cellulose revealed unique peak at 1735cm^{-1} that corresponds to ester carbonyl group ($\text{C}=\text{O}$) [3-4] and confirms planned modification. Nanocellulose (NC) was produced from obtained modified cellulose using cryogenic milling and microfluidizer. Produced NC was used for paper coating and effect on paper properties was investigated. Preliminary results revealed considerable effect of NC on mechanical properties of paper.

Acknowledgements. Financial support for this research is from Latvian State Institute of Wood Chemistry Bio-economic grant "CelFunVol2".

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HOMOGENEOUS SYNTHESIS OF CELLULOSE PALMITATE DERIVATIVES IN IONIC LIQUID VIA TRANSESTERIFICATION

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Nonrenewable resources like oils are mainly used for the production of thermoplastic polymers which are used as packaging materials. These materials are responsible for causing environmental problems such as pollution and depletion of natural resources [1]. There is a strong need to find sustainable alternatives for these materials. Cellulose is a notable raw material for several industries, such as food, paper, textile, cosmetics, pharmaceuticals and biomaterials. Cellulose is one of the major components of biomass and the most abundant natural polymer on Earth and hence it is considered as a carbon neutral renewable material [2]. Cellulose can be chemically modified (e.g. via esterification) and can be converted into valuable cellulose derivatives having various functions such as thermoplasticity. Long chain cellulose esters are bio-based materials which have several industrial applications in plastics, coatings and films [3]. Homogenous functionalization needs cellulose to be fully dissolved. However, cellulose is not soluble in water and organic solvents due to the presence of strong intra- and intermolecular hydrogen bonds. Ionic liquids (ILs) are the most promising sustainable solvents for the dissolution of cellulose as they provide quite stable functionalization environment and have good recycling properties [4]. Addition of co-solvent is needed in certain conditions as it helps to reduce dissolution period for cellulose along with viscosity of final solution making overall synthesis economical. In this work, the preparation of cellulose palmitate (DS \approx 1.5 and more) was investigated through homogeneous transesterification of microcrystalline cellulose (MCC) in the presence of ionic liquid, methyl 1,5,7-triazabicyclo[4.3.0]non-6-enium acetate, [mTBNH][OAc] and co-solvent dimethyl sulfoxide (DMSO) by using vinyl palmitate as an acylation agent. The reaction parameters like the ratio of ionic liquid with co-solvent, molar ratio of MCC with vinyl palmitate, time and temperature along with series of concentrations of MCC (1-3%). The reaction parameters 1:1 ratio of IL: DMSO, molar ratios \geq 1:3 MCC AGU:vinyl palmitate, temperature range 60- 80°C and time 1.5- 2.5 h were giving cellulose ester products with better solubility and DS \approx 1.5- 2.0. All samples were characterized by volumetric titration and FTIR. The structural analysis was carried out by 1D and 2D ^1H and ^{13}C nuclear magnetic resonance (NMR) and X-ray diffraction (XRD). Physical and mechanical properties were studied by using techniques like differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) along with rheological studies.

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ENABLING CIRCULAR BIOECONOMY VIA ESTIMATING THE POTENTIALLY VALORISABLE FOOD LOSS AND WASTE IN THE NORTHERN EUROPEAN REGION

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Food loss and by-product (FLB) estimation has been difficult due to no uniform guidelines for monitoring and measuring FLB, and no obligation or system for reporting FLB. As FLB generation is associated with various environmental, economic and social burdens, its prevention, reduction and valorisation play a crucial role, especially in the context of circular bioeconomy. The generation of FLB is inevitable during the primary production, processing or manufacturing of certain foods. Thus, such FLB require further re-introduction into the bio-based material cycle to avoid their disposal or leakage from the circular resource system. Animal feeding, anaerobic digestion, composting and landspreading are common conventional valorisation methods that provide low economic and environmental benefits [1]. As the world's population increases, so will the amount of produced food and their associated FLB. This makes their sustainable utilization more urgent.

Our study aims to (1) estimate the extent of FLB from the agricultural and food production stages of the top ten most-produced food products (based on their amount) in the Northern European countries (Lithuania, Latvia, Estonia, Finland, Sweden, Norway, Iceland and Denmark), (2) identify the current valorisation pathways, and (3) estimate the potential amount of valorisable FLB and obtainable value-added products based on the emerging biological valorisation approaches reported in literature to sustainably close the bio-based material and resource loop.

We compiled data on the extent of food production using the data from the FAOSTAT database. Potential valorisation pathways of FLB into higher value-added products were estimated through scientific literature analysis. Current valorisation pathways were assessed through an extensive browsing of information provided by food industry and research projects made available on CORDIS database.

Existing state-of-the-art research provides various solutions on how to valorise unavoidable FLB into higher value-added products. Despite the ongoing research and creation of bio-based industry clusters, understanding of the amount, composition, seasonal variability and geographical distribution of FLB generation is limited due to the insufficient data availability and quality, legislative restrictions on FLB definition and use, as well as lack of cooperation among various bio-based industries and stakeholders. Knowledge and data availability on the FLB flows is an essential precondition not only for implementing FLB valorisation pathways at an industrial scale, but also for developing sustainable circular bioeconomy policies at national and regional scales. In the Northern European countries, this is currently missing, and this study is the first attempt to estimate the valorisable FLB and obtainable value-added products in this region.

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THE RESOURCE POTENTIAL OF FERMENTATION RESIDUES

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Successful transition to circular bioeconomy relies on the availability and efficient use of organic feedstocks, which can be transformed to a variety of products through technologies of biorefinery and industrial biotechnology. These approaches in turn create industrial side-residues such as spent microbial biomass (SMB).

This study aims to reflect on the current state of SMB within bioeconomy and to create awareness of this growing industrial resource. To do this we use data from a range of published fermentation processes to estimate how much SMB is formed per unit of a fermentation product (e.g., weight per weight, wt/wt) across different types of bioproducts. To the best of our knowledge, this is the first attempt to estimate how much SMB is generated within the growing biotechnology industry.

The amount of SMB differs across bioproducts and production processes. In general, production of bulk products (e.g., alcohols) generates less SMB than the product itself, whereas production of high-value low-volume specialty products (e.g., vitamins) can generate 10 to even 100 times more SMB than the target product. Thus, SMB from bulk and specialty bioproducts account for roughly equal amounts of global SMB, which is estimated as more than 50 million tons of protein and other nutrient-rich SMB (in 2013).

These results indicate that SMB is a significant, growing, and predictable nutrient-rich industrial residue. These attributes make SMB suitable for nutrient circulation through various valorisation routes (e.g., protein biorefinery, feed or food applications, fermentation substrates, agricultural biofertilizer, energy) providing nutrient links across different industries and contributing to circular bioeconomy.

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WASTE RAPESEED COOKING OIL IS PERSPECTIVE SUBSTRATE FOR BIOSURFACTANT SYNTHESIS VIA YEAST *STARMERELLA BOMBICOLA*

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Synthetic surfactants are one of the most important bulk chemicals. They are used in agriculture, food and feed, cosmetics, oil mining and refinery, etc. However, their biodegradation is poor, therefore the need to find environmentally friendly alternatives increases permanently.

Biosurfactants are microbially derived molecules with similar properties to their synthetic analogues. They can be used as detergents, emulsifiers, and have the potential to substitute synthetic surfactants. They can be synthesized from renewable resources and are biodegradable. Additionally, waste cooking oil is widely available, potentially useful yet cheap substrate [1].

Sophorolipids are amongst the most studied microorganism-derived biosurfactants. Non-pathogenic yeast *Starmerella bombicola* is the main producer of these glycolipid (sugar sophorose linked to fatty acid) surfactants.

We tested if rapeseed waste cooking oil can be used as a source of fatty acids by *S. bombicola* for sophorolipid synthesis. In batch culture experiments we evaluated cell growth, substrate consumption and product formation rate. We also established fast anthrone - DNS based method for sophorolipid determination in cultivation media.

Our results demonstrate that *S. bombicola* is able to produce sophorolipids from raw and waste rapeseed oil. The best results were achieved in the nitrogen poor media. We conclude that waste rapeseed oil can be used as a cheap substrate for sophorolipid production.

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DEVELOPMENT OF LOW-COST MEDIUM FOR *BACILLUS SUBTILIS* SPORE OBTAINMENT

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Bacillus spp. is one of the most commonly used beneficial microorganisms both in research and industry, due to its ability to promote the growth of plants and improve the protective abilities of the plant against the abiotic and biotic effects [1,2]. Among these species, *Bacillus subtilis* is a non-pathogenic bacterium, with can able to colonize most of the habitats with a high growth rate and relatively short fermentation cycle [3,4]. Spores of *Bacillus* are thermotolerant, resistant to mechanical damage, drying, ultraviolet radiation, etc., thus suitable for inclusion in microbial formulations [5]. However, microbial products at the moment cannot compete with conventional products, if the price is compared [6]. Therefore, a search for a low-cost and cost-effective medium for spore production of *B. subtilis* is crucial for sustainable agriculture, including European Green Deal [7] and nature protection in general. Therefore, in this study, a low-cost and cost-effective medium was investigated by changing the traditional nitrogen and carbon sources to by-products, e.g., molasses, a sugarcane industry by-product, and food-grade ingredients, e.g., legume flour.

The experiments were conducted in a laboratory scale in Erlenmeyer flasks. Bacterial growth was monitored with optical density measurements, and colony forming units of total and spore cells were determined by plating appropriate dilutions on agar plates.

Study results show, the by-products and food-grade components as medium ingredients can compete with laboratory grade reagents in terms of spore yield versus medium costs and medium preparation time. Therefore, microbial plant protection and fertilization products can become more available to the end consumer.

By choosing locally available, low-cost by-products and food-grade ingredients for low-cost and cost-effective bacterial growth medium compositions, plant protection products and fertilizers containing microorganisms can break into the market at a lower price, at the same industrial agriculture can become more sustainable and environmentally friendly. However, further studies must be performed to validate the use of the developed medium in the industrial scale bioreactors.

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MEDIUM FORMULATION AND FED-BATCH CULTIVATION OF METHYLOSINUS TRICHOSPORIUM

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Methane and methanol are considered as low-cost, widely available substances, which are produced as part of multiple modern industrial applications. Both mentioned substances can be used as substrates for cultivating methanotrophic bacteria strains and production of valuable bioproducts. Methanotrophic biomass has high contents of unsaturated fatty acids, as well as macro and micronutrients and can be used as a feed supplement for farm animals [1, 2].

Usually methanotrophs show low specific substrate consumption rates. Thus, the most cost effective methane and/or methanol utilization processes using methanotroph biomass are those operated in a continuous mode. However, to reach the required biomass concentrations for enabling continuous methane removal, it is necessary to go through batch as well as fed-batch stages. In order to reduce the time and costs of the cultivation process, it is vital to accelerate the growth of applied organisms as much as possible during the batch and fed batch phases. Usually, methanotrophic bacteria cultivations are carried out using fully synthetic mineral mediums (nitrate mineral salts medium (NMS)) without the addition of any growth factors [3]. Potentially, higher biomass growth and substrate uptake rates can be achieved by supplementing the growth medium with vitamins, amino acids etc. or by using more bioavailable substrates.

The aim of our research was to study the influence of growth factors such as vitamins, and different nitrogen sources (yeast extract, yeast nitrogen base with/without amino acids and tryptone) on the growth of *Methylosinus trichosporium* ob3b. Subsequent tests of the nutrient medium, which promotes higher biomass growth rates, were carried out in laboratory 5 L bioreactor cultivations to study the main process parameters.

Experiments for studying the influence of growth factors were carried out in shake flasks by varying the medium compositions and analyzing the effects of said variations on the kinetics of the cultivation, e.g. specific biomass growth rate and biomass yield from substrate.

From the statistical analysis of experimental data it was observed, that supplementation of the growth medium with yeast extract or tryptone, seems to promote the growth rate of methanotrophs, when methanol is used as the main substrate. Furthermore, specific growth rates observed during cultivations in mediums containing vitamins (including cobolamin) also seem to positively affect the biomass growth rate. Based on the results of lab-scale bioreactor cultivations, using the identified medium composition it was possible to achieve a maximal biomass specific growth rate of $0.15 \text{ L} \cdot \text{h}^{-1}$ and productivity of $0.12 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$.

Further work should be aimed at optimizing the medium composition for the continuous methanotroph cultivation stage.

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BIOECONOMY BASED BIOREFINING SOLUTIONS FOR VALORISATION OF FOOD WASTES TO OBTAIN BIOACTIVE AND FUNCTIONAL INGREDIENTS

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Food loss and food waste are some of the major issues being recognized as a part of modern society. Approximately one third of all the food is lost along the production and supply chain, leading to losses of valuable resources as well as creating environmental problems. The current food processing, production, consumption, and waste management approaches are not corresponding to the principles and aims of sustainability. The food waste and organic waste management problem becomes yet more urgent considering the aims set by a variety of environmental initiatives to abandon fossil material-based production and promote bio-based economy – bioeconomy, thus achieving climate neutrality and development of resource saving practices [1]. Despite the efforts put in place by the EU achieving the set aims and the transition to bioeconomy much more knowledge and innovation is needed also in respect to properties of biomaterials, production and waste processing.

Juice production is an industry that produces fruit or berry press residues (pomace) as a by-product, which is often discarded in landfills or composted. Although these solutions are within the framework of the goals set by the different environmental initiatives, this type of waste lacks the recognition, despite being rich in bioactive ingredients that could be retrieved. The aim of the research is to study composition of *Vaccinium* genus berries, common for NE Europe, as well as biorefining possibilities of their pomaces to support development of extract applications in bioeconomy. The investigated berry press residues contain a variety of ingredients, polyphenols and lipids are the groups of interest due to their application potential in various products, where these compounds could be used as functional ingredients. Anthocyanins are the main polyphenolics of berries – they are plant pigments that provide the vibrant colour of the berries while lipids are plant metabolites that are part of cell membranes and have a regulating function within the plant. Exploring the potential of berries and their industry by-products have the potential to reduce food loss and at the same time provide new, innovative, natural and healthy products with functionality for human consumption (Fig 1).

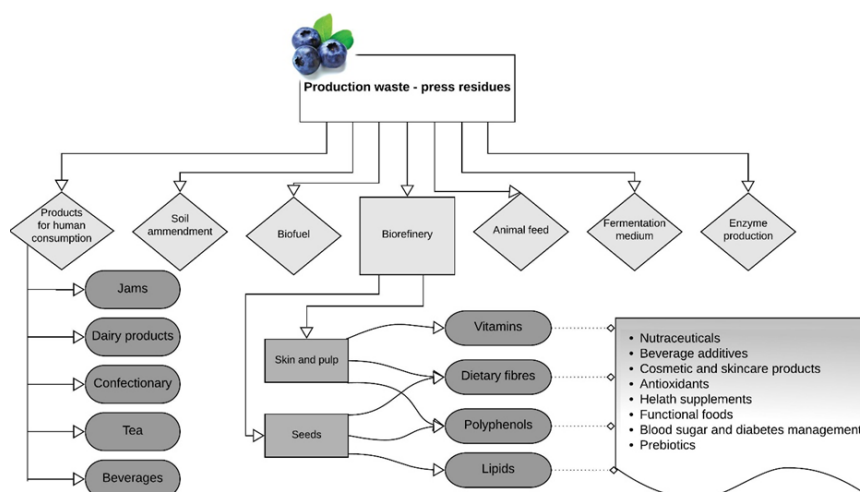


Fig 1. Proposed biorefinery strategies of berry press residues

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VANILLIC AND MELDRUM'S ACID CONTAINING ANTIOXIDANT

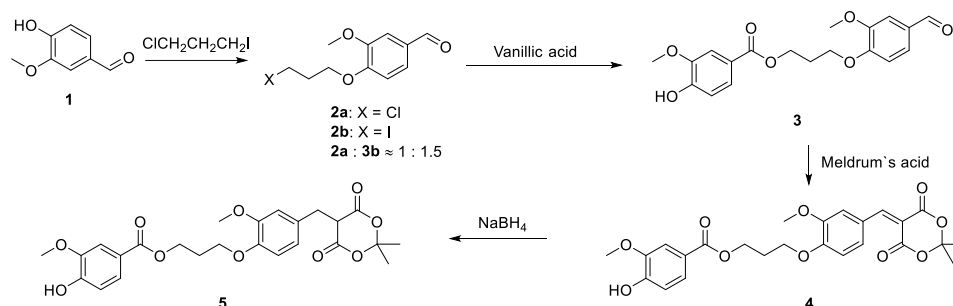
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Oxidation processes are the cause of degradation of various products, such as polymers [1, 2] and food [3]. In living organisms, oxidation processes produce reactive oxygen (ROS) and nitrogen (RNS) species, which work as cell signaling molecules in small amounts [4]. However, an overproduction of these molecules can lead to oxidative stress and related health issues, e.g. cancer [5], Alzheimer's [6], and Parkinson's [7] disease. Antioxidants can be used to regulate the production of ROS.

Some studies have shown a synergic effect when a mixture of antioxidants of different types is used [8–10]. Herein, we provide transformation of naturally occurring phenol type compounds – vanillin and vanillic acid – leading to value added products with higher antiradical activity in comparison to the parent phenol type antioxidants. In this study 2 types of antioxidants – 1,3-dicarbonyl and phenol – were combined in a single molecule to see if this structure gives the synergic effect as well. The synthesis was carried out in 4 steps. First, an aldehyde **3** containing the phenol type antioxidant was synthesized. The aldehyde **3** was then subjected to the Knoevenagel condensation with Meldrum's acid. Finally, the resulting arylidene derivative **4** was reduced affording the target compound **5** (Scheme 1).



Scheme 1. Synthesis of the target compound 5

The antiradical activity of the compound **5** was assessed by measuring its ability to scavenge the DPPH radical. At a 100 μM concentration, compound **5** inhibited 70% of the radical, with an IC_{50} value of 59 μM . This means compound **5** is a more potent antioxidant than BHT.

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DETERMINATION OF ANTIOXIDANT ACTIVITY IN FRACTIONS OF PYROLYSIS LIQUIDS

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Pyrolysis is a well-known biomass processing technology, which has several advantages, it can be reasonably up-scaled and is considered to be suitable for integration in biorefineries [1]. During pyrolysis the feedstock undergoes thermochemical conversion and three kinds of products are obtained – gasses, char and liquids. The liquid products (bio-oil, pyrolysis oil) can be separated to extract value-added chemical products. In our case, fast pyrolysis of sulfuric acid pre-treated birch wood chips gives a high yield of the liquid products with levoglucosan (1,6-anhydro- β -D-glucopyranose) as the main product. Besides levoglucosan, a large number of chemicals ensue as by-products. After levoglucosan is removed from the mixture of condensable pyrolysis liquids, the issue of by-product valorization arises. The biorefinery concept demands obtaining several products from a single feedstock, so this work is related to the investigation and valorization of the phenolic fraction of pyrolysis liquids.

To analyze the chemical composition of the pyrolysis liquids, UHPLC-MS-UV was used with Waters Acquity BEH C18 (2.1 \times 50mm, 1.7 μ m) column as the stationary phase and a gradient system consisting of water/acetonitrile with 0.1% formic acid additive as the mobile phase. Because of the many similar aromatic structure chemicals in the sample, only a few individual chemical compounds could be resolved (the most abundant were vanillin, vanillic acid, syringol, syringic aldehyde). So for the quantitative determination of total phenols the Folin-Ciocalteu method was used. Since phenols are often considered valuable antioxidants [2], we tested the antioxidant activity of the aromatic fractions of the pyrolysis liquids. We used the spectrophotometric free radical 2,2-diphenyl-1-picryl-hydrazyl (DPPH[•])-scavenging test, and found that the dark brown colour of the sample interfered with the results of this method. In this work, we examined two approaches to avoid the interference of the sample colour in the DPPH test results. Firstly, the spectrophotometric method can be adjusted by using a mathematical correction with regard to the absorption value of the sample solution at 517nm wavelength, which is the maximum absorption wavelength for DPPH. Alternatively, the method can be modified to use UHPLC-UV for monitoring the DPPH concentration changes. Fig. 1 shows a typical chromatogram of pyrolysis liquids and DPPH. DPPH has a later retention time than all the phenolic compounds in the sample, showing that UHPLC enables selective detection of DPPH signal.

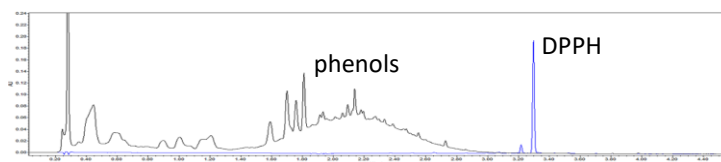


Fig. 1. UHPLC-UV chromatogram of pyrolysis liquids and DPPH

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VALORIZATION OF LIQUID BY-PRODUCTS FROM HEMP CARBONIZATION

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Slow pyrolysis is a process that consists of thermal decomposition of biomass. This latter undergoes a group of complex chemical reactions at high temperature and inert atmosphere resulting in the degradation of the different components, i.e., hemicellulose, cellulose, and lignin [1]. At temperature above 400°C, the process approximately yields 40 wt% or less (depending on the biomass composition) of solid residue called biochar which can be used in several applications as a high added value product (super capacitor, batteries); however, the remaining part is wasted in form of condensable and non-condensable (CO, H₂, CH₄, C₂H₆) gases [2]. To reduce these wastes and increase the profitability of the process, valorisation of the condensable fraction via biorefinery treatments seems to be interesting. Nonetheless, few studies have been published about this topic. Black et al. [3] characterized liquid by-product from fast pyrolysis plants and reported the occurrence of compounds with distinctive properties such as acids, phenolics, and complex sugars-derived molecules with high concentrations. Interesting features are attributed to the detected compounds such as antioxidant and antimicrobial activities, sensorial properties, acidity, etc. To the best of our knowledge, minor efforts have been devoted for the characterization of aqueous condensate from slow pyrolysis.

In this study, liquid condensate from hemp stems slow pyrolysis was investigated. Hemp stems were carbonized up to 1000°C and 4 fractions were collected separately at different temperature ranges (25-150°C, 150-250°C, 250-400°C, and 400-1000°C). The four fractions (F1, F2, F3 and F4) were subjected to several characterization tests including volumetric concentration determination, liquid-liquid separation (using ethanol-acetone mixtures), DPPH antioxidant activity test, total phenolic content determination and high-performance liquid chromatography analysis (UHPLC). The highest products concentration was attributed to F3. Findings indicated the presence of molecules with antioxidant activity in F3 and F4. UHPLC allowed to identify phenolic acids and propoxyphenols in both F3 and F4. Further research is being conducted to identify the potential applications of the different subfractions.

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TORREFACTION OF PULP INDUSTRY SLUDGE: EXPERIMENTAL VALIDATION, OPPORTUNITIES AND CHALLENGES

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Pulp industry is known to produce large quantities of sludge. Sustainable handling of such large quantities of sludge is needed in order to improve the environmental feasibility of the pulp mills and to improve the resource efficiency. On the other hand, recently, under COP26, several countries agreed to phase-out coal from energy systems. In terms of fuel characteristics, torrefied biomass could be an alternative to coal. However, torrefied biomass pellets selling price is significantly higher than coal because of the increased raw material costs. Thus, using low cost organic residues such as pulp sludge could be help to optimize the economic feasibility of the torrefied pellets.

In this study, torrefaction of dewatered pulp industry sludge was studied in a bench scale continuous torrefaction reactor at 250, 275 and 300 °C. The influence of torrefaction treatment on composition and fuel characteristics of the sludge was established. The heating value of the sludge increased from 19 MJ/kg for dried to 22 MJ/kg for torrefied at 300 °C. The dried sludge contained 14 wt.% of hemicellulose, 35 wt.% of cellulose and 12 wt.% of lignin. As expected, torrefaction treatment showed significant effect on the biomass components present in the sludge. For example, at a torrefaction temperature of 300 °C hemicellulose was degraded completely and cellulose content was reduced to 65 wt.%. The fuel ratio of the torrefied sludge varied between 0.27 - 0.61. The ash melting behavior of the pulp industry sludge followed a similar pattern with agricultural wastes i.e. straw. The initial deformation temperature for dried sludge varied between 730 - 740 °C. The ash mainly contained SiO₂, Na₂O and CaO. The theoretical evaluation of several slagging and fouling indexes such as fouling index, acid/base ratio, and bed agglomeration index showed that the ash related issues of the sludge in the medium range.

Torrefaction treatment improved the fuel characteristics of the sludge and torrefied sludge can be compared with low rank coal such as lignite. The high initial moisture content could increase the overall energy input. The low ash melting temperatures could be a threat to combustion equipment. Finally, to conclude, torrefaction of pulp industry sludge can improve the environmental feasibility and generate additional revenue to the pulp mills.

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