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The outlook for bio-based value-added chemicals and their growing markets

Riina Muilu-Mäkelä, Hanna Brännström, Mikko Weckroth and Johanna Kohl



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Tiivistelmä

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Biopohjaiset arvokemikaalit ovat biomassoista saatavia kemiallisia yhdisteitä, joita voidaan hyödyntää monilla eri teollisuudenaloilla. Niiden osuus on noin 7 % EU:n biopohjaisen teollisuuden markkinoista. Biopohjaisella teollisuudella tarkoitetaan biomassoihin perustuvaa tuotantoa, ruoka- ja juomateollisuutta lukuun ottamatta. Tässä raportissa kuvataan metsä-, maatalous- ja vesibiomassoista, saatavia kemiallisia yhdisteryhmiä ja niiden sovelluskohteita eri tuoteryhmissä. Raportissa keskitytään alan tutkimukseen erityisesti erilaisilla uuttoprosesseilla erotettavista biokemikaaleista ja nostetaan tutkimuksia biomassojen sisältämistä yhdisteistä ja niiden soveltuvuudesta erilaisiin käyttökohteisiin. Tavoitteena on hahmotella tulevaisuuden visio biokemikaalien hyödyntämisestä vuoteen 2050 mennessä.

Vallitsevat megatrendit, kuten ilmastonmuutos, erilaiset geopoliittiset jännitteet, huoltovarmuuden merkityksen kasvu, luontokato ja väestönkasvu vaikuttavat biomassojen tuotantomahdollisuuksiin alueellisesti ja globaalisti. Rajallisten resurssien takia teollisuudella on tarve hyödyntää entistä tehokkaammin tuotettu biomassa. Maapallon kantokyvyn rajat saavutetaan joka vuosi aikaisemmin ja siksi biomassapohjaisten tuotteidenkysyntä kasvaa. Biopohjaiset ratkaisut tarjoavat vaihtoehdon fossiilipohjaisille tuotteille, joiden tuotanto on ongelmallista kasvihuonekaasupäästöjen, ympäristön kemikalisoitumisen ja fossiilisten varantojen vähentymisen myötä. Korvattaessa fossiilisia tuotteita biopohjaisilla ratkaisuilla tulee ympäristöhyödyt pystyä osoittamaan selvästi, esimerkiksi elinkaariarviointia hyödyntämällä.

Erilaisista biomassoista saadaan kaskadiprosessoinnilla monenlaisia jakeita teollisuuden käyttöön. Esimerkiksi kuumavesiuutolla voidaan erottaa fenolisia yhdisteitä, kuten kondensoituja tanniineita, stilbeenejä ja flavonoideja. Näille yhdisteille on monia potentiaalisia käyttökohteita. Esimerkiksi tanniineja voidaan käyttää nahan parkitsemisessa, viininvalmistuksessa, rakennusmateriaaleissa, jäteveden puhdistuksessa flokkulantteina ja koagulantteina, liimoissa, lääkkeissä, ravintolisinä, ja kosmetiikassa. Hemiselluloosasta saadaan monenlaisia sokereita jatkojalostettavaksi biotuotteisiin ja hiilenlähteeksi fermentointiin perustuviin tuotantoprosesseihin. Uuteaineisiin perustuvat kaupalliset biokemikaalituotteet kuuluvat tuotteisiin, joilla on pieni tilavuus, mutta korkea yksikköhinta. Tulevaisuudessa biopohjaisten tuotteiden kysyntä kasvaa ja saatavuus tulee nousemaan. Bio-kemikaalien merkittävin kasvava luokka ovat teollisuuden peruskemikaalit, ns. platform-kemikaalit, joita voidaan muokata käyttötarpeen mukaan.

Asiasanat: biokemikaalit, biomassa, sivuvirrat, uuteaineet, kaskadiprosessointi, sidosaineet, maku- ja ravintoaineet, bioaktiiviset yhdisteet, pinnoitteet, alustakemikaalit

Abstract

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Bio-based value-added chemicals are chemical compounds derived from biomass that can be used for a wide range of industrial applications. They account for about 7% of the EU biobased industrial market. Bio-based industry refers to production from biomass, excluding the food and beverage industry. This report describes the different groups of chemical compounds from forest, agricultural and aquatic biomass and their applications in different product groups. The report focuses on biochemicals that can be extracted from biomass by different extraction methods and highlights studies on their suitability for different applications. The aim is to outline a future vision for the use of biochemicals by 2050.

Global megatrends such as climate change, geopolitical tensions, security of supply, loss of biodiversity, population growth will influence the potential for biomass production at regional and global level. Given limited resources, industry needs to make more efficient use of the biomass produced. The limits of the earth's carrying capacity are being reached earlier every year and therefore there is a high and growing demand for biomass-based products. Bio-based solutions offer an alternative to fossil-based products, the production of which is problematic due to greenhouse gas emissions, environmental chemicalization and the depletion of fossil reserves. When replacing fossil products with bio-based solutions, the environmental benefits must be clearly demonstrated, for example through life-cycle assessment.

Cascade processing of different biomasses produces a wide range of fractions for industrial use. For example, hot water extraction can be used to separate phenolic compounds such as condensed tannins, stilbenes and flavonoids, which have applications in leather tanning, winemaking, building materials, flocculants and coagulants, adhesives, pharmaceuticals, food supplements and cosmetics. Hemicellulose can be used to produce a wide range of sugars for further processing into bioproducts and as a carbon source for fermentation. Commercial biochemical products based on novel materials are among the products with belong to the low volume but high unite price. In the future, the high demand for bio-based products will increase the production and availability of bio-based alternatives. The most important growing category of bio-chemicals are the basic industrial chemicals, the so-called platform chemicals, which can be tailored to specific applications.

Key messages

- 1. Agricultural, forest and water-based biomasses contain valuable biochemicals. Biomass is a resource whose exploitation requires the involvement of the whole value chain, from the harvesting, storage and transport of raw materials to the processing, manufacturing and marketing of final products. Cascade utilization of biomass enhance economic and environmental viability of biochemical productions.
- 2. Biochemicals could derived from renewable resources can greatly reduce dependence on fossil-based raw materials and promote a circular economy, aligning with global climate goals. When replacing fossil solutions with bio-based alternatives, the environmental benefits must be clearly demonstrated, for example through life cycle assessment.
- 3. Regulatory support is crucial for market growth, alongside efforts to raise awareness and encourage widespread adoption of bio-based products.

Keywords: biochemicals, biomass, side streams, extractives, cascade processing, adhesives, flavourings and nutrients, bioactive compounds, coatings, platform chemicals

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1. Introduction

Riina Muilu-Mäkelä, Hanna Brännström, Pekka Saranpää, Mikko Weckroth, Juha-Matti Katajajuuri and Johanna Kohl

The circular economy **is an economic system that shifts away from the traditional "end-of-life" model by prioritizing the reduction, reuse, recycling, and recovery of materials throughout production, distribution, and consumption processes** (Kirchherr et al 2017). Circular economy strategies, referred to as R strategies, have emerged as part of the wider circular economy concept and have been developed by several researchers and organisations around the world. R-strategies can be classified under three categories: 1) smarter product use and manufacture (R0 Refuse, R1 Rethink, R2 Reduce), 2) life extension strategies (R3 Reuse, R4 Repair, R5 Refurbish, R6 Remanufacture, R7 Re-purpose), and 3) creative material application (R8 Recycle, R9 Recover). Circular economy principles and strategies have evolved over time in response to the need to reduce resource consumption and environmental impacts (Winquist et al. 2023).

Renewable materials are crucial for sustainable production and green transition. The just green transition means a shift towards economically, socially and environmentally sustainable growth and an economy that is not based on fossil fuels and overconsumption of natural resources. In the shift toward a circular bioeconomy, chemicals and materials derived from biomass play a major role (IEA Bioenergy). With a stronger emphasis on addressing climate change and implementing measures to mitigate its effects, efforts are underway to transition from the current fossil-based economy to a more socially just and acceptable, responsible and environmentally sustainable economy. Hence, circular bioeconomy is grounded in renewable energy, biomass utilization, and recycling that would enable to societies to function within planetary boundaries. By embracing circularity, economic prosperity can be achieved within the Earth's carrying capacity through the reduction of natural resource use and the development of innovative business models and nature resource governance principles.

Biobased products are defined as "the products that are derived from plants and other renewable agricultural, marine, and forestry materials and provide an alternative to conventional petroleum-derived products (other than feed, food, or fuel)" (USDA 2020). The focus of this vision paper is on biochemicals, specifically those produced through various extraction processes, derived from forest, agro and aqua biomasses, as well as side-streams from processing and underutilized biomass (Figure 1). The main groups of biomass-based chemicals include cosmetics, coatings for textiles and other materials, ingredients and additives for food and feed, pharmaceuticals and antimicrobial compounds and solutions. Some of the extractives can be used as platform chemicals that play a role as precursors for various other high value-added products. Bio-based platform chemicals, made from renewable raw materials, offer great potential for decarbonizing everyday products, allowing everything from running shoes to plastics and car parts to be made bio-based. However, the environmental impacts of new bio-based added value production systems, technologies and products should be assessed holistically, with scientific evaluation to demonstrate potential environmental benefits of replacing fossil-based products with new bio-based value-added products.



Figure 1. Forestry, agricultural and aquatic main and side streams contain value-added chemicals that can be classified according to their chemistry and are suitable as feedstock for a wide range of product applications.

Despite the policy frameworks promoting both bio- and circular economies, significant systemic barriers and entrenched practices continue to hinder the transition toward sustainability. These include rigid regulatory frameworks, market lock-ins, and infrastructure dependencies that continue to favour fossil-based industries. Additionally, the scaling of bio-based alternatives faces challenges such as complex supply chains, high initial costs, and limited consumer awareness or acceptance of new sustainable solutions. Furthermore, the targeted sustainability improvements need to be demonstrated.

Overcoming these barriers requires innovative approaches, collaborative networks and interdisciplinary research and development, and systemic change that transcends traditional industry silos. The upcoming vision chapter will explore these opportunities, outlining strategic pathways to address these obstacles and accelerate the adoption of bio-based chemicals and processes.

Cascade processing of biomass for applications

Cascading is the efficient use of resources, where processing and production wastes and materials are used and recycled to increase the overall availability of biomass in a given system. In the cascading biorefinery concept of lignocellulosic biomass, for example, various biomass components, i.e., cellulose, hemicellulose, lignin and extractives are recovered by consecutive unit processes (Jyske et al. 2023a) (Figure 2). The cascade use of biomass increases the cost-effectiveness of processing and the value of individual fractions by separating multiple valuable fractions from the initial biomass. Lignocellulosics can be processed using mechanical, chemical, biochemical and/or thermochemical conversion methods (Alén 2011). Integration of these unit processes enables the production of a wide range of different bio-based products. The process of extracting valuable compounds from biomass involves many stages, starting with the material pretreatment for extraction, and often ending up with the enrichment of target compounds, removal of impurities and chemical modification of the extract after recovery (Varila et al. 2020). Extractives contain a wide variety of different compounds with different chemical structures and, thus versatile bioactive properties. This in turn provides potential functionalities for various types of speciality and platform chemicals.



Figure 2. Cascade processing of (lignocellulosic) biomass enhance the profitability of value chemical fractions.

Similarly, proteins, peptides, phenolic compounds and polyshaccarhides can be recovered from the side streams of the food industries by utilizing different unit processes. These valuable compounds can be applied in food and feed products as nutritional and techno- and bio-functional ingredients as well as in other bioproducts, like cosmetics. The incredients can improve the structure and sensory properties as well as enhance the nutritional composition and health promoting properties of the end products.

2. Vision and challenges of the value-added biochemicals

Riina Muilu-Mäkelä, Hanna Brännström, Mikko Weckroth, Johanna Routa, Eila Järvenpää, Sari Mäkinen, Janne Saarikko, Martin Diaz, Maryam Ghalibaf, Pertti Marnila and Johanna Kohl

In our vision for value-added biochemicals, bio-based products will be widely available to industry and consumers by 2050. Fossil-based and non-renewable raw materials have been replaced by renewable alternatives in various industries. Raw materials and by-products from agriculture, forestry and blue bioeconomy are widely used in high value products.

To achieve this ultimate vision, several technological, social, environmental and economic challenges must be overcome. A key driver for the development of value-added biochemicals is the need to reduce greenhouse gas emissions by shifting from fossil-based materials to bio-based alternatives. Population growth, over-exploitation of natural resources and pollution of environment are drivers for the green transition and the efficient use of biomass within the limits of the planetary capacity.

The development of industrial ecosystems will require systemic changes, better logistics, new industrial platforms and data economy solutions to reduce certain barriers between different actors in the value chain and increase process efficiency. In industrial ecosystems, industrial partners form a chain or network in which one party exploits the by-products of the other. Logistically well-placed actors improve the profitability of production. Industrial platforms can take the form of for example eco-parks and virtual communities where some of the production challenges are solved through collaboration. In the near future, new bio-based innovations will be developed, and the market potential of different biomass fractions will be increased, and awareness, acceptance and empowerment of customers and end-users will be improved. Logistics and timing are major challenges for profitable cascade use of biomass. However, potentially, electric vehicles and consequent lower energy costs in transport will increase the future viability of biomass use. The availability of raw materials, the complexity of processing techniques and logistics determine the overall feasibility of the final value-added product. A variety of digital tools will help to improve and streamline future bioeconomy processes. Luke's Biomass Atlas is an example of a facilitating tool to assess the availability of raw materials in Finland (https://biomassa-atlas.luke.fi/).

The content of extractives in biomass is often relatively low, which means that the volume of biomass required for industrial production is high. On the other hand, eg., bark biomass is abundantly available and contains a lot of potential compounds such as phenols, tannins and terpenes for biochemical applications. Oil plant residues and fish side streams contain valuable proteins and fatty acids. However, the side streams have competing uses, such as energy production, which affects the price at which the biochemicals are worth processing from biomass. In other words, the economic return on the biochemical must be high enough to make it economically viable and exceed the revenue from competing uses. Typically, biochemicals are not considered as 'bulk' products. Their production costs could be lowered through efficient cascade processing, where all side streams and residues are fully utilized and converted into value-added products.

Research is needed to generate new innovations and knowledge to use the compounds in viable ways. Solutions include the development of new pre-treatment and process technologies, the integration of different industries and the cross-use of raw materials. Artificial intelligence (AI) has been applied in recent decades to address challenges related to feedstock variability, conversion economics, and supply chain reliability. In the future, various AI techniques will be further developed and increasingly used to facilitate the prediction of biomass properties, of biomass conversion process performance, and supply chain modelling and optimisation.

Regulations, laws and codes are often one of the barriers to market access, but the laws also guide us towards a fossil-free future. There are several laws that regulate the production, import, distribution, and use of chemicals in different contexts. EU regulations are directly enforceable in Finland and binding for Finnish businesses. The regulations are designed to ensure that chemicals are used safely and sustainably, minimizing the impact on environmental and human health. For example, REACH (Registration, Evaluation, Authorisation and Restriction of chemicals) is the EU regulation to protect health and environment from the risks of chemicals and requires companies to register produced or imported chemicals. CLP (Classification, Labelling and Packaging) regulation ensures that the hazards of chemicals are properly classified and labeled through the EU. BPR (Biocidal product regulation) governs biocidal products against harmful organisms.

Furthermore, regulations and agreements are one way of steering industrial production and markets in a safer and more sustainable direction. The EU's Circular Economy Action Plan of EU (CEAP) is one of the key building blocks of the Green Deal and the following Clean Industrial Deal, Europe's new agenda for sustainable growth. It is also a prerequisite for achieving the EU's 2050 climate neutrality target and halting biodiversity loss. The CEAP targets how products are designed, promote circular economy processes, encourages sustainable consumption, and aims to ensure that waste is prevented, and the resources used are kept in the economy for as long as possible. The value-added chemicals from main and side-streams provide solutions in sectors where the potential for circularity is high. As a result, there are growing markets for sustainable products in a variety of industries and funding for research and innovation activities.

2.1. Markets

The bio-based industry is predicted to show a growing market trend in the future. The biobased economy or bioeconomy is economic activity that uses biotechnology and biomass to produce goods, services or energy. The terms bio-based economy and bioeconomy are both widely used. The **bioeconomy** covers both the bio-based economy and the production and use of food and feed. Instead, the **bio-based economy**, considers the production of nonfood products from produced biomass.

A report published by European Bioeconomy Consortium (BIC) states that the bioeconomy, which covers the entire EU bioeconomy, has grown from around €1.75 trillion to over €2.35 trillion between 2014 and 2021 (Porc et al. 2024). About half of the 2.3 trillion Euro in 2021 came from the food and beverage sector (47%), 1.6% from tobacco products and 19% of the turnover is generated by the primary sectors (agriculture and forestry) (Fig.3a). The rest is attributed to the so-called bio-based industries, having the total turnover around €725 billion in 2021. The Bio-based industry includes paper and paper products (25%) and forest-based industries (24%) turnover together was 352 billion, chemicals and plastics (€55 billion (7%)),

pharmaceuticals (158 billion, 18%), textiles and textile products (65 billion, 9%), biofuels and bioenergy (€122 billion (17%)) (Fig 3b).



Figure 3. Turnover of the bioeconomy in the EU-27 in 2021 if food and feed products are a) included in the categories or b) excluded from the categories to show the turnover of biobased economy modified from Porc et al. 2024.

Using categories that mimic the BIC report's bio-based economy categories in figure 3b, the size of the global bio-based economy market is projected to grow significantly by 2050 if growth remains stable (Figure 4). The estimates shown in Figure 4 are calculated using 2023 market size values and an estimated compound annual growth rate % (CAGR %) ranging from 4–26% (Fortune Business Insights 2024a, Fortune Business Insights2024b, Mordor Intelligence 2024a, Research and Markets 2024a, 2024b, Grand View Research 2024a, Verified Market Reports 2024).



Figure 4. Development of the global bio-based economy markets using current market sizes and estimated CAGR % (Fortune Business Insights 2024a, Fortune Business Insights2024b, Research and Markets 2024a, 2024b, Grand View Research 2024a, Verified Market Reports 2024)

Biobased chemicals in Figure 4 (under the category of biochemicals and plastics) refer to chemicals derived from biomass or biological sources such as sugar, cellulosic raw materials and biodegradable waste. The market for these bio-based chemicals is expected to grow in various industrial sectors and the market is divided into the following categories: platform chemicals, plastic polymers, paints, coatings, inks and dyes, surfactants, cosmetics and personal care, adhesives, man-made fibres and biocides, with platform chemicals expected to be the fastest growing segment of the market. High demand for bio-based fertilizers, biocides, and pesticides due to the biodegradability of the chemicals is driving the growth of the biochemicals market. Moreover, demand for bio-based surfactants is projected to grow in applications such as personal care, textiles, home care, industrial and institutional cleaning. The global bio-based chemicals market is 73 billion in 2023 and is projected to grow at 9.6% CAGR (Fortune Business Insights 2024a, https://www.fortunebusinessinsights.com/bio-based-chemicals-market-106586). Instead, biobased pharmaceuticals, are a complex medicines extracted or semi synthesized from biological sources by biotechnological methods. The biobased pharmaceuticals market includes different product types such as monoclonal antibodies, recombinant growth factors, purified proteins, recombinant proteins, recombinant hormones, vaccines, recombinant enzymes, cell and gene therapies, cytokines, interferons and interleukins, targeted for various therapeutic applications. Many phenolic compounds, peptides and proteins contain properties that are relevant for pharmaceutical applications. Biopharmaceuticals market size was valued at 572 billion in 2023 with 8.4%

CAGR (Fortune Business Insights 2024b, <u>https://www.fortunebusinessinsights.com/biophar-maceuticals-market-106928</u>)

If market developments remain stable and in line with forecasts, it is possible that the turnover of the bioeconomy market will increase tenfold by 2050. However, this development will be influenced by many unforeseen factors, such as new innovations and the ability of societies to produce new products in an economically viable way. The availability of raw materials is probably one of the most important factors influencing the development of bioeconomy markets. If the demand for certain valuable components increases, the price of raw materials will also rise, with a direct impact on the price of final products and the speed of market development. Land use and regional and local specificities are important issues for biomass production. In addition, different societal interests and conflicts influence the development of the market.

Bio-based paper and paper products is a growing market segment worldwide (1059 billion in 2023 with CAGR 7.2%) (Research and Markets 2024a, https://www.researchandmarkets.com/reports/5939789/paper-products-global-market-report). This growth is driven by increased environmental awareness and demand for sustainable products. Main types of paper products are converted paper products, unfinished paper and pulp mills. Moreover, policies to reduce carbon emissions and the energy transition are strongly influencing the growing market for **biofuels** worldwide. Solid biofuels, such as wood pellets and agricultural waste, are mainly used for electricity and heating. Liquid biofuels, such as ethanol and biodiesel, are the most widely used, especially in transport. Gaseous biofuels, such as biogas and biomethane, are a sustainable source of energy and help in waste management (100 billion in 2023 with CAGR 11%) (Grand View Research 2024a, https://www.grandviewresearch.com/horizon/outlook/biofuels-market-size/global). Very often, biomass containing value-added chemicals and potential for upstream solutions is used only for energy production. The upstream product production needs to be more profitable than energy production alone, which is often not possible due to the heavy processing and the lack of advanced industrial systems to support cascade processing. Systems should be evolved so that only the residues from the various stages of cascade processing are ultimately used for energy production and biofuels.

In the global textile industry, the market for **bio-based fibers** is a segment that focuses on fibers made from renewable biological resources, mainly plant or animal-based materials. Bio-based fibers are derived from organic materials that can be naturally replenished through agricultural or forestry practices. The market size of bio-based fibers is now 41 billion but it is expected to grow with CAGR 26% due to demand for sustainable products, raising environmental concerns and need to substitute fossil-based materials (Verified Market Reports 2024, https://www.verifiedmarketreports.com/product/bio-based-fibre-market/)

Moreover,-the **wood products** market (788 billion in 2023, with CAGR 7,3%) is segmented by type into finished wood products, wood processing and manufactured wood materials, the finished wood products market being the largest segment of wood products (Research and Markets 2024b, <u>https://www.researchandmarkets.com/report/wood-products</u>.)The report of the Finnish forest bioeconomy science panel 1/2024 estimates that Finland has the potential to multiply forest-based value-added and the forest-based industry, medical solutions, carbon from lignin production, lignin products in general, cellulose and packaging products with barrier layers, and fibers are estimated to be the main value-adders in the near future

(Österberg et al 2024). For example, 20–40% of the lignin currently produced could be used in value-added products for different markets, with a value-added of €670–1,500 million (Österberg et al. 2024)). In the valuation of forest biomass, the value of biochemicals is not expected to be very significant compared to other products like biofuels or materials. Only ca. 5% of the added value is assumed to be the potential increase in the value-added of chemicals if structural chemicals (lignin, cellulose) are excluded. However, for instance, the volumetric price of some medicinal compounds can be very high. For example, bark biomass and many agricultural biomasses are rich in phenolic compounds with various health-promoting properties and potential for high value products. The seek for sustainable and renewable alternatives to fossil-based chemicals enhance the biochemical markets.

The food and beverages (the main bioeconomy sector) are excluded from the classification of bio-based economy industry categories in Figure 4. However, biomasses, like many by-products of food production, still contain valuable value-added products such as proteins, carbohydrates and bioactive compounds also as ingredients for the food, drink and feed industries. Protein products are one of the opportunities for growth in the food sector. Global protein ingredients market is expanding dramatically due to the growth of global population and consumers increasing awareness of healthy diet. The global protein ingredients market size was USD 79.28 billion in 2023, expanding at a CAGR of 5.7% from 2024 to 2034 (Predence research 2024, https://www.precedenceresearch.com/protein-ingredients-market). New value chains and increasing the processing capacity are seen important for adding the value in Finnish food sector (Jansik et al 2024). The side streams can be refined into various ingredients including e.g. proteins, peptides and polysaccharides and also, they can be utilized as nutrient source for protein production in cellular agriculture. Bioactive peptides are one specific segment of protein ingredients. Increasing prevalence of lifestyle related diseases along with technological advancements in peptide extraction accelerate the global bioactive peptides market growth (5 billion in 2022 with CAGR 10%) (Data Bridge Market research 2024).

2.2. Critical steps in the raw material supply chain

New kind of supply chains need to be developed to guarantee the delivery of fresh raw materials for processing. In the forest industry, the supply chains of wood raw materials are complex and the operating environment is constantly changing. In addition, the seasonality of harvesting and the balancing of different transport and storage solutions to meet the constant demand for wood throughout the year requires well-functioning logistics management. Traditional forest supply chains are often slow when fresh material is needed, so new demand is being placed on supply chains. This requires new thinking and optimisation of logistics. The content of forest biomass extractives declines rapidly, starting to decrease immediately after tree felling, with some compounds disappearing completely during storage. The storage method and season have a significant impact on the loss of these components. In order to develop viable production chain for fresh woody biomass, knowledge of the raw material quality is crucial.

In summer conditions, the supply chain needs to be fast to get the biomass fresh for processing. If bark is the raw material required, the wood should be transported to the biorefinery as a whole and the bark should be removed just before processing. In winter conditions there is a little more time for that process. Storage is a necessary part of the biomass supply chain. During storage, the goal can be to maintain quality, and in some cases, storage can improve the desired quality characteristic. Understanding the natural properties of biomasses and the changes that occur during storage allows us to optimise the quality of biomass during processing (Wendt et al. 2020, Koppejan et al. 2013).

The same applies to agricultural biomass which must be delivered fresh and quickly to the biorefinery for processing in order to obtain value-added ingredients. The length of the logistic chains for food raw materials from the farm, field or greenhouse to fresh food wholesaler or food processing plant is variable and needs to be optimised. Most likely the residues will end up mainly in biogas or composting processes, including nutrient recycling.

Harvest residues of cereals and oil seeds remain on the fields and have an impact on soil carbon content. Residues and side streams generated at food processing sites vary, as their annual volumes depend entirely on the quality and quantity of the food raw material. In a few cases industrial processing lines are built to collect food grade side streams separately from the non-food grade side streams enabling the use of further processing for food and feed ingredients. The harvest residues (e.g. remnants from fruit, berry and vegetable production) and low-quality industrial side streams are usually used for biogas production, heating and processed further as soils amendments.

The operating environment of the Circular bioeconomy is highly decentralised. In this environment solutions that are flexible and suitable for use by small and dispersed operators need to be used. The implementation of traceability requires that items or products can be identified and accompanied by information that can be shared. In order to get the right raw materials to biorefineries in time and to keep the production costs of the whole value chain at a profitable level, biomass logistics requires a wide range of expertise and cooperation at all stages of the chain.

2.3. Potential of biomass extracts for various applications

This value-added biochemicals vision paper presents the utility of different groups of compounds from different biomass sources in different value-added market categories such as functional coatings, cosmetics, detergents, biostimulants, biocides, food and feed ingredients (proteins and bioactive compounds), adhesives and basic industrial chemicals.

Many different solutions exploit the antimicrobial properties of compounds and extracts. In the next chapter (Chapter 3), the antimicrobial properties of biomass fractions and their use in different product groups such as cosmetics, detergents and preservatives are assessed. Chapter 4 focuses on functional coatings and bio-based colours. Lignin, suberin and pigments can be used, for example, as functional coatings or briocoleurs in packaging materials, textiles and wood-based materials. Chapter 5 summarizes the plant biomass containing secondary metabolites originally produced as defence molecules. Therefore, biomass extracts have potential as biostimulants and bioprotectants to replace synthetic pesticides and biocides that are harmful to ecosystems. Chapter 6 deals with biomass polymers such as polysaccharides, lipids and proteins used in food and hybrid food solutions, and Chapter 7 focuses on biomass-derived feed additives. Bioactive compounds also have antioxidant and nutritional properties that can be enriched from food industry waste and non-food by-products and returned to food and feed products. In addition, biomass processing is not always efficient due to complex

structures of biomass and compounds. The extraction and development of some simple chemicals can improve the profitability and provide a source of platform chemicals for industrial purposes (chapter 8). Hemicellulose and carbohydrates serve as basic chemicals that can be processed for various industrial needs (chapter 9). Biomass extracts also have the potential to be used for flocculation or coagulation of harmful substances in wastewater, as summarized in Chapter 10. The chapter (11) brings together the most potential groups of compounds for bio-based chemicals extracted from biomass and summarises Luke's research in this area. The last chapter is a framework chapter and summarises the key messages of this vision paper.

As an interesting annex, the case study on a bark biorefinery is presented at the end of this publication. The bark biorefinery case study presents techno-economic analyses to assess the viability of biorefining wood bark biomass. The economic feasibility of using a given biomass is influenced by many factors. Bark is a large biomass rich in valuable chemicals and the chemical composition of bark is well known. However, it is typically used for energy production in the paper industry, even though it contains a lot of water. Societal and process changes are needed to make the use of bark in higher value-added products more attractive to industry in the future.

3. Antimicrobial properties

Riikka Linnakoski, Jenni Tienaho, Petri Kilpeläinen and Jyrki Ollikainen

Many applications of biomass extracts are based on the antimicrobial properties of the extracts and extracted compounds. Novel antimicrobials¹ are urgently needed to combat both emerging pathogenic microorganisms and existing organisms developing resistance against current antimicrobials. Research at Luke has revealed several natural antimicrobial substances of plant and fungal origin that can be produced by extraction methods and microbial fermenting (Linnakoski et al. 2018, Korpinen et al. 2021, Tienaho et al. 2021, Jyske et al. 2023b), providing innovations and research findings of commercial potential (Table 1). In future, these substances can serve as high value-added biochemicals and other functional solutions in various applications (e.g. biocides, cosmetics, pet welfare, coatings, packaging) on biorefinery approaches, and some can potentially be used to replace the currently used toxic substances. However, these substances are complex natural mixtures, which pose challenges in both scientific and regulatory aspects. Antimicrobials are classified under biocide legislation.

	Substance	IPR status					
Solution	Patent	Patent pending	Innovation disclosure	Research phase	Patent		
Natural Antivirals	Fungal ferment	Х		Х			
Fiber networks	Condensed tannins, tannic acid				Х		

Table 1. Luke's antimicrobial solutions IPR status or commercial potential

Antimicrobials are substance that can protect humans, animals, and plants by either killing these microorganisms or preventing their virulence or ability to cause infection. A well-known type of antimicrobial substance in medical products is antibiotics. Antimicrobial resistance (AMR) occurs when microorganisms transform and mutate over time and no longer respond to the antimicrobial products designed to target them. WHO has declared AMR as one of the top global public health threats facing humanity (WHO 2021). In recent years, also new diseases such as COVID-19 have emerged. With the human population continually increasing, the likelihood of encountering novel zoonotic microbes remains high.

Biocides are antimicrobial agents that are used to control infections and contamination in industry and health care environments. Commonly used biocides are quarternary ammonium compounds (QACs), polyhexamethylene biguanides (PHMB), sodium hypochlorite, hypochlorous acid, hydrogen peroxide and ozone. The mode of action of these compounds varies from destabilizing cell membranes to oxidative damage to bacterial cells. Some of these compounds such as QACs or chlorine releasing agents are used against viruses, for instance coronaviruses (Dev Kumar et al. 2020). Inappropriate use of these compounds could by selective pressure, lead to antimicrobial resistance. Therefore, there is a need to find alternative

¹ Antimicrobials: substances that act against microorganisms, including antibacterial, antiviral, antifungal, antiprotozoal, and antiparasitic agents. While all antibiotics are antimicrobial, all antimicrobials cannot be considered antibiotics.

solutions. Plants produce polyphenols as secondary metabolites (Quideau et al. 2011). For example, flavonoids possess antioxidant, anti-inflammatory, antiallergic, anticancer, antiviral and antifungal properties (Górniak et al. 2019). Compounds can be extracted from the plants and utilized against microbes. The research finding at Luke is to use hot water extracts of willow against enveloped and non-enveloped viruses (Reshamwala et al. 2023).

Currently, **cosmetics** cannot claim antimicrobial properties. However, in cosmetics industry there is growing interest in natural products to replace the currently used synthetic compounds that have been used as preservatives and stabilizers with antimicrobial properties (Rybczýnska-Tkaczyk et al. 2023). Antimicrobial agents are needed in high-water-content cosmetics to increase durability and safety (Neza & Centini 2016). Synthetic preservative compounds include parabens, which can cause side effects such as skin allergies and hormone disruption (Mitra et al. 2021), and via wastewaters pollute freshwater and disrupt aquatic ecosystems (Lee et al. 2020). Considering the commercial potential of natural products in cosmetics preservative use, the amounts in the product can be minimal. For instance, ECHA (European Chemical Agency) has established that preservatives are typically limited to concentrations of less than 1%. Therefore, the multifunctionality of the natural product is needed for the improved revenues. In addition to antimicrobial properties, many natural products do have also e.g. antioxidant and anti-inflammatory properties.

In the EU legislation, a product falls into a single category, while globally (e.g. in the USA), a product like antidandruff shampoo can belong to both cosmetic and drug categories due to its dual intended uses: hair cleaning (cosmetic) and dandruff treatment (drug) (Ferreira et al. 2022). In 2050 EU legislation should recognize the dual use of the ingredient. Also, meeting the regulatory needs should be lower in terms of cost and time.

Since natural products are typically complex mixtures, their active substances or synergy effects are difficult to define. While the EC Directive on **medical products** is oriented toward single or combinations of molecules, the directive for **medical devices made of substances** applies to complex substances (Bilia et al. 2021). Examples of products or equipment designed for medical purposes that benefit from the application of natural antimicrobials include wound dressings, diapers, disinfectants, surfactants (surface-active agents), soaps, and detergents. A few domestic antimicrobial medical device opportunities include resin and fungal ferments and their derivatives (e.g. terpenes and phenolics).

To replace alkyd (polyester) **coatings**, manufacturers have introduced paints with natural oils like linseed and earth pigments, such as Uula products (Uula 2023). These "traditional paints" lack biocides, posing a higher risk of molding. The entire paint industry is now exploring less harmful preservatives to replace biocides, which creates opportunities in the biocide replacement markets in the next decades.

Pet welfare products can utilize antimicrobial, preservative, and other claims of natural ingredient in fur and skin care products. E.g. Botaniqa fur care products have replaced colorants, silicon, parabens and alcohol with natural oils, seeds, and berries (Botaniqa 2023). AniVox pets' ear cleaner is without alcohol and perfumes but contains ingredients from coniferous resin (AniVox 2023). The household expenditures for pet care is expected to increase by 2030 by 5% (Grand View Research 2022)

In summary, bringing new natural product innovations onto the market (in Europe) can pose several challenges. Regulatory compliance is a significant hurdle. EU regulations require thorough testing and documentation to ensure the safety and efficacy of products. Meeting these standards can be time-consuming and costly and require special expertise and testing infrastructure. Natural products are typically complex molecular mixtures, which bioactivity can be due to the synergistic and simultaneous action of several compounds. When the bioactive component is unknown, it may be difficult or impossible to meet the regulatory requirements and obtain necessary approvals.

Development of standard and safety tests are needed. There is currently a lack of pathway to pass the regulations for natural products and bring this type of ingredients/products onto the market, which are complex mixtures of compounds. To fasten the process and improve service, more customer-centric service is needed from the authorities. A holistic legislation in Finland and EU is needed, e.g. testing choices for the natural product might exclude other applications and market opportunities. The high price for passing the safety tests and regulations prevents small and medium-sized enterprises from exporting valuable chemicals to the market.

4. Biobased and functional surface treatments

Pekka Saranpää, Maryam Ghalibaf, Jaakko Hiidenhovi, Risto Korpinen, Anuj Kumar and Susan Kunnas

Functional coatings and biodyes for wood, packaging materials and textiles.

Bio-based paints and coatings still play a rather small role in the coatings business. The current market share is estimated at around 5% in sales. Most of this is also likely to come from long-established natural raw materials. However, the use of biomass for producing materials has increased overall by 5.6% from 2010 to 2015 and within this category, the bio-based chemical sectors have shown a significant increase (almost 50%). The total value of global packaging market was USD 850 billion (2016), global paints and coatings market was USD 146 billion (2019), and global adhesives and sealants market was USD 52 billion (2017). All of the markets are expecting strong growth and are trending towards bio-based solutions. Hopefully we see a greener coatings industry rather sooner than later (https://www.european-coatings.com/news/markets-companies/bio_based-coatings-overview-increasing-activities/).



Figure 5. Schematic overview of bio-based polymers' differences modified from Gigante et al. 2021. This vision is based on polymers derived from biomass: mainly polysaccharides, lipids and proteins.

Lignin based coatings

Being economically attractive, lignin, predominantly as lignosulfonates, is used as a binding and dispersing agent. It can also replace synthetic phenolic compounds in phenolic resins and epoxides, as well as in polyolefin systems. In coating applications, lignins have been used to enhance the poor barrier properties of fiber-based packaging materials that are usually laminated with aluminum or petroleum-based polymers (Alakurtti 2013). Due to the excellent protective properties, lignin can also be used as low cost and active substances in the coating industry for various substrates. Lignin and its derivatives exhibit the appropriate chemical properties for application in coatings, thanks to its hydrophobic nature, particle size, and the ability to form stable mixtures. Numerous studies have also demonstrated the remarkable properties of lignin as an anticorrosive in coatings for steel (stainless steel, iron-phosphated steel) and in different test mediums (physiological solutions and 5% NaCl) (Carlos de Haro et al. 2019). Lignin monomers and non-modified lignin have been demonstrated to have immense potential as corrosion inhibitors when dissolved in acidic, basic, and neutral media.

Suberin as a natural biopolyester

Suberin is a readily available under-utilised material. In the outer bark of birch (Betula sp.) the suberin content is up to 40-50% (Rižikovs et al. 2014). In 2019, the Finnish forest industry alone consumed approximately 15.1 million m3 hardwood logs (13.8 million m³ pulping industry and 1.3 million m³ mechanical forest industry), mainly birch (stat.luke.fi). Theoretically, the amount of oven dry outer bark available is over 160 000 tons and the amount of suberin available is 48 000 tons per year.

Suberin fatty acid mixture isolated from birch outer bark is a natural binder and barrier material and thus will provide bio-based solution in coatings where synthetic polymers are dominating. Packaging represents an excellent opportunity for reducing fossil raw materials and increasing sustainability as it is one of the biggest sectors that uses fossil-based coatings. Altogether, the packaging sector uses over 250 million tonnes of materials annually. Although the recycling rate of fiber-based packaging is excellent today – for paper and board in the EU-28 around 85% (Packaging Europe 2019), it is important to ensure recycling without too much losing the fiber properties. Cascade use is fundamental for bio-based products and applications. New functionalities for fiber-based packaging are created by barriers and coatings which may improve recyclability and biodegradability.

Suberin and lignin based on aqueous dispersions may provide also antimicrobial (Mingjie Chen et al. 2023) and antioxidative functionalities and postpone food spoilage. Dispersion coating trials have been successful, but challenges are still related to variation of raw material quality and testing of biodegradability, safety and recyclability. Suberin extraction from birch outer bark has been optimized by Luke in several strategic and joint projects (PolyCoat, Opti-Bark and SUSBINCO) and natural biopolyester based dispersions and coatings for paper and paper board will be further developed and scaled-up with research and industry partners (COCOBIN, <u>https://clicinnovation.fi/project/cocobin/</u>). Raw material availability and the environmental impact (LCA and safety issues) of alternative paper and textile coatings are also studied.

Wood Coating

As a hydrophilic, hygroscopic, porous, and fibrous material, wood is especially vulnerable to water sorption, because water penetrates rapidly into the wood structure causing swelling and eventually a loss of mechanical strength as well as providing conditions for biological degradation, UV-degradation of wood (Kumar et al. 2017, Petrič 2013). Several wood modification methods have been developed to improve the overall chemical and physical properties of the material. Wood modification can be divided into two main categories: active and passive wood modification. Active modification includes chemical, thermal, and enzymatic modifications of the wood cell wall and surface, whereas passive modification consists mainly of impregnation of the pores and lumen space of the cell wall with chemicals (Hill 2007, Kumar et al. 2021b). Wood surface coating is one of the active chemical modification techniques to improve the service life of wood and wood products, and various synthetic fossil derived polymeric coatings have been investigated for this purpose (Petrič 2013, Petrič & Oven 2015). However, in recent years, polymers and monomers derived from bio-based materials have attracted enormous interest due to the dwindling of non-renewable feedstock such as petrochemicals (Rajput et al. 2014, Kumar et al. 2015). Suberin fatty acid hydrolysate (SFA) extracted from the outer bark of silver birch (Betula pendula Roth.) has been studied also for

coating of solid wood (PolyCoat) (Kumar et al. 2022). Various other biobased extracts from ongoing projects and RDI of Luke, such as biowaxes could be potential biomaterial for wood coating application. Biopolyols from wood and bark liquefaction also had a potential in wood coatings. There are many several other biopolymers such as hemicellulose, tannin, and lignin needs to explore in wood coatings application.

Fish and animal side stream -based coating development

Gelatine has often been used as a suitable starting material for the production of biodegradable or edible films suitable for food packaging. It can also be used as an adhesive or coating, for example with pills and papers. Gelatine is derived from collagen, the most abundant protein in mammals (25-35% of total protein), which is present in animal connective tissues and thereby, commonly in meat- and fish sector by-products. Gelatine can be extracted for example by hot water extraction. Traditionally, gelatine has been isolated from pig and bovine skin and bones. Recently, there has been a significant increase in interest in the use of fish gelatine, due in part to various animal diseases such as mad cow disease. In addition, there are no religious restrictions on the use of fish gelatine. Fish gelatine can be obtained from marine and freshwater fish and from by-products of fish processing - skin, bones, fins and scales (Välimaa et al. 2019).

In Luke, fish gelatine from rainbow trout skin is used as the main component of film-forming preparations. The influence of various additives such as plasticisers, cross-linkers and various forest-based compounds (waxes and tannins) on the techno-functional properties of films has been and is currently studied in several projects (RELOVED, Fish4Func, Blue Products 3.0, PlastLife).

Textile treatments and biocolours

Textile industry is one of the major sources of emissions globally. Clothing production has increased but the service life of clothing has shortened. Textile materials and final products are partly manufactured outside the EU area. Due to the long transport distances and to improve the feel, performance and the look of textile materials, textiles are treated with anti-mold agents, pesticides and different kind of finishing agents. Most of these chemicals used in textiles are harmful or even toxic to humans and nature (Table 2) (ladaresta et al. 2018, Koniecki et al. 2011, KEMI-Swedish Chemical Agency 2014). In addition, textile dyes have a significant environmental impact from production to disposal. First, textile dying is a water and energy intensive process, and secondly, many textile dyes are hazardous chemicals to textile workers and consumers (Chequer et al. 2013, Lellis et al. 2019). Both the textile dye and textile finishing agents bioaccumulate in the environment causing water and soil contamination (Carlos de Haro et al. 2019).

Climate neutrality goals and EU legislation (European Commission 2021; Council of the European Union 2021) combined with the growing interest of consumers and competitiveness on the market, have led the textile industry to take steps towards environmentally friendly, safe and sustainable materials and chemicals. Hence, in recent years, the study of the properties and applications of bio-based alternatives and green chemistry methods has therefore grown strongly (Hermens et al. 2020, Ferreira-Filipe et al. 2021).

Chemicals		Flame retardants	PFAS	Lead	Chro- mium	Phtha- lates	Chlorine bleach	Azo dyes	VOCs
Impact categories	Probable carcinogens	Y	ΧY	Y	Y	Y	ΧY	Υ	Y
	Skin irritants	Х	Х	Y	Y	Х	ΧY	Y	Y
	Hormone disruptors	Y	Y	Y	Y	Y	Y	Y	Y
	Environmental degra- dation (water pollution)	ХΥ	ΧY	Y	Y	ХΥ	Y	Y	Y

Table 2. An example of chemicals used in clothing (Hill 2007).

X = Short-term or acute exposure can lead to health impacts

Y = Prolonged or extensive exposure can lead to health impacts

The exploration of biomimicry or nature-inspired innovations is one approach to mimicking interesting properties from nature in textiles (Coppens et al. 2021). For example plants defend themselves against insects and diseases by using their secondary metabolism products, e.g., essential oils and waxes (Jan et al. 2021, Croteau et al. 2015, Zwenger & Basu 2018). They are therefore commonly used in natural biocides, insect repellents, perfumes, cosmetics and medicine (Franz & Novak 2010, Pandey et al. 2017). Our interest in Future Bio-Arctic Design I & II projects (ERDF 2018-2021, EU React 2021-2023) was in sustainably utilizing the protective properties of plants and substituting harmful chemicals, in textiles or cosmetotextiles for instance, with natural compounds so that their studied properties define the subsequent applications. Especially Angelica (Angelica archangelica L.) and Marsh Labrador Tea (Rhododendron tomentosum Harmaja) proved to be very applicable plant materials to the laboratory scale CO₂ extractions and according to the results, the extracts showed a broad spectrum of antimicrobial activities against the selected microbes (Korpinen et al. 2021). These extracts were microencapsulated with chitosan using the coacervation method, and the microcapsules were impregnated onto the linen- and cotton-based jacquard fabrics using citric acid as a cross-linker to form covalent bonding between the chitosan microcapsule shell and cellulose textile material. The results indicated that the antimicrobial activity of the extracts retains in the textiles during the microencapsulation treatment and the textiles were antibacterial after six cycles of standard domestic washing test (Kunnas et al. 2023). The research results were put into practice by producing five product prototypes with cooperation of Natural Resources Institute Finland (Luke), Department of Art & Design at University of Lapland and Lapland University of Applied Sciences (Lapland UAS) and the network of companies (https://www.ulapland.fi/loader.aspx?id=05d00e26-88f7-433f-8a24-041c4bd20119; https://pohjoisentekijat.fi/2023/10/03/luontoalya-tekstiileihin-kohti-alykkaita-ja-ekologisiaratkaisuja/).

Since the production processes of new innovations and smart textile prototypes demand an added-value natural raw material production in cooperation of networks of different fields, F.BAD II project modelled the whole production process and network and investigated the requirements for the added-value production, legislation frames and preliminary environmental impacts of Marsh Labrador Tea and Angelica. The results show the strong needs of the companies for upskilling as far as green chemistry, drying, extraction and separation technologies are concerned. F.BAD II project results indicated a significant impact of the

drying and extraction technology choice on the carbon footprint of the production process. In addition,

The research of utilizing the oil and wax extracts of for example, conifer needles, berry production residues, caraway and coriander are alternative raw materials that exist in large or emerging quantities in Finland and other Nordic countries will be continued in Business Finland Co-innovation project "Bioproducts from nature – High value-added products from forests and agricultural side streams (BIO4P)" (2023–2026). This project will build an industryacademy -ecosystem for establishing value chains and businesses for these domestic extractive-rich raw materials. Essential oils, phenolics, and waxes that can be extracted from the raw materials above have application potential in various sectors, such as cosmetics, medical, healthcare, food, packaging, rubber and tire manufacturing, construction, coating, paper, and textile industries. In Finland, we have potential natural resources for both domestic wax and essential oil production, but we do not have an existing business ecosystem to commercially exploit this potential. In the BIO4P project, Luke envisions a business ecosystem with a high potential in the Finnish industries (https://www.luke.fi/fi/uutiset/kuusenneulasista-jamarjoista-luonnonvahoja-kosmetiikkaan-sivuvirtojen-arvoaineista-korkean-jalostusasteentuotteita).

Sustainable solutions can be produced by valorizing biopolymers obtained from woody biomasses and forestry by-products by green chemistry. Plant- and woody biomass- based dyes have the potential to replace synthetic dyes in the textile industry. However, to achieve this, it is necessary to overcome several challenges. These challenges include limited color selection, weak and moderate color fastness, low extraction efficiency, high costs, and low profitability. Based on our previous and ongoing research in Business Finland Co-Innovation project Bio-Prot (2021-2024) and Interreg Baltic Sea Reagion project CEforestry (2023-2025) (https://www.luke.fi/fi/uutiset/bioprot-tahtaa-biopohjaisiin-kayttajaystavallisiin-maskeihinjotka-nujertavat-virukset; https://www.luke.fi/en/projects/ceforestry), different forestry biomass-derived components have very good bioactivity properties to be used as such in novel functional biomaterials (Tienaho et al. 2021, Reshamwala et al. 2023). The pressurized hot water extracts and other solvent extracts are tannin-based and the colors of the extracts depend on the extraction conditions and solvent. The ongoing research in Luke aims also to add these extracts on non-wovens, textiles and other materials without losing any of the effectiveness (Jyske et al. 2023b). In addition, the research cooperation with Aalto University will focus on using these extracts as biocolors, as well.

Roadmap to biobased solutions

The RoadToBio bio-based chemicals roadmap for the European chemical industry aspires to increase the share of bio-based or renewable feedstock to 25% of the total volume of organic chemicals raw materials/feedstock used by the chemical industry in 2030 (<u>https://roadto-bio.eu/uploads/publications/roadmap/RoadToBio action plan.pdf</u>). Paints and coatings are complex formulations. It is challenging to exchange only one component for another without adjusting the whole formulation. Thus, replacement of one chemical often requires the development of a completely new formulation. Especially if they need to suite for the existing technology and machinery. This is a barrier, but also an opportunity for the introduction of new components with new functionalities that might not have worked in existing formulations.

In order to meet standards, bio-based alternatives should deliver the desired mechanical performance characteristics and water resistance requirements in adhesives. Most feasible way to meet these requirements is to mix bio and fossil-based adhesives. Legislation may lead to accelerating the transition from synthetic to bio-based adhesives by regulating the presence of VOCs and the presence of recyclable materials, especially in the building industries.

Luke's road to develop biobased surface treatments

Finland has potential to be a leading country in creating the solutions for biobased market and reducing dependency to the fossil-based chemicals locally and globally due to vast forest-based biomass. Hence, Luke's role is important due to the knowhow and strong points of research including the competent resources, accessibility to the reasonable infrastructure for fundamental research within multi-disciplinarity research teams. There is a huge need by 2050 for the development of sustainable biopolymers and materials that can be used as barriers, coatings or films. On the other hand, research at Luke has not been progressed evenly, for instance the product development technology of suberin has reached in the laboratory scale to a technical readiness level (TRL 3-4) compared to production of tannin and gelatine which has been piloted (TRL6). Besides, currently, market potentiality of the products is challenged with the competition with energy producer sectors, and secondly with various type of legislation policies such as, Reach and CLP legislation (established by European Chemicals Agency) which resulted in costly end products. The future market can be achieved by changes in the company's business strategy and end user awareness.

5. Biostimulants and biopestisides from plant-based biomass

Riina Muilu-Mäkelä, Francoise Martz, Marleena Hagner, Taina Pennanen, Pirjo Yli-Hemminki and Ansa Palojärvi

Synthetic chemicals are currently widely used in conventional agriculture for crop protection. Although effective against pathogens and crucial to ensuring crop yields, they have been shown to have a wide range of adverse effects on ecosystems. The compounds accumulate into environment and affect the viability of plants, animals and microbes, as well as soil health (Hagner et al.2024). Resistance of pathogens to chemical compounds also leads to reduced efficacy, cross-resistance to different types of compounds and increased virulence (Fisher et al 2022). Therefore, new farming practices are urgently needed. The problems cannot be solved by a single solution, but a combination of new soil improvement practices, targeted and broad-spectrum biocontrol agents and biostimulants, crop rotation and new crop varieties is needed to achieve sustainable farming. The aim of EU is to phase out synthetic chemicals by 2050.

Many biomasses contain useful natural defence compounds that could be developed for plant protection purposes. However, limiting factors for biomass extraction agents are the high solvent volumes required in extraction processes, the preservation of biomass to retain active components, the affordability of synthetic methods and the efficacy against the target pathogen. However, in addition to their economic value, bio-based control methods can offer other benefits such as biodegradability, safety and health. These properties need to be demonstrated, and legislation is also stringent for molecules extracted and concentrated from biomass. Biostimulants can support global food security by increasing crop yield and relieving plants from climate-related stress.

Biostimulants are substances applied to plants or root systems to stimulate natural processes and promote nutrient uptake, use efficiency, or crop quality. The most common categories of biostimulants are humic acids, seaweed extracts, liquid manure composting and beneficial bacteria and fungi. **Biopesticides**, on the other hand, are pesticides derived from natural materials that reduce the viability of harmful organisms. Biopesticides can be divided into biochemical pesticides, microbial pesticides, and plant-derived protectants (PIP). Because of their adverse effects, biopesticides are regulated as plant protection products under EU plant protection Regulation 1107/2009, which does not recognize "biopesticides" as a regulatory category. Regulation is carried out in conjunction with other EU Regulations and Directives (e.g., the Regulation on Maximum Residue Levels (MRLs) in food; Regulation 396/2005) and the Directive on sustainable use of pesticides; Directive 2009/128/EC). Instead, bio-stimulants are covered by EU fertilizer legislation (Fertilising Product Regulation (EU) 2019/1009), which facilitates their market access if compared to biopesticides.

EU standardization committees CEN/TC 455 Plant biostimulants (and CEN/TC 223 Soil improvers and growing media) have prepared 33 standards for the assessment of the safety and efficacy of the **biostimulant** products. The effectiveness of biostimulants can be based on a wide range of cellular and molecular mechanisms. Biostimulants can enhance or protect photosynthesis (humic acids, seaweed extracts, phytohormones), facilitate nutrient availability and utilization in plants (humic acids, fulvic acids), and protect seedling establishment and

early growth stages (plant growth promoting microbes, seaweed extracts). Biostimulants can protect against abiotic stress by inactivating reactive oxygen species (ROS) and harmful oxidative reactions in cells. Osmoprotectants (include i.e. amino acids, betaines, sugar alcohols and unreduced sugars) protect against protein denaturation and degradation of cell structures without interfering with the normal metabolism of the plant.

However, the challenge in developing biostimulants is to investigate and demonstrate different mechanisms of action at the cellular and molecular level, depending on the application. Apart from a few examples, the exact mechanism of action of biostimulants is not yet known. In addition, standardized and target-specific methods are needed to demonstrate the efficacy of bio-stimulants. There are several biostimulant products on the market, but their efficacy and mechanisms of action are often relatively unclear. The market is very wild and there is no guarantee of efficacy. There is therefore a growing need for research-based evidence and products that promote plant vitality.

Compared to synthetic pesticides, **Biopesticides** are environment-friendly, specific in their mode of action and sustainable. They do not leave residues and are not associated with the release of greenhouse gases (Borges et al., 2021). Biopesticides are divided into three categories according to the source material; phytopesticides (plant origin), microbial pesticides (microbial origin), and nanobiopesticides (nanoparticles produced from biological agents) (Ayilara et al. 2023). Biopesticides act through different mechanisms, including inhibition and destruction of plasma membrane and protein translocation of pathogens/pests. They act by regulating gut disruption, pest growth, and pest metabolism. Biopesticides are often very specific to their targets, have a short shelf life, are less persistent in the soil environment and are derived from sustainable raw materials, unlike synthetic pesticides (Kumar et al., 2021a). These characteristics contribute to the acceptability of biopesticides for environmental use but are also challenges for the use of biopesticides. The rapid degradability of the product and the exact target organism will not work in situations where long lasting control of multiple species is required.

Market potential

Climate change, soil degradation and increasing abiotic and biotic stress factors are the main drivers for the market and development of biostimulants and biocontrol agents. New solutions are needed to mitigate stress factors and promote plant growth under changing conditions. Market growth in Europe is expected to be driven by a strong focus on sustainability in food production practices in the region and changing food demand. The EU has set the target to reduce the use of synthetic plant protection products and even phase them out by 2050. Thus, the markets of biopesticides and bio-stimulants are expected to be growing market. The Europe Biopesticides Market size is estimated at USD 1.97 billion in 2024, and is expected to reach USD 3.20 billion by 2029, growing at a CAGR of 10% during the forecast period (2024–2029) (Mordor Intelligence 2024b). The market for biostimulants is expected to grow by 8% by 2029 reaching 2.3 billion USD (Mordor Intelligence 2024c). This includes both extraction and microbial products.

The European Biostimulants Industry Council (EBIC) influences on a European market for biostimulants and recognises their contribution to sustainable agricultural production, green innovation, economic growth and other societal goals. EPIC aims to promote the role of the biostimulants sector in helping farmers to grow sufficient quantities of high-quality crops profitably and using resources wisely.

Non-microbial bio-stimulant and biopesticide research in Luke

As stated in Luke's path in biopesticide research 2023-2030 report, Luke's work permits and promotes the wide-ranging and safe use of biopesticides in agricultural and forest environments. Our expertise in biocontrols provides practical tools to support green transition in soils and crop production.

Forest and agricultural biomasses contain various plant-based compounds that can be used as bio-stimulants and/or biopesticides depending on their mechanisms of action. Plant-based biomass contains many different active compounds like terpenes and polyphenolics including phenolic acids, stilbenes, flavonoids, lignans and tannins. These compounds play crucial role in direct biochemical processes in environment like for example terpenes can decrease fungal growth, tannins can create complexes in soil with nitrogen compounds and thus stabilize carbon balance (Chen et al. 2020).

The effects of terpenes and lignans against plant fungal diseases have been studied at the Luke. Di- and triterpenes inhibited growth of fungi on petri dishes, with efficacy like that of a known synthetic fungicide preparate (Adamczyk. et al 2023). Monoterpenes indicate antimicrobial properties (Muilu-Mäkelä et al. 2022). In addition, the beneficial effects of lignans in enhancing cellular defence responses protected strawberry seedlings from infection by grey mould (Pennanen et al. unpublished). The impact of chemistry of wood chips on forest tree seedling growth has been evaluated and green chemistry-driven methods for extracting lignans and terpenes from woody biomass developed (Adamzcyk et al. 2022).

Microbial plant protection products and biostimulants, such as plant growth promoting bacteria and mycorrhizae, are studied at Luke, but do not fall under the category of value-added chemicals and are therefore excluded from this report.

Moreover, pyrolysis oil from hardwood biomass has been shown to have repellent activity against molluscs (Lindqvist et al. 2010) and insects (Hagner et al. 2015) as well as herbicidal and fungicidal properties (Hagner et al. 2020a, 2020b, 2023, Korkalo et al. 2022). Pyrolysis oil is generated as a waste residue from biochar production and has a cocktail of compounds with biopesticide efficacy. For instance, potato cultivation is plant control product intensive. Also, oil plant cultivation is challenging without pesticides. Low content of pyrolysis oil stimulated growth of the plant roots, whereas high content was cytotoxic (Hagner et al. 2020b). The pyrolysis liquid inhibited the growth of oilseed rape but did not damage wheat seedlings, indicating that it can act as herbicide against dicotyledonous plants (Hagner et al. 2023). Some commercial herbicides are based on acetic acid, which is one of the main components of the pyrolysis liquid and can be isolated during the process.

Pyrolysis oil has plant protection effects, but its market price is difficult to determine. To produce pyrolysis oil to be profitable, its market value would have to exceed its market value considerably as a fuel for thermal energy in a pyrolysis plant for own use or for sale. The sale of pyrolysis oil as a chemical product also involves heavy and expensive regulation, as well as some form of fractionation, to ensure quality and safety of use. As a chemical, it should be consistent from batch to batch, so that it can be marketed as a safe chemical for a particular purpose. Also, the efficacy of the chemical, e.g. as a pesticide, should remain equal and that is a challenge as well. Understanding the quality of raw materials, developing extraction methods, and demonstrating the efficiency of the final product are crucial factors in creating profitable products. The same principles apply to all biomass and biomass processing. For example, bark biomass contains many components suitable as biopesticides and/or biostimulants, but at present they are mainly used for combustion and energy production. More knowledge is needed on the mechanisms of action and applications of biostimulants and biopesticides. In addition, potential biomass processing technologies need to be developed in order to stabilize production costs and product quality.

Circular Bioeconomy solutions offer the opportunity to develop new biostimulants and biopesticide innovations. This will require intensive research against various plant pathogens and standardisation of efficacy assessment methods. This research must be multidisciplinary and include physiological and molecular biological methods at the organism and cellular level, but also cultivation practices, risk assessments and life cycle analyses.

By 2050, different biobased methods to protect plants against pathogens have been found and convential agrigulture is free of synthetic chemicals. Most of the new plant protection solutions are based on microbes, but extractives play an important role as growth and defence enhancers, biostimulants. Production is part of the cascade processing, enhancing profitability. In some cases, effector molecules may also be produced in cell cultures in an energy-efficient way without the use of organic solvents. Biomass extracts are widely used as biostimulants and biopesticides and are part of sustainable food production. Local biorefinery operations have also been developed on farms to accelerate the processing of valuable biochemicals.

6. Food value-chain: Proteins and bioactive compounds

Martin Diaz, Anne Pihlanto, Sari Mäkinen, Nora Pap and Eila Järvenpää

A wide range of components (i.e., protein and fibre fractions) and compounds (i.e., peptides and phytochemicals) can be extracted from side-streams of plant and animal origin. Utilization of these high value fractions offers possibilities for comprehensive use of food processing side streams (Fig 6). For instance, protein fraction can be extracted from undervalued biomass arising from traditional agriculture (Pihlanto et al. 2020, 2021, 2022). Green plants (e.g., legumes, grasses) are widely available and formidable source of protein that remains unexploited due to regulatory issues, although they have good techno-functional properties, such as foaming, emulsifying properties and nitrogen solubility (Pap et al. 2022, Pap et al. 2024). On the other hand, fish side-streams have been a conspicuous source of valuable compounds – hydrolysates and peptides – with various food application involving e.g., tasteenhancing, techno-functional activities, and potential health effects on consumers (Välimaa et al. 2019, Mäkinen et al. 2022, Partanen et al. 2023, Wang et al. 2024). Traditionally, Finnish berries and plants have been an outstanding source of polyphenols; compounds with wide potential for human and animal health promotion, as well as for adding value for food products through techno-functionalities (Mäkinen et al. 2020, Pap et al. 2021, Granato et al. 2022).

LUKE has substantial experience on protein recovery and modification into functional hydrolysates and peptides. Even though milk peptides have been studied extensively (e.g., Pihlanto 2006, Korhonen & Pihlanto 2006, 2007), bioactive peptides can be produced from a wide variety of side-streams (Mäkinen et al. 2012, Mäkinen et al. 2016, Logrén et al. 2022) and—in addition to health promotion—peptides can present taste-enhancing properties in food involving salty and umami (Hoppu et al. 2017). Peptides, under the frame of a cascade valorization vision, can enhance the profitability of the process as they could become valuable commercial ingredients (Du & Li 2022). In the future, peptides offer an opportunity for new highend applications of the circular economy. Cereals, such as oats, wheat and rye, can be source of useful bioactive compounds, and their amounts can be further increased by bioprocessing techniques (Pihlava & Oksman-Caldentey 2001). Evidence suggests that compounds extracted from rye, such as benzoxazinoids and alkylresorcinols, may have anticarcinogenic properties (Mattila et al. 2005, Adhikari et al. 2015, Pihlava et al. 2015, 2018) and avenanthramides in oats have anti-inflammatory properties (Mattila et al. 2005, Martínez-Villaluenga & Peñas 2017, Multari et al. 2018); this can bring us one-step closer to a nutraceutical approach and preventive medicine. Overall, the major strengths of LUKE are (i) capacity to handle a wide range of biomasses/side-streams derived from food chain, forestry, and aquatic sources, and (ii) tackle conceptual and practical challenges with a cross-sectional and comprehensive vision of the whole food chain and bio-circular system.

TEA perspectives for the cascade use of fish side streams

In fish filleting industry, by-products such as head, fins, skin, frame and bones comprise approximately 60% of the total weight of the fish (Ghaly et al. 2013). In addition to fish processing side streams, there are vast amount of underutilized indigenous fishes with high potential for food applications (Wessels et al. 2023). In Finland, 10–20 mil. kg of fish by-products are formed annually and in addition to this, approximately 24 mil. kg of undervalued fish,

mostly Baltic herring and sprat, comprise a remarkable raw material stock (Setälä et al. 2021). According to Luke's studies, various high value ingredients can be produced from fish byproducts and undervalue fishes by biorefinery concepts. Fish oil, gelatin, protein and collagen hydrolysates, as well as mineral ingredients can be recovered by straight forward cascade processing enabling comprehensive utilization of the fish materials. The yield of fish protein hydrolysate (protein content >90%) is typically around 6% from the fresh weight of fish raw material and the yield of fish oil is at the same level. The yields vary depending on the proximate composition of the raw material and processing method applied, however these mean values were utilized for preliminary assessment of feasibility. Considering the investment costs, running costs, as well as raw material and end product prices in 2021, profitable business for cascade use of fish by-products would be possible by processing at minimum of 5,8 mil. kg fish by-products annually. However, end product prices affect greatly on the profitability. Thus, if the protein hydrolysate product would be for example a specific health promoting peptide ingredient for Asian markets, the value would be exponentially higher in comparison to a common food protein ingredient and enable a profitable business already with smaller volumes (Setälä et al. 2021).

Future perspectives

Despite Luke's outstanding achievements, there are still various challenges around the scalability, functionality, consumer attitude and techno economic feasibility of protein fractions, hydrolysates, peptides, and polyphenols. For instance, some protein sources can be unknown by potential consumers thereby jeopardizing fast brand positioning, competitiveness, and market share growth. More attention should be paid on raising consumer awareness about new protein sources. The regulations around health claims and novel foods could bring about bureaucratic constraints which increases the cost of product development, slows down the entering and take-up on market (novel food procedure), and therefore the product's availability and consumption within EU. However, efforts could be diverted into products and solutions for non-EU markets located in countries with less restrictive legislation to novel processing technologies and solutions. More science-based evidence and know-how is needed concerning the health effects and structure-function relationships to enable the use of peptides and polyphenols in personalized nutrition.

Big opportunities and enablers are foreseen in the coming years beyond the Euro-centric paradigm. One example is a South Korean company Lotte Corporation, which succeeded in incorporating egg yolk immunoglobulins (IgYs) against *Streptococcus mutans* into a commercially available chewing gum. As the time goes by—and surely by 2050—the increase of databases will enable the development of efficient tailor-made solutions within the frame of personalized medicine, diet, and nutrition.



Figure 6. Comprehensive use of food processing side streams.

7. Bioactive compounds as feed additives

Gabriel Da Silva Viana, Marketta Rinne and Pertti Marnila

Feed additive consepts

Feed additives have been long used in livestock nutrition to: 1) fulfil partially animal requirements for nutrients; 2) improve sensory aspects and physical quality of feeds, 3) improve the digestibility and efficiency of nutrient utilization by animals; 4) maintain and/or boost animal health and welfare; 5) improve sensory and microbiological quality of final products (e.g., eggs, meat, milk, etc.); and 6) to reduce the negative environmental impact of livestock production. Although some feed additives influence several of the processes mentioned above, most of the existing commercial products have specific mechanisms of action and targets, which makes livestock industry explore the synergism among multiple additives to maximize the efficiency of animal production on economic, environmental, and health grounds.

The strategy regarding the combination and/or doses of additives to be supplied in feeds requires 1) the understanding of the environmental stressors (e.g., sanitary challenge, thermal stress, etc.) faced by the targeted animal, 2) the knowledge about the physiology of the category of the animal to receive the additive (e.g., ruminant versus monogastric animals, and within these groups, animal species, age, and type of production, e.g., piglets, sows, chicks, etc.), 3) the costs related to the administration of the additive, and finally, 4) the revenue, i.e., economic return, from the supplementation. Recently, societal demands to increase the sustainability and welfare of animal production have stimulated the investigation and exploitation of bioactive compounds originated from side streams from local industries.

The potential feed additives must fulfil several criteria to be considered feasible. At first, it must be, obviously, effective. Secondly, the intended material must be free from microbiological contaminations and toxins, palatable and easily accepted by animals. In the industrial level, the availability of the material must be compatible with the continuous demands from feeding industry, stable during storage and feed manufacturing, and of low acquisition cost. As a final step, once investigated the efficacy and safety of the potential additive, all findings must be submitted and accepted by EFSA if the supplements are to be used within EU countries. This brief narrative addresses the potential utilization of bioactive compounds of relevance in Finland as feed additives in monogastric (poultry and pigs) and ruminant feeds.

Some examples of feed additives for poultry, pigs and ruminants

Caraway oil

Essential oils might be defined as mixtures of bioactive volatile compounds synthesized by plants, whose chemical structures consist mainly of terpenes, terpenoids, and phenylpropanoids (Lukas et al. 2009, Movahedi et al. 2024). In livestock feeds, essential oils gained relevance and attention due to restrictions in antibiotic utilization in animal nutrition. The antibacterial properties of EOs against pathogens relies mainly on the capacity of their hydrophobic compounds of disrupting the permeability of bacterial cell bacteria, which leads consequently to cell lysis (Brenes & Roura, 2010, O'Bryan et al. 2015). A Finnish company Nordic Caraway is in the process of patenting caraway oils as an antimicrobial feed additive for

livestock. The company received Agri-Inno prize for the innovation in 2022. Finland produces significant amounts of caraway (*Carum carvi*), and field area in 2024 was 20 000 ha (Luke statistics 2024). Recently, FEEDAP Panel established safe concentrations of caraway oil in complete feed for different farming animal species. For poultry and pigs, safe concentrations range from 9 to 24 mg/kg depending on the category, and for horses and ruminants from 10–25 mg/kg (EFSA 2024). In Luke, so far, there is no research activity towards exploring caraway oil in poultry or pig feeds. Literature regarding the topic confirm the potential benefits of both caraway oil as a feed additive.

Silage juice

Green Biorefining is an emerging technology where green biomass is processed into novel products (Rinne 2024). Using the juice pressed from grass enables the use of soluble grass nutrients also for monogastric farm animals. Because liquid feeding is commonly by swine industry in Finland and Europe, the administration of silage juice in pig feeds is more relevant and feasible compared with poultry feeds. Apart from the nutrients, the fresh or fermented juice may also contain bioactive compounds with potential additional benefits, including the maintenance or improvement of intestinal integrity, and the modulation of intestinal microbiome. Such benefits are of great interest for weaning piglets. Weaning is perhaps the most traumatic event that a pig will ever face. At the beginning of this phase, piglet gastrointestinal tract (GIT) is not entirely prepared to cope with new substrate from complex diets. Consequently, the presence and fermentation of undigested substrates in the hindgut is a common phenomenon, - one that might predispose pathogen outbreaks in the GIT, which damage intestinal mucosa, cause diarrhea and impairments in performance, and mortality.

Recently, Luke started exploring the potential benefits of silage juice in pig nutrition. Keto et al. (2021) reported a feeding trial where juice extracted from silage was fed to growing pigs. Regarding the palatability and performance, the results observed in pigs fed silage juice equalled those obtained by using traditional feed ingredients. Although silage juice can potentially modulate intestinal health and microbiome, no differences were noticed between pigs fed silage juice and those fed control feeds. Both groups exhibited good intestinal status, which might be presumably correlated to the high sanitary status of experimental facilities during the trial. The organic acids included in the silage juice (mainly lactic, acetic, and formic acids) do, however, possess proven benefits for liquid feed stability and intestinal status of pigs.

Tall oil fatty acids

Tall oil fatty acid (TOFA) mixture contains natural fatty acids and resin acids from coniferous trees is a novel feed material that has not been studied in periparturient cows. The material has an antimicrobial activity against Gram-positive pathogens such as *Clostridium perfringens* and *Staphylococcus aureus* in vitro, while the Gram-positive commensals such as *Lactobacillus* spp. seem to be relatively tolerant to it. TOFA has been shown to improve the composition of intestinal microbiota and productivity of pigs and poultry. In monogastric animals, dietary resin acids have been suggested to reduce inflammation-associated upregulation of intestinal matrix metalloproteinases and therefore to enhance intestinal integrity and homoeostasis. However, a feeding trial with dairy cows using TOFA as a feed additive failed to show positive effects on production or immune response (Kairenius et al. 2020.
Berry and fruit pomaces

As a side streams of berry processing, substantial amounts of berry oils and pomace are generated. The berry oils are mainly used for cosmetics and health products and in minor amounts in pharmaceutical industry. The oils contain valuable fatty acids as well as antioxidants and vitamins. The pomaces still contain substantial amounts of oils and water-soluble valuable compounds such as phenolics, terpenoids, other antioxidants like carotenoids, vitamins and a variety of nutrient fibers. As examples of novel ideas in feed sector include feed additives for improving piglet gut health and antioxidant and fibre additive for working and sporting dogs. The need of additional antioxidants of sport dogs is substantial due to 3-8 times higher energy metabolism as compared to human. In strenuous exercise the antioxidant levels as well as red blood cells and hemoglobin levels decrease. Cell and tissue damages and consequent inflammations are developed during heavy work. According to research these could be alleviated by adding berry and fruit derived fibers, antioxidants and related phytochemicals to dog feeds.

Reduction of enteric methane production by ruminants

Massive research efforts have been put towards mitigating the production of methane from ruminal fermentation. Some chemical compounds have been found effective (3-NOP, nitrate, bromoform), but a lot of effort has also been given to different plant extracts and other natural compounds such as biochar and tanniferous plants or various plant extracts (e.g., garlic). The effects have mostly been, however, rather small and the results variable not allowing to obtain clear conclusions regarding the matter. In vitro studies conducted at Luke did not indicate much potential of microcrystalline cellulose (Stefanski et al. 2018) or bark extracts (Stefanski et al. unpublished) as methane mitigating agents.

Market size of feed additives

The feed additive solutions promote substantially the competitiveness of the Finnish feed companies in international markets. Due to the good hygienic and health status of animal production in Finland, the benefits of some additive types may be greater in other areas than Finland. Also, regulatory restrictions may be lighter outside EU. If commercial use is reached, large volumes of products are needed, which may be a problem for minor side streams such berry pomaces etc. The global animal intestinal health market size is expected to reach USD 6.37 billion by 2030, according to a new study by Polaris Market Research. In EU 85 million households have at least one pet animal including. These include 77.4 million cats and 68.5 million dogs (25% on households). In EU, the annual revenue in pet food sector is 252 M€ and it grows 2.6% every year. The created export potential is high as compared to R&D investments needed. In the future, the R&D augments the companies to renew and develop. Novel animal intestinal health and well-being promoting products are introduced to markets. Reduced need for antibiotics lower veterinary costs and diminish the risk of emerging antibiotic-resistant bacteria.

8. Platform chemicals and bio-based adhesives

Anuj Kumar and Veikko Möttönen

The direct usage of most biomass resources is **not always practical and efficient due to their complex structures**. For better utilization, **biomass needs to be transformed into simpler or more useful molecules**, that is the so-called **platform chemicals** or building blocks or intermediates (Schutyser et al. 2018). There are two major pathways towards transformation of renewable feedstocks into bio-based platform chemicals, i.e., fermentation and chemical treatment. These bio-based platform chemicals demonstrate favorable properties, including economic viability, low toxicity, as well as environmental-friendly and renewable features, thus attracting enormous attention (Mathers 2012).

Biomass and its derivates have extremely diverse chemical structures or behavior that often varies by small details, and their reaction activities and performance of related polymers vary dramatically (Schutyser et al. 2018). For example, the successful utilisation of complex lignin biopolymer as a feedstock for chemicals is governed by an interplay of (i) the biomass fractionation method, (ii) the lignin depolymerisation technology, and (iii) subsequent upgrading towards targeted chemicals. According to Liu et al. (2021) the bio-based platform chemicals suitable for instance for thermoset resins are classified into four categories a) carbohydrates, b) lignin, c) vegetable oil, and d) plant extracts. These four categories will be divided into different bio-chemical types as demonstrated in Table 3.

Biomass based Bio-polymers	Bio-polymers in- termediates and derivatives	Platform chemicals		
	Polyols	Sorbitol, mannitol, isohexides, ethylene glycol, 1,4-butanediol and 1,2- propanediol		
Carbohydrates	Furan derivatives	5-Hydroxymethylfurfural: Levulinic acid and 1,4-butanediol, 2,5-fu- randicarboxylic acid and maleic anhydride, 1,6-hexanediol Furfural: 2,5-furandimethanol and 1,6-hexanediol, furfurylamine, cyclo- pentanone		
	Carboxylic acids	Dicarboxylic (succinic acid, fumaric acid, itaconic acid, maleic acid and muconic acid), others (quinic acid, lactic acid and amino acids)		
	Diphenols	Resorcinol, hydrocatechol and catechol		
Lignin	Phenols	Guaiacol, catechol, vanillin, eugenol, <i>p</i> -hydrobenzoic acid, <i>p</i> -coumaric acid, ferulic acid, phloretic acid and gallic acid		
Vegetable oils	Base oil Derivatives & polyols	Glycerol, lactic acid, amination and esterification products of fatty acids		
	Flavonoids	Apigenin, naringenin, daidzein, and catechin		
	Tannins	Condensed tannins (flavonoids, catechin (resorcinol), pyrogallol) Hydrolyzable tannins (pyrogallol, gallic acid)		
Plant and tree	Terpenes and ter-	Rosin acid (dihydroabietylamine and rosin acid oligomer), limonene and		
bark extracts	penoids	pinene		
	Others	Thymol, sesamol, coumarin, benzaldehyde, cinnamic acid, salicylalde- hyde, chavicol, deoxybenzoin, urushiol, resvatrol, catechin, magnolol, and arbutin		

Table 3. Bio-based platform chemicals used for thermosetting resins synthesis (Liu et al. 2021)

Carbohydrate-derived furan compounds are seen as promising platforms for a renewable value chain. The high reactivity of such bio-based intermediates requires the development of new catalytic chemistry to improve product yields. Lignocellulosic biomass is first converted into lignin, hemicellulose and cellulose. Subsequently, the holocellulose fraction is further converted into hexoses and pentoses after removal of the lignin component. Subsequent dehydration of these carbohydrates yields various furan compounds which can be further processed into chemical building blocks. The protection of reactive functional groups provides a means to improve product selectivity (Coumans et al. 2022). The higher oxygen content of bio-based feedstocks compared to petroleum-derived hydrocarbons is of particular interest for the production of chemical building blocks. However, the presence of reactive oxygen-containing groups also makes bio-based molecules susceptible to non-selective side reactions leading to less interesting high molecular weight products such as humic acid. The availability of suitable protection strategies depends on the type of functionality, which for furan compounds is mainly limited to carbonyls, hydroxyls and carboxyls to reduce side reactions.

Biobased Adhesives

Carbohydrates derived bio-chemicals especially consider for thermoset resin production are polyols (polyurethane type adhesive production); furan derivatives; carboxylic acid; and diphenols. **The C5 and C6 sugars carbohydrates are the two most important furan derivatives for production of 5HMF (hydroxymethyl furfural)** and furfural. 5HMF and furfural or furfural alcohol considered to be potential replacement of fast curing amino resins. However, the **main challenges lie in efficient and large-scale production of C5 and C6 sugars into 5HMF and furfural or furfural alcohols. Until now only 2,5-furandicarboxylic acid (FDCA) is starts producing at industrial scale and it is defined as a chemical compound, which is manufactured from the two classes of carboxylic acids and these acids are bound to a central furan channel. Various carbohydrates are used in the production of FDCA and used in PET, Polyamides, Polycarbonates, Plasticizers, Polyester Polyols, and others.**

Lignin is the second most abundant biopolymer on the earth, and most of the available lignin comes as a by-product of the pulping process. These lignin derived fragments have low value and usually serve as fuel for the recovery boiler of pulp and paper mills. They are very heterogeneous in their structure with structural units that range from almost native to highly degraded. The structure of lignin plays a key role in the required extensive modifications and crosslinking to allow for better adhesive properties of the derived adhesive. **Tannins** as a raw material for adhesive applications poses certain issues, like short pot life, high viscosity, reactivity, and poor weather resistance. Comprehensive investigation and introduction of newer concepts like copolymerization, chemical modifications etc., can catalyse the development of tannin as a sustainable raw material for adhesive applications (Dhawale et al. 2022).

Soy Protein as an adhesive date back to the ancient times but its commercial use in plywood production began only in the 1930s. The soy proteins used as plywood adhesives were typically denaturized by caustic treatment. The products had typically short pot lives, poor biological stability, low solid content, slow pressing times and very poor water resistance, which limited them to mainly interior applications. In the 1960s, most soy-based adhesives were replaced with synthetic adhesives, such as phenol-formaldehyde (PF) and urea-formaldehyde (UF) adhesives. The new developed soy adhesives have higher moisture tolerances and are stronger than those known before the 1960s. As a wood adhesive, soy protein is inexpensive,

easy to handle, has low pressing temperatures and can bond wood with relatively high moisture content. Protein adhesives are also quite sensitive to changes in temperature, pH, ionic strength and pressing conditions. The adhesive properties highly depend on protein content. However, **there are no commercial production of soy protein adhesives for wood products bonding**.

Starch is a polysaccharide derived from the seeds, roots and leaves of plants. It acts mainly as the energy storage unit of plants and can be found in large quantities in corn, wheat, potato, rice, tapioca and sago. Starch consists of glucose units joined by glucosidic bonds. The two fractions of starch are amylose and amylopectin. Starch has relatively low bonding strength, making it unsuitable for wood-based panel products in its native form. Thus, starch needs to be highly modified or cross-linked when used in the wood industry. The main types of modifications for starch-based adhesives are chemical, physical, enzymatic and genetic.

Wood adhesives are polymeric materials that can interact physically or chemically, or both, with the surface of wood in such a manner that stresses are transferred between bonded members, hopefully without rupture of the adhesive or detachment of the adhesive from the wood. Adhesives and the physicochemical phenomenon of adhesion play an important role in more than 80% of all wood-based materials in use today, that's include plywood, laminated veneer lumber (LVL), particleboard, oriented strandboard (OSB), fiberboard (MDF, HDF), laminated beams and cross laminated timber (CLT), edge- and end-jointed products, windows and frames, architectural doors, and fiberglass insulation (USDA 2001, Hemmilä et al. 2017). Most of the wood adhesives used in engineered wood products are thermosetting resins and classified into Amino resins, phenolic resins, and isocyanates as described in Table 3.

Adhesive types	Adhesives
Amino resins	Urea Formaldehyde (UF) Melamine Urea Formaldehyde (MUF) Melamine Formaldehyde (MF)
Phenolic resins	Phenol Formaldehyde (PF) Phenol resorcinol Formaldehyde (PRF)
Polyurethanes	diphenylmethane diisocyanate (MDI): di- or polyfunctional isocyanate

Table 4. Types of Thermosetting resins used in wood products bonding.

Amino resins (aminoplasts) are condensation thermosetting polymers of formaldehyde with either urea or melamine and mainly used for interior grade wood panels. Melamine is a condensation product of three urea molecules. It is also prepared from cyanimide at high pressure and high temperature. The nucleophilic addition reaction of urea to formaldehyde produces mainly monomethylol urea and some dimethylol urea. When the mixture is heated in presence of an acid, condensation occurs, and water is released (Solt et al. 2019). This is accompanied by the formation of a cross-linked polymer as described in Figure 1c. A similar reaction occurs between melamine and formaldehyde and produces methylolmelamine derivatives.

Phenolic resins are the most important commercial phenolic adhesives include phenol-formaldehyde (PF), resorcinol-formaldehyde (RF), and phenol-resorcinol-formaldehyde (PRF). Phenolic adhesives are thermosets with excellent bond strength to wood for exterior applications. They are also extremely stiff, highly resistant to water, more thermally stable than wood, and possess long-term durability. Due to their high resistance to hydrolysis when cured, phenolic adhesives have no significant release of formaldehyde once the product is placed in service. PF resins are formed by a step-growth polymerization reaction between phenol and formaldehyde in either acid or base catalysed environment (Figure 1a and 1b) (Mark 2013). Depend on the formaldehyde to phenol (F/P) molar ratios, the phenolic resins further divided into two groups: 1) Novolacs, when F/P molar ratio less than one, 2) resoles, when F/P molar ratio more than one. Novolacs resins require external crosslinking agents to fully harden, while resoles did not needed external cross-linking agent.

Isocyanates are important industrial chemicals used in injection molding and to produce poly-urethane foams and also known as PMDI resins. All isocyanates of industrial importance contain two or more isocyanate groups (-N = C=O) (see Figure 2) per molecule. MDI has become an important adhesive in the wood products industry, especially for bonding OSB, MDF (Bekhta et al. 2021). The higher cost of the PMDI resins is offset by the faster reaction time, compared to PF, the very high bond strength and the superior resistance to water and climatic conditions. These adhesives are marketed as formaldehyde-free systems in Europe. However, PMDI adhesives need special precautionary protection measures when used in the industry, and press-sticking problems need special care, when used in the face layer.

The global wood adhesives and binders market size reached 15.8 billion USD in 2020 and ~20 million tons adhesives produced, and it is expected to reach 21.9 billion USD by 2028 (Verified Market Research 2024, <u>https://www.verifiedmarketresearch.com/prod-</u> uct/wood-adhesives-and-binders-market/). Formaldehyde-based adhesives are counted as approximately 90–95% of the total wood adhesives used in the industry (Kristak et al. 2023).

Bottle-neck issues in the wood-based industry are associated with the adhesive system used in panel manufacturing due to **toxic formaldehyde emission and dependency on fossil materials** (Kristak et al. 2023). However, current formaldehyde based adhesive systems exhibit versatile properties such as flexibility, low cost, high thermal stability, low curing temperature, water, and chemical resistance. So, finding the replacement of the present adhesives has been rather complicated because bio-based solutions have not been able to provide all the versatility mentioned above. All the currently available biobased adhesives solutions are failing to fulfil several parameters, most importantly they suffer from high cost, high curing temperature, lack of suitable biobased crosslinkers and, most importantly, very low stability in wet conditions, which hinders the applications of bonded products in exterior conditions such as plywood, OSB and LVL.

Luke's role in Bio-adhesives innovation and future road map

In Luke, we successfully delivered two R&D&I projects; a) Positive Fibers (Internally funded) https://www.luke.fi/en/projects/posfibes and Nature2Bond project (Research to Business) https://www.luke.fi/en/services/biobased-sustainable-adhesive-system-for-plywood-lvl-andwoodbased-panels funded by Business Finland. In the Nature2Bond project. Luke has developed a new and inventive method, Nature2Bond, to produce sustainable and non-toxic bioglues that have a potential to replace the formaldehyde adhesives in the production of wood-based panels and engineered wood products. Luke's process is straightforward, costeffective and can utilize abundant supply of renewable raw materials. Using the new production method several intermediate steps of purification and functionalization can be avoided, which results in cost savings. New bio-glues are suitable to be used in exterior grade wood panels as well as in interior grade wood panels. The solution developed by Luke follows the principles of circular bioeconomy; low-value raw materials are processed into high valueadded products and wood panels bonded with new bio-glues are sustainable and environment friendly. In Nature2Bond project, upscale of bioglues is achieved at semi-industrial process and third-party validation were achieved by semi-industrial of bio glues in wood-based panels production.

Luke own several IPR and patents on the bioglues such as biomass processing, bioglues formulations, and different applications. In the current time in future, Luke will going play thecrucial role in bio-adhesives production innovation as well as all kind of testing facilities and services.

9. Hemicellulose-based products

Petri Kilpeläinen, Risto Korpinen and Hanna Brännström

The second most abundant renewable component in lignocellulosic biomass is the natural polysaccharide hemicellulose, which typically comprises between 15 and 35% of the biomass (Gírio et al. 2010, Rao et al. 2023). Hemicellulose is an attractive but currently underutilized source of biopolymers (Geng et al. 2020). In the development of sustainable biorefineries, extraction and utilization of hemicellulose is of key importance. Hemicellulose has excellent physical and chemical properties providing possibilities for the utilization in multitude of different applications and wide potential markets. Seed storage hemicelluloses, guar and locust beam cum (galactomannans), konjac gum (glucomannan) and tamarind gum (xyloglucan) are widely used in food industry. Hemicelluloses isolated from forest industry wood side-streams or agricultural byproducts can be used to replace starch in the food and beverage industry. It may be used as an emulsifier, thickening and stabilizing agent in foods and cosmetics, as a dietary fiber and as ingredients in bio-based films and coatings, in fine chemicals (e.g., xylitol, ethanol, furfural), and energy storage applications. According to Cognitive Market Research (2024), the global Hemicellulose market size is USD 1.5 billion in 2023 and will expand at a compound annual growth rate (CAGR) of 7% from 2023 to 2030.

Hemicelluloses, which are cell wall polysaccharides other than cellulose, predominantly have a β -1,4 glycosidic bond structure (Ebringerová et al. 2005, Pauly et al. 2013, Scheller & Ulvskov 2010). This category includes xyloglucans, xylans, mannans, glucomannans, and mixed linked β -(1 \rightarrow 3,1 \rightarrow 4)-glucans. The function of hemicelluloses is to strengthen the cell wall by linking cellulose microfibrils. Different sources of biomass contain different hemicellulose compositions, structures and contents. Xylans and glucomannans are the most relevant hemicelluloses, and xylan is also the most abundant one. Good sources for xylans include agricultural crops and their residues (e.g., sorghum, sugarcane, corn stalks and cobs, cereal straws and husks), and forest industry side-streams from hardwoods. Glucomannans are the major hemicellulosic components in softwoods.

Methods which have been used to extract hemicellulose from woody tissues include dilute acid pretreatments, alkaline extraction, alkaline peroxide extraction, liquid hot-water extraction, steam treatment, microwave treatment, ionic liquid extraction, and also others. At Luke PHW extraction (pressurized hot-water extraction) of hemicelluloses has been in focus as it provides advantages over conventional extraction methods for being typically faster and greener approach (Kilpeläinen et al. 2014, Geng et al. 2020). Hemicelluloses can be extracted from biomass prior to other processing steps by using PHWE. For more comprehensive utilization of biomass two-stage (90 °C + 160 °C) PHWE methods have also been developed to extract first hydrophilic, phenolic extractives, and to obtain a hemicellulose-rich fraction in the second extraction stage.

10. Wastewater treatment: Flocculants and coagulants

Risto Korpinen, Petri Kilpeläinen and Hanna Brännström

The global flocculant and coagulant market size was estimated to be 10.4 billion USD in 2023 and projected to reach 12.6 billion USD in 2028 at a compound annual growth rate of 3.8% (MarketsandMarkets 2024, <u>https://www.marketsandmarkets.com/Market-Reports/flocculant-and-coagulant-market-243584994.html</u>)

Clarifying agents are used to remove suspended solids from liquids by inducing flocculation, causing the solids to form larger aggregates that can be easily removed after they either float to the surface or sink to the bottom of the containment vessel.

Most commercial flocculants are synthetic water-soluble polymers with average molecular weights in the region 1000 to 30·10⁶. They are generally supplied as powders that have a limited storage life, particularly when made up into solution. The examples of synthetic flocculants can be seen in Figure 8 (Tarleton & Wakeman 2007).



Figure 7. Examples of cationic, anionic and non-ionic flocculants used in the industry.

Coagulation is one of the common methods used by water treatment plants to clean water to users. Coagulants are chemicals that are used to remove suspended solids from water. They are made up of positively charged molecules, which help to provide effective neutralization

of water. Coagulants are usually iron or aluminium salts such as ferric sulfate, aluminium sulfate and ferric chloride (Campbell, B. 2022)

Especially flocculants can be replaced using biobased alternatives. Tannin-based coagulants are effective at removing various contaminants from water, for example, they are reported to remove turbidity, color, suspended solids, chemical oxygen demand, total phosphate, algae, and heavy metals (Tomasi et al. 2022). Due to abundance of tannins in nature and ease of their chemical modification, they are an attractive option for the production of coagulants. Tannins are anionic, so they are often cationized to produce coagulants effective in removing anionic colloidal particles from water and wastewater.

Commercially available tannin-based flocculants, such as Acquapol, SilvaFLOC, and Tanfloc, demonstrate the feasibility of using tannins in coagulation-flocculation processes (Carlqvist et al. 2020). These products are produced from well-known sources of condensed tannins, including quebracho (*Schinopsis balansae*) and black wattle (*Acacia mearnsii*). However, tannins from tree species abundant in subarctic climates, such as Norway spruce, are currently not utilized in commercial products. Softwood tannins have been used in collaboration with project partners for instance in TanWat and OptiBark projects. The tannins obtained from Norway spruce bark by hot water extraction have been cationised by so called Mannich reaction and used in water purification tests. The scheme of cationisation can be seen in Figure 9.



Figure 8. Cationisation of tannin.

11. Summary of extractives groups, their applications and potential sources

Hanna Brännström, Riina Muilu-Mäkelä and Sari Mäkinen

Phenolic extractives: condensed tannins, flavoinoids, stilbenes, lignans

Polyphenols are a broad group of different compounds including **tannins**, **flavonoids**, **stilbenes**, **lignans and phenolic acids**. Polyphenols have antioxidant and anti-inflammatory properties and contain pigment molecules such as anthocyanins with great potential as natural colourants. Polyphenols are used as flavourings, health ingredients and preservatives. New health foods and beverages are a growing market for polyphenols. The size of the polyphenols market was estimated at USD 2.2 Billion in 2023. The polyphenols industry is projected to grow to USD 3.3 billion by 2032, exhibiting a compound annual growth rate (CAGR) of 4.5%. Tannins are widely used in various industries such as food and beverages, leather tanning, wood glues, healthcare and animal feed (SkyQuest Technology 2024, https://www.skyquestt.com/report/tannin-market).The tannin market is expected to grow at a CAGR of 5.6% by 2031. **Table 5.** Summary of extractives groups, their applications and examples of their biomass sources

Compound group Applications		Examples of biomass sources		
Phenolic extractives				
Condensed tannins [1–7]	leather tanning, winemaking, building materials, flocculants, coagulants, adhesives, pharmaceuti- cals, food supplements, ingredients in animal feeds, cosmetics, dietary supplements, food in- gredient, beverages, adsorbents for proteins and antibiotics	Bark of trees (e.g., oak, pine, spruce) Heartwood (quebracho) Plants and fruits, in various parts of plants including, barks, seeds, stem tis- sues, roots, and leaves.		
Flavonoids [8–11]	Pharmaceuticals, food ingredients, cosmetics	Fruits, vegetables Berries (e.g., blueberries) Stemwood of both softwoods and hard- woods, pine needles Rich sources of these e.g., aspen knots		
Stilbenes [12–16]	antioxidants, antimicrobials, and preservatives in cosmetics, technochemical products, or pharma- ceuticals cosmetics, nutraceuticals	Grapevine Peanuts Berries Trees (spruce bark, heartwood and knots of Pine species)		
Lignans [10,16–18]	Dietary ingredient, insecticide-synergist, pesti- cide, cosmetics	Flax Fibre rich plants, incl. grains (e.g., wheat, oats, barley) Legumes (e.g., beans, lentils, soybeans) Vegetables (e.g., carrots, broccoli) Nuts, fruits Softwoods and hardwoods (stemwood), softwood knots		
Terpenes and terpenoids				
Monoterpenes [10,19–22]	Cosmetics, household, natural insect repellent, fragrances, pharmaceuticals, plasticisers, explo- sives, food additive, pesticides, detergents, disin- fectants, solvents, flavourings, cleaning agents, insect attractants, insecticides	Softwoods berries, tropical fruits, Citrus fruits (e.g., orange) Herbs		
Sesquiterpenes [20,22]	Food additive, cosmetics, biofuels, insect repellent, chemical industry, fragrance, pharmaceutical	Softwoods		
Resin acids [20,23,24]	paper sizes, adhesives, chewing gum bases, coatings, disproportionated rosin soaps, printing ink resins, rubber processing aids, rosin resin es- ters, sealants, tackifiers, medical applications	Softwoods		
Triterpenoids (betulin etc.) [25,26]	Cosmetics, nutraceuticals, pharmaceuticals	Birch bark medicinal herbs, marine sponges, fruit, vegetables, spices, and cereals common sources of pentacyclic triterpenoids		
Steroids (sitosterol etc.) [10,27,28]	Pharmaceuticals, health enhancing food addi- tives	Vegetable oils, tall oil, wood, microalgae, grains, vegetables, fruits and berries		
Fats, waxes and their con	nponents			
Fatty acids [19,29–31]	Soaps and detergents adhesives, coatings, cos- metics, epoxy resins, defoamers, emulsifiers, and surfactants, among many others, biofuels, phar- maceuticals	Fish and animal fats (e.g., tallow) Oilseeds (e.g., sunflower, canola) algae Wood, bark, and other biomass assort- ments from trees		
Waxes [24]	cosmetics, food, and biomedical applications, coatings for the packaging, paper, and textile in- dustries, lubricants, plasticisers, candles	Plants (e.g., carnauba, candelilla, jojoba, tree foliage), beeswax, algae, fruit peels, berries, agricultural waste residues		

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Currently, the primary sources of **condensed tannins** are the bark of black wattle (*Acacia mearnsii*) and the heartwood of quebracho (*Schinopsis balansae* and *S. lorentzii*) (Holmbom 2011, Bianchi 2017). However, extracting tannins from pine and spruce bark has also proven to be economically viable (Lacoste et al., 2015). For instance, the tannin content in the bark of Norway spruce (*Picea abies*) has been reported to range from 4% to 15% (Kemppainen 2015). At Luke we have studied the effect of supply chain on the tannin content bark sidestreams (Routa et al. 2021, Jyske et al. 2020, Jylhä et al. 2021, Halmemies et al. 2022), optimized extractions methods (Kilpeläinen et al. 2023), developed methods for extract refining (Varila et al. 2020). Tannin-based extracts have been tested e.g., in following applications: rigid carbon foams (Varila et al. 2020, Korkalo et al. 2023), flocculants (Carlqvist et al. 2020), smart functional fiber surfaces (Jyske et al. 2023b), and as sustainable preservative and aroma (Raitanen et al. 2020).

The flavonoids are found in almost all plants, and thus, they are the most common group of phenolic plant compounds (Nisula 2018). Flavonoids have antioxidant, anti-inflammatory, anti-mutagenic, and anti-carcinogenic properties, along with their ability to regulate key cellular enzyme functions, and they have been linked to beneficial effects on human and animal health (Panche et al. 2016). For this reason, they are regarded as essential components in various applications (e.g., nutraceutical, pharmaceutical).

Stilbenes have been subject of several studies due to their bioactivity and potential benefits for human health (El Khawand et al. 2018). At Luke we have carried out studies on the effect of geographical origin and supply chain on the stilbenoid content of Norway spruce bark (Jyske et al. 2020, Jylhä et al. 2021, Halmemies et al. 2022, Jyske et al. 2022), developed extraction and purification methods (Jyske et al. 2022), and studied the stability of biologically interesting and readily available stilbenes such as astringin and isorhapontin and their aglucones piceatannol and isorhapontigenin (Latva-Mäenpää et al. 2021).

Lignans exhibit a wide range of biological activities and are broadly distributed throughout the plant kingdom, having been identified in species from more than seventy different families (Saleem et al. 2005). Earlier studies have included topics such as distribution of lignans in knots and stem, within-stem variation of lignans (Piispanen et al. 2008, Willför et al. 2005) and the effect of fertilisation. Also, potentially rich source for lignans and stilbenes, root neck of Norway spruce, has been identified (Latva-Mäenpää et al. 2013).

Terpenes and terpenoids: mono- and sesquiterpenes, resin acids, triterpenoids, steroids

The **terpenes** market size was 1.46 billion in 2023 and is expected to grow at a CAGR of 8.9% (Value Market Research 2024, <u>https://www.valuemarketresearch.com/report/terpenes-market</u>) over the next decade. Terpenes are aromatic hydrocarbons with a strong smell. They have anti-cancer, anti-inflammatory and anti-microbial properties and hence their market is therefore focused on cosmetics, pharmaceuticals, food and beverages, skin care products, as well as rubber. On the basis of product, the market is segmented by product into pinene, limonene, linalool and others. The main challenge in the terpene market is the increasing price of high-quality products. The production of the purest terpenes can be very expensive, as it can cost hundreds of kilograms to extract one kilogram of pure terpene from plants. Terpenes are therefore often produced using petrochemicals.

Essential oils primarily consist of monoterpenes, sesquiterpenes, and their derivatives, and have been used for centuries as essential ingredients in perfumes and aromas (Royer et al. 2012). Terpenes and monoterpenes have a wide range of biological effects, including antimicrobial, antiparasitic, anti-inflammatory, antioxidant and anti-tumour effects (De Alvarenga et al. 2023, Kim et al 2020). The chemical structure of monoterpenes provides double bonds and reduced functional groups that are susceptible to oxidation and have been shown to have antioxidant properties (Noacco et al. 2018). However, our biosensor and eye cell model experiments showed that the four main monoterpenes of conifers (α - and β -pinene, S-limonene and 3-carene) have antibacterial properties, but no clear antioxidant stress-protective properties could be demonstrated (Muilu-Mäkelä et al. 2022). The antibacterial effect of monoterpenes is based on the ability to damage cell membranes and they can affect cellular respiration and energy metabolism by inhibiting the respiratory chain complex, leading to cell death of bacteria (Sandasi et al. 2008, Shu et al. 2019). Crude sulfate turpentine (CST) is the cheapest and most widely available source of monoterpene biomass, with around 260 000 tonnes of CST produced as a waste by-product of the paper industry annually. The acid catalyzed ring opening reaction of CST can be used to produce a variety of bioproduct fragrances, pharmaceuticals, polymers and biofuels.

Resin acids in softwoods are primarily tricyclic diterpenoids, typically constituting 0.2–0.8% of the wood's weight (Nisula 2018). Diterpenes and -terpenoids are of great industrial importance (Alén 2000). Tall oil resin is primarily utilized as a chemical intermediate, undergoing further modification for applications in the production of adhesives, coatings, and other products listed in table 4.

Triterpenes and triterpenoids are widely found throughout the plant kingdom, consisting primarily of oxygenated derivatives (Alén 2000). They are traditionally classified into two groups: triterpenoids and steroids. Pentacyclic triterpenes with lupane structures have been associated with various bioactivities, including bactericidal, antiviral, anti-inflammatory, cyto-toxic, and antitumor effects (Royer et al. 2012). Betulin is the most well-known triterpenoid from the lupan series, possessing valuable pharmacological properties and hydrophobic effects (Yadav et al. 2024). At Luke life cycle assessment of suberin and betulin production from birch bark has been carried out.

Fats, waxes and their components: fatty acids, waxes

Historically and currently, oils and fats derived from both vegetable and animal sources are the most significant renewable feedstocks in the chemical industry (Biermann et al. 2021). **Fatty acids** (FAs) and their derivatives possess value beyond their biological properties, serving as essential starting materials for a wide range of chemicals across various industrial sectors, including food, pharmaceuticals, cosmetics, oleochemicals, and plastics (Cerone et al. 2021). Additionally, polyunsaturated fatty acids are crucial for human health and disease prevention. Conversely, FAs derived from wood extractives, such as tall oil FAs, provide alternatives not only to fossil feedstocks but also to edible vegetable oil-based FAs (Routa et. al. 2017). Typical applications for FAs (incl. tall oil based FAs) and their derivatives are included in Table 4.

Biogas production and volatile fatty acids

Volatile fatty acids (VFAs) are intermediates in the methane formation pathway of anaerobic digestion and they can be produced in similar reactors as biogas to increase the productivity of a digestion plant, as VFAs have more varying end uses compared to biogas and methane (Tampio et al. 2019). VFAs, including acetate, propionate, butyrate, and valerate are the essential precursors for the productions of bioplastic, biodiesel, and biofertilizer (Atasoy et al. 2020). Anaerobic digestion of food wastes and cow slurry have been studied in Luke in BIO-FVA, GÖDSELVFA and Era-SUSFOOD2 projects.

The plant cuticle serves as a protective interface between plants and their environment, covering leaves, stems, and fruits (Trivedi et al. 2019). It is composed of cutin, a polyester-type and cuticular wax, which is a complex mixture of very-long-chain fatty acids, their derivatives (e.g., alkanes, ketones, primary and secondary alcohols, aldehydes, esters), and secondary metabolites (e.g., triterpenoids, sterols, tocopherols and phenolic compounds) (Szakiel et al. 2012). The composition of cuticular wax varies by species, plant organ, developmental stage, geography and environmental conditions and it exists as intracuticular wax embedded in cutin and epicuticular wax. Waxes have a wide range of potential applications across industries (see Table 4 and chapter 4). Bio-based waxes derived from domestic raw materials are valuable alternatives to fossil and non-renewable waxes with potentially harmful properties, as well as animal-based wax products and other natural waxes with non-transparent supply chains. The market for waxes is large and expanding, valued at \$9.9 billion with a 2.8% CAGR (Blended Waxes, Inc. 2021, <u>https://blendedwaxes.com/blog/upcoming-trends-in-the-indus-trial-wax-market/</u>).

One interesting group of molecules are **hemicelluloses**, which in the past were mainly used as ingredients in paper products. Today, many of the properties of hemicelluloses are being exploited in new applications. **Xylan** is one of the major components of hemicelluloses and can be used as a dietary fibre, pharmaceutical and food binder. **Furfural**, derived from the degradation of hemicellulose, is a flexible base chemical in bioplastics and pharmaceuticals, and xylene glycosaccharides are increasingly popular as prebiotics. In addition, the properties of hemicellulose can be tailored for different applications by changing molecular weight, charge and other properties through chemical and enzymatic treatments. This increases the potential market for functional coatings, durable adhesives and high performance composites. The hemicellulose market is forecast to grow to USD 2.7 billion by 2030, growing at a CAGR of 6.6% by 2030, assuming steady growth without barriers or other factors affecting development (https://www.verifiedmarketreports.com/product/hemicellulose-market-size-and-forecast/). The interest in the potential applications of polymeric hemicelluloses has been limited by the high cost of the extraction process.

12. Framework for sustainable value creation

Mikko Weckroth, Juha-Matti Katajajuuri, Esa-Jussi Viitala, Johanna Kohl, Hanna Brännström, and Riina Muilu-Mäkelä

In 2050, the cascade use of biomass will have evolved so that valuable extracts will be part of the processing and value-added products. Raw material supply chains have evolved so that most of the potential biomass residues are stored and processed in a way that does not degrade the valuable components. Sensing and monitoring technologies have been developed to monitor molecular concentrations to optimise biomass processing for different needs.

The next step should be to develop processes that make it profitable to produce valuable materials from biomass. Market demand is needed to change processes. By working with companies, it is possible to develop products for different markets. Simultaneous developments in biomass knowledge, process development and market understanding are needed to get production going. Luke's strengths are in lignocellulosic feedstocks and pretreatment process technologies that can be used to produce a range of biochemicals for various products, such as food and feed additives, biocomposites, adhesives, biostimulants and biopesticides. There is scope to develop research-based new products in these areas in collaboration with other research institutes and companies.

In this framework chapter, several systemic barriers that have been identified in the transition to a bio-based and circular economy are highlighted. A key issue is the existing regulatory framework, which often still favors traditional, fossil-based industries due to complexity and rigidity of regulation. These regulations can slow down the market entry of bio-based innovations, by imposing higher compliance costs and documentation requirements on these new technologies. On the other hand, regulation can also contribute to the transition towards a fossil-free economy. Currently, infrastructure and logistical dependencies are still designed around fossil-based supply chains, making it difficult for bio-based alternatives to scale up and compete. Overcoming these barriers will require new policies and decision making to support and favor bio-based solutions and the creation of supportive infrastructure and economic incentives to facilitate the growth of sustainable bio-based industries.

Another major challenge is the limited consumer awareness and acceptance of bio-based products and circular economy principles. Consumers tend to be familiar with conventional products and may be hesitant to switch to new sustainable alternatives, especially when the environmental benefits are not reliably proved, demonstrated and clearly communicated. There is therefore an urgent need for targeted research and communication strategies to raise consumer awareness of the long-term benefits of sustainable products, both for human well-being and for the health and environment. Effective campaigns and educational initiatives could also help demonstrate the potential of sustainable bio-based solutions in reducing the environmental footprint of consumer choices.

A critical issue preventing the wider adoption of bio-based products is that negative externalities, such as nature and biodiversity loss, are not yet priced into the costs of fossil-based products. This gives fossil-based industries a competitive advantage, as they do not bear the full cost of their environmental impact. To level the playing field, policy measures such as carbon pricing, environmental taxes, or subsidies for bio-based solutions could help internalize these externalities. By adjusting market dynamics to reflect the true environmental costs, biobased products could become more economically viable and competitive with their fossilbased counterparts.

The bark biorefinery case study (see the appendix, page 58) exemplifies the potential for biobased innovation but also underlines the challenges. The development of bark-based biorefineries has shown promise in converting waste materials into valuable chemicals, but the market adoption of these technologies remains limited due to logistical challenges and regulatory hurdles. For instance, the need for fresh biomass within tight timeframes poses logistical difficulties, requiring new supply chain solutions and cooperation between different actors. Policy interventions should focus on facilitating the development of biorefinery supply chains by investing in logistics infrastructure and incentivizing cross-industry collaborations. The bark biorefinery case serves as a valuable example of the need for coordinated efforts across policy, industry, and research to build sustainable value chains and foster the transition to a bio-based economy.

In conclusion, while supportive policy frameworks are emerging, more targeted measures are needed to overcome these systemic barriers. Policies should not only promote technological innovation but also address market failures, such as the failure to account for environmental externalities. Research and consumer engagement will be crucial in ensuring that bio-based and circular products gain widespread acceptance.

12.1. Political tools for change: the EU taxonomy, green claims

Governments can play an important role by providing incentives and support policies that encourage the uptake of sustainable practices and technologies. As part of the Green Deal the European Commission has adopted the Sustainable Finance Framework (EU Taxonomy) which aims to direct capital flows to those economic activities and solutions that can significantly contribute to Union's environmental targets. EU Taxonomy is a voluntary scheme that is based on technology-agnostic approach. This means that any activity and solution that wishes to be aligned with Taxonomy and its environmental criteria, often reflecting "best-inclass" category, needs to substantiate its environmental performance in terms of verifiable impacts (e.g. GHG emissions, water use, pollution prevention, circular economy, biodiversity protection and restoration). However, bio-based industries and solutions, including new and emerging biobased chemicals, could be more widely incorporated in the Taxonomy than currently. This would facilitate flow of capital to these endeavors.

Other policy tools with potential for accelerating the shift towards more sustainable solutions, consumption and production include the Green Claims Directive (under legislative procedure), the Ecodesign for Sustainable Products Regulation (ESPR), and the new type of sustainability reporting requirements for companies and financial institutions (CSRD, SFDR, CSDDD), all of which will be implemented during the next years. The ESPR aims to significantly improve the circularity, energy performance and other environmental sustainability aspects of products placed on the EU market. The scope of ESPR is wide and through implementation will cover progressively an increased number of products. It will also introduce a Digital Product Passport (DPP), a digital identity card for products, components, and materials, which will store relevant information to support products' sustainability, promote their circularity and strengthen legal compliance. The sustainability reporting requirements in turn stipulate companies to disclose how much of their turnover, operational expenses and capital expenses are taxonomy-eligible and taxonomy-aligned. This requirement is expected to leverage the impact of EU Taxonomy and direct financial flows to sustainable economic activities in the EU and beyond.

12.2. Regulation

Added value chemicals often face stringent regulation and they are categorized under different regulations. For example, in the EU, biopesticides are regulated under the Plant Protection Products Regulation (EC) No 1107/2009, which aims to ensure a high level of protection for human and animal health and the environment. The regulation process involves rigorous testing and evaluation to confirm the safety and efficacy of biopesticides before they can be approved for use. In the EU, novel foods are regulated under the Novel Food Regulation (EU) 2015/2283 and cosmetics are regulated by the EU Cosmetics Regulation (1223/2009/EC). In the future regulations could become more stringent as the EU continues its push for sustainability and safety. The trend is towards increased scrutiny of environmental and health impacts, which might initially seem like a block to innovation but can ultimately drive more sustainable and safer product developments. Embracing green chemistry and alternative testing methods are ways industries can innovate within these frameworks.

12.3. Need of demonstration and verification on environmentally sustainable solutions – importance of life cycle assessment view

Fossil chemical solutions and chemicals should be replaced by bio-based alternatives when bio-based solutions are more environmentally sustainable than conventional fossil systems. Evaluation and comparison should always be based on a systematic Life Cycle Assessment (LCA) to provide a holistic picture and understanding. To promote bio-based alternatives, clearly proven, research-based facts and data are needed to show, on a case-by-case basis for different product categories and alternatives, whether the bio-based alternatives are more environmentally friendly than existing fossil alternatives.

When comparing the environmental sustainability of fossil and bio-based alternatives, both the negative environmental impacts (such as climate impact, eutrophication effects, etc.) and possible differences in the technical performance of the products need to be understood and taking into account. For example, for packaging materials such as cellulose-based food packaging materials (compared to traditional fossil-based plastics), the ability of different packaging systems to prevent food waste should also be considered. In traditional LCA, chemicals derived from fossil feedstocks were often compared against bio-based chemicals without considering land use and land use change impacts to climate change. From a climate perspective, these assessments should include all elements affecting global warming, ie. fossil and biogenic greenhouse gas emissions and also all carbon emissions and removals from land use and land-use change, without ignoring other LCA factors. If only a few LCA or GWP factors are considered, comparisons are not fair.

When assessing the environmental sustainability of competing products, it is important to consider all relevant stages of the life cycle. Raw material chains are needed to be fully taking

into account. Life cycle impacts need to be assessed on the basis of a number of life cycle aspects, e.g. recoverability, compostability or resource use, or some other characteristics. Environmental sustainability needs to be considered on a whole product system basis. For example, short transport distances or the use of recycled or reduced raw material use do not allow a system to be claimed as environmentally sustainable. Similarly, the compostability or recyclability of some materials is only one parameter, and the analysis needs to be extended to include even expected consumer behaviour if relevant.

To assess the environmental sustainability of bio-based alternatives compared to fossil alternatives, in addition to comparing carbon footprints, key environmental impact categories such as eutrophication, water scarcity based on water footprints, ecotoxicity impacts and biodiversity need to be considered.

In addition, the LCA assessment of competing schemes should be based on similar harmonised LCA methodologies, such as the European Commission's Product Environmental Footprint methodology, which is still evolving, as well as harmonisation work at national level and some of Luke's ongoing research projects (https://www.luke.fi/en/projects/biolca, https://www.luke.fi/en/projects/lcafoodprint, https://www.luke.fi/en/projects/modilca-01). In practice, more detailed rules for product categories would benefit internal comparisons within specific product categories to make comparisons more robust and consistent.

12.4. Optimized value chains

Biomass production has regional specificities. For example, Finland's strength is our large surface area relative to population, which makes us a large producer of biomass per capita. On the other hand, our arable land area is the smallest in the EU, which puts the emphasis on forest biomass production. Northern conditions also influence biomass production, i.e. growth rate and plant species suited to our conditions (cascading). Long distances and the regional nature of biomass create challenges for biomass processing. In the future, different technologies and the electrification of transport will ease logistical problems and energy issues.

In the future, digital tools will facilitate the identification of the most promising biomass sources, such as agricultural waste, forestry by-products and underutilised biomass streams, and enable efficient design of bio-based production processes. Al-based tools enable industry to optimise their supply chains, reduce transport costs and ensure timely availability of fresh raw materials, which is crucial for processes such as bark biorefining (see bark biorefinery case study). The Biomass Atlas developed by Luke is an example of an important tool that can significantly support the transition to a bio-based economy by providing detailed information on the availability and location of biomass resources throughout Finland. It can also help policy makers to identify regional opportunities for bioeconomy development and ensure that investments are targeted at areas with the greatest biomass potential.

Several strategies exist to optimise biomass processing and the use of by-products and residues. The introduction of advanced technologies, such as biorefineries, can improve the conversion of biomass into valuable products. These plants combine different processes and treatment steps to maximise the recovery of useful components, reduce waste and improve overall efficiency. For example, combining thermal, chemical and biological treatments can help to extract more value from biomass. Locating biorefineries close to the biomass production site and in some cases using mobile biorefineries will improve the recovery of rapidly degradable compounds. Exploring new applications for new co-products can provide new income streams for farmers and local producers, for example. For example, using agricultural waste to produce bio-based chemicals, materials and energy can diversify production and increase profitability. This can be demonstrated at Luke, for example in the LivingLab Biopaja in Jokioinen. In the circular economy, it is essential to create closed systems where waste from one process becomes an input to another. Continuous research and development is needed to find new methods and applications.

12.5. Key messages

- 1. Agricultural, forest and water-based biomasses contain valuable biochemicals. Biomass is a resource whose exploitation requires the involvement of the whole value chain, from the harvesting, storage and transport of raw materials to the processing, manufacturing and marketing of final products. Cascade utilization of biomass enhance economic and environmental viability of biochemical productions.
- Biochemicals could derived from renewable resources can greatly reduce dependence on fossil-based raw materials and promote a circular economy, aligning with global climate goals. When replacing fossil solutions with bio-based alternatives, the environmental benefits must be clearly demonstrated, for example through life cycle assessment.
- 3. Regulatory support is crucial for market growth, alongside efforts to raise awareness and encourage widespread adoption of bio-based products.

Case study: bark biorefinery

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Introduction

Bark is an underutilised biomass produced at large quantities by the wood processing industry. This case study reviews the potential of tree bark for value added products. The purpose is to provide background information of the availability of bark from different tree species, its structure and chemical composition, as well as the potential the bark has as an industrial raw material. Based on the review of scientific research in the area, a concept of bark biorefinery is presented, and preliminary techno-economic assessment concerning a biorefinery utilising spruce bark as the feedstock is introduced.

Bark as a side stream

The industrially most relevant tree species in Finland are Norway spruce (*Picea abies* L. Karst.), Scots pine (Pinus sylvestris L.), silver birch (Betula pendula Roth.) and white birch (*Betula pubescens* Ehrh.). The total annual industrial utilization of these species in 2000–2022 was ca. 65.5 million cubic metres (Mm³/a) on the average. As the wood material normally has very different properties compared to the bark, the standard procedure is to remove the bark from trunks before processing them into valuable products at the industrial sites, such as sawmills or pulp mills. Based on the wood utilization, the estimated amount of bark produced annually in Finland is shown in Table 1.

Table 1. The average annual industrial utilization of the most relevant wood species in Finland, reported as cubic metres over bark (Luke 2023). Based on this data, the oven dry weight (o.d.w.) of the bark residue can be estimated, when the volume of the bark in the roundwood (%) (Heiskanen & Rikkonen 1976, Saikku & Rikkonen 1976), as well as the bark basic density (kg/m³) (Heiskanen & Rikkonen 1976, Saikku & Rikkonen 1976, Alakangas et al. 2016), is known. ND stands for "not determined".

2000-2022	Norway spruce (Picea abies)		Scots pine (<i>Pinus sylvestris</i>)		Birch (<i>Betula</i> sp.) ^{(a}		TOTAL
	Pulpwood	Logs	Pulpwood	Logs	Pulpwood	Logs	
Average utilization, Volume over bark, Mm ³	10.4	14.1	15.7	11.3	12.7	1.4	65.5
Relative bark volume, V-%	12.8	10.1	11.8	12.2	12.0	10	ND
Total bark volume, Mm ³	1.3	1.4	1.8	1.4	1.5	0.1	7.6
Basic density, kg/m ³	346	383	286	292	550	550	ND
Bark amount, Mt (o.d.w.)	0.46	0.55	0.53	0.40	0.84	0.08	3.0

^{a)}Including silver birch (Betula pendula) and white birch (*Betula pubescens*); no separate data available

The amount of bark from the wood processing industry is significant, a total of 7.6 million m³ or 3.0 million tonnes. Currently, this feedstock is combusted to supply energy – steam and electricity – and utilised for the industrial processes at the sawmills, plywood industry, as well as paper and pulp mills. It is estimated that the energy content of the side-streams resulting from producing one cubic meter of plywood is more than twice the amount of energy

needed for the actual manufacture of the product, making the plywood mill energy-wise more than self-sufficient (Siitonen 2010). Additionally, the energy content of the bark side-stream is 21% of the total side streams' energy content, which indicates that utilizing the bark for any other purpose than energy production would not compromise the energy demand of the plywood manufacturing.

Bark can be structurally and physiologically divided into two parts: outer bark (cork) and inner bark (phloem). The volume of the outer bark of birch is 3–4% and the volume of the inner bark is 8–9% of the whole trunk's volume. It means that e.g. one cubic meter of birch trunks contains 10.6 oven dry (o.d.) kg of outer bark (Rizhikovs et al. 2014). Thus, based on the information shown in Table 1, it can be estimated that 150 000 t of birch outer bark could be collected as a side-stream in Finland.

Value-added chemicals and their applications

Birch outer bark contains suberin and triterpenoic compounds, such as betulinol and lupeol. The content of the two latter components in the outer bark is ca. 30–35 wt.% (Ekman 1983) oven dry weight (o.d.w.), while the amount of suberin is ca. 45 wt.% o.d.w. The rest of the birch outer bark consists of other extractive components (5–10 wt.%), as well as carbohydrates (6 wt.%) and lignin (9 wt.%). (Pinto et al. 2009) Betulinol can be converted to betulinic acid, which is reported to have biological and pharmacological functionalities. It can suppress malaria and some inflammations; additionally, betulinic acid and its derivatives have anti-HIV and anti-cancer activity. (Alakurtti et al. 2006) Betulinol is an extremely lipophilic compound, making it and the derivatives of the compound good raw material for manufacturing water repellent textiles. (Huang 2019) Other reported applications for betulinol are preservative, antioxidant, or dietary supplement in foods, as well as an agent in cosmetic products. (Alakurtti et al. 2006, Zhang et al. 2019)

The suberin-derived fatty acids (FAs) are suitable for production of water-repellent coatings, e.g for hydrophobizing paper. (Korpinen et al. 2019) Other reported applications for suberin FAs range from construction and oil industry to cosmetics products, where the compounds' ability to function as dispersing and emulsifying agents is exploited. (Laine 2020) Moreover, suberin-derived FAs and their derivatives are suitable as wood preservatives, antioxidants, coatings, co-polymers (polyurethan), food preservatives, flocculants, textile dyes, and additives in foods and pharmaceuticals. (Cordeiro et al. 1999, Krasutsky et al. 2004, Rizhikovs et al. 2014, lvdre et al. 2023)

Spruce and pine bark contain substantial amounts of polyphenolic compounds called tannins. These compounds have many possible applications. Traditionally, tannins have been used in leather tanning, where the very name of this versatile component group derives. Tannins have been investigated and utilised in multitude of applications, such as glues, foams, antioxidants, antivirals, anti-inflammatory agents, rust protection, antibiotics, as well as food and beverage supplements. (Feng et al. 2013, Jablonsky et al. 2017, Shirmohammadli et al. 2018, Fraga-Corral et al. 2020) For industrial-scale applications, the best options are the traditional use in leather manufacture, as well as adhesives and glues in wood based products. (Pizzi 2019) Usually, the tannins are not isolated from Nordic softwood bark, but in recent years there has been increasing interest, and e.g. optimising the extraction conditions has been investigated. (Kilpeläinen et al. 2023)

As all lignocellulosic materials, pine bark consists of cellulose, hemicelluloses, lignin, and extractives. (Raitanen et al. 2020) The outer bark contains much more lignin than the inner bark, but both contain many types of easily extractable components, such as sugars, lignans, flavonoids, catechins, and pyrocyanidins. (Karonen et al. 2004) The inner bark is especially rich in extractives: 24 wt.% compared to only 6 wt.% in the outer bark. Due to its sugar – glucose, fructose, sucrose – content, pine inner bark was used as flour substitute for bread in Finland in the years when the rye crop was poor.

In spruce, the inner and outer bark content of extractives does not differ as markedly: inner bark's extractives content is 22 wt.%, while the outer bark contains 17 wt.% of extractives. In contrast, lignin content follows the same trend in both pine and spruce: lignin is more abundant in the outer bark also in the case of spruce. (Raitanen et al. 2020) The principal extractive compounds in spruce bark are condensed tannins, stilbenes, stilbene glucosides, and different sugars. Research into the antioxidant and antimicrobial potential of the tannin-rich water extracts from pine and spruce has shown that it may be possible to produce preservatives from these components. It was observed that the extracts successfully prevented the oxidation of triglycerides when liposome model compounds were tested. Even though the results were promising compared to other plant-based extractives, more research is needed before the bark-derived extracts can be proven safe for using as food additives and flavouring agents. (Raitanen et al. 2020) The photo-sensitive stilbene-containing extracts from spruce bark do not lose their antioxidant or antimicrobial properties even after exposure to UV light, which indicates that stilbenes could be utilized in short-term protection of surfaces. (Välimaa et al. 2020).

Which raw materials could be replaced?

The compounds extracted from bark could be used to replace synthetic chemicals derived from fossil resources (see Table 2). They could also be used to replace toxic wood preservative agents (chromium, copper, creosote etc.) the use of which is not anymore permitted.

Table 2. Examples of potential practical applications for tannins isolated from softwood bark.

Traditional utilization	New products and innovations
 Leather tanning Protein precipitation in various industrial processes of (chemical) industry 	 Water-resistant glues/adhesives Water and effluent purification (removal of heavy metals, surfactants, or other organic contaminants) Tannin foams for thermal or audio insulation, improving properties of special fire-resistant foams Coatings, laminates Antioxidative, antimicrobial tannin-treated textiles (e.g. silk) Active ingredients in cosmetics and pharmaceuticals Animal feed products Biobased resin manufacture Tannin-furfuryl-alcohol-resin-based brake pads for automotive industry Tannic acid and polyethylenglycol based biological binder for intravascular bleeding medical care Tannin-based biosorbents for recovery of dissolved valuable metals (e.g. gold, silver, palladium, platinum) from waste electronic equipment and in hydrometallurgical processes Utilization of the antimicrobial properties of sol-gel encapsulated tannin extracts

Supply chain notably affects the chemical composition of the bark raw material

Freshly removed bark is essential for bark biorefinery and this sets new requirements for the supply chain. (Routa et al. 2020, 2021) The content of extractives decreases rapidly, leading to some compounds disappearing completely. Especially the content of the valuable phenolic extractives, such as tannins and stilbenes, decreases rapidly during bark storage. Also, the storage method has a significant impact on the loss of these components. (Jyske et al. 2020, Routa et al. 2021)

Routa et al. (2020, 2021) investigated the effect of storage on the properties of pine and spruce bark at sawmill when used as fuel. They paid special attention on the extractive content of the bark. Spruce and pine bark were stored for eight weeks in piles. Samples were taken after two, four, and eight weeks of storage time. After eight weeks of storage, the extractive content of spruce bark had decreased to 66% of the original content; for the pine bark the corresponding value was 56%. The most significant changes took place already during the first two weeks of storage. The loss of the condensed tannins in the pine bark was 60% during two weeks of storage. Thereafter, a slight decrease in the content was observed. Jyske et al. (2020) studied the effect of storage on non-debarked spruce logs during 24 weeks. Similar experiments were conducted both during summer and winter. During winter storage, the content of the condensed tannins remained unchanged during the first 12 weeks, after which a significant decrease was observed. During the storage in summer, the tannin content of the outer bark started to decrease immediately. The stilbene content of the bark also decreased rapidly even during wintertime at low temperatures (Figure 1). Halmemies et al. (2018) stored spruce sawmill bark in a pile for 24 weeks. They reported that the stilbenes in the bark had completely disappeared already after four weeks of storage time.





Figure 1. Yield of stilbene glycosides and aglycons in bark of Norway spruce saw logs during storage treatments in winter (bars on the left) and summer (bars on the right). The colours of bars indicate the stilbene compounds: green, sum of stilbene glycosides; blue, sum of stilbene aglycones. The whole bark was analysed without separation to inner and outer layers. (Jyske et al. 2020)

The chemical composition of wood bark, as well as the antioxidative properties of the extractives, remain less affected when the logs are stored with bark, compared to the case when the wood is debarked, and the separated bark is stored in a pile. (Jyske et al. 2020) The key to the isolation and utilization of the extractives is to speed up the supply chain so that the bark raw material is transported to the processing site immediately after debarking. Especially the content of valuable components, such as tannins and stilbenes, starts decreasing after log felling.

Estimation of the current TRL (Technical readiness level)

There are commercial companies having activities in producing certain compounds from birch bark; thus, TRL is 7 or higher.

Examples of companies utilizing birch bark:

- Innomost (Kokkola, Finland) https://www.innomost.com/
- Nature Science Technologies (Riga, Latvia) https://nstchemicals.com/
- BetulinLab (Riga, Latvia) https://betulin-lab.com/en/betulin/
- KoivuBioTech (Helsinki, Finland) https://www.rasweet.com/

Company utilizing pine bark

- Eevia Health Oy (Kauhajoki, Finland) https://eeviahealth.com/
- Ravintorengas Oy (Siikainen, Finland) <u>https://ravintorengas.fi/</u>

Estimation of the current SRL (Social readiness level)

There are commercial companies having activities in producing certain compounds from birch bark; thus, SRL is 9 or higher.

Future research including scale-up

Although some applications do exist also in the industrial level, research into the derivatization of the of the bark components and testing of the resulting products is still required. Techno-economic assessment (TEA) for scaling up the processes from the laboratory scale to pilot and finally to the industrial scale is needed. The production must be economically feasible and sustainable. Full utilization of the bark e.g. via cascade processing (combining the unit operations) is one possible practical solution for increasing the sustainability of the production, but this approach calls for more research. (Rasi et al. 2019) The novel products also need to go through the administrative approval protocol, depending on the target application, e.g. novel food legislation, chemical legislation.

Techno-economic assessment of bark biorefinery

In this TEA, the bark biorefinery is a cascade process (Ding et al. 2017, Rasi et al. 2019) where the principles of green chemistry (Anastas and Warner 2000) are considered.

Process steps

Pulp mills, sawmills and plywood mills are using different debarking methods. At pulp mills, the tree trunks are customarily sprayed with water prior to debarking (Willför et al. 2011), due to which water-soluble extractives are partially washed out from the bark. Additionally, the

log diameters are different: usually, the pulp mills are using smaller diameter tree trunks compared to sawmills and plywood mill. This affects the bark content and composition.

In Finland, the most relevant transportation method for bark is by land using lorries. As the bark material's freshness has a significant effect on the amount and quality of the compounds to be extracted, the location of the biorefinery should be in a vicinity of sawmills and pulp mills or other wood processing facilities. Mechanical and chemical wood processing sites are often situated close to each other, which creates synergy to the processes: e.g., steam and electricity from pulp mill's recovery boiler can be utilised for paper and board production, or a material side stream from one process can be exploited as the raw material of another process. According to this scenario, an optimal site for a bark biorefinery would be a forest-products mills integrate, where, for example, bark raw material and energy, as well as effluent treatment plant, are readily available.

The bark is fed into the process and pre-treated so that the material's particle size and moisture content are optimal for the extraction process. The subsequent extraction process can consist of several sequential extraction stages, during which different solvents can be used. Mostly, the process is water-based but small-molecule organic solvents, such as ethanol, may be used for isolating more lipophilic components e.g., from birch outer bark. The process should be such that the highly water-soluble components, which do not withstand high temperatures or low pH values (tannins, stilbenes, mono- and oligomeric sugars, etc.), can be isolated first, and thereafter the extraction process proceeds to collect other components, such as hemicelluloses.

The extracts are further purified through water removal (e.g., ultrafiltration) and spray drying; also, enzymes can be applied to aid purification (Kyllönen et al. 2023). The technology for isolating the components is based on the application's requirement: for some applications high purity of the individual components is required while for others, a mixture of many components is suitable.

Material balance

The material balance is calculated for a process using annually 40 000 o.d.w. tonnes of spruce bark. The dry matter content (DMC) of the bark is 43%. The block diagram with the material streams of the bark biorefinery is shown below (Figure 2).



Figure 2. Bark biorefinery block diagram and principal material streams. The numbers in dark brown colour refer to organic material o.d. weight and the numbers in blue colour also include the weight of water. The water additions are shown in light blue. The bark raw material used annually is 40 000 o.d.t. The streams are given both in annual tonnes (t/a) and kilograms in hour (kg/h). The figure shows the o.d. weights for the dissolved tannins and hemicelluloses; however, these streams also contain other dissolved components, the amounts of which can be found below in tables and text. PHWE stands for Pressurised Hot Water Extraction.

Pre-treatment and Water Extraction

The chemical composition of the bark is presented in Table 3.

Table 3. Chemical composition of the raw material, fresh spruce whole bark from a sawmill. (Raitanen et al. 2020) The part named "Other" contains extractive components other than tannins, as well as inorganic salts.

Component	wt.% of dry matter
Lignin	31.0
Cellulose	22.0
Hemicelluloses and pectin	28.0
Tannins	10.0
Stilbenes	2.0
Other	7.0
TOTAL:	100.0

The pre-treatment methods of the bark include diminution (e.g. shredding, grinding), screening and drying of the bark to a suitable DMC. The material loss in screening (reject) is estimated to be 2 wt.%. After pre-treatment, the bark is extracted at 90 °C for 60 minutes at liquid-to-solids (L/S) ratio of 10 l/kg, after which the extract is separated from the solid material (DMC=30%). In this process, 10 wt.% of the original dry matter is dissolved into the extract. Table 4 depicts the chemical composition and other properties of the dissolved material.

Table 4. Chemical composition of the dissolved material in the first extraction (90 °C, 60 min., L/S=10). The resulting tannin content in the extract is approximately 0.7 wt.%, while the overall

content of the solid material is 1.2 wt.%. In the process, 320 522 t/a of extract is produced, corresponding to 40 065 kg/h. During the first extraction stage, no lignin or cellulose dissolves. The part named "Other" contains extractive components other than tannins and stilbenes, as well as inorganic salts.

Component	wt.% of dry matter
Hemicelluloses and pectin	30.0
Tannins	53.0
Stilbenes	10.0
Other	7.0
TOTAL:	100.0

Pressurized Hot Water Extraction

The next stage in the process for the solid material is the Pressurized Hot Water Extraction (PHWE), carried out at 160 °C for 60 min. at L/S ratio of 10 l/kg. During this step, 30 wt.% of the solids dissolve, yielding a solution rich in lignin and hemicellulose (Table 5). Cellulose is inert at this temperature; therefore, it does not appear among the dissolved components.

Table 5. Chemical composition of the dissolved material during PHWE (160 °C, 60 min., L/S=10). The resulting hemicellulose content in the extract is approximately 2.1 wt.%, while the overall content of the solid material is 5.3 wt.%. In the process, 210 504 t/a of extract is produced, corresponding to 26 313 kg/h. During PHWE, no cellulose dissolves. The part named "Other" contains extractive components other than tannins and stilbenes, as well as inorganic salts.

Component	wt.% of dry matter
Lignin	37.7
Hemicelluloses	38.9
Tannins	8.7
Stilbenes	3.4
Other	11.3
TOTAL:	100.0

Table 6 presents the chemical composition of the solid material after the PHWE step.

Table 6. Chemical composition of the solid material after PHWE (160 °C, 60 min., L/S=10). The total amount of the material is 24 696 o.d. t/a, corresponding to 3 087 o.d. kg/h (DMC 30%). The part named "Other" contains extractive components other than tannins and stilbenes, as well as inorganic salts.

Component	wt.% of dry matter
Lignin	33.1
Cellulose	34.9
Hemicelluloses	23.0
Tannins	3.7
Stilbenes	0.1
Other	5.1
TOTAL:	100.0

Comparison to published bark biorefinery cases

Ajao et al. (2021) and Wijeyekoon et al. (2021) have published techno-economic assessments of bark biorefineries in Canadian and in New Zealand context, respectively. In both cases, tannins are extracted. Additionally, the targeted products include lignin and cellulose rich residue (Ajao et al. 2021), as well as bark briquette (Wijeyekoon et al. 2021). In the Canadian scenario, an option for producing polyurethane bio-based foam incorporating 20% of lignin, as well as polypropylene biobased composites from cellulosic fibres was also investigated (Figure 3).



Figure 3. Block diagram of the bark biorefinery proposed by Ajao et al. (2021).

Currently, we are lacking a detailed economic analysis of our bark refinery concept; however, some aspects of the bark biorefineries can be compared (Table 7).

	Bark biorefinery case			
	Ajao et al.	Wijeyekoon et al.	Luke	
Bark input (o.d.t/a)	300 000 (900 o.d.t/d)	20 000	40 000	
Bark type	Black spruce, yellow birch	Radiata pine	Norway spruce	
Tannin yield (wt.% of o.d. bark)	6 (spruce); 3 (birch)	20	5	
Other products	Lignin, fibrous residue (a	Bark briquette	Hemicellulose, solid stream	
Tannin price (USD/t)	1500	1644	NA	

Table 7. Comparison of bark biorefinery cases.

^{a)}Additionally, the products can be used in manufacture of bio-based polyurethane foam, as well as composites from cellulosic fibres

NA = not available

The capacities of the industrial scale scenarios are very different: ranging from 300 000 to 20 000 o.d.t annual utilisation of bark. Another notable difference can be seen in the tannin yield: Wijeyekoon et al. (2021) assume a 20 wt.% yield for their extraction process, which seems very high compared to the other cases.

When looking into the economic viability, both of the cited bark refinery concepts (Ajao et al. 2021, Wijeyekoon et al. 2021) show favourable economic figures, depending on the conditions chosen. The feasibility is increased along with increasing tannin yield, and naturally the other products' selling prices have a big effect on the feasibility. In addition to annual bark processing volumes, there are also very big differences in the estimated CAPEX and OPEX (capital and operating expenditures, respectively) of the bark biorefineries. These differences are, on one hand, at least partially explained by the differing intended production volumes, but on the other hand it is not easy to explain why the Canadian bark biorefinery CAPEX (Ajao et al. 2021) is 67 times higher than the respective figure for the New Zealand case (Wijeyekoon et al. 2021) (1 014.8 and 15.2 million USD, respectively).

Another important factor affecting the economy is the type of products manufactured: when looking into the economic feasibility of the bark biorefinery, Ajao et al. (2021) found that it was not very profitable to produce and sell directly lignin and tannin extracts; the economic performance was improved if polyurethane bio-based foam was produced, despite the increased capital investment and operating costs. Furthermore, due to synergy provided by existing infrastructure and resources, substantial economic benefits are achieved if the bark biorefinery is placed alongside with an existing forest industry installation, which is especially highlighted by Wijeyekoon et al. (2021)

As mentioned in Table 2, tannin-based chemicals can be utilized in effluent purification. According to Table 1, the average annual amount of bark generated in Finland was roughly one million o.d. tonnes for Norway spruce and 0.9 million o.d. tonnes for Scots pine. In our bark biorefinery example, the tannin yield is ca. 5 wt.%, meaning that approximately 45 000 o.d.t tannins could be produced from the processed softwoods in Finland with this technology (the total theoretical yield of tannins is approximately 97 000 o.d.t). For example, municipal wastewater treatment plants in Finland generate 150 000 – 160 000 o.d.t sludge per year. The dosage for an average cationic polyacrylamide (PAM) flocculant for digested wastewater sludge ranges from 5 to 15 kg active polymer per tonne dry matter. If the modified tannins can be dosed similarly to treat wastewater sludge, 750 - 2400 o.d.t of tannins are required for municipal wastewater treatment plants in Finland; hence, the existing bark biomass is well sufficient for manufacturing flocculants to replace the synthetic polymers (cationic PAM).

Conclusion

Based on the discussion above, these conclusions can be made about the bark biorefinery case presented in this report:

- 1) The bark biorefinery concept is technically viable, and comparable to other concepts presented in literature.
- 2) For favourable economic performance following should be carefully considered:
 - i. synergy with existing sawmills and pulp mills is essential, and therefore the bark biorefinery should be placed in vicinity of existing sawmills, pulp mills etc.
 - ii. bark type and quality have a strong effect on the bark biorefinery feasibility, and this can be affected by optimizing the supply chain
 - iii. for the viability of the process, it is of utmost importance that marketable products are manufactured from all the streams: tannins, hemicelluloses, as well as the solid stream (the latter contains more than 50 wt.% of the raw material's dry matter)
- 3) Making direct comparisons with other presented bark biorefinery concepts is challenging because the product portfolios suggested are somewhat different and because the markets at least for some of the products are still developing.
- 4) A more detailed TEA of the bark biorefinery case should be constructed, taking carefully into account all the equipment and materials needed in the process, as well as its total energy consumption, and the market value of the product portfolio.

Scenario for 2035 and 2050

Although currently the profitability of the presented bark biorefinery is somewhat questionable, we believe that by 2035 we will have at least one industrial-scale bark biorefinery operating in Finland. By 2050, due to climate change mitigation actions and stringent legislation, the market situation has been changed to favour bio-based materials and products over the fossil based alternatives. Therefore, virtually all bark side-streams are used for marketable products, meaning that bark biorefineries exist alongside with all the major forest products industry sites. Based on this scenario, Finnish industry will be a significant player in isolating the bark-based tannins, stilbenes, hemicelluloses, lignin, and fibres, as well as manufacturing products from thereof.

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