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VTT

PL 1000

02044 VTT

Puh. 020 722 111

<https://www.vtt.fi>

VTT

P.O. Box 1000

FI-02044 VTT, Finland

Tel. +358 20 722 111

<https://www.vttresearch.com>

Engineered Lignin Products

Lignin Based Polyacids to Substitute Fossil-Based Materials in Coatings Formulations

Olesya Fearon¹, Viviana Polizzi², Pieter Vandezande², and Anna Kalliola¹

¹VTT Technical Research Centre of Finland Ltd, Espoo, Finland

²Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium (VITO)

Corresponding author: Olesya Fearon <olesya.fearon@vtt.fi>

Abstract

Coatings provide protection against moisture, can improve fire resistance properties and simultaneously act as decoration. The aim of this work is to develop sustainable bio-based polyacids to substitute fossil-based materials in polyester and alkyd resin coatings. A sustainable process aims for reduced energy use, efficient resource use, minimal waste production and utilization of renewable and non-toxic products. However, very few commercial options and technologies for biobased materials are currently available.

Lignin, a renewable side stream from pulp mills and biorefineries, is currently underutilized. However, it has a high potential to provide not only higher economic returns, but also environmental benefits by substituting fossil-based coating formulations. The LigniOx technology, where lignin is oxidized by O₂ under alkaline conditions, produces water-soluble polymeric lignin by increasing its anionic charge. These oxidized lignins have successfully been applied as concrete plasticizers and versatile dispersants. Currently, the LigniOx process conditions were adjusted to produce lignin based polyacids at high yield. The target is to obtain low molecular fractions of lignin polyacids for alkyd coatings. The high molar mass fraction is utilized as dispersants for coating formulations.

The development of sustainable alternative for synthetic polyacids for coatings using the LigniOx process also supports the feasibility and commercialization of other end-use applications developed and tested for the LigniOx lignins as well as aids in reaching the European target of carbon neutrality.

Introduction

Coating- formulations consist of several components: resin (binder), liquid (solvent or water), pigments, and additives. Today, majority of resins, paints and varnishes are produced from fossil- based raw materials. The key feature that distinguishes alkyds from other polyesters is the presence of monoacids (commonly fatty acid) as a major part of the composition (Jovičić et al., 2020). Alkyds are mainly solvent-born formulations, which leads to high fossil-based VOC content in the final product.

Water-based solutions reduce VOC content, however, derive a major proportion of their resin components from fossil-based sources.

Synthetic polycarboxylic compounds utilized in alkyd coatings could be replaced by bio-based alternatives. The use of bio-based carboxylic acids in coating systems usually is limited to plant oil-delivered fatty acids utilized in the formulations of alkyd resins (Derksen et al., 1995). Nowadays, the development of bio-based polyacids for above mentioned applications is strongly supported by the industry. Bio-based carboxylic acids can be produced from carbohydrates in lignocellulosic materials (basically cellulose) e.g. lactic acid, formic acid, levulinic acid, glycolic acid (Yang 2015). Additionally, lignin can be treated in different ways to recover the carboxylic acids. Lignin carboxylation e.g. by carboxymethylation (Konduri et al., 2015) or using anhydrides (Kazzaz et al., 2019) are well known methods. Recently, also more sustainable enzymatic carboxylation (Tommasi 2019) has been reported. In carboxymethylation, toxic chemicals are used, and the enzymatic means are still far from industrial applicability. Furthermore, lignin remains in polymeric form without reduced molecular weight, which would ease the application in resin formulation similarly to the current monomeric aromatic di- tri- or polyacids. Oxidative degradation of lignin is an approach to produce monomeric/dimeric aromatic acids. However, lignin is rather recalcitrant for depolymeration; the monomer yields are typically rather low (< 15 %), and complex mixtures of aromatic aldehydes and acids, quinones, and aliphatic (di)carboxylic acids are formed (Costa and Rodrigues 2021; Zhou et al., 2022). These are also prone to secondary repolymerisation reactions. Objective of the current work is to develop a new conversion route to produce intermediate chemicals based on lignin, specifically to produce oligomeric lignin-derived polyacid fractions (for alkyd coatings) at high yield by alkali-O₂ oxidation.

Approach

Technical lignins have been explored as polyols in polyester coating applications (Haridevan et al., 2021). However, to perform as polyacids, lignin has to be modified and new carboxylic acid functionalities should be introduced to its structure. In the current work, industrial lignin raw materials: softwood kraft lignin (KL) and wheat straw organosolv lignin (OSL) (provided by Stora Enso and CIMV, respectively) are oxidized to perform as polyacids in alkyd and polyester coating formulations. The scheme of lignin polyacids production is illustrated in Figure 63. Industrial lignins are oxidized under different process conditions (e.g. pH profile, catalyst, O₂, pressure, time, temperature and concentration). Further, oxidised lignins are fractionated according to the molecular weight by cross-flow membrane filtration, to produce fractions with low enough molecular weight for the alkyd and polyester applications. The remaining larger molecular weight fractions are tested as dispersants in coating formulations. The fractionation and purification of oxidized lignin solutions has special emphasis on removal of sodium to produce material with less than 0.5-1 % of Na. The optimization of oxidation and post-treatment parameters for the variable lignin raw materials is performed according to the feedback of project partners on the performance of lignin-based polyacids in applications.

Batch reactor is used for screening of the oxidation conditions, after which the oxidation will be scaled up using a pilot reactor (215 L) constructed by ANDRITZ. Membrane filtration protocols are elaborated and optimised for the recovery, fractionation, and purification of all variable oxidized lignin types. Bench-top crossflow test rigs (1-20L) are used for screening trials, proof-of-concept testing and process optimization of membrane filtration, whereas the actual samples for application testing and product demonstrations are produced on pilot test units (20-200L).

Final lignin fractions are analysed for the molecular weight, acid value, anionic charge, inorganic compounds, Gardner index, TGA as well as ³¹P NMR for lignin functionalities and GC/MS for composition

of small molecular weight compounds. Acid value and Gardner index parameters specifically important for coating formulations preparation.

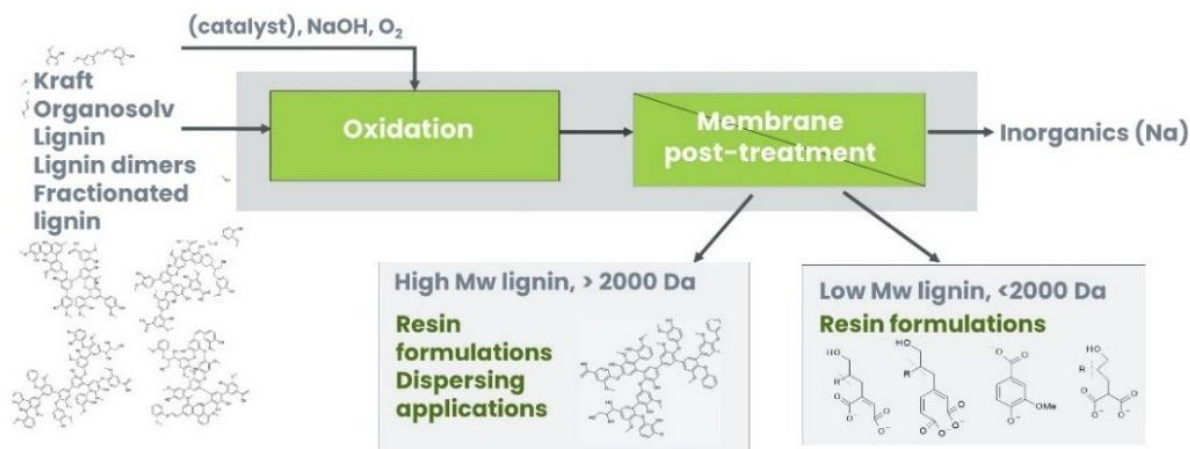


Figure 63. Concept for production of lignin polyacids.

The major challenge for converting lignin into small lignin-based polyacids is the selective bond cleavage during the oxidation process. The reaction mechanism, product yield, and product distribution of lignin oxidation strongly depend on processing conditions, especially pH and selection of an oxidant. Oxidative conversion of lignin through LigniOx technology for concrete plasticizers and versatile dispersants aims to retain the polymeric structure of lignin (Kalliola et al., 2022). Varying the LigniOx oxidation conditions towards more degrading process, gives a complex mixture of lignin structures as well as a high share of secondary oxidation products such as aliphatic acids. Yield of lignin polyacids should be high enough to allow a feasible conversion process. However, it is well known that lignin is difficult to degrade with high yield at any conditions, e.g. vanillin could be recovered with the highest yield ~14 % (Wang et al., 2018). The yield of lignin has direct correlation with a final molecular weight as presented in Figure 64. Preferably, having a lignin raw material with rather low molecular weight at the start would ease the production of lignin polyacids with acceptable yield.

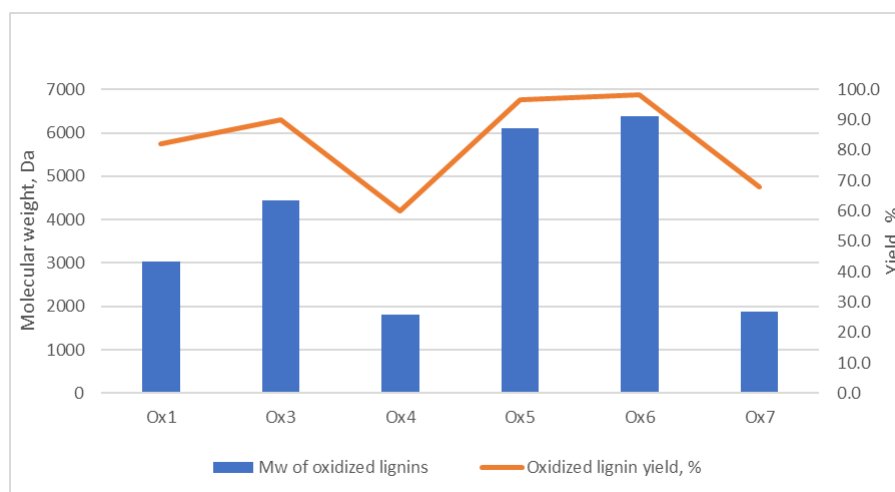


Figure 64. Molecular weight and yield of oxidized lignins with varying oxidation parameters. Should you include the initial Mw of KL in the fig? Yield axis without a decimal.

Carboxylic acid functionalities could be introduced to lignin structure in relatively fast and mild oxidation conditions (Kalliola et al., 2022). However, to decrease lignin molecular weight - harsh oxidation conditions should be applied to break bonds. It leads to secondary degradation of lignin

structures to aliphatic acids with low yield of lignin (Kuitunen et al., 2011). Therefore, refining lignin using organic solvents, e.g. EtOH/water, is a promising strategy to obtain homogenous fractions with controlled quality in terms of structure and properties. The EtOH/water soluble lignin fraction poses low molar mass, higher phenolic (PhOH) and carboxylic groups (-COOH) content than insoluble fraction (Jääskeläinen et al., 2017). The soluble fraction, having molar mass below 2000 Da, is preferable used for coating applications after being alkali-O₂ oxidized to increase the -COOH content in the lignin fragments. The insoluble fraction having molar mass of > 5000 Da, is preferable carbonized to produce lignin based hard carbon. End-uses of lignin based hard carbons include energy storage and harvesting. The insoluble fraction can also be valorised to a versatile dispersant by applying the alkali-O₂ oxidation (LigniOx). The lignin starting material can be fully used after the EtOH/water fractionation and by applying the given modification strategy to produce modified lignins for high-performance applications as presented in the Figure 65.

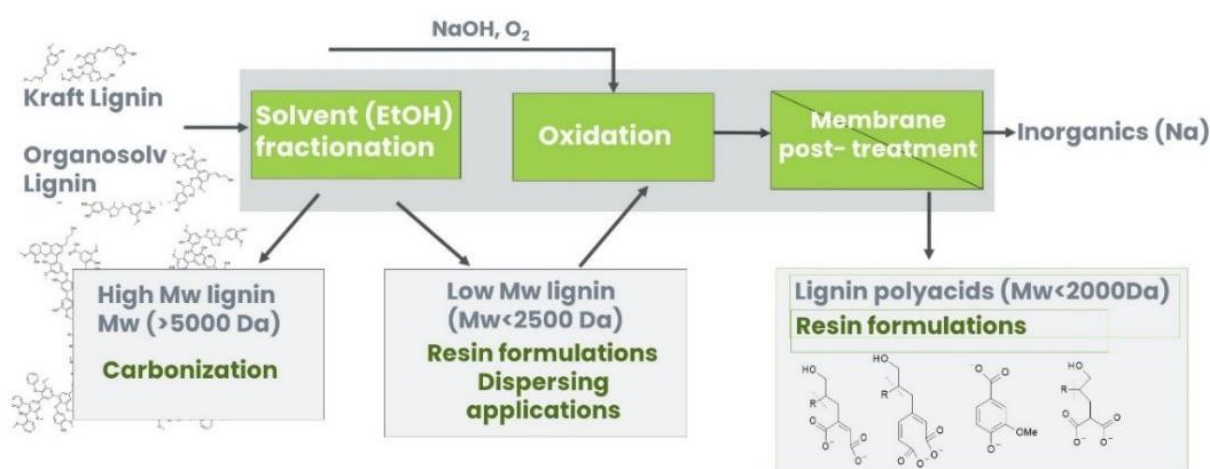


Figure 65. Lignin polyacids production concept with fractionation step

Utilizing already fractionated lignin for the oxidation gives freedom in oxidation parameters which could be tuned to modify structure of lignins (functionalities) and not focusing on breaking lignin bonds. Sodium content in the final fraction could be also decreased by fractionation step, due to lower alkali (NaOH) dosing in oxidation and more efficient membrane post treatment.

Conclusions

Alkali-O₂ oxidation technology with tuned process parameters converts various industrial lignin raw materials to low molecular weight lignin-based polyacids. However, it is critical to have application(s) for high molecular weight fractions to have a feasible process. The final decision, between oxidation at harsh conditions or solvent fractionation and mild oxidation will be done based on the performance in application test and techno-economic analysis.

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