Esterification: A feasible approach to improve structural properties of *organosolv* lignin

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Keywords: esterification, *organosolv* lignin, structural properties.
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Introduction: Lignin is one of the main components in biomass, with the presence up to 30% in the total composition. It is notably as a second most abundant natural biopolymer (after cellulose) with an aromatic-enriched structure, and mainly composed by three main building blocks that so-called p-hydroxyphenyl (H), guaiacyl (G), syringyl (S) (figure 1A) (Constant et al. 2016). Thanks to the special structural feature of lignin as well as appointed hydroxyl groups that can be easily modifed, lignin is offerring a potential renewable source for making biopolymer. In order to get lignin become ready-to-use macropolymer building blocks, the structural transformation is inevitable. Among several modification pathways, the substitution of long chain hydrocarbon via esterification between aliphatic/aromatic hydroxyl groups in lignin and fatty acid chloride is the most feasible approach. As consequences, the hydrophobicity, thermoplasticity and miscibility in common organic solvent properties of lignin would be improved, providing better possibility of using lignin in polymer industry.

Organosolv delignification is sulfur-free process and considered as the best treatment for lignocellulosic biomass (LB) in terms of purity and highly preserving lignin structure (Galbe and Wallberg 2019). In this study case, lignin extracted from pine by using organic solvent (e.g., 1,4-dioxane) in the presence of hydrochloric acid as catalyst, also known as *organosolv* lignin, mainly focused for the modification tests. The extracted lignin was then modified with active compound (e.g., octanoyl chloride, C8) (figure 1B) with the use of catalyst pyridine or triethylamine have been comparatively investigated.

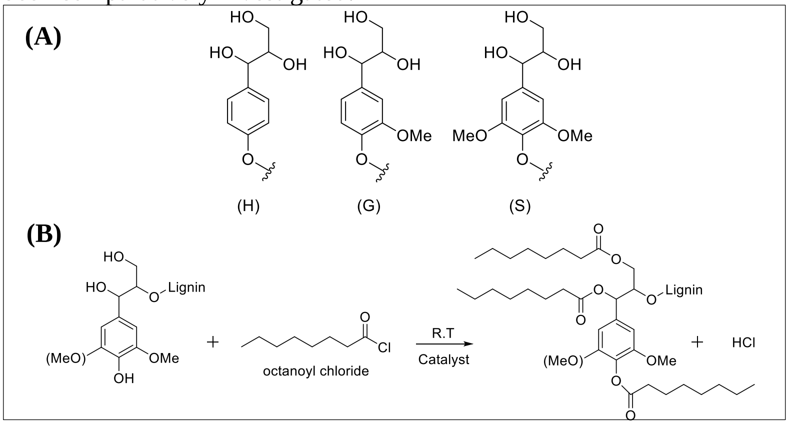

Figure 1. *Three main monomers in lignin (A); esterification scheme between fatty acid chloride and aliphatic/aromatic hydroxyl groups in lignin (B).*

Materials and method: octanoyl chloride (C8, 99%, ThermoFisher), pyridine (anhydrous, 99.8%, Sigma-Aldrich), triethylamine (TEA, 99.8%, Fisher Scientific), tetrahydrofuran (THF, HPLC grade 99.9%, Fisher Scientific), 1,4-dioxane (99%, analytical grade, Fisher Scientific), *organosolv* lignin (extracted from pine in 1,4-dioxane/0.28 M HCl, 6h, well described elsewhere (Piia et al. 2022)).

Esterification with different catalyst: 0.5 g of *organosolv lignin* extracted by 1,4-dioxane (4.2 mmol OH/g of lignin, previously determined by phosphorous NMR (Piia et al. 2022)) was weighted into the 100 ml round bottom flask. 10 ml of THF was additionally added and kept stirring until completely dissolve lignin. Catalyst (pyridine or TEA) was then added at a certain amount of 9.4 mmol/g of lignin (Koivu et al. 2016), stabilized for 10min. The excess amount of octanoyl chloride was pipeted to the mixture (1.3 equiv. to OH groups in lignin). The reaction was kept at R.T for 2 hours. Upon completeion, reaction quenching by adding 50 ml of water/ethanol mixture (1:1, v/v%), and then washing with the same volume for three times to remove the excess reagent and unreacted lignin. Finally, the esterified lignin was dried in the oven at 35^{o}C, overnight.

Results and discussions: The obtained materials were checked by ATR-FTIR. All spectra were recorded using 5 scans from 400 to 4000 cm^{-1}, corrected with zero-baseline correction function, and normalized at 1508 cm^{-1}, signal of C=C aromatic skeleton vibration. From figure 2, it shows that the synthesis pathway was sufficient to get lignin modified when either using pyridine or TEA, confirmed by the appearance of vibration at 1737, 1759 cm^{-1} imply for carbonyl groups (C=O) from aliphatic, and aromatic ester, respectively. In addition to that, the successful attachment of long chain hydrocarbon to the functional OH groups in lignin was further confirmed by the significant decrease in OH band, broadening around 3400 cm^{-1}, together with the increase in CH, CH_2, alkyl stretching from 2850 to 3000 cm^{-1}. Further evidence also shown in the fingerprint region, all esterified lignin samples give rise to the rocking vibration of CH_2 from the attached long chain hydrocarbon.

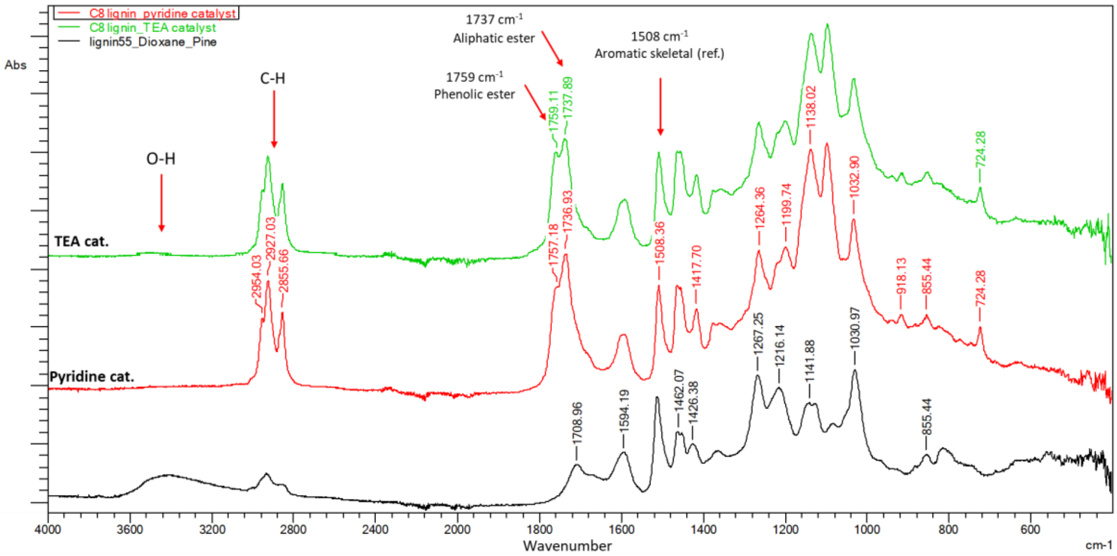

Figure 2. *FT-IR spectra of ethanol lignin from pine wood (black) and esterified lignin materials with octanoyl chloride (C8), using pyridine or triethylamine (TEA) as catalyst.*

Conclusions: The esterified lignin was successfully obtained by using either pyridine or triethylamine with the testing protocol. The efficiency of reaction when interchangably used two catalyst do not show significant difference in the degree of substituion that confirmed by FT-IR with OH band completely dissapear after modification. Due to the cost effective reason, further investigation will be carried out by using TEA for catalyzing lignin esterification reaction, and more variety of lignin from different treatment conditions as well as biomass sources will be examined. Fatty acid-derivatized lignin with improvement in hydrophobicity will be easier to be miscible within polymer matrix, providing better property for making biodegradable polymer.

References

Constant, Sandra, Hans L. J. Wienk, Augustinus E. Frissen, Peter De Peinder, Rolf Boelens, Daan S. Van Es, Ruud J. H. Grisel, Bert M. Weckhuysen, Wouter J. J. Huijgen, Richard J. A. Gosselink, and Pieter C. A. Bruijnincx. 2016. “New Insights into the Structure and Composition of Technical Lignins: A Comparative Characterisation Study.” *Green Chemistry* 18(9):2651–65.

Galbe, Mats, and Ola Wallberg. 2019. “Pretreatment for Biorefineries: A Review of Common Methods for Efficient Utilisation of Lignocellulosic Materials.” *Biotechnology for Biofuels* 12(1):1–26.

Koivu, Klaus A. Y., Hasan Sadeghifar, Paula A. Nousiainen, and And Jussi Sipila Dimitris S. Argyropoulos. 2016. “Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin.” *ACS Sustainable Chemistry & Engineering* 4:5238–47.

Piia Jõul, Tran T. Ho, Urve Kallavus, Alar Konist, Kristiina Leiman, Olivia-Stella Salm, Maria Kulp, Mihkel Koel, and Tiit Lukk. 2022. “Characterization of Organosolv Lignins and Their Application in the Preparation of Aerogels.” *Materials*.