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

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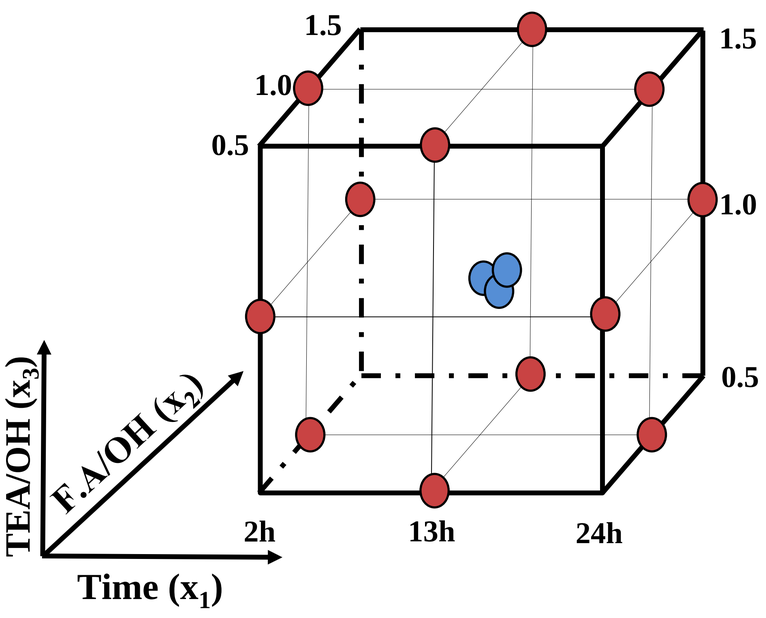
1. Introduction

Up to 30% presence in lignocellulosic biomass, lignin is a second natural aromatic polymer (after cellulose), composed mainly by three monolignols, p-hydroxyphenyl (**H**), guaiacyl (**G**), syringyl (**S**) [1]. Due to the depletion of fossil resource nowadays, producing bio-based thermoplastic material is remaining as a hot topic, especially in the field of lignin valorization. Herein, we reported the way of converting *organosolv* lignin into the ready-to-use macropolymer building blocks by chemically modifying via esterification reaction with fatty acid chloride in the presence of catalyst.

Lignocellulosic biomass | ***Organosolv* pulping** | ***Organosolv* lignin** | **Monolignols**

2. Method

Box-Behnken design of experiment (B-DoE) has been applied using three factors for investigating the optimal condition of lignin esterification (**Fig.1**) in accordance with the responses obtained from FT-IR (aliphatic, aromatic carbonyl stretching).



Optimal condition

$x_1 = 4h$, $x_2 = 1.5$, $x_3 = 1.5$

Figure 1. *A set of 15 experiments, created by Box-Behnken design to investigate the optimal condition for pine lignin extracted by 1,4-dioxane [2]. Three variables are considered, time (x_1), molar ratio of fatty acid chloride (F.A) and triethylamine (TEA) to OH content [2] (x_2, x_3, respectively).*

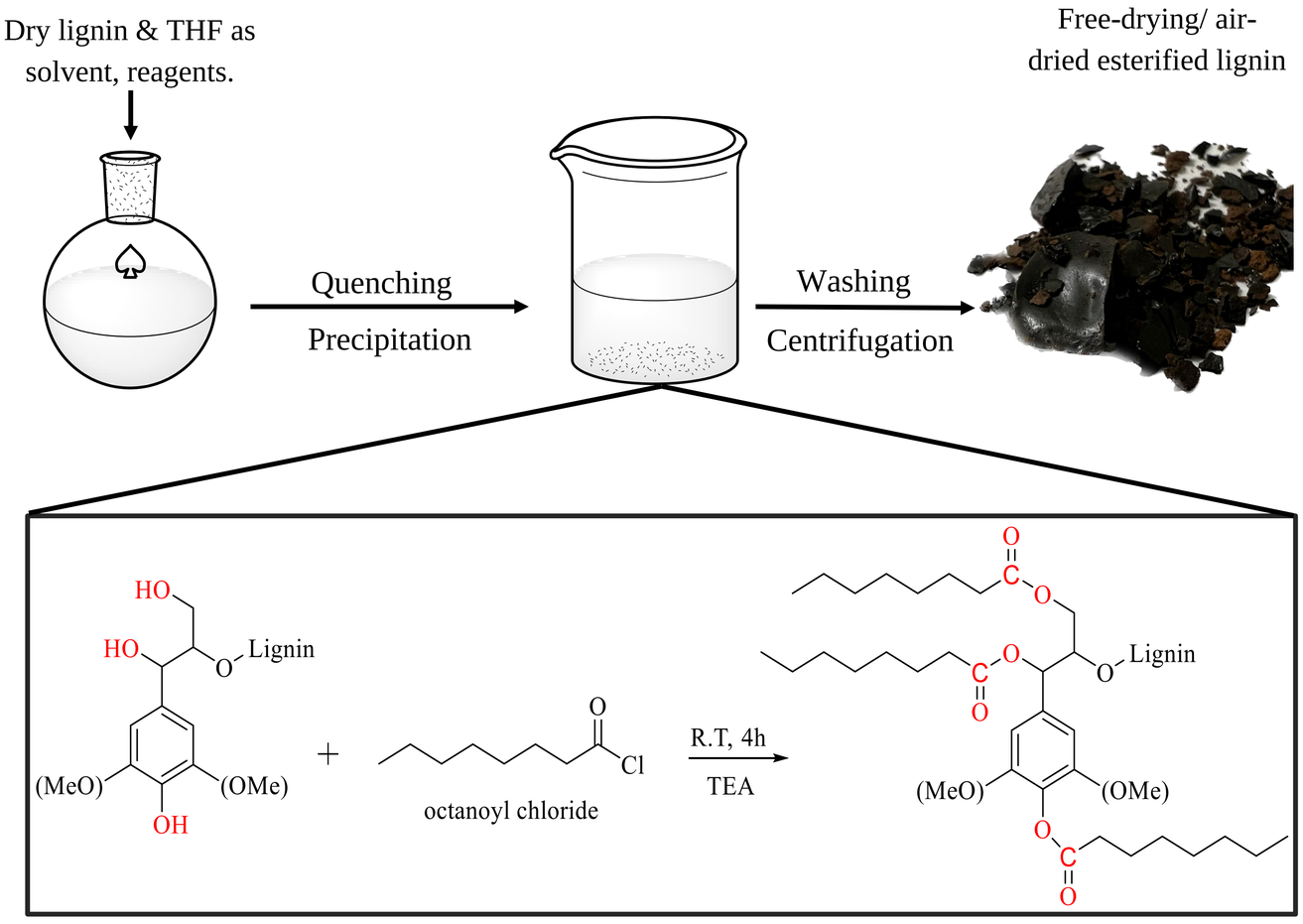


Figure 2. *Esterification reaction scheme between OH groups in organosolv lignin and octanoyl chloride catalyzed by triethylamine (TEA) under optimized condition obtained from Box-Behnken design of experiment.*

3. Results and Discussion

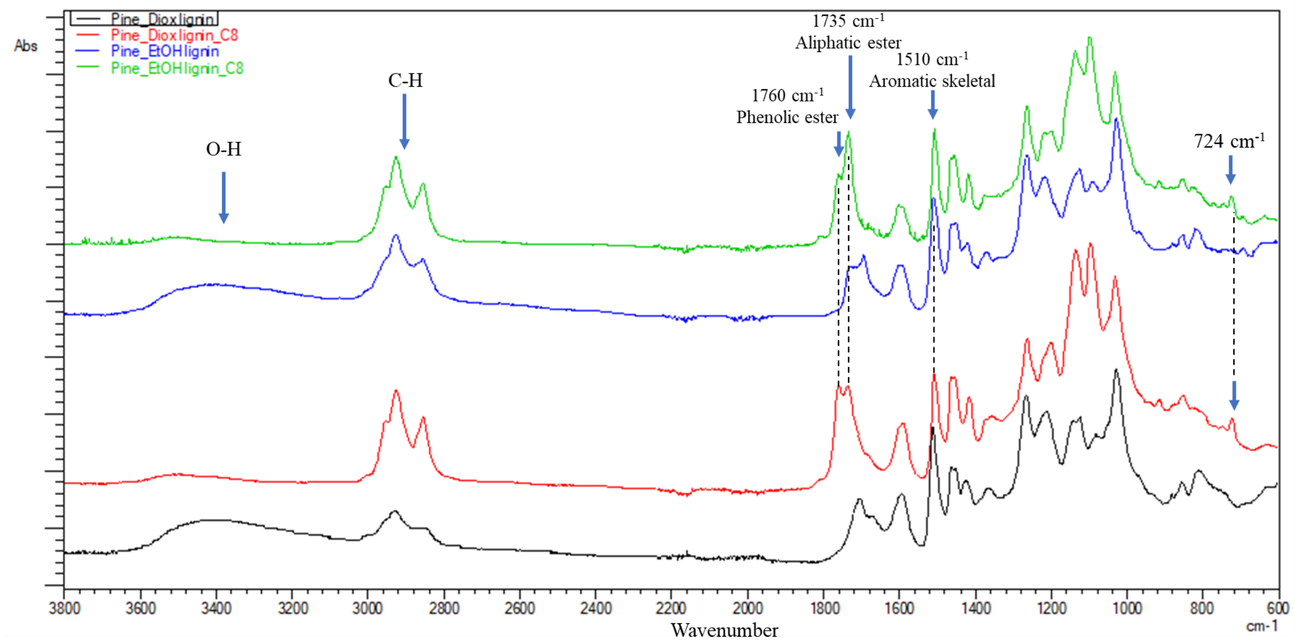


Figure 3. *FT-IR spectra of lignin extracted by ethanol, and 1,4-dioxane from pine sawdust and its esterified derivatives with eight carbon sidechain attachment (C8).*

- ✓ OH stretching broad band around 3400 cm^{-1} substantially decreased while the alkyl chain stretching from 2850 to 3000 cm^{-1} increased due to the attachment of long chain hydrocarbon.
- ✓ New carbonyl (C=O) stretching, 1760 & 1735 cm^{-1} are clearly observed that assigned for aromatic, aliphatic ester, respectively.
- ✓ The rocking vibration of CH_2 (724 cm^{-1}) appeared in all modified lignins.

4. Conclusions and Outlooks

- ➢ *Organosolv* lignin was successfully modified by primarily observed in FT-IR spectra.
- ➢ B-DoE results show the substitution degree on hydroxyl groups correlated with the excess of acid chloride and catalyst.
- ➢ The attachment of long chain hydrocarbon improves hydrophobicity of lignin that is beneficial for polymer blending application.
- ➢ Esterification modification will be tested with lignin from different biomass sources.
- ➢ More characterizations will be carried out to further confirm and study the new properties of esterified lignin.

References

[1] H. Luo and M. M. Abu-Omar, "Chemicals From Lignin," in Encyclopedia of Sustainable Technologies, Elsevier, 2017, pp. 573–585. doi: 10.1016/B978-0-12-409548-9.10235-0.

[2] P. Jõul et al., "Characterization of Organosolv Lignins and Their Application in the Preparation of Aerogels," Materials, vol. 15, no. 8, Apr. 2022, doi: 10.3390/ma15082861.

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