The Catalytic Depolymerization of Kraft Lignin (Valorization of Industrial Byproduct) via a Clamshell-Derived Calcium Oxide Catalyst for the Synthesis of High-Value Aromatic Monomers

Ui Jin Seo, Masud Rana, Shubho Ghosh, Md Ishtiaq Hossain Khan, Young-Tae Jo and Jeong-Hun Park*

Department of Environment & Energy Engineering, Chonnam National University,

77 Yongbong ro, Bukgu, Gwangju 61186, Republic of Korea.

* corresponding author: parkjeo1@jnu.ac.kr

Abstract

This study investigates the synthesis and application of a calcium oxide (CaO) catalyst, derived from clamshell, for the depolymerization of Kraft lignin obtained from black liquor, a by-product in pulp mills. The research explores various process parameters, about reaction solvents, temperature, and duration. The optimal conditions resulted in a peak bio-oil yield of 35.8 wt% at 340 °C using water as the solvent. However, the introduction of an alcoholic solvent, specifically methanol, significantly enhanced lignin depolymerization. The maximum bio-oil yield of 72.4 wt% was achieved utilizing a 10 wt% CaO catalyst in methanol solvent at 340 °C during a 4-hour reaction. Bio-oil analysis revealed that the non-catalytic reaction yielded bio-oil with a low total area percentage of phenolic compounds, predominantly comprising alkyl phenols with a minor presence of methoxy phenols. Interestingly, the CaO catalyst facilitated the promotion of lignin macromolecule depolymerization, resulting in an increased selectivity (58.7%) toward catechol compounds. Fourier transform infrared (FT-IR) spectroscopy analysis demonstrated a higher functionality of aromatic and methoxy compounds in catalytic bio-oils compared to non-catalytic counterparts. These findings underscore the efficacy of the clamshell-derived CaO catalyst in augmenting lignin depolymerization, thereby enhancing bio-oil yield and influencing the bio-oil composition. The study contributes valuable insights into sustainable practices by repurposing industrial by-products and advancing catalytic processes for lignin conversion.

1. Introduction

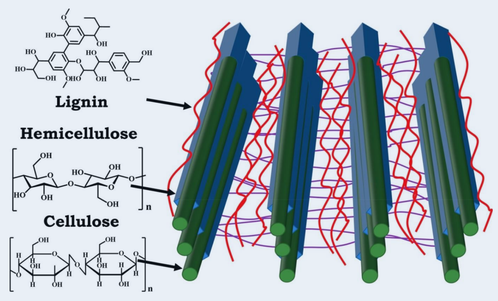


Fig.1 Components of plant cell

- Biomass is an alternative renewable energy source
- Black liquor contains about 40% of pulping chemicals and about 60% of the organic compounds (lignin, cellulose and hemicellulose)
- A rich aromatic polymer of lignin → Suitable for aromatic chemicals and energy production

2. Materials and Methods

2.1 Materials

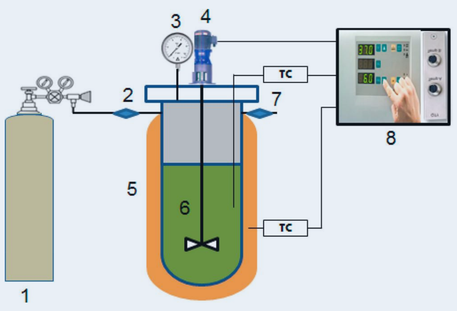


Fig. 2 Hydrothermal reactor

- Black liquor
- Methanol (Sigma-Aldrich), Ethanol (Sigma-Aldrich), Ethyl Acetate (Honeywell Burdick & Jackson), H_2SO_4 (Daejung)
- 300 mL-high-pressure Hastelloy-C-276 HR-8300 reactor (Hanwoul Eng. Ltd., ROK)

2.2 Lignin extraction (a) and Catalyst preparation (b)

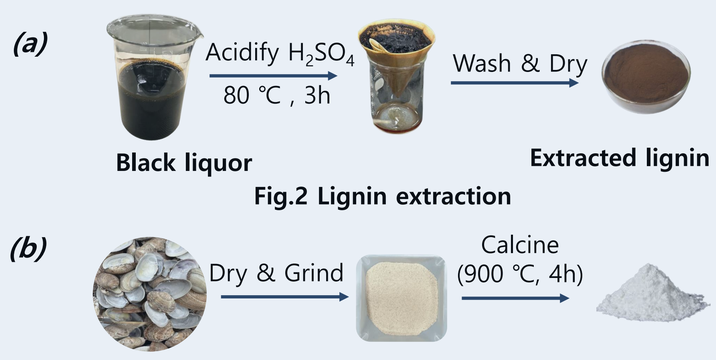


Fig.2 Lignin extraction

Fig.3 Catalyst preparation

2.3 Lignin depolymerization and product separation

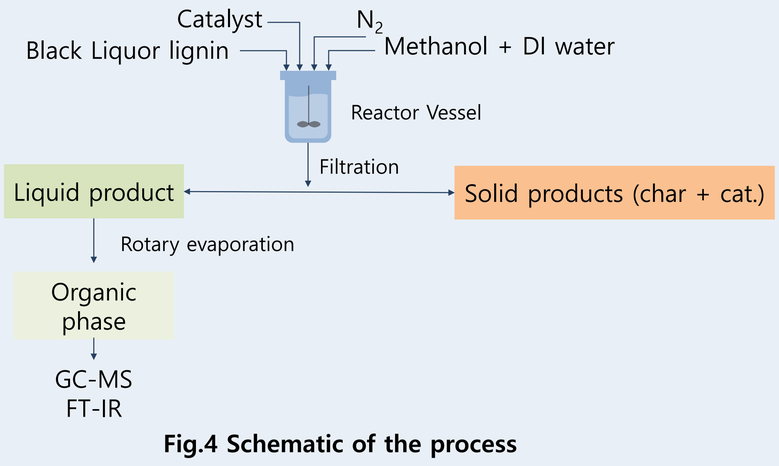


Fig.4 Schematic of the process

3. Results and Discussion

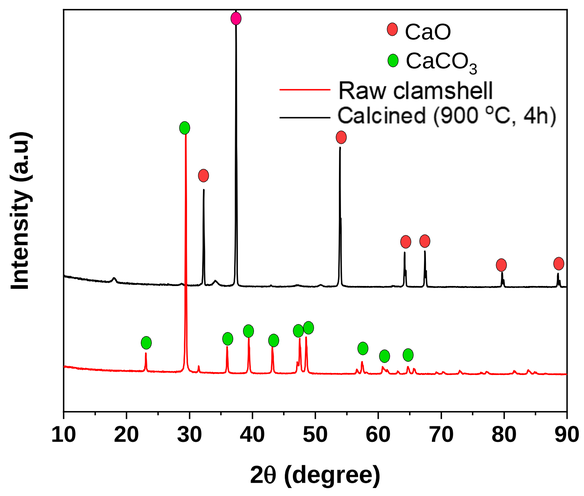


Fig.5 XRD patterns of raw clamshell and calcined clamshell.

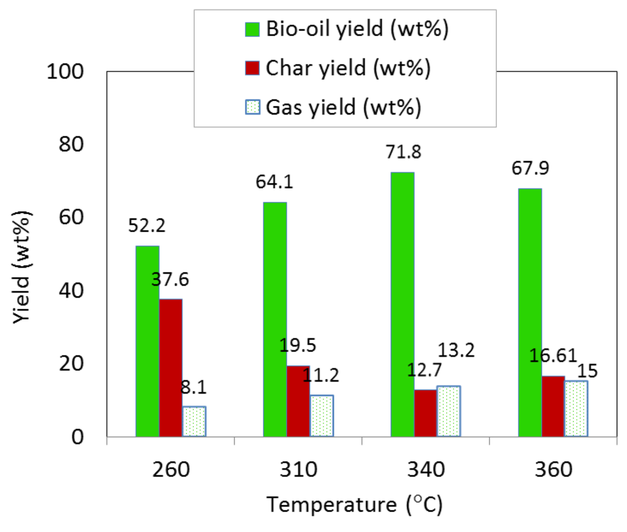


Fig.6 Effect of temperature on the yield of depolymerized products.

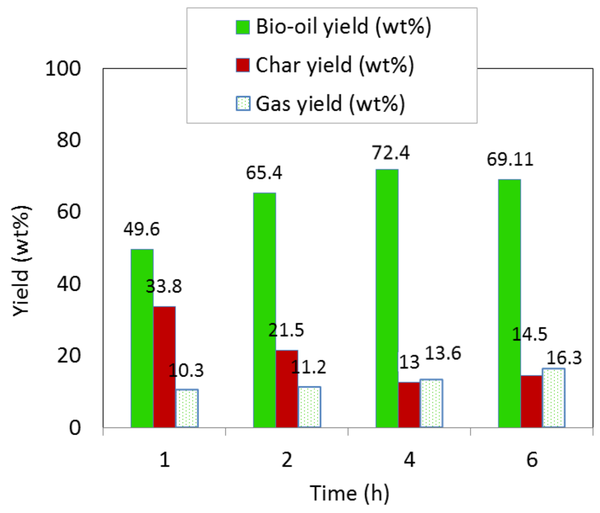


Fig.7 Effect of time on the yield of depolymerized products.

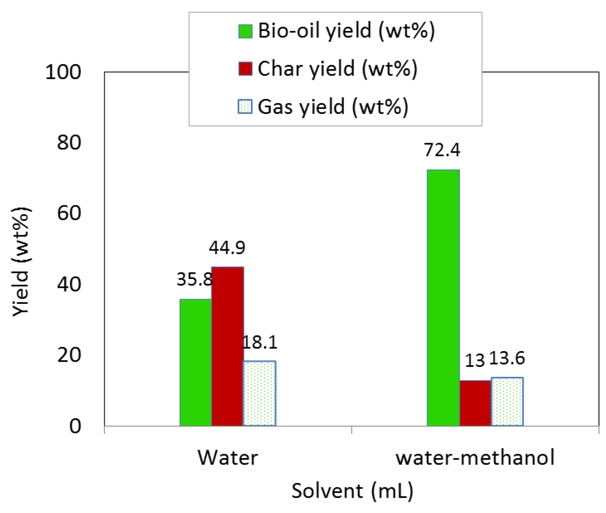
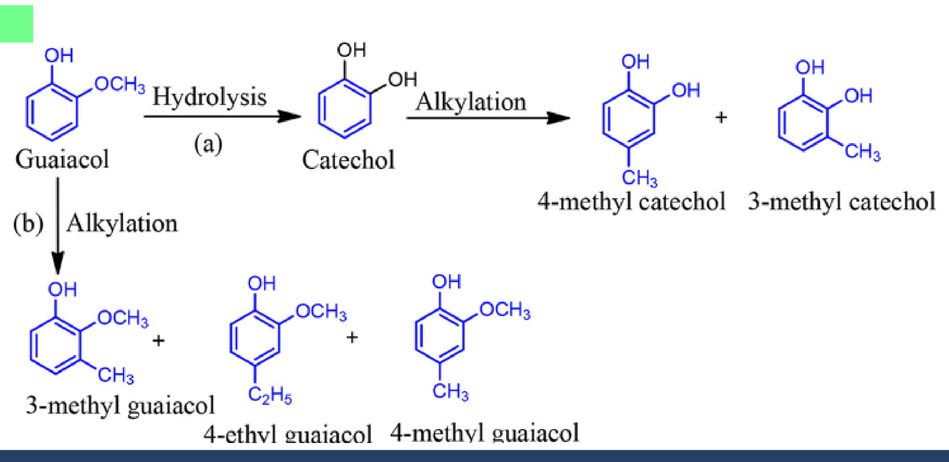


Fig.8 Effect of solvents on the yield of depolymerized products.

Mechanism:



4. Conclusion

- In this study, depolymerization of Kraft lignin in black liquor was performed under various conditions of reaction solvent, temperature, and time using a CaO catalyst.

- A maximum bio-oil yield of 72.4wt% was obtained under conditions of methanol+distilled water and catalyst at 340℃ for 4hours.

- Analysis of bio-oil revealed that CaO catalyst enhanced the production of catechol compounds.

- The main compounds were 1,2-Benzenediol (catechol), 1,2-Benzenediol, 4-methyl (4-methyl catechol) and 1,3-Benzenediol, 4-ethyl.

This work was supported by the National Research Foundation of the Republic of Korea (NRF - 2022R1A2B501002469).