

Biopolyol production from black liquor via ultrafast depolymerization in supercritical water

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1. Introduction

According to the McKinsey's report¹, despite the decreasing trend in printing papers because of digitalization, the pulp & paper industry compound annual growth rate (CAGR) still projects positive because of the packaging industry shift from plastic cutlery to cardboard or corrugated boxes. For this reason, it can be expected that traditional pulp & paper industries will keep alive for a while. Thus, black liquor stream will still be an important waste resource to valorize for production of aromatics and biopolyols rather than low efficiency incineration for energy recovery².

The polyols (compounds that contain more than two hydroxyl group in one molecule) produced from black liquor or kraft lignin can be used for lubricant and/or polyurethane production replacing the petroleum-based polyols². In this study, black liquor depolymerization into biopolyols and aromatics were investigated under ultrafast depolymerization in supercritical water. Different refining techniques on the products were also examined. The experiments were conducted in three different operations in a pilot plant, each one of them was done for 1 hour of operation at steady state. The average reaction temperature and pressure were 385 °C and 260 bar, while the average reaction time was evaluated between 0.36 and 0.39 s. According to our group's previous contribution, below 0.5 s reaction time was selected to prevent char-like formation from undesirable condensation reactions (repolymerization) by controlling the reaction time³. Considering the results, the most suitable separation method was chosen. Also, the total biopolyol (oligomers + monomers) fraction was increased 30 wt.%, whereas the syringol monomer amount was almost doubled compared to Black Liquor.

2. Materials and Methods

A description of the operating details and procedure of the ultrafast SCW Pilot Plant can be found in the previous work of our research group, in addition to a discussion of scaling up the process from laboratory to pilot plant⁴. Briefly, the design of the plant provides short reaction times due to the small reactor volume and a fast flow through the reactor. The instantaneous mixing of biomass and SCW at the inlet of the reactor, reduces degradation reactions that could occur during the ramping heat-up.

Three refining methods were used to decide which one is best to follow. These can be named as: freeze drying, oven drying and biopolyol fractionation method. In freeze drying and oven drying methods, the product is directly subjected to these drying techniques after acidification. Then, a solid liquid separation was done with ethyl acetate. In fractionation method, the product was separated to 2-phases via centrifuge after acidification and then, an ethyl acetate extraction was done for both phases. Carbohydrates and insoluble lignin analysis (NREL protocol) was done for the raw material and product's composition characterization. GC-MS, FTIR, TGA/DTG, GPC, Elemental Analysis were conducted for further characterization analysis.

3. Results and discussion

Total Dissolved Solids analysis was performed to understand the pH evolution of both black liquor (BL) and its depolymerized product (SHP) see if there is any difference. The results showed that dissolved solids (DS) and suspended solids (SS) amount of BL and SHP are similar. However, the pH evolution slightly differs. The evolution diagrams can be seen in figure 1. After that, some separation methods (freeze drying, oven drying, fractionation method) were applied. Freeze dried and oven dried particles were not being separated well from the complex material by using ethyl acetate and water. Hence, fractionation method

was performed to separate the particles. The results showed that biopolyol fraction amount was increased 30 % at pH 2. Although the difference in the final DS and SS does not differ, during the fractionation it can be seen that the separation continues between phases until pH of 2. This outcome is demonstrated in figure 2.

GC-MS results shows that the syringol amount in SHP was almost doubled. It was increased from 1.8 % to 3.4 wt.% in biopolyols fraction. Other biopolyols that were found in this fraction was guaiacol, vanillin, acetovanillone, syringaldehyde, and acetosyringone. In syringaldehyde, a slight decrement was observed. However, other biopolyols either kept their percentages or slightly increased compared to BL. Figure 3 shows these results.

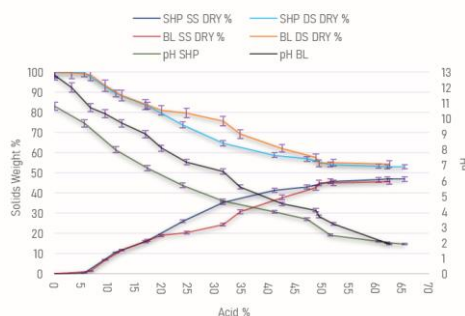


Fig. 1. Total Dissolved Solids Analysis

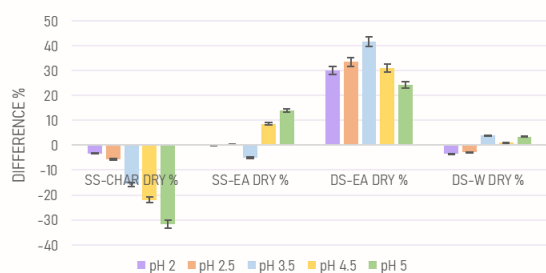


Fig. 2. Black Liquor (BL) vs Depolymerized Black Liquor (SHP) Fractionation Comparison

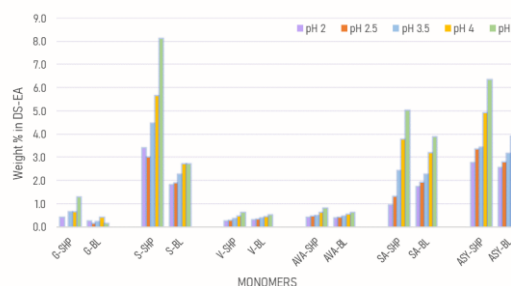


Fig. 3. Biopolyols analyzed by GC-MS

Considering these results, five different products were determined for further characterization. BL was used as blank test, and SHP was used as the unmodified product. Besides these products, spray dried (SD), oven dried (OD), and ethyl acetate extracted from oven dried (EA) products were characterized. Compositional Analysis showed that the highest lignin amount, and minimum ash amount were observed from EA product. Elemental Analysis revealed that during the depolymerization and the fractionation, dehydration occurs. H:C ratio for the products were found as BL > SHP > SD=OD > EA. That means, the aromaticity is the highest in EA fraction. TGA/DTG results were also in accordance with compositional, and elemental analysis results. Interestingly, GPC results demonstrated the difference of a drying method makes slight structural differences in the matrix.

4. Conclusions

This study was performed to find an easy, quick, and optimized separation methods to make the product ready to be processed in the industry. Minimizing time and cost was the primary objective to create an efficient method. However, SHP and SHP derived products were only separated by fractionation. Biopolyols fraction was increased 30 wt.%, and syringol amount was almost doubled. Moreover, this fraction can be used for lubricant or polyurethane production. Among the other products EA was step ahead. Overall, the most important point was being able to successfully operate 20 wt.% solid loaded slurry in continuous pilot plant to produce biopolyols which can be implemented to pulp & paper industry in the future.

References

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