KnE Materials Science

FibEnTech21
1st International FibEnTech Congress (FibEnTech21) New opportunities for fibrous materials in the ecological transition
Volume 2022

Knowledge E
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Research article

Efficient Recovery of Lignin and Hemicelluloses from Kraft Black Liquor

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Abstract.

Black liquor (BL) from kraft pulping industries contains a large fraction of lignin and hemicelluloses and their efficient separation can open up new possibilities for integrated biorefineries. In this work, lignin and hemicelluloses were separated from BL and concentrated BL (obtained by ultrafiltration), by precipitation using acidification and antisolvent precipitation method, respectively. For lignin precipitation, different organic acids, namely acetic, lactic and citric acid, were used and the yield and purity of the extracted lignin were compared with the lignin precipitated using inorganic acids, namely sulphuric and phosphoric acid. Among the organic acids, the highest yield of lignin (57.2%) was obtained by lactic acid, but the extract also contained the highest levels of inorganic impurities (9.2%). The extract obtained from acetic acid contained lower inorganic impurities and the lignin yield was 48.1%. The hemicellulose was extracted from BL liquor that was concentrated using the ZnO-based PES mixed matrix ultrafiltration membrane, which was started by first separating lignin (at pH 3.5, 4 and 4.5) from it. The supernatants from the lignin precipitation process were used as a source of hemicellulose and this was precipitated by using acetone as an antisolvent. The highest hemicellulose yield (54.4%) was obtained from the supernatant with the lowest lignin content and highest acetone to supernatant ratio.

Keywords: acidification, antisolvent precipitation, hemicelluloses, kraft black liquor, lignin

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Published 10 August 2022

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the FibEnTech21 Conference Committee.

1. Introduction

Kraft black liquor (BL) contains inorganic (pulping chemicals) and organic (mainly lignin and hemicelluloses) components. Pulping chemicals are majorly recovered and reused while its organic part often undergoes for energy conversion process to make the pulping process economically viable. Such components, rather going for energy conversion process, require efficient separation methods as these have great potential to transform into high value-added products [1]. The most studied process for separation of lignin from BL are the precipitation by acidification and the membranes filtration [2,3]. For the acidification process commonly, sulfuric acid is considered in spite of its inorganic nature and difficulties of special handling, therefore the focus is shifting towards the use of greener acidifying agents.

The hemicelluloses are second most abundant organic component of BL, but it is challenging to recover it from BL due to less efficient recovery processes and its lower concentration in BL than lignin. So, sequential recovery of lignin from BL and hemicelluloses from the leftover of lignin recovery process was seen a better solution. Also, prior to recovery process, concentrating these organic components in lower volume of BL can lead in reduction of chemicals consumption in recovery process [4]. It can further improve the efficiency of separation processes by increasing purity or higher separation yield of organic components; also least possible imbalance of inorganic components of BL to maintain the conventional process of chemical recovery in paper industries [5–7]. In light of the aforementioned findings, we studied the separation of lignin by acidification of BL using various organic acids and compared with the precipitated lignin obtained using inorganic acids. Further, a sequential recovery of both lignin and hemicelluloses was carried out, to exploit the full potential of BL, through the acidification and antisolvent precipitation methods. To enhance the efficiency of separation processes, BL was pre-filtered by lab-made ZnO- based PES mixed matrix ultrafiltration (UF) membranes to concentrate the lignin and hemicelluloses in the retentate stream and this UF retentate was referred as concentrated BL [8].

2. Material and methods

Industrial BL—with a total dissolved solid (TDS) content of ~17%—was used as a source for lignin and hemicelluloses. The composition of BL and concentrated BL (UF retentate) is shown in Table 1. The lignin separation by acidification was performed using various acids namely sulfuric acid (SA), phosphoric acid (FA), sulfuric acid + acetic acid (SA+AA), acetic acid (AA), lactic acid (LA) and citric acid (CA). For that purpose, the pH of BL was reduced to 3 - 3.5 using sulfuric acid and sulfuric acid + acetic acid whereas it was reduced to 4 - 4.5 for other acids. The precipitated lignin was separated by centrifugation followed by three times washing with acidic water (pH ~3). The precipitates were dried at 100 °C and analyzed for organic and inorganic contents by thermogravimetric analysis at 650 °C. The lignin content was measured using UV-Vis spectroscopy by measuring the absorption at 295 nm wavelength.

As an improvement in the recovery process, hemicelluloses were separated from supernatant of lignin separation process and concentrated BL was used instead of BL. Prior to separation process, BL was prefiltered by using ZnO-based PES mixed matrix UF membranes (lab-made) for the reduction of volume upto 60%. The pre-filtration step increased the concentration of lignin and hemicelluloses in retentate

TABLE 1: Composition of BL samples used for lignin and hemicelluloses recovery.

Sample	TDS (g/L)	*Inorganic content (%)	*Organic content (%)	Lignin conc. (g/L)	Hemicellulose conc. (g/L)
Black liquor	187 ± 1.42	48.26 ± 0.55	51.74 ± 0.55	84-92	8-13
Concentrated BL	267 ± 2.12	37.10 ± 0.16	62.89 ± 0.16	135-142	19-23

*Organic and inorganic contents comprise the composition of TDS content.

stream (see table 1), which facilitated the desirable recovery of organic components with comparatively less acid and antisolvent consumption. First, lignin was separated from retentate using acetic acid followed by the separation of hemicellulose from lignin-lean supernatant by antisolvent precipitation using acetone (90% v/v to BL). The process of lignin and hemicellulose separation from concentrated BL is shown in Fig.1. First lignin was precipitated by reducing the pH of BL to 3.5, 4 and 4.5 and the supernatants with different concentration of lignin were used for hemicellulose recovery. The yield of hemicellulose was analyzed as a function of lignin concentration in the supernatant and the ratio of acetone to supernatant. The precipitate was analysed for organic and inorganic content similar to lignin precipitates whereas hemicellulose content was analysed by HPLC analysis. The yield of TDS was measured as amount of precipitate separated per litre of BL whereas, the yield of lignin or hemicellulose was determined as the amount of lignin or hemicellulose extracted to the amount of lignin or hemicellulose present in BL.

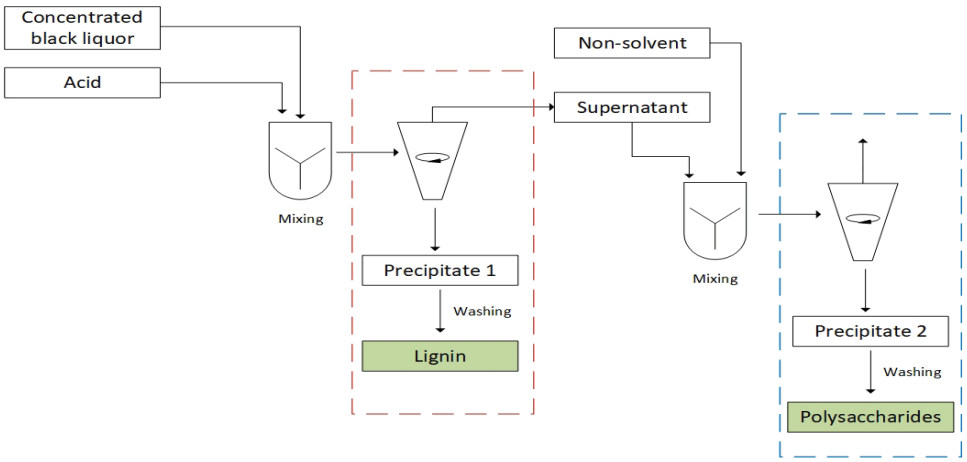

Figure 1: Schematic representation of process for separation of lignin and hemicelluloses from black liquor.

3. Results and discussion

In lignin separation process, the highest yield of separated solids (approx. 56 g/L) was obtained when a combination of sulfuric acid and acetic acid was used as acidification agent. But the organic content of these solids were lower than the solids separated using organic acids, except for lactic acid, and phosphoric acid, see Fig. 1. In terms of purity of lignin, it was higher for the fractions with high organic content and the highest purity was obtained by acetic acid, citric acid and phosphoric acid. When the recovery performance of different organic acids was compared, the highest yield of lignin was obtained with lactic acid (57.2%) however, the separated solid had the highest amount—around 9.2%—of inorganic impurities in it.

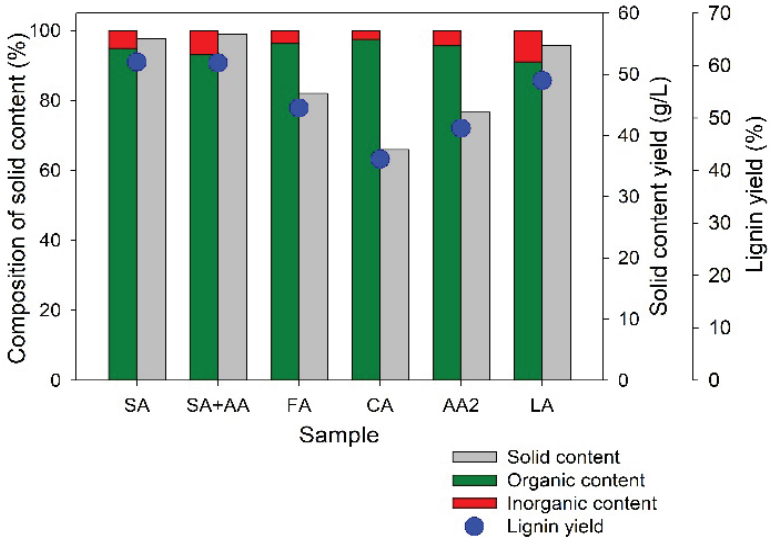

Figure 2: Composition and yield of solid content and the yield of lignin from various acids.

Further for the recovery of both lignin and hemicelluloses from concentrated BL, the acetic acid was used for first acidification step for two reasons: (a) high purity and (b) satisfactory yield of lignin among all organic acids. The highest lignin yield from concentrated BL was 32.7% at pH 4. However, this yield was ~10% lower (with the same acid and same level of pH reduction) from concentrated BL compared with yield from BL. This reduction can be due to the presence of less amount of lower molecular weight lignin in concentrated BL. As a benefit of prefiltration step, separated lignin from concentrated BL has the narrower molecular weight distribution (not shown here). Also, despite of lower yield, the total amount of lignin separated from concentrated BL was similar to the total amount separated from unfiltered BL. Further, the second precipitate, precipitated from the supernatant using acetone, contained mainly polysaccharides, particularly hemicelluloses. The organic and inorganic content of the second precipitate

as a function of lignin concentration in supernatant and acetone to supernatant ratio is shown in Fig. 3. It can be seen that the highest yield of TSD with 75.8% organic content and 24.2% inorganic content was obtained from the supernatant with lowest concentration of lignin in it and highest acetone to supernatant ratio. As the BL was received from kraft pulping of Eucalyptus species, the major portion of hemicelluloses was composed of xylans. Therefore hemicelluloses yield and purity was determined considering arabinose, xylose, uronic acids and acetic acid monomer units. The lignin and other polysaccharides mainly glucose were considered as the organic impurities in the extracted hemicellulose. The yield of hemicelluloses at different conditions is shown in Fig 4. It can be observed that the highest yield of hemicelluloses was 54.4% which was also obtained from same sample with highest yield of organic content. However, the precipitates contained some lignin and other organic impurities which still remained challenging to obtain high purity hemicelluloses.

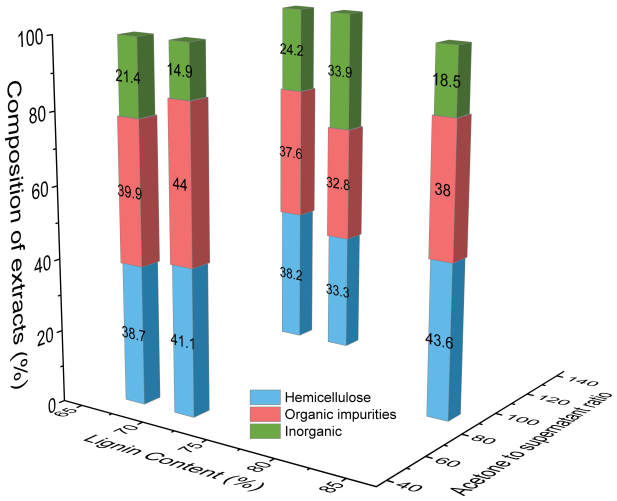

Figure 3: Composition of hemicellulose extracted from concentrated black liquor.

4. Conclusions

In this study, the comparative separation of lignin from BL was shown using organic and inorganic acids and observed that the precipitation by organic acids resulted into lower yield of lignin but with higher purity. Therefore, organic acids can be considered greener alternative for the separation of high purity lignin from BL. Further, by this study, it can be concluded that combining membrane filtration with recovery processes of lignin and hemicelluloses to their higher can lead to higher recovery with less chemical

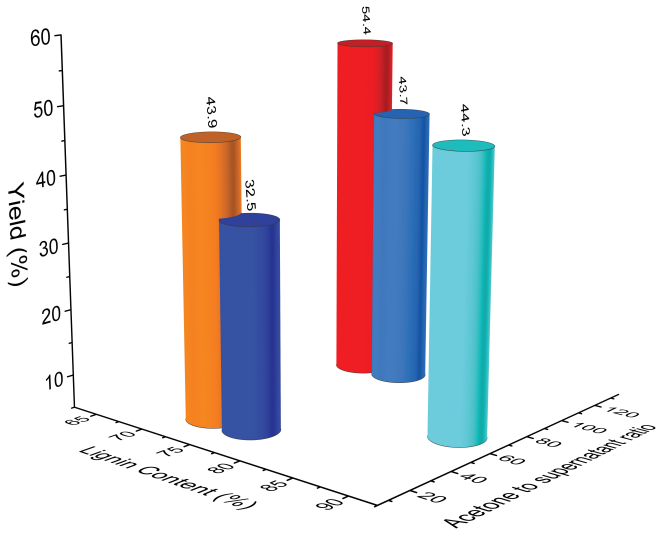

Figure 4: Yield of hemicellulose extracted from concentrated black liquor.

consumptions. In this sense, 32.7% lignin and 54.4% hemicelluloses were recovered from the BL concentrated using membranes filtration.

Acknowledgments

This work was carried out under the Project inpactus – innovative products and technologies from eucalyptus, Project N.º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017. Manorma Sharma acknowledges the PhD grant BDE 08|POCI-01-0247-FEDER-021874.

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