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Production of biophenolics from industrial black liquor by catalytic oxidation in a continuous reactor

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PURPOSE OF THE ABSTRACT

Black Liquor is an aqueous effluent massively produced in the pulp and paper industry. It comes from wood by Kraft pulping process where cellulose is transformed in paper pulp and lignin and hemicelluloses are solubilized and degraded in black liquor [1]. It contains mainly lignin with an important fraction of carbohydrates and carboxylic acids, and a significant amount of inorganics (NaOH, NaHS, Na2S, Na2CO3 and K2CO3). Earlier studies on black liquor oxidation were mostly focused on total oxidation as an alternative to the combustion currently used in Kraft pulp mills, or on partial oxidation to produce small acids [2]. The oxidation of Kraft lignin was also investigated in literature and led to a small production of phenolic compounds such as vanillin and syringaldehyde [3].

The main objective of this work is to produce value-added compounds from lignin in black liquor: phenolic compounds but also aliphatic compounds are targeted. Lignin in black liquor was depolymerized by catalytic oxidation, with air as an oxidant and a copper-based catalyst. The reaction was carried out in a continuous fixed reactor to achieve a better control of operating conditions (pressure, temperature and contact time).

Black liquor was provided by a pulp mill (Smurfit Kappa, Facture, France) working with softwood maritime pine. The reactor was filled with catalyst (5% CuO/TiO2), placed in a tubular oven and fed with diluted black liquor and air. Experiments without catalysts were also performed to investigate the homogeneous reactivity. Liquid samples were collected periodically. The lignin residue (Klason phase) was characterized by elementary analysis, FTIR, NMR HSQC, SEC. The liquid residue was analysed by HPLC-UV.

Lignin conversion reached 80 % without catalyst and 94 % with catalyst at 150°C. At 200°C, it reached 95 % without catalyst and 100 % with catalyst. Lignin conversion was attributed to hydrothermal depolymerization mainly due to temperature and OH- reactivity in solution. Figure 1 shows the yield (on lignin basis) in phenolic compounds obtained at 150°C and 200°C. The main product of lignin oxidation was vanillin, although other oxidation products were observed (acetovanillone, vanillic, homovanillic and anisic acids) as well as non-oxidised products such as phenol and guaiacol. The presence of a copper catalyst drastically increased the yield in monomers (+ 37 %), evidencing catalytic activity, whereas increasing contact time had a detrimental impact on total yield, attributed to the degradation of phenolic compounds over time. Therefore, the application of a continuous fixed bed reactor, allowing short reaction times and limiting degradation reactions, is particularly appropriate for this reaction.

In conclusion, the feasibility of direct catalytic oxidation of black liquor in a continuous fixed bed reactor was demonstrated. Kraft lignin in black liquor was converted to vanillin, homovanillic acid, acetovanillone, phenol and

other phenolic compounds, in alkaline medium, under air pressure. The presence of catalyst had only a minor influence on lignin conversion but a great impact on the production of phenolic compounds. Temperature had a strong impact on both lignin depolymerisation and phenolic compounds production. However, the degradation of phenolic compounds was observed when contact time increased. The production of phenolic compounds from black liquor oxidation is relevant for the future design of integrated forest biorefineries. This work is a promising first step for the design of a continuous process of black liquor oxidation.

FIGURES

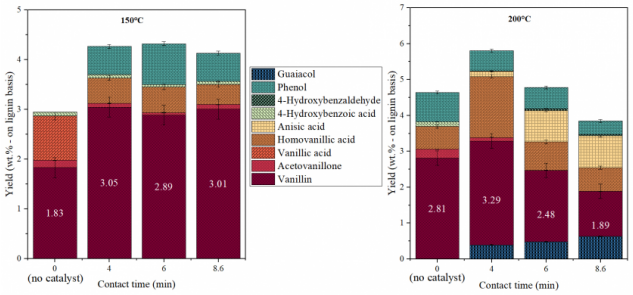

FIGURE 1

Figure 1.

Yields of phenolic monomers during black liquor catalytic oxidation at 150°C and 200°C. Operating conditions: 80 bar, 15 NL.h-1, catalyst CuO/TiO2.

FIGURE 2

KEYWORDS

Black liquor | Green oxidation | Copper catalyst | Fixed bed reactor

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