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Black liquor valorization via reactive distillation and heterogeneous catalysis

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PURPOSE OF THE ABSTRACT

Carboxylic acids are one of the most important raw materials for the production of fine chemicals, aromatics, polymers among others. However, their production is largely based on derivatives of petrochemical processes. To ensure their long-term sustainable production, it is necessary to exploit renewable raw materials. A potential alternative route is the recovery of the carboxylic acids present in black liquor (BL)[1]. This solution is a by-product of the Kraft process in pulp industry and comprises an important carboxylic acid fraction (?30%). Usually, BL is valorized as energy through its combustion. Different technologies have been considered on a laboratory scale for recovering aliphatic acids from BL.[2] Reactive distillation (RD) stands out as one of the most promising recovery processes.[3][4] RD can facilitate the recovery of carboxylic acids from BL by broadening the relative volatility between the compounds through the transformation of the carboxylic acids into their derivative esters. In this project, the inclusion of active structured column internals is also considered. The envisaged strategy for the carboxylic acid recovery from BL is displayed in fig 1.

Before developing a process for the reactive distillation of crude BL, it is necessary to consider the reaction parameters, operational conditions, a screening for possible catalysts, reaction kinetics and the correct selection of the column internals. In a first approach, the esterification of glycolic acid with ethanol was considered as a model reaction. The preliminary study focused on operating conditions such as the temperature, the influence of the acid/alcohol ratio and the presence of water in the medium were studied. The results of catalytic tests suggest that the amount of active sites represents the most important parameter in catalytic activity, followed by the size of the pores, limiting factor during the diffusion of the reagent molecules towards the active sites of the catalyst. [5]

Various support materials for the chosen catalyst (mixed oxides) were also considered, among them the one that showed the most affinity for the type of catalysts was the aluminum-based structures. As structure of the internals of the column, foams with different pore sizes (10, 20 and 30 ppi) were chosen. This type of packing has a significant effect on process intensification. However, it is also a challenging strategy because the efficiency of the process can be compromised by the hydrodynamics of the column and catalyst deactivation.

Continuous and hydrodynamic characterization tests were carried out in a laboratory distillation column (ø32 mm*1 m).The study of liquid hold-up in the column suggests that in a range of 10 to 30 ppi, macroporous foams are comparable to glass beads internals (ø?7mm). It was also observed that regarding separation and number of theoretical plates, foams, regardless of porosity behave similarly to spheres. However, the greatest advantage of foams over beads is that foams may potentially reduce the problems associated with pressure drop, column flooding as well as allowing catalyst deposition over the full length of the packing and limiting internal mass

transfer effects. Then, the impact of the column internals in the RD was studied on esterification and separation of different acids representative of BL. Additionally, a strategy is currently being developed for the pretreatment of crude BL in order to extract the carboxylic acid fraction, conceiving the study of BL esterification in batch and RD.

FIGURES

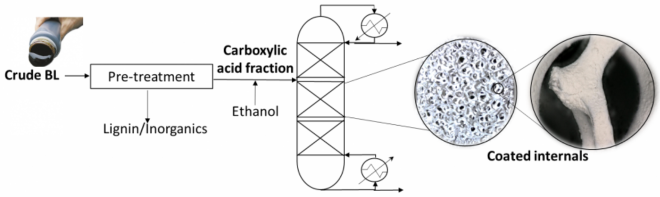

FIGURE 1

Fig 1.

Envisaged strategy for the carboxylic acid recovery from BL

FIGURE 2

KEYWORDS

Reactive distillation | Biomass | Heterogeneous catalysis | Esterification

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