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Levulinic acid esters production via heterogeneous catalysis: from batch to continuous technology

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PURPOSE OF THE ABSTRACT

1. Introduction

The esterification of carboxylic acid with alcohols is a very actual topic of the modern bio-refinery. It is normally performed to produce value-added products, such as solvents and plasticizers [1]. This reaction is promoted by acid catalysts and occurs with the production of an ester (the main product) and water as by-product. Different catalysts have been already tested in the literature [1,2]. Recent findings demonstrate that acid resins, such as Amberlyst-15, show good activity. SMOPEX-101 is an ion exchange resin characterized by no porosity, thus eventual intraparticle mass transfer limitations are avoided when using this catalyst to promote ethyl levulinate synthesis. In the present work, an effort was made to develop the technology to produce ethyl levulinate in continuous reactors. The idea was to investigate the kinetics in classical batch reactors and scale the operation to continuous packed bed.

2. Methods

The experiments have been performed in a 300 cm3 hastelloy cylindrical autoclave. The continuous operation was performed in two different reactors: (i) a single bed (FBR), short reactor (20 × 0.9 cm diameter); (ii) a glass tube with the length and internal diameter of 60 and 1.9 cm, respectively (FBRm). This reactor contained four sampling lines to facilitate the sampling at different residence times. In the case of FBRm, the transient was measured more punctually with the aim to describe the dynamic behavior of this reactor.

3. Results and discussion

Experiments were performed in batch reactor by varying different operative conditions, i.e. temperature, catalyst loading and reactants ratio. The catalyst loading effect was evaluated to check the eventual existence of fluid-solid externa mass transfer limitations and the reaction order referred to the catalyst bulk density (Figure 1).

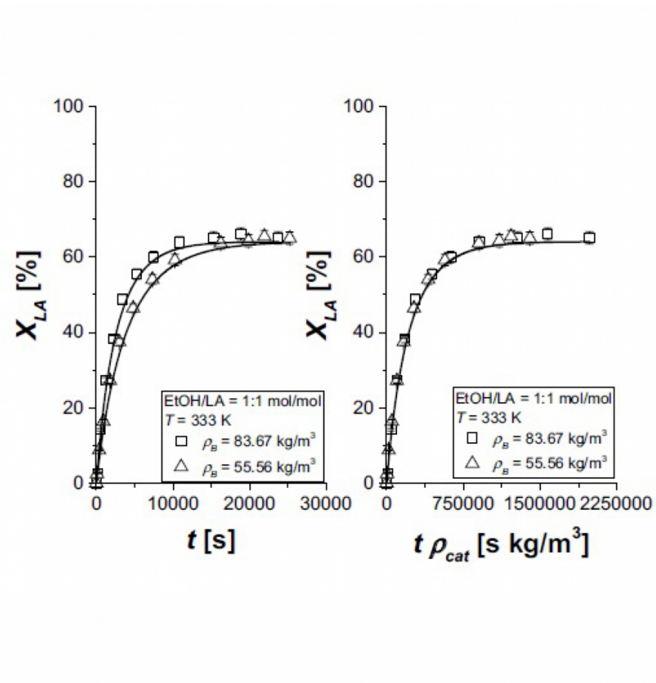
As revealed by the time scaled by the catalyst bulk density plot, a reaction order of 1 was determined for SMOPEX-101. The plot suggests that no external mass transfer limitations are present. The collected data were interpreted developing a O.D.E. system, based on the mass balance equations for each component, and a second order equilibrium reaction rate law.
As the SMOPEX -101 catalyst is nonporous, the internal diffusion resistance plays no role in the process. Thus, reactants and products cannot diffuse in the solid particle. The results of the model predictions are satisfactory as shown in Figure 1. From the parameter estimation activity, an activation energy of 39.38 ± 0.78 kJ/mol was obtained.
The behavior of the continuous fixed bed reactor was predicted. Experiments were conducted by using either a

standard fixed bed reactor (FBR), or a fixed bed reactor with different withdrawn points (FBRm). The experiments were simulated using axial dispersion packed bed reactor model.
As revealed by Figure 2, the model was able to correctly interpret the collected data at different lengths of the pipe both in steady-state and dynamic conditions.

4. Conclusions

The scale-up process from batch to continuous for the levulinic acid esterification, promoted by SMOPEX-101, was successful. Experimental data were collected in a wide spectrum of operation conditions. Kinetic and mass transfer mechanisms were considered in elaborating the experimental data, obtaining in every case a good fit. The results can be considered as good starting point for continuous reactors optimization.

FIGURES



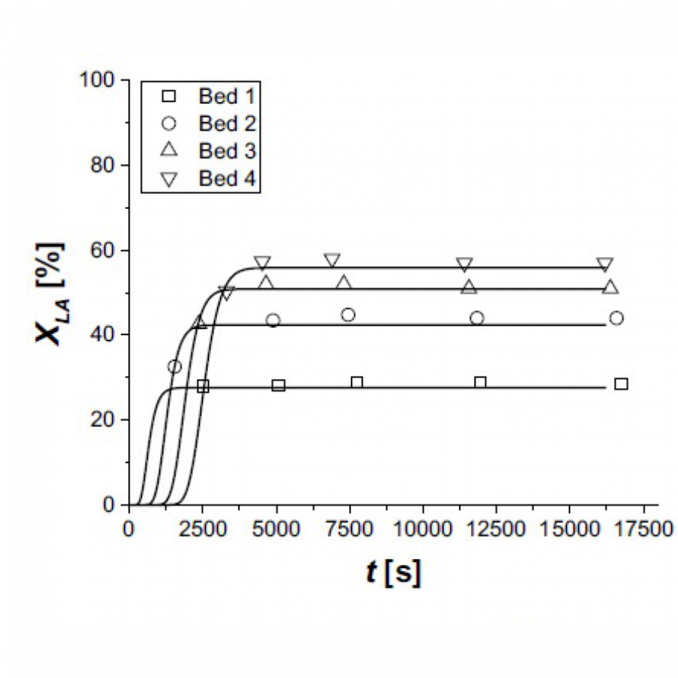


FIGURE 1

Figure 1

The effect of Smopex-101 bulk density on the levulinic acid esterification, fixing the EtOH-to-LA 1:1 molar ratio: (left) raw data; (right) time scaled by the catalyst bulk density. Symbols are the experimental data, lines the model predictions.

FIGURE 2

Figure 2

Levulinic acid esterification in FBRm. The symbols are the experimental data collected at the outlet of the four catalytic beds, continuous lines represent the simulations.

KEYWORDS

Levulinic acid esterification | Ethyl levulinate | SMOPEX-101 | Scale-up

BIBLIOGRAPHY

[1] D.R. Fernandes, A.S. Rocha, E.F. Mai, C.J.A. Mota, V.T. da Silva, Appl. Catal. A-Gen 425 (2012) 199-204.

[2] H.J. Bart, J. Reidetschlager, K. Schatka, A. Lehmann, Ind. Eng. Chem. Res. 33 (1994) 21-25.