Use of 3D-printed CSTRs in the ketalization of ethyl levulinate with glycerol

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Highlights

- 3D-printed CSTRs applied to ketalization reaction.
- Mixing in high-viscous system enhanced.
- Experimental data successfully described by a mathematical model.
- RTD experiments performed.

1. Introduction

The valorization of biomass for the development of sustainable chemical processes represents a key strategy for replacing fossil-based products with renewable alternatives. In this context, levulinic acid and its derivatives play an important role [1]. Among them, ethyl levulinate is particularly attractive, as it is derived from biomass-based feedstock and ethanol, combining low production costs with renewable resources. Additionally, the use of glycerol, a by-product of biodiesel production, enhances process sustainability by promoting industrial waste valorization. One advantage of using esters such as ethyl levulinate is the avoidance of competitive esterification reactions. Its reaction with glycerol produces ketals, versatile compounds with a wide range of industrial applications.

Catalysis plays a crucial role in this process and can involve either homogeneous catalysts, such as mineral acids, or heterogeneous catalysts. While homogeneous catalysts often provide high conversions, heterogeneous catalysts offer important environmental and operational benefits, including reusability, higher thermal resistance, and easier separation from the reaction medium [2].

This study focuses on the kinetic investigation of the ketalization of ethyl levulinate with glycerol promoted by heterogeneous catalysts. A preliminary catalytic screening was performed in a batch reactor to evaluate the activity of several acidic ion-exchange resins. The highly viscous nature of the reaction mixture, combined with resin swelling, a common limitation in packed-bed reactors, makes their use difficult. Moreover, in tubular reactors, achieving high residence times requires low flow rates, resulting in low local turbulence and significant external mass transfer resistance. In contrast, the use of stirred reactors provides enhanced mixing, making them more suitable for these types of systems. For these reasons, a cascade of miniaturized 3D-printed CSTRs, arranged in a vertical configuration, was employed. Operating multiple CSTRs in series allows the system to approximate plug flow behavior while maintaining the mixing benefits typical of stirred reactors [3]. This configuration also offers modularity and scalability, which are key aspects of process intensification.

2. Methods

Catalytic screening of different ion-exchange resins was conducted in 0.3 L Hastelloy stirred reactor. Samples were periodically withdrawn over a 2h reaction and analyzed by ^{1}H-NMR spectroscopy to determine conversion. Subsequent experiments were performed using 3D-printed CSTRs at T=25°C, volumetric flow rates of 0.1 and 0.2 mL/min fixing an ethyl levulinate/glycerol molar ratio of 5:1. The number of reactors in series ranged from 1 to 4, with each reactor loaded with the same catalyst amount. Experimental data were described using a mathematical model developed in Matlab R2024b.

3. Results and discussion

All tested ion-exchange resins showed good catalytic activity in the batch experiments (Figure 1).

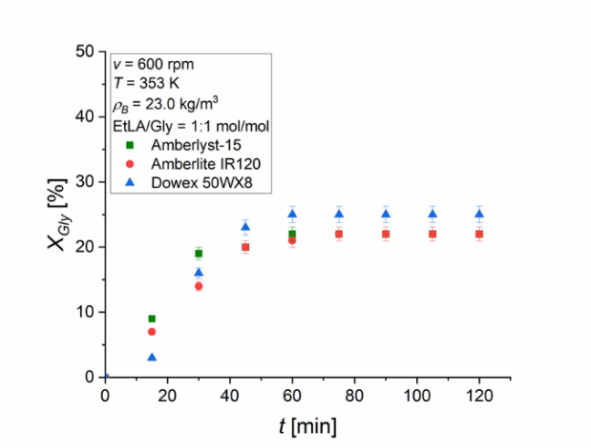

Figure 1. Results of the ion-exchange resins screening.

Based on these results, Amberlyst-15 was selected for tests in the 3D-printed CSTRs. The ketalization reaction was investigated by varying the flow rates and the number of reactors in series. As shown in Figure 2, glycerol conversion increased with the number of CSTRs. Conversely, increasing the volumetric flow rate led to lower conversion due to the reduced residence time. A mathematical model was developed and successfully described the collected experimental data.

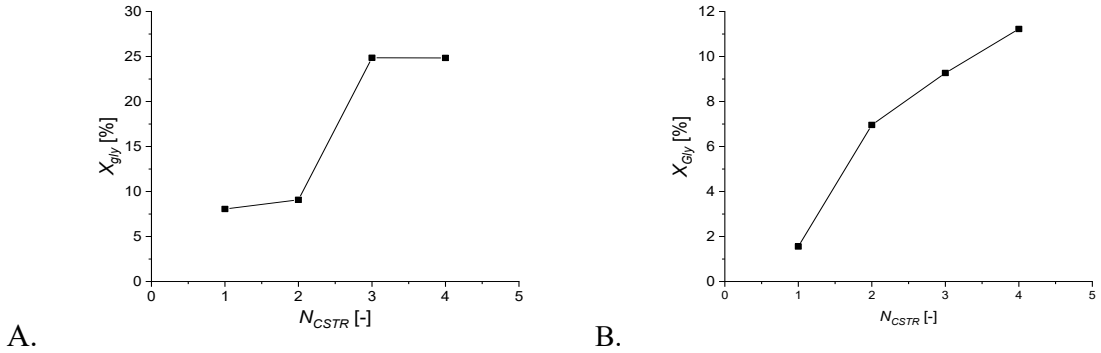

Figure 2. Glycerol conversion at different numbers of CSTRs using Amberlyst-15 as the catalyst. Tests were conducted at A. Q = 0.1 mL/min, w_{cat}/CSTR = 0.1 g/CSTR. B. Q = 0.2 mL/min, w_{cat}/CSTR = 0.1 g/CSTR.

Additionally, a fluid-dynamic characterization was performed to investigate the reactor behavior under different operating conditions, providing information on residence time distribution.

4. Conclusions

The ketalization of ethyl levulinate with glycerol was investigated in a cascade of miniaturized 3D-printed CSTRs using Amberlyst-15 as a heterogeneous catalyst. A preliminary batch screening confirmed the good activity of ion-exchange resins. The use of CSTRs proved particularly suitable for highly viscous systems and for overcoming limitations related to resin swelling. The influence of flow rate and number of reactors in series was systematically evaluated, and a mathematical model was developed to accurately describe the experimental results.

References

[1] R.A. Sheldon, Green Chem. 16 (2014) 950–963
[2] F. Taddeo, R. Tesser, M. Di Serio, V. Russo, Chem. Eng. Process.: Process Intensif. 197 (2024) 109712
[3] G. Gkogkos, L. Storozhuk, J. Piovesan, M.R. Penny, S.T. Hilton, N.T.K. Thanh, A. Gavriilidis, Chem. Eng. Sci. 294 (2024) 120081

Keywords
3D-printed CSTRs; ion-exchange resins; viscous reaction system; ketalization.