Process intensification applied to overcome thermodynamic equilibrium conversions for reversible reactions: the case of levulinic acid esterification

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Highlights

- Process intensification of levulinic acid esterification with ethanol was explored via several advanced technologies
- Reactive chromatography was successfully applied to the reaction leading to full levulinic acid conversion
- Transient techniques were investigated, showing that it is possible to overcome the thermodynamic equilibrium values
- Numerical reactor models were developed for future process scale-up actions

1. Introduction

Esterification reactions are industrially performed in batch systems. The reaction is reversible, and water is formed as byproduct. In order to shift the equilibrium to the product side, normally water is removed by stripping, operation that requires high energy consumption. A possible solution would be exploring the scale-up from a batch to continuous operation, adopting packed bed reactors where acid heterogeneous catalysis (e.g., ion exchange resins) could be employed. The main drawback of the mentioned technology in using packed bed systems is the achievement of low conversion due to the formation of water, that keeps the system at the thermodynamical conversion degree
Different technologies could be used to overcome the mentioned problem, in the frame of Process Intensification, namely reactive chromatography (RC) or transient techniques (TT). RC is an adsorptive separation process, where the components are separated based to their different affinity towards the adsorbent. Similar performance could be obtained by using TT, i.e., varying one of the main operation conditions gradually during the operation of the reactor. In particular, by varying the flowrate, it would be possible to separate molecules in flow exploiting their different affinity with the solid phase. [1]

In this work, we decided to test both technologies with a specific esterification reaction, i.e., levulinic acid esterification with ethanol to produce ethyl levulinate. The focus on ethyl levulinate (EL) is due tue its high potential applications as additive for fuels, for its use in perfume formulations, as plasticizer in bio-degradable plastic polymers and as additive in de-icer formulations. Dowex 50WX-8 and Amberlite IR120 were tested as heterogeneous catalysts as they shown good performance in similar systems. Several experiments were conducted to investigate how the different operation conditions would affect the final conversion of the system trying to overcome the thermodynamic limitations of the reaction.

2. Methods

Two different laboratory-scale continuous packed bed reactors were constructed: i) a chromatographic packed-bed reactor, ii) a classical packed-bed. The general setup consists of an HPLC pump with which the reactants are fed to the pipe, a Rheodyne injector valve (combined with a 20 μL loop) used wither for fluid-dynamic characterizations or for the reactive chromatography experiments, an online detector (Reach Device RD4 equipped with UV 250 nm and 280 nm, RI and conductivity detectors) put in series with the reactor, used to analyze the liquid phase exiting the reactor, a pressure and temperature regulator. The reactors consist of a steel tube of 0.3 m length and 0.0078 m diameter jacketed with a heater regulated by a PID system. The pipe was packed either with 6.5 g of Dowex 50 WX-8 (RC experiments) or with 7.0 g of Amberlite IR-120 (TT experiments). The computations were performed with gPROMS ModelBuilder software.

3. Results and discussion

RC experiments were conducted pulsing levulinic acid (6mol/L in ethanol) at T=303 K to a stream of ethanol, varying the volumetric flow rate. The UV spectra collected are reported in Figure 1A. As revealed, the LA retention time decrease when the flow rate increase. This is what we expected because at higher flow rates the time required to flow through the reactor is lower. In more detail, looking at the curves shape at the intermediate flow rate (0.9 and 1.1 cm^3/min tests) it can be noted the formation of a second peak. The test at 0.8 cm^3/min flow rate shows a single, broad peak detected at a retention time similar to the second peak shown in the two tests at intermediate flow rates. An explanation of this behaviour can be ascribed to the time of interaction of the reagents with the resin that makes the reaction happen. At lower flow rates, 0.8 cm^3/min, the entire quantity of LA pulsed into the reactor has enough time to interact with Dowex 50 WX-8 and it is totally converted, resulting in a single EL peak at the detection point. At intermediate flow rate values, LA is only partially converted, and both the carboxylic acid and the ester are detected by the UV analyser with detection times that are in line with their affinity values. Thus, it was possible to achieve full LA conversion to EL. The made assumptions were confirmed by injecting a solution of EL 6M in ethanol into the chromatographic reactor at the same operative conditions and the UV spectra were com-pared with the corresponding LA spectra.

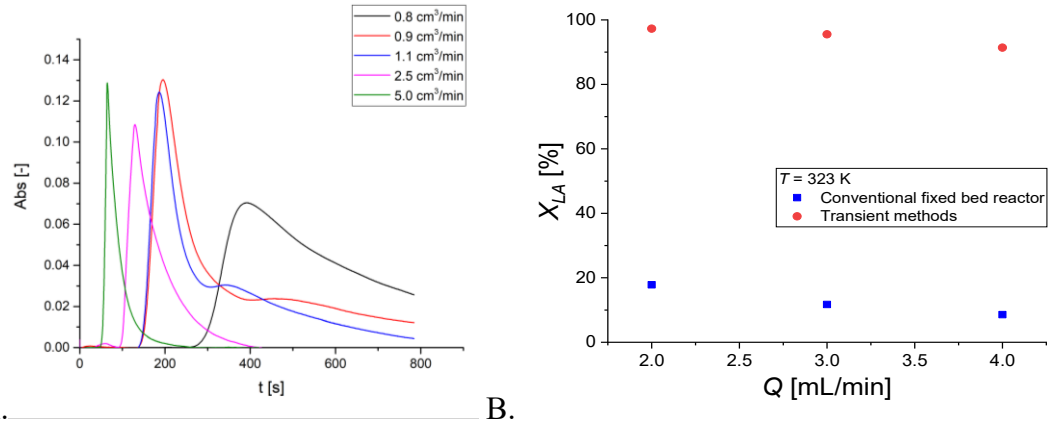

Figure 1. A. UV spectra of LA 6M injected in the chromatographic reactor working at T=303 K and at different flow rates. B. Comparison between conventional fixed bed reactor and transient methods for levulinic acid conversion at different volumetric flowrate fixing T=323 K.

TT experiments also allowed to reach full conversion of levulinic acid (Figure 1B). By comparing the experimental results collected at T=323K working either with constant flowrate (conventional packed bed) or varying the flowrate gradually from 2 mL/min to 4 mL/min. As revealed, the transient mode allowed to achieve full LA conversion at 2 mL/min, while only 18% was obtained with classical packed bed reactor.

4. Conclusions

The possibility of conducting LA esterification with ethanol for production of EL in both a chromatographic reactor and a transient state packed bed was successfully verified using ion exchange resins as catalysts, demonstrating that it is possible to achieve full LA conversion. These promising reactive setups could be further investigated for scale-up purposes.

References

[1] S. Haase, P. Tolvanen, V. Russo. Process Intensification in Chemical Reaction Engineering. *Processes* **2022**, 10(1), 99.

Keywords
Process intensification, Levulinic acid esterification, Reactive chromatography, Transient techniques.