

# Levulinic acid esterification kinetics with ethanol catalyzed by Amberlyst-15

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### Highlights

- Ethyl levulinate synthesis was investigated.
- Amberlyst-15 chosen as heterogeneous catalyst.
- Kinetics and mass transfer were investigated with dedicated experiments.
- Experimental data described with advanced intraparticle model

## 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 catalyzed by acid catalysts and occurs with the production of an ester (the main product) and water as byproduct. Different catalysts have been already tested in the literature [1,2]. Recent findings demonstrate that acid resins, such as Amberlyst-15, show good activity. This behavior is due to the nature of the catalyst itself. In fact, acid catalysts with high acidity, porosity and surface area are much more active in the reaction itself. Moreover, the chemical nature of the starting reactants (steric hindrance and carbon chain length) strongly affects the rate of the overall process due to possible diffusion limitations inside the catalyst particle. Ethyl levulinate shows promising applications in the field of inks and paints. It is synthetized from levulinic acid and ethanol in the presence of an acid catalyst, normally homogeneous (H<sub>2</sub>SO<sub>4</sub>). In the present work, an effort was made to investigate the kinetics of the levulinic acid esterification with ethanol in the presence of Amberlyst-15.

## 2. Methods

The experiments have been performed in a 300 cm<sup>3</sup> hastelloy cylindrical autoclave, supplied by Parr Instrument and allows to work at a maximum of 55 bars. Temperature and pressure have been acquired through a built-in data acquisition system and controlled by PID systems. Samples of 2 cm<sup>3</sup> have been withdrawn in vials, using a pin valve, connected to a tube that reaches the bottom of the reactor. At the end of this tube, a sintered AISI 316 filter of 10  $\mu$ m mesh, has been mounted to avoid catalyst drainage. The samples have been analyzed by acid-base titration. The samples withdrawal at the end of the experiment were analyzed by GC-FID, to detect eventual by-products. Amberlyst-15 and all the reagents employed have been supplied by Aldrich at the highest level of purity available, used as received without further purification.

#### 3. Results and discussion

Experiments were performed by varying different operative conditions, i.e. stirring rate, temperature, catalyst loading and reactants ratio. The stirring rate effect was evaluated to check the best operative condition to neglect the fluid-solid mass transfer resistance (Figure 1A). A maximum in the reaction rate was determined by working at 200 rpm, thus all the experiments have been performed at this value. Several experiments have been performed by varying the catalyst amount and fixing the other operation conditions (Figure 1B). It is evident that two different regimes can be individuated: at low catalyst concentration, the initial reaction rate follows a linear trend with the catalyst loading, while at high catalyst loading, no differences in the reaction rate have been observed. This evidence can be explained assuming that at high catalyst loading, the fluid-solid mass transfer resistance becomes dominating.





Figure 1. Reaction rate trend as a function: A. stirring rate (T=70°C, CLA,0=2.5mol/L, 2.5% Amberlyst-15); B. catalyst loading (T=70°C, CLA,0=2.5mol/L); C. temperature (CLA,0=2.5mol/L, 2.5% Amberlyst-15). D. Levulinic acid conversion trend for experiments performed at different temperatures.

Finally, several experiments have been performed at different temperatures (Figure 1C-D). It is evident that also in this case we observed two regimes: (i) a kinetic regime operating at temperature lower than 70°C; (ii) a mass transfer limited regime operating at temperature greater than 70°C. The collected experimental data were interpreted with reliable models considering both the chemical and mass transfer phenomena involved in the reaction network, such as external and internal mass transfer limitations. The mixed PDE/DAE systems given by the mass balance equations, Eq. 1 were solved with advanced numerical techniques.

$$\frac{\partial C_{i,s}}{\partial t} = \frac{D_{eff,i}}{\varepsilon \cdot x^s} \cdot \frac{\partial}{\partial x} \left( x^s \cdot \frac{\partial C_{i,s}}{\partial x} \right) + \sum_{k=1}^{N} \frac{\rho}{\varepsilon} \cdot r_k \tag{1}$$

An example of data fit can be appreciated in Figure 1D. From the data elaboration, we got an activation energy value of 6.5 kcal/mol.

#### 4. Conclusions

The kinetic investigation of the ethyl levulinate synthesis, catalyzed by Amberlyst-15 was the topic of the present paper. 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.

#### References

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#### Keywords

Levulinic acid; esterification; ethyl levulinate; kinetics.