Solvent-free condensation of ethyl levulinate with phenol promoted by Amberlyst-15: kinetics and modelling

Federica Orabona[1,2], Salvatore Capasso[2], Francesco Taddeo[2], Kari Eränen[1], Wander Perez Sena[1], Letizia Verdolotti[3], Martino Di Serio[2], Dmitry Murzin[1], Tapio Salmi[1], Vincenzo Russo[1,2*]

1 Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Åbo Akademi University, Turku, Henriksgatan 2, FI-20500; 2 University of Naples Federico II, via Cintia, IT-80126 Napoli; 3 Institute of Polymers, Composites and Biomaterials, National Research Council, IT-80055 Portici

**Corresponding author: v.russo@unina.it*

Highlights

- DPA and its ester derivatives (DPEs) are promising bio-based monomers for different applications.
- Kinetic study of ethyl levulinate condensation with phenol revealed the influence of different parameters on the reaction rate.
- Intraparticle reaction-diffusion model enabled to describe the experimental data.
- Kinetic and adsorption parameters were successfully estimated by non-linear regression analysis.

1. Introduction

Diphenolic acid (DPA) and its derivatives (DPEs) are considered as the most promising bio-based alternatives to the toxic bisphenol A in the synthesis of epoxy resins and polycarbonates [1]. After further treatments, DPA could also be employed as a precursor of non-isocyanate polyurethanes [2]. DPA is usually synthesized by solvent-free condensation or Friedel-Crafts hydroxyalkylation of two molecules of phenol and levulinic acid (or levulinic esters) in the presence of a Brønsted acid catalyst [3]. Both levulinates and phenol can be derived from lignocellulosic biomass. In this work, an extensive kinetic investigation of the condensation of ethyl levulinate with phenol was performed in a laboratory-scale batch reactor, employing Amberlyst-15 as the heterogeneous catalyst. An intraparticle reaction-diffusion model has then been utilized to describe the experimental data and non-linear regression analysis allowed the estimation of kinetic and adsorption parameters.

2. Methods

Friedel-Crafts hydroxyalkylation (or condensation) of ethyl levulinate with an excess of phenol under solvent-free conditions has been carried out in a batch reactor employing Amberlyst-15 as the acid catalyst. The reaction scheme is displayed in Fig. 1.

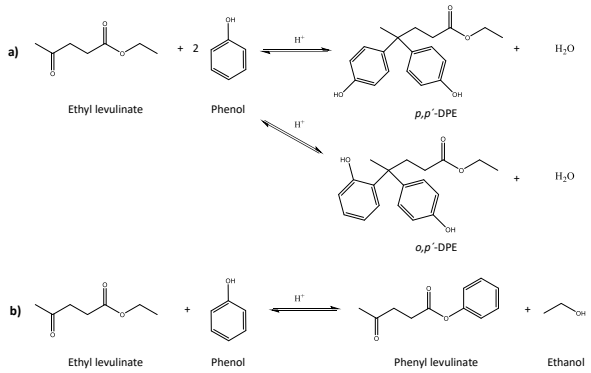

Figure 1. Reaction scheme.

The kinetics of the reaction has been investigated and the collected data have been implemented in a mathematical model employing gPROMS Model Builder as main software. A classical batch reactor

model was utilized for the liquid phase whereas concentration profiles inside the catalyst pores have been considered for the solid phase. The swelling of the catalyst particles and the role of water on the reaction rate have been taken into account as well. Finally, the estimation of kinetic as well as adsorption parameters has been performed via non-linear regression analysis.

3. Results and discussion

The kinetic investigation revealed that the reaction temperature and the Amberlyst-15 load have a positive effect on the ethyl levulinate conversion and the DPE yield (Fig.2), while water was revealed to be detrimental on both parameters. External mass transfer limitations did not affect the system, as revealed by experiments conducted at different stirring rates. On the contrary, the internal mass transfer resistance was revealed to limit the reaction rate and, therefore, it was included in the mass balance for the solid phase. On the basis of the experimental data, a two-step reaction mechanism was proposed considering that the reaction takes place between adsorbed ethyl levulinate and bulk phenol through the formation of an intermediate and in two elementary steps. In particular, the quasi-equilibrium approximation was employed to retrieve the concentration of the intermediate. The resulting kinetic model managed to successfully describe the experimental data.

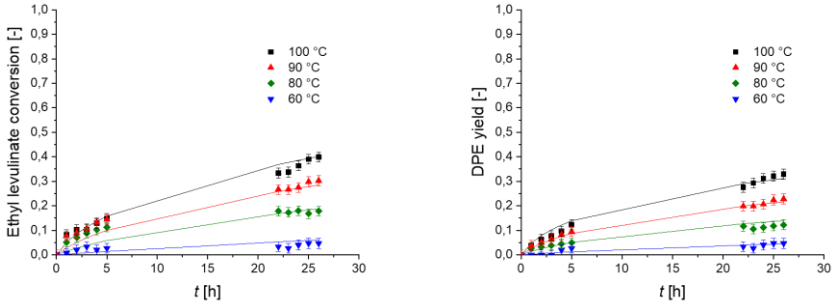

Figure 2. Temperature effect on ethyl levulinate conversion and DPE yield. The solid lines represent the model prediction.

The parameters estimated were used to simulate the concentration profiles of ethyl levulinate along the dimensionless radial coordinate of the catalyst. As a result, the diffusion resistance inside the catalyst pores played a quite prominent role in the first hours of reaction to then flattens at the end of the experiment. Amberlyst-15 is an ion-exchange resin with a macroreticular network generated by macromolecules i.e. styrene-divinylbenzene crosslinked to each other. Compared to ceramic materials, there is an uncertainty on the value of porosity and tortuosity. Therefore, a sensitivity study was performed to evaluate its influence over the results of the kinetic modeling and the parameter estimation.

4. Conclusions

The reaction kinetics between ethyl levulinate and phenol to produce *p,p'*-DPE was investigated under solvent-free conditions. Amberlyst-15 was employed as the heterogeneous catalyst, showing high activity even after recycling. An accurate kinetic model was developed to describe the experimental data. Internal mass transfer as well as swelling of the catalyst particles due to the formation of water were considered in the model, which accurately described the experimental data. The adsorption of ethyl levulinate and the monophenolic intermediate was suggested to take place following an Eley-Rideal-like mechanism. The parameters estimated resulted not to be correlated to each other and the parameter errors resulted to fall into the 95% confidence interval.

References

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Keywords
Diphenolic acid, ethyl levulinate, kinetic study, NMR.