

Condensation of ethyl levulinate with phenol on Amberlyst-15: kinetics and modelling

Federica Orabona^{1,2}, Salvatore Capasso², Francesco Taddeo², Kari Eränen¹, Wander Perez Sena¹, Letizia Verdolotti³, Martino Di Serio², Dmitry Murzin¹, Tapio Salmi¹, 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.
- Only the *p,p'*-DPE isomer was observed in the investigated conditions.
- 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.

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]. Traditionally, DPA is produced by solvent-free condensation of two molecules of phenol and levulinic acid (or levulinic acid esters) in the presence of Brønsted acid catalysts, generating two stereo-isomers [3]. However, *p,p'*-DPA, has a higher market value as it mimics the chemical structure of BPA. In this work, ethyl levulinate rather than levulinic acid has been employed as the substrate in the condensation reaction, reducing the kinetic probability to produce by-products. In particular, 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 (Fig. 1) under solvent-free conditions has been carried out in a batch reactor employing Amberlyst-15 as the acid catalyst.

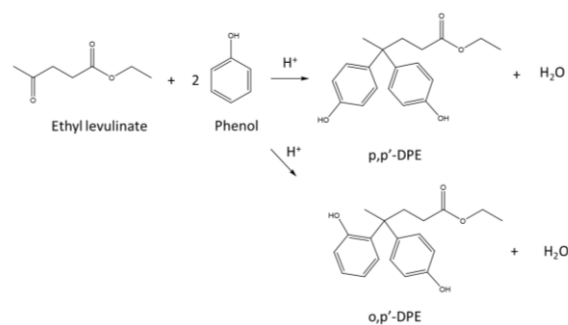


Figure 1. Reaction scheme.

In particular, reaction temperature, molar ratio phenol-to-ethyl levulinate, catalyst load and mixing rate were varied. Moreover, the effect of water i.e. the co-product of DPE on the reaction rate was investigated. Different liquid samples were withdrawn during the reaction and analyzed via ¹H-NMR

500 MHz. The results were evaluated with MestReNova. A classical batch reactor model was employed, considering chemical kinetics, intraparticle diffusion limitations, swelling of the catalyst particles as well as the role of water on the reaction rate. gPROMS Model Builder was utilized as main software.

3. Results and discussion

^1H - and ^{13}C -NMR analysis revealed that only the p,p' -DPE isomer is produced in the main reaction under the investigated conditions, which is a very positive result as p,p' -DPE has a potentially higher market value since it mimics the most the chemical structure of BPA. The yields to DPE are quite high, however the transesterification of ethyl levulinate with phenol took place as a side reaction. 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 selectivity (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. The density and viscosity of the reaction mixture were measured, revealing a dependence on the temperature and reaction time. 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. The parameter estimation allowed to obtain the activation energies, kinetic and adsorption constants.

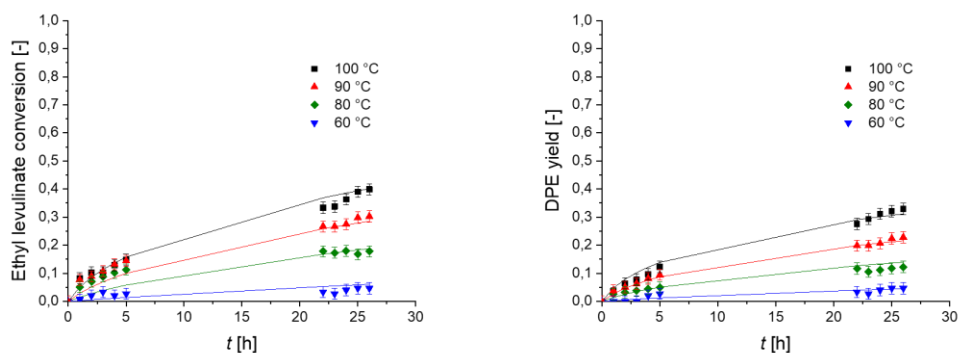


Figure 2. Temperature effect on ethyl levulinate conversion and DPE yield. The solid lines represent the model prediction.

4. Conclusions

The kinetics of the reaction between ethyl levulinate and phenol to produce p,p' -DPE has been investigated under solvent-free conditions. Amberlyst-15 was employed as the heterogeneous catalyst, showing a high activity even after recycling. The ethyl levulinate conversion and the DPE yield were registered with quantitative ^1H -NMR. Internal mass transfer limitations in the system were taken into account in the mathematical model, which accurately described the experimental data. Numerical values of the kinetic constants, adsorption constants were estimated with nonlinear regression analysis.

References

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Keywords

Diphenolic acid, ethyl levulinate, kinetic study, NMR.