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Development of a kinetic model for polyurethanization from carbonated vegetable oils.

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Highlights
- Non-isocyanate route for the production of polyurethane.
- Establishment of a kinetic model for polyurethanization.
- Calorimeter-aided for the determination of thermodynamic constants.

1. Introduction

Polyurethanes are among the polymers with more applications in the modern technologies, occupying the rank 6th with an annual production of 18 Mt in 2016. During the past years, many different routes to synthetize non-isocyanates polyurethanes have been explored, one of the most promising is the reaction of cyclic polycarbonates with amines [1-2]. Nevertheless, the kinetic study of this reaction can be cumbersome due to the high viscosity of the reaction mixture and the presence of side-reactions. To overcome the issue of viscosity, fatty acid methyl ester was used. Urethanisation of carbonated methyl oleate by n-butylamine was studied in semibatch reactor under isothermal conditions. The goal is to develop a kinetic model for polyurethanization on a test chemical system.

2. Methods

A huge effort has been made for the production of carbonated methyl oleate. Different stages were needed: esterification of oleic acid, epoxidation of methyl oleate [3-4] and carbonation of epoxidized methyl oleate [5-6]. Concentrations of unsaturated and epoxide groups were followed by titration methods. Kinetic experiments of polyurethanization of carbonated methyl oleate by n-butylamine were performed in a semibatch reactor, where amine was added, at different reaction temperature (50-70°C). Concentrations of carbonated and amide groups were determined by FTIR. Reaction enthalpies were determined by a Tian-Calvet calorimeter.

3. Results and discussion

Based on our experimental data, two reactions occurred during the process: reaction between carbonated group and amine to create the urethane function (polyurethanization) and the reversible reaction between the ester group and amine to produce the amide group (Figure 1). Thus, to limit the side reaction of amidation, it is compulsory to establish a kinetic model.
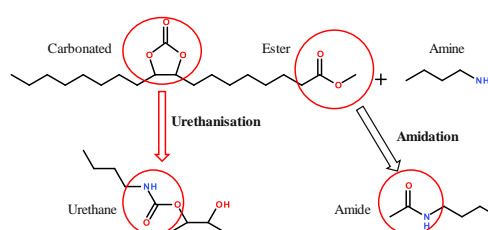

Figure 1. Simplified scheme for polyurethanization and amidation reactions.

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By calorimetry, it was found that the reaction enthalpy for urethanization is equal to -19 kJ/mol and the one for amidation is equal to -5kJ/mol. Due to the low values of reaction enthalpies, one can neglect the exothermicity of these reactions.

Kinetic equations for urethanisation and amidation were expressed as:

$$R_{Ure.} = k_{Ure.}[Carbonated][Amine]$$

$$R_{Amid} = k_{Amid} * \left([Ester][Amine] - \frac{[Amide][MeOH]}{K_c}\right)$$

The equilibrium constant K_C was expressed by using a van't Hoff equation.

For the kinetic model, the kinetic constants of these reactions were determined by non-linear regression methods using the concentrations of carbonated and ester groups as observables. Different experiments were performed at different reaction temperatures and concentrations. The ordinary differential equations of the different mass balances were solved out by using ODESSA algorithm. Figure 2 shows the fitting of the model to the experimental data.
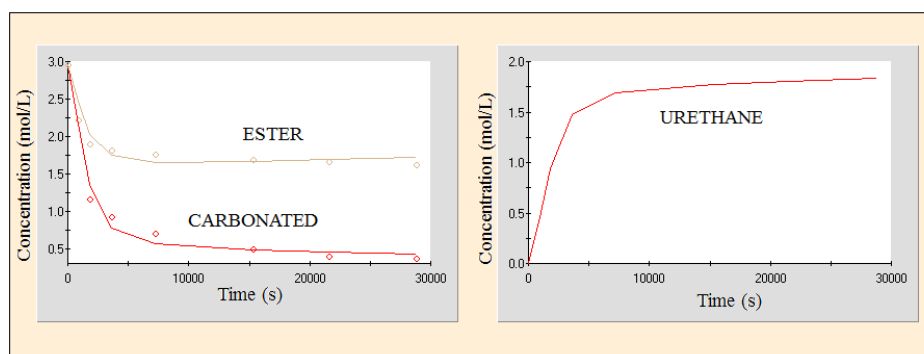

Figure 2. Fit of the model to the experimental data at 70°C.

4. Conclusions

A kinetic study for the urethanization of carbonated methyl oleate was performed in a semibatch reactor under isothermal conditions. It was observed that the side reaction of amidation could not be neglected and should be taken into account. Furthermore, this reaction system is not very exothermic. The built model fits properly the experimental data.

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