



Microreactor modelling for ethoxylation reactions

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1. Introduction

The ethoxylation of fatty alcohol is an important process to produce non-ionic surfactants. Ethylene oxide reacts rapidly with long chain alcohols, reaction promoted by strong base catalyst, reaching almost full selectivity to the desired products, as no-side reactions are favoured in the presence of base catalysts. The reaction occurs via anionic polymerization, where ethylene oxide molecules are added to a growing ether chain, leading to a statistical distribution of the products. The alkoxylation reactions are generally performed in semibatch reactors [1], also in series, in which the catalyst and the substrate (alkyl phenols, fatty alcohols or acids) are initially charged while epoxide (ethylene or propylene oxide) is added during the reaction course. This synthesis strategy is due to the high reactivity of alkoxides and also to the high heat involved in alkoxylation reaction. The use of semibatch reactors, however, have some drawbacks that can be summarized in the following points: (i) the reactor volume is relatively high; this aspect could represent a serious problem for safety issues due to the high quantity of alkoxide present in the reactor at a certain time; (ii) the productivity of the system is quite low for the various steps involved in a semibatch process (reactant and catalyst charge, chemical reaction, products discharge); (iii) the safety of the overall process is not optimal, fact due to possible epoxide accumulations that could lead easily to runaways reactions.

A possible solution that could allow overcoming the mentioned drawbacks is the adoption of a continuous reactor that can be properly designed for the achievement of the desired alkoxylation degree. The shift from the traditional semibatch process to the continuous ones could really represent the start of a new era in the alkoxylation technologies. In the scientific and patent literature both traditional tubular reactors and more innovative reactor configurations, like microreactors, have been proposed for the alkoxylation reactions. These last are particularly suitable for exothermic and multiphase reactions, thanks to the high heat and mass transfer exchange [2-3]. Such reactors were tested in the literature, showing good performances in terms of reaction conversion and thermal control, allowing to work at relatively high temperatures (240°C) [4-5]. Even though in the adopted experimental conditions it was demonstrated that the flow-pattern is laminar [6], the collected data are normally simulated with a plug-flow model approach [4]. This approximation certainly leads to a non-rigorous determination of the parameters related to the intrinsic kinetics of the reaction. At this purpose, in the present work a laminar-flow model was applied to the description of the experimental data collected in the literature.

2. Methods

A laminar-flow reactor model was tested to determine the kinetic and equilibrium parameters for octanol ethoxylation data reported in the literature [4-5].

The partial differential equation (PDE) system describing the single liquid phase reactor was solved with the method of lines already implemented in gPROMS Model Builder v. 4.0. The reaction occurs in a liquid system, considered non-isothermal [6] hence it is necessary to write both mass and energy balance equations. The model was written in a time-dependent form, to simulate the evolution of the concentration and temperature profiles along the reactor length and reactor radius.

$$\frac{\partial c_i}{\partial t} = -u(r) \frac{\partial c_i}{\partial z} + D_i \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) + \sum_j v_{ij} r_j \quad (1)$$

$$\frac{\partial T}{\partial t} = -u(r) \frac{\partial T}{\partial z} + \left(\frac{\lambda}{\bar{c} \bar{\rho}} + D_i \right) \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \frac{\sum_j v_{ij} r_j (-\Delta_j)}{\bar{c}_p \bar{\rho}} \quad (2)$$

3. Results and discussion

The developed model was firstly applied to conduct a sensitivity study, showing high flexibility of the model, simulating for a very exothermic reaction temperature gradients along the radial coordinate. Then, the model was applied to describe the experiments conducted at different temperatures (from 180 to 240°C) taken from the literature [4-5]. All the required physical properties were taken from the literature [4]. In every case, a good fit was obtained (Figure 1).

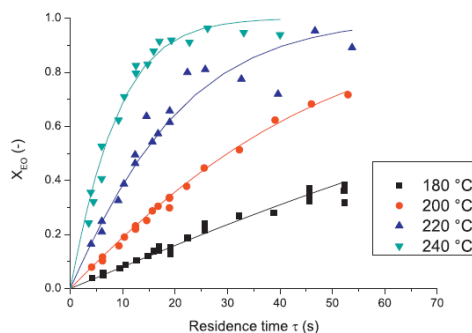


Figure 1. Ethylene oxide conversion along the residence time of the microreactor. Experiments conducted at different temperatures, taken from the literature [4-5].

The kinetic parameters shown a deviation from the ones obtained using a plug flow-approach (30% deviation), demonstrating the validity of the present model.

4. Conclusions

A laminar-flow reactor model was developed to describe ethoxylation reactions. The modelling approach consists of the simultaneous dynamic solution of both liquid mass and heat balance equations along the axial and radial coordinate. No rate-determining steps were assumed. The model showed a high flexibility in interpreting the experimental data and a good prediction power that will allow the design of a continuous equipment intensifying ethoxylation processes.

References

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