

Propoxylation of fatty amines

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RESEARCH ARTICLE

Propoxylation of fatty amines: Switching from batch to flow

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Abstract

The ethoxylation and propoxylation of fatty amines are important industrial reactions commonly performed in de-intensified semi-batch reactors. The present study aims to intensify these reactions by transferring the process to continuous processing. Therefore, the propoxylation of octylamine, as model system, was performed in a batch reactor and in a micro tubular reactor. The micro tubular reactor operated with a single liquid phase at 15 bar pressure. The batch study found valuable kinetic and solubility information in the temperature range of 120°C–160°C. Moreover, a switch-flow method in the micro tubular reactor combined with inline FTIR gave a more detailed understanding of the reaction kinetics. In the micro tubular reactor, all PO was added in the feed according to stoichiometry, which led to a process intensification factor of 3.7 compared to fed-batch gas phase addition at maximum 2 bar.

1 | INTRODUCTION

Ethoxylated and propoxylated fatty amines are widely used as nonionic surfactants, leading to a steady increasing industrial demand over the past six decades.^[1,2] The intermediate products, with 2 mol of ethylene (EO) or propylene oxide (PO), react in a second step via a chain growth polymerization of EO or PO to di-polyetheramines (Figure 1). Other uses are as starting material for the production of quaternary salts or amine oxides. We focus in the present work, on the reaction to the 2 M di-alcohol amines.

One key limitation of the reaction processes are the severe safety measurements necessary due to the hazard potentials of EO, as explosive, flammable, and toxic gas.^[3–5] Therefore, commonly reported reactor types for ethoxylation or propoxylation of fatty groups, like alcohols, phenols, or acids, are semi-batch reactors,^[6] spray-tower-loop reactors^[7,8] and Venturi-loop reactors.^[9–11]

These three reactor types differ in the way that the liquid is brought in contact with the gas phase or vice versa. In semi-batch (Figure 2a), EO or PO enter from the top to the preheated liquid. Venturi-loop reactors (Figure 2b) spray the gas into the liquid phase, whereas spray tower-loop reactors (Figure 2c) disperse the liquid in the gas phase. Usually, a high circulation of the crude through a heat exchanger is necessary in those cases to avoid thermal runaway due to the exothermic reaction enthalpy of $-120 \text{ kJ/mol}_{\text{EO}}$. The advantages of those newer reactor types are the increased mass and heat transfer while allowing product treatments after each batch according to di Serio et al.^[12] A considerable amount of detailed models and intensive optimizations have been performed on those processes.^[7,13,14] Optimal process conditions were reported to be 180°C, the pressure not exceeding 5 bars, working entirely oxygen free and without the use of a catalyst (for fatty amines). Di Serio and coworkers

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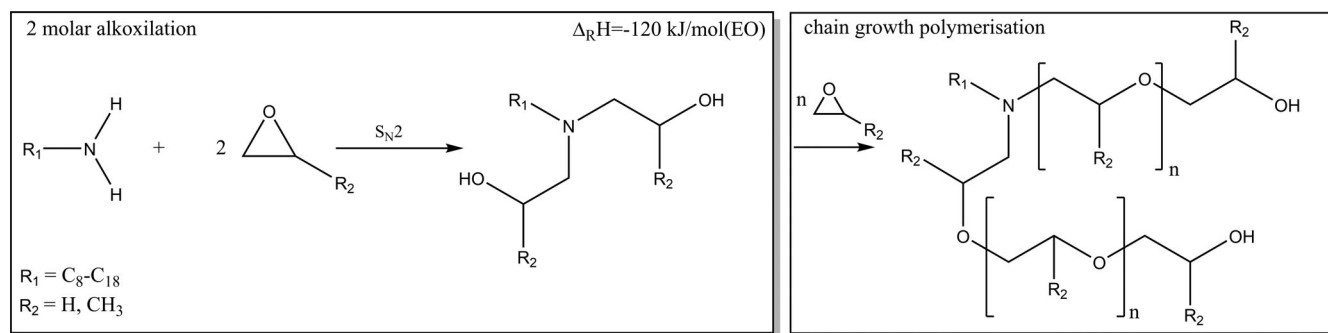


FIGURE 1 Ethoxylation or propoxylation of fatty amines gained from organic sources like coco, tallow or soya. In a next step, those products get polymerized with a variable amount of EO and/or PO based on the property demand for the specific product

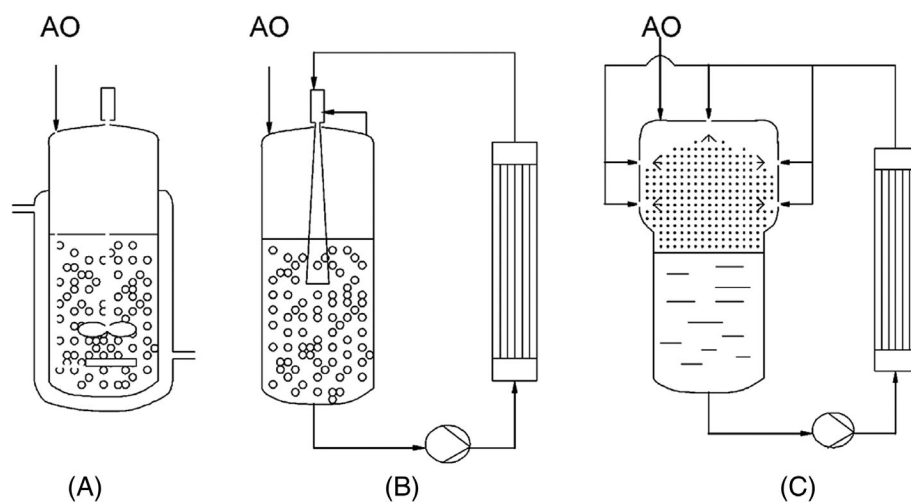


FIGURE 2 Schemes of semi-batch reactors mainly employed industrially for ethoxylation/propoxylation processes: (a) stirred tank reactor; (b) Venturi loop reactor; (c) spray tower loop reactor. AO stands for alkyl oxides in general including EO and PO (taken from Di Serio et al.^[12])

compared those three most applied reactor systems in regard to safety and performance behavior.^[12]

They concluded that Venturi-loop reactors and spray-tower-loop reactors are safer because of the absence of mechanical agitation, which could lead to spark formations. However, no significant improvement of process time could be achieved because the addition of EO per time step stays limited due to the high explosion and hazard potential of EO. In the 1950s, semi-batch processes were constructed that are still running today. Venturi-loop and spray tower loop reactors are presented as most recent technical advances, although they already date back to 1980.^[15] Innovation is tardy due to the high investment costs and risk avoidance. Although industrial intensification of ethoxylation and propoxylation is not seen applied, some alternatives were discussed in literature^[16–19] and seen patented.^[20–22] Two main directions can be discerned: (a) a catalytic route to accelerate the reaction, especially the slow initial phase^[23–25] and (b) the adoption of continuous systems using higher EO or PO concentrations on which we will focus.

In this article, we demonstrate a switch-flow method combined with inline FTIR analysis and compare this with batch analysis of kinetics. We will show that significant

more qualitative and quantitative information can be collected in a shorter time frame and with less chemicals. Furthermore, we will show that the reaction time can be reduced from hours to minutes by operating at more extreme pressure, leading to a significant reduction in reactor size. Finally, we will compare the conventional fed-batch process of 50 t of product per day in a 30 m³ autoclave (including batch down times) with a continuous process in a 0.1 m³ continuous reactor with an equivalent production rate as the conventional process. As additional benefits to the lower equipment costs, the significantly smaller reaction volume is less hazardous and the shorter residence time gives a higher product quality.

2 | METHODS

2.1 | Experimental

2.1.1 | Chemicals

All reactants were sourced from commercial parties, that is, Acros Organics, EMD Millipore, and Sigma-Aldrich.

TABLE 1 Process conditions and deviations

		Batch	Flow
Volume (mL)/volumetric flow rate (mL/min)	Total	50 mL	0.06 or 1.0 mL/min
	Per reactant	7 ± 1 mL(PO)	0.0265 or 0.458
		43 ± 0.05 mL(OA)	±5 10 ⁻⁴ mL/min (PO) 0.033 or 0.542 ±10 ⁻³ mL/min (OA)
Molar ratio	4 × 0.5 to 1 M ratio PO/(OA + SEC + TERT)	2 to 1 M ratio PO/OA	
Pressure (bar)		0.1-2.0	15
		± 0.05	± 0.5
Temperature (°C)		130-160°C	120-160°C
		± 2	± 0.5 K

The highest available purity was chosen. A detailed list is available in Table S1. The pure reaction products are not commercially available. The final product could be purified to 99%_{mol} as established by GCMS, whereas the intermediate secondary amine could be obtained at a concentration of 75%_{mol} from the reaction crude in batch.

2.1.2 | Set-up batch

The experimental set-up is briefly explained for the comparable experiments in semi-batch. A complete description is given in Müller et al.^[26] The fatty amines were preloaded to a heated and vacuumed stirred 100 mL tank reactor. PO was added via a syringe at the top of the reactor. All reactions were conducted between 130°C and 160°C for PO. An experimental scheme is presented in Figure S1).

2.1.3 | Set-up flow

The set-up is depicted in Figure S2. In short, octylamine was pumped with an HPLC pump from Shimadzu AT-2010, whereas PO was added via a syringe pump (Nexus 2000) from Chemyx. The chemicals were stoichiometric mixed and pumped through the 16 m long capillary (ID = 7.8 10⁻⁴ m), which was heated in an oil bath (Lauda-E300). The reaction pressure was kept constant at 15 bar using a backpressure regulator (Equilibrar LF Series, Pressure Control Solutions). For both systems for convenience, the process conditions are summarized in Table 1:

2.1.4 | Analytics

The reaction mixture was analyzed by taking samples for GC in a GC-FID (Shimadzu) with a DB-5 column using

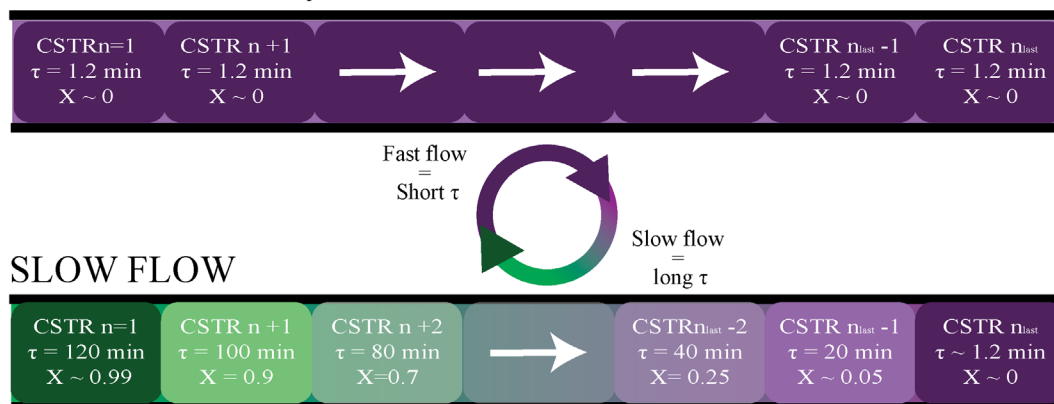
helium as mobile gas. Samples needed to be analyzed in maximal 12 hours to avoid sample degradation. For the batch experiments, the vapor pressure of the epoxides was used to determine the concentration in the liquid phase. Therefore, a NRTL model was fitted to solubility data collected. More information can be found in Data S1. For the flow experiments additional to GC, FTIR spectra were in-line recorded Nicolet iS50-FTIR with a liquid flow-cell from Harrick with a volume of 7.5 µL and ZnSe windows.

2.1.5 | Switch-flow procedure

To improve the data collection, we herein describe a method allowing the use of all intermediate points. This method requires a characterization of the mixing behavior and the fluid dynamics (more information can be found under micro tubular modeling and the Data S1, sections 1.5 and 1.6) to know the dispersion behavior inside the micro tubular reactor. The procedure is as follows: An equilibrium is initially reached with a residence time shorter than a reaction time with negligible conversions leading very low conversion gradients along the microtube (first part Figure 3).

In the next step, the flow rates of both reactants are lowered aiming for a high residence time compared to the reaction rate, achieving therefore full conversion at steady state. Important criteria are identical transient behavior of the pumps and the switch time being negligible short compared to the reaction time. At the low flow rate, each fluid element has another residence time in the reactor (middle section Figure 3), which gives a complete overview about the conversion trends in the micro tubular reactor. The switch-flow technique is reversible. The concentration gradients are seen for both switches in Figure S6.

FAST FLOW steady state



SLOW FLOW steady state



FIGURE 3 Switch flow technique, after achieving steady state conditions at a fast flow rate, the pumps are lowered. Achieving a complete conversion profile because every fluid element has a defined residence time in the reactor

TABLE 2 List of elementary steps used for modeling the reaction of PO with OA. Elements on the arrow signify catalytic processes. The difference is in the explicitness of the catalytic terms are lumped up, whereas for flow, a catalytic complex is formed in a reversible reaction

	New proposed model
r1	$OA + PO \xrightarrow{k_1} SEC$
r2	$PO \xrightleftharpoons[k_{-2}]{k_2} SEC \xrightarrow{k_3} PO^{SEC}$
r3	$PO \xrightleftharpoons[k_{-3}]{k_3} TERT \xrightarrow{k_4} PO^{TERT}$
r4	$OA + PO^{SEC} \xrightarrow{k_4} 2SEC$
r5	$SEC + PO^{SEC} \xrightarrow{k_5} SEC + TERT$
r6	$OA + PO^{TERT} \xrightarrow{k_6} SEC + TERT$
r7	$SEC + PO^{TERT} \xrightarrow{k_7} 2TERT$

2.2 | Modeling

2.2.1 | Kinetic fitting

The modeling was conducted using MATLAB version 2018a. All kinetic parameters were determined by means of nonlinear fitting of the reaction mechanisms (Table 2) using a least-square fitting procedure (lsqnonlin) toward

the experimental data. The confidence intervals were calculated using the nlparci function using the jacobian matrix gained from lsqnonlin.

The rate equations are shown in Data S1. The data for butylene oxide with dodecylamine was fitted, preliminary, with a model previously developed.^[26] This model fitted the results in batch for butylene oxide with dodecylamine very well and was therefore initially tested in this work assuming similar kinetic mechanism of the reactants. However, as this model proved insufficient for flow, a new model was developed. Herein, we propose a new model based on the found results in flow.

2.2.2 | Modeling micro tubular reaction assumptions

The flow system was modeled as one liquid phase, in contrast to batch, where PO was added to a vacuumed reactor and the pressure was taken as measure of the PO concentration. At the experimental conditions, PO is completely mixable in OA. The system pressure was set to be at least 3 bar above the mixture vapor pressure based on the NRTL study. Therefore, the gas phase could be excluded from the modeling. The flow is in the laminar regime ($Re < 30$) at the used conditions and the theoretical dispersion was with maximal $D/ul = 1.3 \times 10^{-3}$ (with D dispersion, u velocity, and l characteristic length) below the by Levenspiel defined limit for ideal plug flow behavior of 0.01.^[27]

A RTD experiment was performed to study the flow response. The flow response was modeled with a tank in series model,^[28] minimizing the numbers of tanks used. The lowest value found was 130 tanks in series, showing that the system behaves as a plug flow.^[29] This minimum (130 tanks) was chosen to model the kinetics due to the strong linearity of the change in concentrations at this dispersion regime. Higher numbers of tanks in series did not have an influence on the model, however on the modeling time. More information can be found in Data S1. The following mole balance was used for flow:

For CSTR index, $i = 1-130$, for component index $k = \text{PO}, \text{PO}^{\text{SEC}}, \text{PO}^{\text{TERT}}, \text{OA}, \text{SEC}, \text{TERT}$

$$\frac{dC_{k,i}}{dt} = \frac{F_W \rho_{\text{mix}}(T^0)}{V_{R,i} \rho_{\text{mix}}(T)} (C_{k,i-1} - C_{k,i}) + R_k \quad (2.1)$$

with

$$R_{\text{PO}} = -k_1 C_{\text{OA}} C_{\text{PO}} - k_2 C_{\text{PO}} C_{\text{SEC}} + k_{-2} C_{\text{PO}^{\text{SEC}}} + k_3 C_{\text{PO}} C_{\text{SEC}} + k_{-3} C_{\text{PO}^{\text{TERT}}} \quad (2.2)$$

$$R_{\text{PO}^{\text{SEC}}} = +k_2 C_{\text{PO}} C_{\text{SEC}} - k_{-2} C_{\text{PO}^{\text{SEC}}} - k_4 C_{\text{OA}} C_{\text{PO}^{\text{SEC}}} - k_5 C_{\text{SEC}} C_{\text{PO}^{\text{SEC}}} \quad (2.3)$$

$$R_{\text{PO}^{\text{TERT}}} = +k_3 C_{\text{PO}} C_{\text{TERT}} - k_{-3} C_{\text{PO}^{\text{TERT}}} - k_6 C_{\text{OA}} C_{\text{PO}^{\text{TERT}}} - k_7 C_{\text{SEC}} C_{\text{PO}^{\text{TERT}}} \quad (2.4)$$

$$R_{\text{OA}} = -k_1 C_{\text{OA}} C_{\text{PO}} - k_4 C_{\text{OA}} C_{\text{PO}^{\text{SEC}}} - k_6 C_{\text{OA}} C_{\text{PO}^{\text{TERT}}} \quad (2.5)$$

$$R_{\text{SEC}} = +k_1 C_{\text{OA}} C_{\text{PO}} - k_2 C_{\text{PO}} C_{\text{SEC}} + k_{-2} C_{\text{PO}^{\text{SEC}}} + 2k_3 C_{\text{OA}} C_{\text{PO}^{\text{SEC}}} + k_6 C_{\text{OA}} C_{\text{PO}^{\text{TERT}}} - k_7 C_{\text{SEC}} C_{\text{PO}^{\text{TERT}}} \quad (2.6)$$

$$R_{\text{TERT}} = -k_3 C_{\text{PO}} C_{\text{TERT}} + k_{-3} C_{\text{PO}^{\text{TERT}}} + k_5 C_{\text{SEC}} C_{\text{PO}^{\text{SEC}}} + k_6 C_{\text{OA}} C_{\text{PO}^{\text{TERT}}} + 2k_7 C_{\text{SEC}} C_{\text{PO}^{\text{TERT}}} \quad (2.7)$$

Outside the micro tubular reactor, no reaction was assumed, due to the rapid cooling of the reaction mix by the high heat transfer from capillary to air (heat transfer time < 0.5 seconds for $\Delta T = 100$). Only the change in volumetric flow rate based on the density temperature dependency was considered.

For batch, intrinsic kinetics, without mass transfer or heat transfer limitations, were calculated (section S1.8). For each successive addition step, new initial concentration was given as conditions for the solver.

For an accurate residence time determination, the density of the liquid needed to be corrected for temperature. The volume extension of the liquid inside the reactor was considered through the Antoine equation for OA

(Equation 2.8) and an empiric correlation taken from the VDI Wärmeatlas,^[30] which proved more accurate than the known Antoine parameters (Equation 2.9). An ideal solution was assumed for the mixture with the density ρ_{mix} .

$$\rho_{\text{OA}} = 1028 - 0.831T \text{ [kg/m}^3\text{]} \quad (2.8)$$

$$\rho_{\text{PO}} = -2.9 \cdot 10^{-3} (T - 273.15)^2 - 1.308 (T - 273.15) - 859 \text{ [kg/m}^3\text{]} \quad (2.9)$$

3 | RESULTS

3.1 | Batch to flow

The results of the batch experiments are shown in Figure 4b. The most significant finding from the batch experiments is the clear sigmoidal curve, typical for auto-catalytic reaction. PO follows in batch the same trends as butylene oxide in our previous reported work, but is a factor of 1.5 faster.^[26] The findings in batch were used to design the micro tubular flow set-up. Initial tests defined the experimental window and allowed a calibration and absorption range in the FTIR; further information concerning the FTIR method can be found in Data S1.

The results based on FTIR and GC in flow are shown in Figure 4a. Clearly, full conversion is achieved in one step at a residence time of 2 hours. The number of data

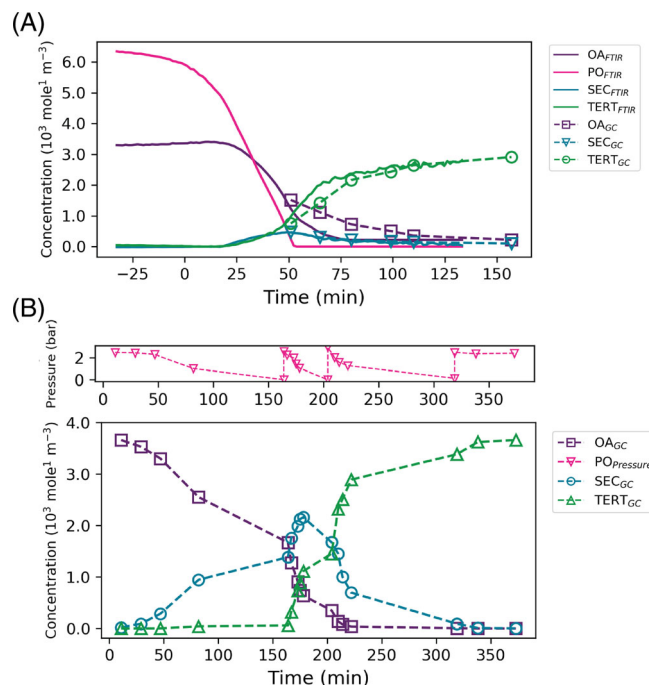


FIGURE 4 Reaction of propylene oxide with octylamine, (a) in flow, (b) in batch both at 150°C. The residence time in flow was 120 minutes. The first 35 minutes are due to the volume between reactor and FTIR cell

points available for fitting the kinetic rate is very high, leading to a much higher accuracy of kinetic rate constants. For comparison, the reaction performed at the same temperature in batch is given in Figure 4b. Apparently, the flow system leads to a significant increase in conversion rate. Full conversion to TERT is achieved in less than half the reaction time of the semi-batch experiment. Both set-ups show a sigmoidal curve for the conversion from OA to TERT. The slow initial and completion reaction rates are due to not enough reactants, for the initial step these are SEC and TERT as catalyzers and for the completion rate PO and SEC. In the semi-batch experiments, the addition of PO was manually performed leading to an uncertainty of 1 mL of approximately 5 mL per addition, which led to already after three additions nearly full conversion. From the data in Figure 4, it is apparent that the FTIR as inline technique leads to a better resolution of the data and to less errors due to sample degradations as explained in the Method section. In addition, PO could be directly measured in the solution without exposure risk to toxic vapors. An interesting result from comparing batch to flow is the difference in concentration of SEC inside the different processes: the amount of intermediate SEC was twice as high for the batch process as for the flow process. A possible explanation for this could be a faster conversion rate of SEC to TERT when the concentration of PO compared to the amine is as high as in the flow experiments. The mass balances of the amines closed to 98%. In addition in GC, no side products as polyglycols were detected, implicating no other species being present. The present finding is in accordance with experiments with butylene oxide (Figure S10).

An interesting feature is the clear disappearance of the PO signal in all flow experiments before stoichiometric corresponding amounts of products were formed or detected. This rather unexpected finding could be explained by the formation of complexes or intermediates diminishing the absorption of PO in FTIR by epoxides oxygen bonding to an alcohols proton, as known from literature.^[31]

3.2 | Process window

The experiments in batch and flow were performed at 120–160°C. Although the batch experiments showed a temperature dependency, the flow experiments revealed a complete independence from temperature above 130°C (Figure 5). Exception are the experiments at 120°C, which showed a lower initial rate and therefore reached only a conversion of 80% after 2 hours residence time. These findings contrast with the reaction system with butylene oxide, where a direct temperature effect was found in batch and flow (Figure S11). One interesting

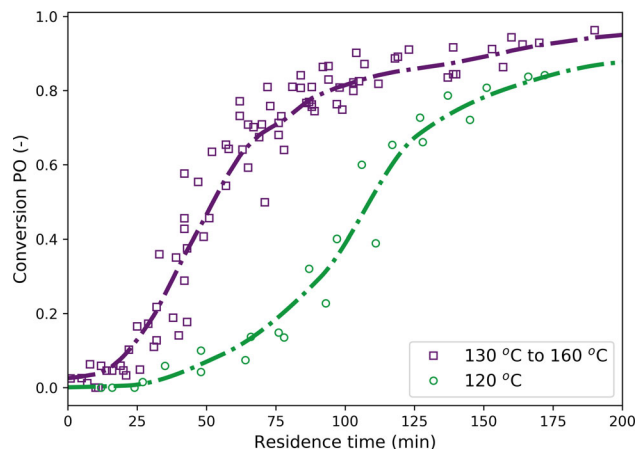


FIGURE 5 Conversion of PO with octylamine based on GC results of all experiments in a reaction ratio of 2 to 1. All experiments above 130°C showed a similar conversion behavior represented by the trend line. At experiments, at 120°C, a lower conversion rate was seen

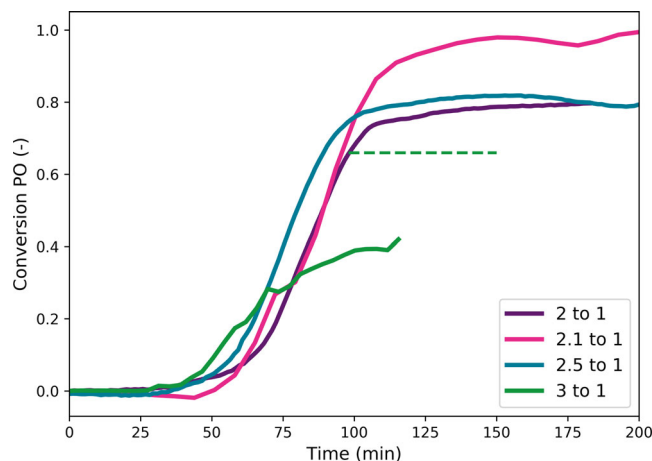


FIGURE 6 Experiments with excess of PO ranging from stoichiometric addition (2 mol PO per mole OA) to 3 to 1. In dotted line is the theoretical maximal conversion of PO given at a ratio 3 to 1. In all experiments, in excess residue, PO was measured in FTIR

feature was that the highest found conversion was only 98%, typical seen as residue SEC in the GC. This is typical for the co-dependent S_N2 mechanism where the chance for reactive encounters of both reactants decreases drastically at low concentration leading to close to infinite reaction times when approaching full conversion.

One common method to avoid this extensive reaction times for full conversion is working in excess of one of the reactants. Herein, experiments using PO in excess were performed.

It is apparent from Figure 6 that the conversion rate of PO depends on the excess used, which was not clear from the amine species results. At a ratio of 2.1 to 1, an

increase in conversion is observed. Increasing the excess of PO to 3 to 1 surprisingly leads to a decrease of PO conversion to the theoretical possible conversion ratio, which is represented by the dotted line. Below the ratio of 2 to 1 preliminary experiments found that the maximum asymptotic conversion rate increase was from 0.5 to 1 mol PO per mole OA, but seemed to be independent from 1 mol to 2 mol of PO toward OA.

As described before, a possible explanation is that an excess of PO accelerates the formation of TERT more than the formation of SEC, so that the concentration of SEC is lower than in experiments with a lower concentration of PO present as in batch. A low concentration of SEC compared to PO leads to most of SEC being bound to the PO in the catalytic complex and therefore possibly not being accessible for the further reaction to TERT and consequently slowing down the reaction rate. The formation of complexes with SEC and TERT can also explain the high solubility of PO in the amine alcohol mixtures. The dependency of SEC concentration of the PO concentration is elucidated using following kinetic scheme (Equation 3.1-3.5).



Leading to the following kinetic rate equations:

$$[POSEC] = \frac{k_1[PO][SEC]}{k_{-1}[POSEC]} \quad (3.2)$$

$$SEC_{tot} = [SEC] + [POSEC] \quad (3.3)$$

$$\frac{k_1}{k_{-1}}[PO] \gg 1 \quad (3.4)$$

$$[POSEC] = SEC_{tot} \quad (3.5)$$

For TERT, the same equations would be valid. The existence of those complexes was not measurable by GC likely due to their instability. The whole concept of working in excess is to the best of our knowledge not published or practically performed in industry. One reason is the safety risk of free remaining PO or ethylene oxide and additional side reactions. We proof however that the latter can be avoided (Table S3).

3.3 | Modeling

The experimental results of batch and flow were modeled using the mechanism shown in Table 2 including the rate

TABLE 3 Fitted temperature independent reaction coefficients for the proposed model

Reaction coefficient (k_i) [–] valid from 130 to 160°C	
k_1	$5.7 \pm 0.7 \times 10^{-11}$
k_2	$7.2 \pm 1.0 \times 10^{-7}$
k_{-2}	$1.4 \pm 0.5 \times 10^{-7}$
k_3	$2.7 \pm 1 \times 10^{-7}$
k_{-3}	$2.8 \pm 0.7 \times 10^{-6}$
k_4	$5.6 \pm 1.0 \times 10^{-6}$
k_5	$3.0 \pm 0.3 \times 10^{-6}$
k_6	$1.5 \pm 0.6 \times 10^{-5}$
k_7	$4.9 \pm 1.3 \times 10^{-6}$

Equations 2.1-2.7. The rate coefficients are given in Table 3. The results of the previously reported model fitting are presented in Table S5.

The reason for the change in model from the previous reported batch model to the new proposed model becomes clearly evident when comparing the flow results to the batch model prediction (Figure 7c).

The previously reported batch model achieved a good fit for experiments in batch, but cannot sufficiently predict the flow experiments. New aspects, such as the early PO disappearance and lower quantity of SEC are not considered because they are based on the extended process window. For a laboratory scale set-up, the batch model gave enough information to design the flow process. However, designing an industrial process based on the batch data alone would very likely not lead to a successful industrial scale process, proofing the importance of continuous experiments.

The newly introduced plug flow model based on tanks in series in combination with the new kinetic model, based on the experimental findings, are able to predict the experimental behavior of the amine species and PO well. The intermediate could not be detected; therefore, they were not considered for the fitting. The unreactive early disappearance of PO is explained by the formation of a PO-SEC and PO-TERT activated state. Figure S7 shows that the PO peak used for analytics at 1450 cm^{-1} , overlaps with a strong carbon absorption band, which has an impact for the accuracy of low concentration. The change in model from batch to flow is leading to better fitting results. The model is also able to fit the batch data (Figure 7b) proving that it is general applicable. This is due to the flow experiments using a bigger experimental window with the addition ratio of up to 3-1 mol PO per mole OA compared to only 0.5-1 mol in batch.

NOTATION

PO	propylene oxide
BO	butylene oxide
DDA	dodecylamine
SEC	mono-(hydroxypropyl) or hydroxybutyl dodecylamine
TERT	bis-(hydroxypropyl) or hydroxybutyl dodecylamine
GC	gas chromatography
FID	flame ionization detector
FTIR	Fourier transform Infrared Spectroscopy
CSTR,	describes the micro tubular set-up regarded
Flow	as plug-flow
CSTR,	describing the semi-batch autoclave; contin-
Batch	uous stirred tank reactor

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SUPPORTING INFORMATION

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