Octanol ethoxylation in microchannels

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ARTICLE INFO

ABSTRACT

The propagation kinetics of the ring opening polymerization of ethylene oxide with octanol ("octanol ethoxylation") was studied in a continuous microstructured reactor. Temperature was varied from 130 °C to 240 °C, and application of elevated pressure ensured a homogeneous liquid phase process. The activation energy was found to be $E_A = 72.2 \pm 0.9$ kJ mol^{-1}. A numerical model was developed which was able to predict ethylene oxide consumption as function of residence time.

The new kinetic parameters were used to determine the process intensification potential of this reaction and to study the limits of stable reactor operation.

1. Introduction

The productivity of fast, exothermic liquid phase reactions can be drastically increased if they are converted from semibatch operation to continuous processes under intensified conditions, i.e. higher temperatures and pressures, without the use of a solvent and/or at stoichiometric composition. For this type of reaction conditions, Hessel et al. [1] coined the term "novel process windows".

Microstructured reactors are often required to manage the large increase in heat release rates accompanying the higher reaction rates. These devices have characteristic dimensions in the sub-millimeter range, which creates a surface to volume ratio (A_W/V) which is several orders of magnitude higher than that of a stirred tank or a conventional tube reactor. The high specific heat removal rates and the small holdups of microchannels improve process safety concerning toxicity, thermal runaway and explosion prevention [2,3].

In this case study, fatty alcohol ethoxylation is used as example to evaluate the possibility of process intensification by continuous operation in a microstructured reactor. This reaction is fast and highly exothermic with a reaction enthalpy of $\Delta_R H = -95$ kJ mol^{-1} of converted ethylene oxide. No solvent is required in the process, resulting in a severe adiabatic temperature rise of several 100 K, depending on the ratio of ethylene oxide to starting alcohol.

This reaction is applied on large scale to produce nonionic surfactants. It is conventionally carried out in semibatch mode in a cooled stirred tank reactor at low pressures below 5 bar and temperatures in the range of 130 °C to 180 °C. Ethylene oxide is slowly fed into the reactor to control reaction temperature, resulting in long batch times and a low specific productivity.

Publications on continuous operation of fatty alcohol ethoxylation are scarce. Using tubular reactors with diameters in the range of several millimeters at higher pressures [4,5] lead to severe hot spots, which are disadvantageous for stable reactor operation and product quality. Recently, several patents proposed the use of a high pressure process in microreactors for industrial ethoxylate production, claiming that the increase in specific heat transfer rate would lead to an efficient and controllable operation [6–8], but no scientific publications could be found to substantiate this claim.

In literature, reaction kinetics has been studied up to 200 °C in semibatch reactors. Theoretically, higher reaction temperatures up to 250 °C can be sustained if microreactors are used, and are an important variable for increasing reaction rates as required for process intensification. Therefore, a microreactor setup was utilized to determine reaction kinetics at high temperatures, and to investigate the potential of microreactor technology for fatty alcohol ethoxylation under high pressures. This comprises process intensification evaluation as well as design considerations based on experimental results and estimation criteria.

2. Theory and methods

2.1. Reaction scheme

The base-catalyzed ethoxylation of octanol was studied. In that reaction, ethylene oxide is added to octanol, with potassium

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Symbols

a–f	parameters in Eq. (16)
A–C	parameters in Eq. (18)
A_i, A_{IS}	GC peak area (a.u.)
a_f	thermal diffusivity (m^2 s^{-1})
A_W	reactor surface area (m^2)
B	parameter in Baerns' criterion
c_{EO}, c_{Cat}	molar concentration (mol m^{-3})
C_p	heat capacity (J kg^{-1} K^{-1})
D	inner reactor diameter (m)
E_A	activation energy (J mol^{-1})
f, g	parameters in Hagan's criterion
i	number of EO units in homologue i
$K_{i,j}$	equilibrium constant
k_p	propagation rate constant (m^3 mol^{-1} s^{-1})
$k_{p,\infty}$	preexponential factor (m^3 mol^{-1} s^{-1})
k_W	heat transfer coefficient (W m^{-2} K^{-1})
L	reactor length (m)
m	mass (kg)
M_P, M_i	molar mass (kg mol^{-1})
n_i	amount (mol)
n	reaction order
$\dot{n}_{EO,0}$, $\dot{n}_{Oct,0}$	molar flow rate (mol s^{-1})
Nu	Nusselt number
$[O/C]_i$	oxygen to carbon ratio in ethoxylate species i
p	pressure (bar)
R	universal gas constant (J mol^{-1} K)
RF_i	FID response factor
r_p	propagation reaction rate (mol m^{-3} s^{-1})
S'	heat production potential
T	temperature (K)
T_C, T_R	coolant/reactor temperature (K)
t_R	characteristic reaction time (s)
u	velocity (m s^{-1})
V	reactor volume (m^3)
X_{EO}	conversion
z	axial coordinate (m)

Greek symbols

α_m	parameters in Hagan's criterion
γ_0	Arrhenius number
$\Delta_R H$	reaction enthalpy (J mol^{-1})
ΔT	temperature increase (K)
ΔT_{ad}	adiabatic temperature increase (K)
ΔT_{rad}	radial temperature difference (K)
ε	ethylene oxide to alcohol ratio (mol mol^{-1})
ϑ	temperature (°C)
κ	catalyst to alcohol ratio (mol mol^{-1})
λ	thermal conductivity of the fluid (W m^{-1} K^{-1})
ρ	density (kg m^{-3})
τ	residence time (s)

Abbreviations

BPR	back pressure regulator
C_2H_4O	ethylene oxide
$C_8H_{17}OH$	1-octanol
$C_8H_{17}O^-K^+$	potassium-octanolate
$C_8H_{17}[OC_2H_4]_iOH$	ethoxylate
CFD	computational fluid dynamics
CSTR	continuously stirred tank reactor
ECN	effective carbon number
EO	ethylene oxide
FID	flame ionization detector
GC	gas chromatograph

H_2	hydrogen
H_2O	water
HCl	hydrogen chloride
ICP-OES	inductively coupled plasma optical emission spectrometry
IS	internal standard
KOH	potassium hydroxide
LAP	living anionic polymerization
Oct	octanol
PI	pressure transducer
TC	temperature controller

Subscripts

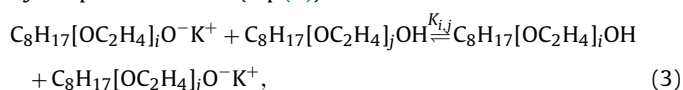|	
0	inlet/initial value
ad	adiabatic
C	coolant
calc	calculated value
Cat	catalyst
center	center of reaction channel
crit	critical
EO	ethylene oxide
exp	experimental value
FA	fatty alcohol/octanol
i, j	number of $[C_2H_4O]$ units
IS	internal standard
mix	mixture
Oct	octanol
p	propagation
P, Prod	product
R	reactor
rad	radial direction
W	Wall

octanolate acting as catalyst. The alcoholate is formed prior to the reaction by dissolving potassium hydroxide in the alcohol and removing water by applying vacuum at elevated temperatures:

$$C_8H_{17}OH + KOH \rightarrow C_8H_{17}O^-K^+ + H_2O \uparrow . \tag{1}$$
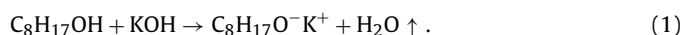
The actual ethoxylation reaction is a S_N2-type polyaddition of ethylene oxide to the alcoholate [9]:

$$C_8H_{17}[OC_2H_4]_iO^-K^+ + C_2H_4O \xrightarrow{k_{p,i}} C_8H_{17}[OC_2H_4]_{i+1}O^-K^+ . \tag{2}$$
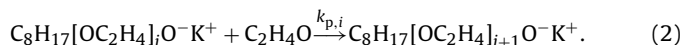
As there are no chain-terminating reactions, ethoxylation can be considered a special case of living anionic polymerization ("LAP"). The difference to normal LAP lies in the pool of alcohol species present, which is virtually inert to ethylene oxide until activated by the proton transfer (Eq. (3))

$$C_8H_{17}[OC_2H_4]_iO^-K^+ + C_8H_{17}[OC_2H_4]_jOH \overset{K_{i,j}}{\rightleftharpoons} C_8H_{17}[OC_2H_4]_iOH$$

$$+ C_8H_{17}[OC_2H_4]_jO^-K^+ , \tag{3}$$

so that while the number of growing chains remains constant, most alcohols will be ethoxylated to a certain degree, resulting in a distribution of the ethoxylate homologues in the product.

There is some discussion in literature whether or not the propagation rate constant $k_{p,i}$ is dependent on the length of the polyether chain. Some authors [10,11] claim that the relative rate constants increase with increasing chain length, whereas others [12,13] show that good agreement between model and experimental data can be obtained by using only a single rate k_p for all chain lengths i, which was also assumed in this work. This means that all species i in Eq. (2) react with ethylene oxide in the same fashion, making the rate of ethylene oxide consumption independent of chain length