Dynamic modelling of homogeneously catalysed glycerol hydrochlorination in bubble column reactor

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HIGHLIGHTS

- Homogeneous glycerol hydrochlorination studied over wide range of reaction conditions.
- Fluid dynamic behaviour analogous to vertical tubular absorbers.
- RTD and high-speed camera images used to characterize the flow inside the tube.
- Axial dispersion concept used to model the dynamic behaviour of the system.
- Fluid dynamic and mass transfer parameters successfully estimated.

ARTICLE INFO

ABSTRACT

The homogeneously catalysed glycerol hydrochlorination was thoroughly investigated in a continuous isothermal co-current bubble column reactor over a wide range of reaction parameters, such as temperature (70–120 °C), catalyst concentration (3–12%), liquid flow rate (6–12 mL/min) and gas flow rate (0.4–1.0 L/min). The flow patterns inside the reactor were studied by means of step response residence time distribution experiments and by high-speed camera images. The fluid dynamics of the system presented an unusual behaviour due to the extremely high solubility of HCl in the reaction mixture. Interestingly, the fluid dynamics imposed severe limitations to the reaction conversion. The axial dispersion model was applied for describing the dynamic changes in concentrations of compounds. Kinetic and solubility data were collected from previous work on glycerol hydrochlorination in semi-batch reactor conducted by our research group. The bubble column model was able to successfully describe the dynamic behaviour of 29 experiments, as well as estimate hydrodynamics and mass transfer parameters.

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1. Introduction

During the past 15 years, the scientific community has turned its attention to the development of more sustainable and environmentally friendly technologies, focusing on the use of biomass and waste as alternative energy sources to fossil fuels (Naik et al., 2010). In this sense, the transesterification reaction has been extensively applied as a route to produce diesel-like fuel from vegetable oils, animal fats and bio waste raw materials (Leung et al., 2010).

Glycerol is a by-product of the transesterification reaction, constituting approximately 10% in weight of the crude biodiesel produced nowadays (Tan et al., 2013; Yazdani and Gonzalez, 2007). For this reason, the global market supply of glycerol has become rather saturated, causing companies, such as Dow and Procter and Gambler, to shut down their glycerol production units (MCCoy, 2006). On the other hand, the glycerol originating from biomass is of low-quality and requires expensive purification techniques to be used in the production of pharmaceuticals, cosmetics and alimentary (Ayoub and Abdullah, 2012), as these were the niche applications in the past (Guerrero-Pérez et al., 2009; Karinen and Krause, 2006) . In fact, modern analysis reveal that glycerol has potential to become a platform chemical of the future, once a bio-based economy is matured (Tuck et al., 2012). For this reason,

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Nomenclauture

a	ratio between the gas-liquid interfacial area and reactor volume [dm^{-1}]
A	cross-sectional area [dm^2]
A	gas-liquid interfacial area [dm^2]
A	fitted parameter for estimation of C_{HCl}^{sat} [-]
B	fitted parameter for estimation of C_{HCl}^{sat} [-]
b	fitting parameter Eq. (14) [$L^2 mol^{-1} min^{-1}$]
C	concentration [$mol\ L^{-1}$]
D	dispersion coefficient [$dm^2\ min^{-1}$]
D	tube diameter [dm]
k	mass transfer coefficient [$dm\ min^{-1}$]
k'	reaction rate constant [$mol L^{-1} min^{-1}$]
K	distribution coefficient [-]
$\dot{m}$	mass flow rate [$g\ min^{-1}$]
m	mass [g]
M	molar mass of compound [$g\ mol^{-1}$]
n	amount of substance [mol]
$\dot{n}$	flow of amount of substance [$mol\ min^{-1}$]
N	molar flux [$mol\ dm^{-2}\ min^{-1}$]
P	pressure [bar]
Pe	Péclet number [-]
Q	objective function [$mol^2 L^2$]
r	reaction rate [$mol\ L^{-1}\ min^{-1}$]
R	
R^2	degree of explanation [-]
t	time [min]
$\bar{t}$	mean residence time [min]
T	temperature [K]

u	fluid velocity [$dm\ min^{-1}$]
w	mass fraction in the liquid-phase [-]
$\dot{V}$	volumetric flow rate [$dm^3\ min^{-1}$]
V	volume [dm^3]
x	molar fraction
$\kappa', \alpha_{HCl}, \alpha_w, \gamma', \delta'$	kinetic parameters in rate equations
ε	holdup [-]
ρ	density, [$g\ dm^{-3}$]
σ^2	variance of E(t) curve [min^2]
$\omega_0, \omega_1, \omega_2$	fitting parameters Eq. (41)

Subscripts and superscripts

G	gas phase
GL	gas-liquid interface
i	component index
L	liquid phase
0	initial condition or standard ambient temperature or pressure
exp	experimental value

Abbreviations

Gly	glycerol
α, α-MCP	3-chloro-1,2-propanediol
β, β-MCP	2-chloro-1,3-propanediol
$\alpha\gamma$, $\alpha\gamma$-DCP	1,3-dichloro-2-propanol
$\alpha\beta$, $\alpha\beta$-DCP	1,2-dichloro-3-propanol
GCD	glycerol and chlorinated derivatives, formed from glycerol, α, β, $\alpha\gamma$ and $\alpha\beta$

several research groups around the world have been studying different glycerol upgrading alternatives (Guerrero-Pérez et al., 2009; Karinen and Krause, 2006; Pagliaro et al., 2007). The present paper aims to investigate the glycerol hydrochlorination to produce dichlorohydrins, as this is the first step for the production of bio-based epichlorohydrin (Carrà et al., 1979), an important building block for the production of epoxy resins and plasticizers (Bell et al., 2008; Santacesaria et al., 2010, 2013).

Glycerol hydrochlorination is a parallel-consecutive reaction, usually carried out in the presence of simple organic acid catalysts, e.g. acetic, propionic and malonic acids, in the temperature range of 70–120 °C. The HCl can be introduced in the system either in gaseous form or as an aqueous solution of hydrochloric acid (Santacesaria et al., 2013). It is experimentally observed that, the first chlorination can take place in either of the OH positions, however, the second chlorination can only proceed via the 3-chloro-1,2-propanediol (α-MCP) compound. One molecule of water is produced for each chlorine atom added. Fig. 1 shows an overview of the glycerol hydrochlorination reaction.

Recently, de Araujo Filho et al. (2014) published a paper in which several novel aspects of the solvent-free glycerol hydrochlorination in semi-batch reactor were revealed. For the first time, the influence of HCl absorption on increasing the liquid phase volume was described and quantified; the volume increase is an important phenomenon which affects significantly the concentration of compounds, as was demonstrated. An important novelty of that work was that the non-catalytic reaction pathway was included in the reaction mechanism, yielding a more complete kinetic model for the reaction. A proper description of the HCl solubility as a function of partial pressure and reaction temperature was also presented for semi-batch experiments.

Indeed, the vast majority of papers concerning glycerol hydrochlorination are focused on batch and semi-batch kinetic studies and catalyst screening (Bell et al., 2008; Santacesaria et al., 2010, 2013; Dmitriev and Zanaveskin, 2011; Lee et al., 2008; Vitiello et al., 2014, 2016). However, in industrial scale, continuous reactor technology is often preferred over batch/semi-batch operation due to its higher throughput capacity, lower operating costs, stable operation and easy to control (Walas, 1990). Interestingly, only few sources have focused on the use of continuous technology for performing glycerol hydrochlorination. Luo et al. (2009) have studied the performance of a reactive distillation apparatus for the glycerol hydrochlorination, investigating the process design aspects based on steady-state analysis.

The present paper intends to study the performance of the homogeneously catalysed glycerol hydrochlorination in a continuous co-current bubble column reactor. A classic bubble column was selected due to the simplicity of its construction, which allows a high liquid content and high interphase mass transfer rates (Salmi et al., 2011). A wide range of experimental conditions were investigated, including different temperatures (70, 80, 90, 105 and
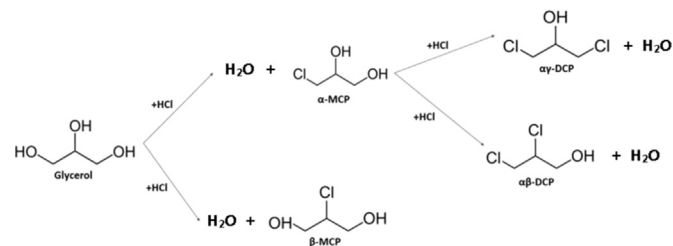

Fig. 1. Overview of the glycerol hydrochlorination process: reactants and products.