Chemical Engineering Journal 258 (2014) 229–239

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Sorption enhanced reactive process for the synthesis of glycerol ethyl acetal

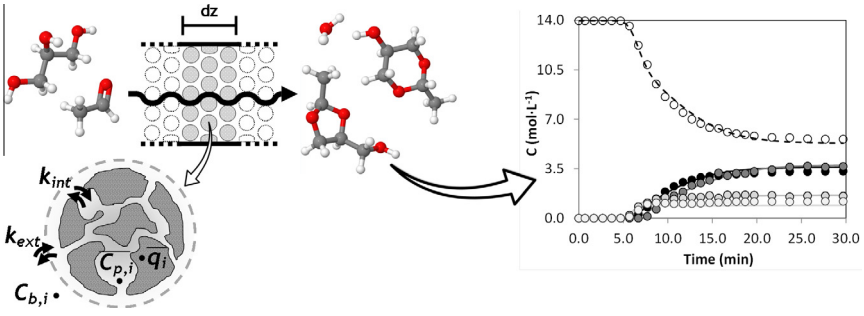
Rui P.V. Faria, Carla S.M. Pereira *, Viviana M.T.M. Silva, José M. Loureiro, Alírio E. Rodrigues

Laboratory of Separation and Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering of University of Porto, 4200-465 Porto, Portugal

HIGHLIGHTS

- Experimental adsorption equilibrium data fitted by a competitive Langmuir model.
- Glycerol acetal produced in a fixed bed adsorptive reactor packed with Amberlyst-15.
- Dynamics of the fixed bed adsorptive reactor described by a mathematical model.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 March 2014
Received in revised form 3 July 2014
Accepted 17 July 2014
Available online 27 July 2014

Keywords:
Glycerol valorisation
Glycerol acetal
Amberlyst-15
Acetalization
Adsorption
Chromatographic reactor

ABSTRACT

The synthesis of glycerol ethyl acetal via acetalisation of glycerol with acetaldehyde, using dimethyl sulfoxide as solvent, in a fixed bed adsorptive reactor packed with Amberlyst-15 wet, operated isothermally at 303 K, was investigated. The study comprised the determination of fundamental adsorption equilibrium data, performing several breakthrough experiments with non-reactive pairs of the species involved in the synthesis of the acetal and fitting the results by Langmuir competitive isotherms. The response of the fixed bed to reactive mixtures was also analysed demonstrating that a conversion of approximately 79% could be achieved at the steady state when an equimolar mixture of acetaldehyde, glycerol and dimethyl sulfoxide was fed to the reactor at 5.0 mL min^{-1}. Additionally, considering the adsorption data gathered, and accounting for the reaction kinetics, the effects of the dispersive plug flow, the velocity variations due to the changes of the bulk composition and the internal and external mass transfer mechanisms, it was possible to develop a mathematical model that could effectively describe the dynamic behaviour of a fixed bed adsorptive reactor applied to the synthesis of glycerol ethyl acetal.

1. Introduction

Chromatography is one of the most important and powerful techniques for continuous separation of complex multicomponent mixtures, finding successful applications in pharmaceutical, food and petrochemical industries. Chromatographic separation occurs as a consequence of the different affinities of the chemical compounds present in a fluid mobile phase towards a solid stationary phase. As a mixture is fed to a chromatographic column, the components with stronger interactions with the adsorbent will be more retained than the components with weaker interactions, originating concentration band profiles that travel at different velocities along the column. This allows collecting purified fractions of the target compounds in the outlet stream. The virtually

Abbreviations: DMSO, dimethyl sulfoxide; GEA, glycerol ethyl acetal; gPROMS, general process modelling system; LHHW, Langmuir–Hinshelwood–Hougen–Watson; UV–VIS, ultraviolet–visible.

* Corresponding author. Tel.: +351 22 508 1686; fax: +351 22 508 1674.
E-mail address: cpereir@fe.up.pt (C.S.M. Pereira).

http://dx.doi.org/10.1016/j.cej.2014.07.073
1385-8947/

Nomenclature

$C_{0,i}$	molar concentration of compound i in the bulk phase at the beginning of a breakthrough experiment mol L^{-1}
$C_{b,i}$	molar concentration of compound i in the bulk phase mol L^{-1}
$C_{in,i}$	molar concentration of compound i fed to the fixed bed reactor during a breakthrough experiment mol L^{-1}
$C_{p,i}$	molar concentration of compound i in the intraparticle fluid mol L^{-1}
$\overline{C_{p,i}}$	average molar concentration of compound i in the intraparticle fluid mol L^{-1}
$C_{out,i}$	molar concentration of compound i at the fixed bed reactor outlet during a breakthrough experiment mol L^{-1}
D_{ax}	axial dispersion coefficient cm^2 min^{-1}
$D_{eff,i}$	compound i effective diffusion coefficient cm^2 min^{-1}
$D_{i,mix}$	diffusion coefficient of compound i in a mixture cm^2 min^{-1}
d_p	particle diameter μm
$E(t)$	residence time distribution min^{-1}
E_a	reaction activation energy kJ mol^{-1}
k_{c_0}	arrhenius pre-exponential factor dm^6 mol^{-1} g_{Cat}^{-1} s^{-1}
K_{eq}	thermodynamic equilibrium constant-
$k_{ext,i}$	external mass transfer coefficient for compound i cm min^{-1}
$k_{int,i}$	internal mass transfer coefficient for compound i cm min^{-1}
K_i	equilibrium constant for the Langmuir adsorption isotherm of compound i L mol^{-1}
$k_{LDF,i}$	global mass transfer coefficient for compound i cm min^{-1}
$K_{s,D}$	DMSO adsorption constants (reaction rate law) L mol^{-1}
$K_{s,W}$	water adsorption constants (reaction rate law) L mol^{-1}
L	fixed bed length cm
$n_{ads/des,i}$	molar amount of compound i adsorbed/desorbed during a breakthrough experiment mol
NC	number of compounds –
NE	number of breakthrough experiments performed –
NP	number of concentration data points for a breakthrough experiment –
Pe	Peclet number –
q_i	adsorbed molar concentration of compound i mol L_{Ads}^{-1}
$\overline{q_i}$	average adsorbed molar concentration of compound i mol L_{Ads}^{-1}
Q	volumetric flowrate mL min^{-1}
$Q_{max,i}$	maximum monolayer capacity for the Langmuir adsorption isotherm of compound i mol L_{Ads}^{-1}
$\Re$	reaction rate based on the local intraparticle composition mol g_{Cat}^{-1} min^{-1}
R^2_{Correl}	correlation factor –
Re_p	reynolds number at the particle conditions –
Sc	Schmidt number –
Sh_p	sherwood number at the particle conditions-
t	time min
T	temperature K
$\overline{t_r}$	mean residence time min
u	interstitial velocity cm min^{-1}
V_{FB}	fixed bed column volume cm^3
$V_{M,i}$	molar volume of compound i cm^3 mol^{-1}
z	fixed bed reactor axial coordinate cm
α_i	adsorption/desorption coefficient-
ε_b	bulk porosity –
ε_p	catalyst particle porosity –
η	effectiveness factor –
μ	fluid phase viscosity cP
v_i	compound i stoichiometric coefficient –
ρ	fluid phase density g cm^{-3}
ρ_b	bulk density g cm^3
σ^2	residence time distribution variance min^2
τ	reactor space time min

unlimited combinations of mobile and stationary phases, together with simple configuration, operation and scale-up procedures endow this technology with a tremendous versatility which constitutes one of its major advantages [1]. The limitations in terms of productivity and the large eluent consumption associated with standard single column chromatographic processes have been overcome through the development of alternative operation modes [2] and multicolumn units [3].

The fixed bed adsorptive reactor was designed according to the innovative concepts behind process intensification, combining chromatographic separation with chemical reaction. As reaction proceeds, the synthesised products are continuously separated from each other and from the reactants due to the differences in their sorption properties. Thereby, it is possible to increase the conversion by displacing the thermodynamic equilibrium, enhancing the global process yield and target species purity. The performance of a chromatographic reactor is the result of the contribution of a complex series of physical–chemical phenomena. Generally, it comprises the forced convection of a fluid through a packed bed, which can be affected by axial and/or radial dispersion effects, the mass transfer from the mobile phase to the stationary phase and the internal diffusion of the species to the catalyst or adsorbent active sites where reaction and/or adsorption occur. In order to understand the fixed bed reactor behaviour and to predict its internal concentration profiles and breakthrough curves, numerous mathematical models [4–8] and numerical methods [9] have been developed.

Common applications of this sorption enhanced reactive process include esterifications [10–13], ester hydrolysis [14,15], etherifications [16] and acetalisations [17–20]. In most of the aforementioned works, advantage is taken from the sorption and catalytic properties of ion exchange resins. This dual behaviour presented by this type of materials, especially by Amberlyst-15, has demonstrated to be particularly effective, even for more complex chromatographic reactors as the simulated moving bed reactor [21–28]. Such ion exchange resins are constituted by cross-linked styrene divinylbenzene copolymers functionalized with acid sulfonic groups. The polymeric matrix is responsible for its bidisperse pore size distribution, with micro and macropores, while its diffusion and adsorption properties result, mainly, from the interactions developed between the acid active sites and the chemical compounds [29–31].

Similar performances to those reported in the open literature for other organic synthesis are expected to be achieved applying the fixed bed adsorptive reactor to the production of glycerol ethyl acetal (GEA) using Amberlyst-15 wet as catalyst/adsorbent. This cyclic acetal has shown interesting results when applied as a green fuel additive [32–34] and, at the same time, represents a sustainable alternative for the valorisation of the excess glycerol, obtained as a byproduct of the increasing biodiesel production [35]. The acetalization of glycerol with acetaldehyde is the most common pathway for the synthesis of GEA, obtained as an isomeric mixture containing cis-5-hydroxy-2-methyl-1,3-dioxane, trans-5-hydroxy-2-methyl-1,3-dioxane, cis-4-hydroxymethyl-2- methyl-1,