



Study of the selective hydrogenation of 1,3-butadiene in three types of industrial reactors



Douglas Pérez, Claudio Olivera-Fuentes, Susana Curbelo, Mirléth J. Rodríguez, Susana Zeppieri*

Departamento de Termodinámica y Fenómenos de Transferencia, Universidad Simón Bolívar, Caracas 1080, Venezuela

HIGHLIGHTS

- The solubility of hydrogen in the liquid is increased, when a solvent is employed.
- Higher values of yield and selectivity for 1-butene were obtained for SBC reactor for the feed 1.
- Transfer resistance of gas–liquid mass is important to the FB reactor inlet and decreases along the same.
- Minor variations in the inlet temperature cause important changes in the selectivity of 1-butene.
- Selectivity increases in the slurry reactors, when the Rsc ratio increases.

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ABSTRACT

A computational study of the selective hydrogenation of 1,3-butadiene in liquid phase is performed, using toluene as solvent and a Pd/Al₂O₃ catalyst, in three different types of industrial reactors: continuous stirred slurry, slurry bubble column and fixed bed. Simulations are run for specific operating conditions that include 380 bbl/d hydrocarbon feed entering at 300 K and 1200 kPa, with 1:1 hydrogen/butadiene and 1:2 solvent/hydrocarbon molar feed ratios. Reactor performances are compared in terms of conversion of reactants and selectivity for products for two feed compositions used by previous researchers. The feed stream used by Galiasso et al. (6% butadiene, 36% 1-butene, 58% butane) is found to give better selectivities for 1-butene and higher yields of this compound, and is therefore used to analyze the effects of inlet temperature, pressure and solvent/feed ratio on the behavior of each type of reactor. The results show that an increase of less than 2% in feed temperature increases the selectivities in the fixed bed reactor, but decreases them in the slurry reactors; these changes amount to about 2–8% in all cases. The effects of inlet pressure and solvent/feed ratio on selectivities are found to be negligible.

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1. Introduction

Polymerization of 1,3-butadiene (BD) at high temperatures produces high molecular weight compounds that may contribute to fouling and loss of capacity of petrochemical plant equipment, and to poisoning and deactivation of solid catalysts in chemical reactors. To prevent these troubles, the diolefin is partially hydrogenated to 1-butene (1BE) in a selective process that should minimize product losses by complete hydrogenation to n-butane (BA) or isomerization to cis- and trans-2-butene (c2BE and t2BE, respectively). The desired product is thus 1BE, used e.g. in the petroleum (alkylation processes) and petrochemical (polyethylene production) industries [1]. When carried out in the gas phase, the selective hydrogenation of BD demands high temperatures that result

in catalyst deactivation [2]. This problem can be avoided by carrying out the reaction in the liquid phase, which requires much lower operating temperatures, typically between 303 and 333 K [3,4].

Bressa et al. [3] studied the effect of operational variables such as feed temperature, pressure and composition and hydrogen/hydrocarbon feed ratio on the performance of a fixed-bed three-phase reactor, and found that reactor yield is favored by increases in both inlet hydrogen concentration and reactor operating pressure. Alves et al. [1] found that adding isoprene to the feed stream helped reduce 1BE losses from secondary reactions, and also that the partial pressure of hydrogen had a crucial effect on the selectivity of the process.

Galiasso et al. [5] investigated the importance of mass transfer resistances in the selective hydrogenation of BD over a PdNiCe/SiAl-SS-316 catalyst, using benzene as solvent and taking into account its possible hydrogenation. Their results showed that diffusional control is important only in the reactor inlet region.

* Corresponding author.

E-mail address: zeppieri@usb.ve (S. Zeppieri).

Nomenclature

1BE	1-butene (-)	t2BE	trans 2-butene (-)
A_r	cross section area, m^2	V	reactor volume, m^3
a_p	surface area of catalyst per unit reactor volume, m^2/m^3	w_{max}	maximum concentration of solid in SBC reactor (-)
a_b	ratio of surface area to volume for bubble, m^2/m^3	X	conversion
BA	n-butane (-)	x	liquid phase mole fraction
BD	1,3-butadiene (-)	Z	height of SBC reactor
C	molar concentration, mol/m^3	z	mole fraction
C_p	isobaric heat capacity, $J/(mol K)$		
c2BE	cis 2-butene (-)		
D	diffusivity, m^2/s	<i>Greek symbols</i>	
D_{ef}	effective diffusivity, m^2/s	δ	dimensionless temperature (-)
d_{ps}	particle diameter (also d_p), m	ΔH_{rxn}	heat of reaction, J/mol
E_a	activation energy, J/mol	$\Delta P_{G,L}$	pressure drop for packed bed, kPa/m
F	molar flow rate, mol/s	ΔT	temperature difference ($T - T_0$), K
f	auxiliary variable defined in Eq. (10) (-)	$\Delta T_{s,b}$	temperature difference ($T_s - T_b$), K
G	gas molar flow rate, mol/s	$\Delta T_{pc,s}$	temperature difference ($T_{pc} - T_s$), K
H	enthalpy, J/mol	η	effectiveness factor of catalytic particle (-)
h	convective heat transfer coefficient, $W/(m^2 K)$	λ	dimensionless radial distance (-)
ISO	2-butene isomers (-)	λ_T	thermal conductivity, $W/(m K)$
K_e	chemical equilibrium constant (-)	ρ	density, kg/m^3
k	kinetic rate constant, $mol/(g_{cat} \cdot s)$	ν	stoichiometric coefficient (-)
k_{ad}	adsorption constant (-)	ξ	auxiliary variable defined in Eq. (14) (-)
k_L	vapor-liquid mass transfer coefficient in the liquid phase, m/s	ψ	dimensionless concentration (-)
k_s	solid-liquid mass transfer coefficient in the liquid phase, m/s		
L	liquid molar flow rate, mol/s	<i>Subscripts and superscripts</i>	
l	axial distance (length), m	b	bulk fluid (-)
N	rotational speed of agitation, $1/s$	cat	catalyst (-)
N_{min}	minimum rotational speed of agitation, $1/s$	eq	vapor-liquid equilibrium (-)
P	pressure, kPa	G	gas (-)
Pe	Péclet number	HC	hydrocarbons (-)
Pe'	corrected Péclet number ($Pe' = Pe \cdot (l/d_{ps})$) (-)	i	component i (-)
P_s	hydrostatic pressure, kPa/m	j	component j different from i (-)
Q	rate of heat transfer, W	k	k -th reaction (-)
R	particle radius, m	L	liquid (-)
r	radial distance, m	o	inlet (-)
rxn	rate of reaction, $mol/(g_{cat} \cdot s)$	p	particle (-)
S	selectivity (-)	pc	center of the particle (-)
S_T	surface tension, N/m	s	external surface of the particle (-)
T	temperature, K	T	total or global value considering both liquid and gas phase (-)
		un	unsaturated hydrocarbons (olefins and diolefins) (-)

They identified temperature and benzene/olefin ratio as having the most influence on selectivity.

Rodríguez [6] compared the use of n-hexane, benzene and toluene as solvents, running simulations for an isothermal packed-bed reactor with reaction kinetics taken from the literature [7]. All three solvents were found to promote the solubility of hydrogen in the liquid phase, but toluene and benzene were preferable to n-hexane in terms of selectivity toward 1BE. Pérez et al. [8] extended the study to include energy and momentum balances, modeling an adiabatic, non-isobaric reactor with toluene as solvent at various operating conditions (feed temperature and pressure, hydrogen/butadiene and toluene/feed ratios). Their analysis showed that selectivity toward 1BE improved with increasing feed temperature and toluene/feed ratio. Further extension of this work by Pérez et al. [9] incorporated mass transfer effects and the kinetic model proposed by Bressa et al. [3]. Hot spots were found to arise beyond a certain reactor length leading to complete vaporization of the reacting liquid, but this operational failure could be avoided by limiting the feed temperature and hydrogen/BD ratio. The authors also concluded that 1BE yield increased with increasing solvent/feed ratio and inlet pressure.

All the above mentioned studies [1,3–9] assume that the hydrogenation reaction is carried out in a packed trickle-bed reactor, a type commonly used in industrial applications because of its good performance in terms of liquid distribution, high conversions, ease of design and maintenance, and wide range of reactor sizes and operating temperatures and pressures. However, this type of reactor uses relatively large catalyst particles, with consequently low effectiveness factors, and may exhibit large pressure drops if smaller particles are used. Also, hot spots may develop as a result of liquid maldistribution at low flow rates [10,11]. Other reactor types are available that use smaller catalyst particles, thereby reducing heat and mass transfer resistances, yet avoid high pressure losses by keeping the solid in circulation. Examples of these are the continuous stirred slurry (CSS) and slurry bubble column (SBC) reactors that have also found application in catalytic hydrogenation [12,13]. By comparison with the fixed bed (FB) type, CSS reactors have better temperature control and catalyst effectiveness, lower external mass transfer resistance and pressure drop, but give lower conversion, are more difficult to scale up, and may necessitate costly separation processes for recovery of catalyst fines entrained in the outlet streams [14]. SBC reactors share some

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