



# Heterogeneous reactive extraction for isopropyl alcohol liquid phase synthesis: Microkinetics and equilibria



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## ARTICLE INFO

### Article history:

Received 6 June 2016

Received in revised form

14 July 2016

Accepted 4 August 2016

Available online 5 August 2016

### Keywords:

Microkinetics

Ion exchange resin catalyst

Liquid-liquid-solid system

Olefin hydration

Isopropyl alcohol

Heterogeneous reactive extraction

## ABSTRACT

The reaction kinetics for the liquid phase synthesis of isopropyl alcohol (IPA) from propene (P) and water (W) using a macroporous sulfonic acid ion exchange resin as catalyst were determined experimentally in a multiphase CSTR in the temperature range 398 K to 433 K at 8 MPa. This high pressure is necessary to dissolve propene in the aqueous phase and to ensure a liquid or supercritical state of all components. At typical reaction conditions, the reactants form two immiscible phases; the reaction takes place in the water swollen gel phase of the catalyst microspheres. Due to the large excess of water in the gel phase the compositions in the gel phase, in the macropore fluid, and in the catalyst surrounding aqueous phase are assumed to be identical. For temperatures up to 413 K the reaction kinetics for the used catalyst size are not influenced by mass transfer resistances within the catalyst matrix. Two reactions, the formation of IPA and the condensation reaction of two IPA molecules forming the by-product diisopropyl ether (DIPE), are investigated. The experimental results can be described sufficiently by pseudo-homogeneous rate expressions in aqueous phase activities. For the formation of IPA, the forward reaction is first-order in propene and water while the reverse reaction is first-order in IPA. The activation energy of the forward reaction was determined to 115.3 kJ/mol. The formation of DIPE is second order with respect to the activity of IPA. The reverse reaction is first order with respect to the activities of DIPE and water. The activation energy was determined to 85.6 kJ/mol. Simultaneous chemical and phase equilibria were investigated theoretically using the volume translated Peng-Robinson equation of state (VTPR-EoS) in combination with a  $g^E$ -mixing rule. Parameters of the used  $g^E$ -model were adjusted to experimental liquid-liquid equilibrium (LLE) data.

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## 1. Introduction

Isopropyl alcohol is primarily used as solvent for paints, printing inks, in the production of silicon wafers, as reaction solvent in the manufacture of drugs, and as drying agent in fuels. Some IPA is employed as intermediate for the production of acetone and manufacture of base chemicals for cosmetics and pesticides. It is also used as antiseptic alcohol and as cleaning agent in industrial soldering of electrical circuits (Papa, 2010).

IPA can be produced either by the indirect or by the direct hydration process. In the indirect process sulfuric acid is used to form mono- and dialkyl sulfates which are subsequently

hydrolyzed by water forming the desired secondary alcohol. In the direct hydration process heterogeneous acid catalysts are employed to convert propene directly into IPA. This work focuses on the liquid phase direct hydration catalyzed by strong acidic ion exchange resins.

An example for a liquid phase direct hydration process is given by Brandes et al. (1982), and Neier and Woellner (1972, 1973). In this process propene is directly converted with water using an acidic ion exchange resin as solid catalyst in a co-currently operated trickle bed reactor. The direct hydration can also be applied in gas phase processes using heteropolyacids or supported phosphoric acid as catalyst. A comparison of different industrial reactors for direct ion exchange resin catalyzed hydrations of propene and butenes is provided elsewhere (Pfeuffer et al., 2009).

For many years the major drawback for the application of ion exchange resins was the limited thermal stability. But, nowadays improved resins are available which can be operated at temperatures exceeding 420 K (e.g. Amberlyst 70, Dow Company, 2015).

**Abbreviations:** DIPE, diisopropyl ether; IPA, isopropyl alcohol; LLE, liquid-liquid equilibrium; P, propene; VTPR-EoS, volume translated Peng-Robinson equation of state; W, water

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<http://dx.doi.org/10.1016/j.ces.2016.08.005>

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Nomenclature			
$a$	activity	$X$	conversion
$a$	cohesive energy parameter of the (VT)PR-EoS ( $\text{Pa}(\text{m}^3)^2/\text{mol}^2$ )	$x$	mole fraction
$a_{ij}$	binary interaction parameter of the UNIQUAC model (K)	$z$	compressibility factor
$b$	co-volume parameter of the (VT)PR-EoS ( $\text{m}^3/\text{mol}$ )	$\Delta h_r$	reaction enthalpy (kJ/mol)
$c_p$	heat capacity (J/mol/K)	<i>Greek letters</i>	
$E$	reactor exit stream (mol/s)	$\gamma$	activity coefficient
$E_a$	activation energy (kJ/mol)	$\varepsilon$	extent of reaction (mol)
$F$	reactor feed stream (mol/s)	$\mu$	chemical potential
$f$	fugacity (partial molar) (MPa)	$\nu$	stoichiometric coefficient
$g$	Gibbs free energy (kJ/mol)	$\bar{\varphi}$	fugacity coefficient (partial molar)
$g^E$	excess Gibbs free energy (kJ/mol)	$\omega$	acentric factor
$h$	enthalpy (kJ/mol)	<i>Subscripts</i>	
$K_a$	chemical equilibrium constant	$c$	critical
$k$	reaction rate constant (mmol/eq/s)	$calc$	calculated
$k^\circ$	pre-exponential factor (mmol/eq/s)	$ij$	component
$M$	mass balance error (mol/s)	$obs$	observed
$N^I$	interfacial mass transfer rate (mol/s)	$res$	residual
$n$	number of moles (mol)	$rev$	reversible
$n_c$	number of components	$0$	initial
$P$	pressure (MPa)	$+$	forward reaction
$q$	van der Waals surface parameter of the UNIQUAC model	<i>Superscripts</i>	
$R$	gas constant (J/mol/K)	$\alpha$	fluid phase
$r$	chemical reaction rate (mmol/eq/s)	$0$	standard or reference conditions
$r$	van der Waals volume parameter of the UNIQUAC model	$398$	value at 398 K
$S$	selectivity	'	organic phase
$T$	temperature (K)	"	aqueous phase
$v$	molar volume ( $\text{m}^3/\text{mol}$ )		

Since the work of Petrus et al. (1984), to our knowledge, no kinetic data for these resins was published. The research group studied the rate of propene hydration with propene-saturated aqueous feeds in fixed bed tubular reactors. This approach is hardly comparable with the real system which comprises mass transfer of all components between two immiscible phases. The amount of converted propene is low due to the very limited solubility of propene in water (1.0 mol-%). It is for these reasons why our study was conducted in a multiphase CSTR. The kinetics of the hydration of butenes using acidic ion exchange resins were determined in the same reactor and published in 2011 (Pfeuffer et al., 2011).

The formation of diisopropyl ether as fuel oxygenate (octane enhancer) was investigated by Heese et al. (1999, 2000). They used Amberlyst 15™ as catalyst for their study. As reactants stoichiometric mixtures of P/W and P/IPA were employed. Unfortunately, the authors provide the reader neither with a kinetic model nor tabulated experimental data.

According to Nowlan and Tidwell (1977) the IPA formation reaction follows an electrophilic addition mechanism of second order ( $A_E2$ ). In a first step propene forms a secondary carbenium ion which is transformed to IPA by consecutive addition of water. The formation of the carbenium ion is the rate determining step of the  $A_E2$  mechanism. According to Markownikow's rule only the secondary alcohol IPA is formed from the carbenium ion.

The reactants propene and water are nearly immiscible. Due to the hydrophilic nature of the acidic ion exchange resin only the aqueous phase wets the catalyst. The liquid or liquid-like supercritical state of propene can be maintained by a pressure of 5 MPa

which is slightly above the critical pressure of propene. However, in order to maximize the amount of dissolved reactant propene in the aqueous phase pressures up to 10 MPa are applied. The reaction product IPA is formed in the aqueous pore liquid of the catalyst, and is transferred through the aqueous bulk phase into the organic phase. That means propene is reactant as well as extractant. The simultaneous extraction of IPA from the reacting aqueous phase is a beneficial feature with respect to selectivity, reaction kinetics, and the limitation on equilibrium conversion. This aspect is analyzed by simultaneous phase and chemical equilibrium calculations.

## 2. Material and methods

### 2.1. Reactants and catalyst

Water is purified by ion exchange (conductivity < 5  $\mu\text{S}$ ). Propene 2.5 is supplied by Linde. IPA is of analytical grade, supplied by Fluka ( $\geq 99\%$ ). Diisopropyl ether is supplied by Sasol Solvents Germany having a purity of  $\geq 97\%$ .

Amberlyst DT is used as catalyst; it is similar to Amberlyst 70. The ion exchange resin passes through a special pretreatment procedure by the industrial operators of the hydration process to reach a higher thermal stability accepting a lower capacity compared to Amberlyst 70. In order to obtain reliable kinetic data not being influenced by catalyst deactivation a catalyst sample from an industrial unit after 130 days time on stream is employed. After

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