Oxygenated Biofuels from Butanol for Diesel Blends: Synthesis of the Acetal 1,1-Dibutoxyethane Catalyzed by Amberlyst-15 Ion-Exchange Resin

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The synthesis of 1,1-dibutoxyethane or acetaldehyde dibutylacetal was studied in a batch reactor by reacting butanol and acetaldehyde in a liquid phase, using Amberlyst-15 as the catalyst. The reaction equilibrium constant was experimentally determined in the temperature range 20–40 °C at 6 atm, where $K_e = 0.00959 \exp[1755.3/T$ (K)].

The standard properties of the reaction at 298.15 K were estimated: $\Delta H^\circ = -14.59$ kJ mol$^{-1}$, $\Delta G^\circ = -3.07$ kJ mol$^{-1}$, and $\Delta S^\circ = -38.64$ J mol$^{-1}$ K$^{-1}$. Kinetic experiments were performed in the temperature range 10–50 °C at 6 atm. A two-parameter kinetic law based on a Langmuir–Hinshelwood rate expression, using activity coefficients from the UNIFAC method, was used. The kinetic parameters are $k_e = 2.39 \times 10^9 \exp[-6200.9/T$ (K)] (mol g$\_\text{cat}$$^{-1}$ min$^{-1}$) and $k_{D,D} = 2.25 \times 10^{-4} \exp[3303.1/T$ (K)].

The activation energy of the reaction is 51.55 kJ mol$^{-1}$. This work is an important step for further implementation of an integrated reaction–separation process, such as a simulated moving-bed reactor.

1. Introduction

In the last years, there has been a growing interest in the development of environmentally friendly gasoline and diesel fuels. Oxygenated additives can be used in order to reduce HC and CO emissions and provide a high octane quality of unleaded gasoline.$^1$ The increase of the oxygen content in diesel fuel reduces significantly the particulate levels; studies showed that the Bosh smoke number (a measure of the particulate or soot levels in diesel exhaust) falls from about 55% for conventional diesel fuel to less than 1% when the oxygen content of the fuel is above about 25% by mass.$^2$ Methyl and ethyl tert-butyl ether (MTBE and ETBE, respectively) are widely used as gasoline additives, providing enhancement of the octane number and a significant reduction of tailpipe pollution. However, these ethers are not suitable as diesel oxygenates because they drastically reduce the cetane number in diesel blends; for example, the ETBE cetane number is 2.5,$^3$ with the minimum value being 51, according to directive 2003/17/EC. Acetals have been under consideration as oxygenated additives to diesel fuel.$^4$ The use of the acetal 1,1-diethoxyethane as a diesel fuel additive has shown a marked reduction of exhaust smoke.$^5$ Moreover, acetals are useful as raw materials for perfumes, agricultural chemicals, and pharmaceuticals;$^6$ they also can be used in the flavoring of food, in the design of synthetic perfumes,$^7,8$ as a mineral oil substitute,$^9$ in the production of poly(vinylc ether)s, and as an intermediate in condensation reactions.$^{10,11}$

Acetals can be produced by the acid-catalyzed addition of 2 mol of monohydric alcohol and 1 mol of aldehyde.$^{12}$ There is a particular interest in the use of ethanol and acetaldehyde as reactants because they are subproducts of the cane sugar industry, and therefore DEE or acetaldehyde diethylacetal can be produced by means of natural resources.$^{13}$ Recently, butanol has been considered as an alternative to ethanol as a biofuel.$^{14}$ Butanol has several advantages over ethanol, such as higher energy content, lower water absorption, better blending ability, and use in conventional combustion engines without modifications. Therefore, butanol is a possible bioderivable reactant to produce the acetal DBE or acetaldehyde dibutylacetal.

The synthesis of acetals is typically carried out under conditions of homogeneous catalysis,$^{15}$ however, the use of strong liquid inorganic acids like H$_2$SO$_4$, HCl, and HI as the catalyst brings some disadvantages, namely, separation problems due to miscibility with a reaction medium and equipment corrosion at a high catalyst concentration.$^{16,17}$ Therefore, heterogeneous catalysts, such as ion-exchange resins and zeolites,$^{18,19}$ become a safer alternative for acetal production. Previous works report the use of heterogeneous catalysts for synthesis of the acetal 1,1-diethoxyethane using Amberlyst-15 and -18,$^{13,20}$ and the acetal 1,1-dimethoxyethane using Amberlyst-15, a Y-type zeolite, and SMOPEX 101 fibres.$^{21,22}$

Amberlyst-15 proved to be an efficient catalyst for acetalization of butanol with heptanal$^{23}$ and formaldehyde;$^{24}$ however, it was verified that side reactions are influenced by the type of ion-exchange resins in the esterification of $n$-butanol with acetic acid at 100–120 °C. The observed side reaction products using Purolite CT 269 (monosulfonated) and Amberlyst-48 (bisulfonated) were isomers of butene, di-$n$-butyl ether, and sec-$n$-butyl-$n$-butyl ether as well as sec-$n$-butanol and sec-$n$-butyl acetate, whereas with Amberlyst-46 (surface-sulfonated), side reactions were almost negligible.$^{25}$

In this work, synthesis of the acetal 1,1-diethoxyethane (DBE) from butanol and acetaldehyde by means of a liquid-phase reaction catalyzed by Amberlyst-15 is studied in order to obtain thermodynamic and kinetic data for further implementation of the integrated reaction–separation processes of fixed-bed reactors and simulated moving bed reactors (SMBRs). Because the reaction is equilibrium-limited, the use of an integrated reaction–separation process, such as a SMBR, allows the displacement of chemical equilibrium toward product formation.$^{20,26}$

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The temperature of the injector was set at 150 °C and the gas used was Helium N50.

To maintain the reacting mixture in the liquid phase over the whole temperature range, the reactor was pressurized with helium. Figure 1 shows a schematic representation of the experimental setup. A dry catalyst is placed in a basket at the top of the reactor, which injects 0.1 mmol of a solution into the reactor. The reactants used were butanol (99.5% pure) (Sigma-Aldrich, Madison, WI) and acetaldehyde (>99.5% pure) (Sigma-Aldrich, Madison, WI).

2.2. Catalyst. The catalyst used was the ion-exchange resin Amberlyst-15 (Rohm and Haas, Philadelphia, PA). The ion-exchange capacity is 4.7 mequiv g\textsuperscript{−1} dry resin, and the surface area is 53 m\textsuperscript{2} g\textsuperscript{−1}.

2.3. Chemicals. The reactants used were butanol (>99.9% pure) and acetaldehyde (>99.5% pure) (Sigma-Aldrich, Madison, WI).

2.4. Analytical Method. The samples were analyzed on a gas chromatograph (Chrompack 9100; Varian, Palo Alto, CA), and the compounds were separated in a fused-silica capillary column (Chrompack CP-Wax 57 CB), 25 m × 0.53 mm i.d., and df = 22.0 μm using a thermal conductivity detector (TCD 903 A) for peak detection. The column temperature was programmed with a 5 min initial hold at 75 °C, followed by a 25 °C min\textsuperscript{−1} ramp up to 100 °C, where it was held for 1.5 min. The temperature of the injector was set at 150 °C. The carrier gas used was Helium N50.

3. Thermodynamic Equilibrium Constant

DBE and water are produced by the acid-catalyzed addition of 2 mol of butanol and 1 mol of acetaldehyde:

2\text{butanol (A)} + \text{acetaldehyde (B)} ⇌ \text{DBE (C)} + \text{water (D)}

The equilibrium constants based on activities\textsuperscript{27} as shown in eq 1 were calculated for different temperatures (in the range of 293.15−323.15 K), at 6 atm, at a stoichiometric initial molar ratio of reactants butanol/acetaldehyde (\(\text{r}_{\text{AB}} = 2.2\)). The total volume of the reactants was 530 mL and the mass of the catalyst 1.8 g. It was ensured that, for these conditions, the amounts of adsorbed species are negligible, and there was only one liquid phase in spite of the fact that water and \(n\)-butanol are only partially miscible; therefore, the equilibrium composition is only related to the thermodynamic reaction equilibrium. Moreover, it was not detected any byproduct. The equilibrium constants were calculated from the experimentally measured equilibrium composition and activity coefficients of the species (\(\gamma_i\)) calculated by the UNIFAC method (Table 1).\textsuperscript{28} The parameters used are presented in Appendix A.

\[
K_a = \frac{a_C a_D}{a_A^2 a_B} = \frac{\gamma_C \gamma_D}{\gamma_A^2 \gamma_B} = K_X K_Y
\]

At equilibrium, the standard free-energy change is related to the equilibrium constant by

\[
\Delta G^\circ = -RT \ln K_a
\]

By definition, the standard free-energy change is related to standard enthalpy and entropy changes by

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

Therefore, temperature dependence of the equilibrium constant is given by

\[
\ln K_a = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \frac{1}{T}
\]

The standard free energy, enthalpy, and entropy changes for this reaction can be estimated by fitting experimental values of \(\ln K_a\) vs 1/\(T\) (Figure 2). From the slope, it is concluded that the reaction is slightly exothermic with \(\Delta H^\circ = -14.593.6\) J mol\textsuperscript{−1}, and from the intercept, \(\Delta S^\circ = -38.6.1\) J mol\textsuperscript{−1} K\textsuperscript{−1} and \(\Delta G^\circ = -3074.6\) J mol\textsuperscript{−1} calculated from eq 3.

4. Kinetic Results

The influence of the external mass-transfer resistance was studied by performing experiments at different stirring speeds. The external mass-transfer resistance is eliminated for a stirring speed above 800 rpm. Therefore, all further experiments were carried out at 800 rpm.
4.1. Effect of the Particle Size. Determination of the concentration of acidic sites of Amberlyst-15 resin for different particle diameters shows that the concentration of acid sites is independent of the particle size; therefore, any difference in reaction kinetics for different particle sizes can only be attributed to the internal mass-transfer resistance. Experiments carried out with different particle sizes of the catalyst show internal diffusion limitations for experiments with particle diameters greater than 0.5 mm (Figure 3). For diameters of particles below 0.5 mm, it is not possible to make conclusions about internal diffusion limitations. Therefore, the kinetic parameters will be estimated by using a detailed model accounting for intraparticle diffusion.

4.2. Mass of the Catalyst Effect. The conversion increases with an increase in the mass of the catalyst (Figure 4) for the same experimental conditions. The maximum reaction rate occurs at the beginning of the reaction, where the slope of the plot conversion versus time is higher. The initial slopes for catalyst masses of 1.8 and 3.0 g are 0.0176 and 0.0296, respectively. The ratio between the catalyst mass is 3.0/1.8 = 1.67, and the ratio between the initial slopes is 0.0296/0.0176 = 1.68. These results show that the initial reaction rate increased in the same proportion as the mass of the catalyst.

4.3. Effect of the Temperature. Experiments performed at different temperatures show that the rate of reaction increases with the temperature; however, the equilibrium conversion of acetaldehyde decreases because of the exothermic nature of the reaction (Figure 5). For batch or fixed-bed reactors, this could be an issue because the conversion decays from about 57% at 20 °C to about 48% at 50 °C. However, from the perspective of process intensification by means of a reactive separation such as the SMBR technology, it is more important to enhance the kinetics of the reaction because equilibrium is displaced by product removal, with complete depletion of the reactants being possible to achieve. At higher temperatures, the mixture viscosity decreases, benefiting also the mass-transfer mechanisms and reducing pressure drops in the bed. Moreover, for multicomponent adsorption equilibria, the effect of the temperature on the selectivity of the resin will play a critical role. For ethyl lactate synthesis, the selectivity of water/ethyl lactate decreases by a factor of 3.5 (from 86.7 to 24.8) when the temperature is increased from 20 to 50 °C.

4.4. Effect of the Initial Molar Ratio of the Reactants. It is known that one way of increasing the conversion is to use an excess of one reactant, in order to shift the equilibrium toward product formation. However, when the catalyst productivity is
analyzed for the same catalyst loading (mass of the resin per volume of reactants), the maximum quantity of DBE is achieved for the stoichiometric ratio of the reactants \( (r_{A/B} = 2) \), as shown in Figure 6. Moreover, the initial molar ratio \( (r_{A/B}) \) does not significantly affect the rate of the reaction; therefore, there is no need to operate at a molar ratio of the reactants far from the stoichiometric one.

5. Batch Reactor Model

As shown in Figure 3 for particle diameters greater than 0.5 mm, the kinetics of the reaction is affected by internal mass-transfer resistances; for smaller diameter particles, it is not possible to conclude about internal mass-transfer resistances. Therefore, an isothermally operated batch reactor model that considers diffusion of the components inside the catalyst particle will be used. In this work, surface diffusion was neglected; however, Dogu et al. showed that although molecular diffusion is the main transport mechanism in macropores, surface diffusion could also have a significant contribution. From our knowledge, this behavior was not reported or noticed for esterification or acetalization reactions. Therefore, surface diffusion was not considered in this work.

Mass balance in the bulk fluid:

\[
\frac{dC_{b,j}}{dt} = - \frac{A_p}{V_{liq}} \frac{\partial C_{p,j}}{\partial r} \bigg|_{r=r_p} \quad (j = A-D) \tag{5}
\]

with

\[
A_p = \frac{3}{r_p} V_p
\tag{6}
\]

where \( C_{b,j} \) is the bulk concentration of component \( j \), \( C_{p,j} \) is the concentration of component \( j \) inside the particle pores, \( A_p \) is the external area between the fluid and particle, \( V_{liq} \) is the volume of liquid inside the reactor, \( D_j \) is the effective diffusivity of component \( j \) inside the particle pores (Appendix B), \( r_p \) is the particle radius, \( V_p \) is the total volume of particles, \( r \) is the particle radial position, and \( t \) is the time coordinate.

Mass balance in the particle:

\[
\varepsilon_p \frac{\partial C_{p,j}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial C_{p,j}}{\partial r} \right] + (1 - \varepsilon_p) v_j \rho_j \mathcal{R} \tag{7}
\]

where \( \varepsilon_p \) is the particle porosity, \( v_j \) is the stoichiometric coefficient of the component \( j \), \( \rho_j \) is the true density of the resin, and \( \mathcal{R} \) is the reaction rate relative to the local concentration (in mol g\(^{-1}\) min\(^{-1}\)).

Initial conditions:

\[
t = 0, \quad C_{b,j} = C_{b0,j}, \quad C_{p,j} = C_{p0,j} \tag{8}
\]

Considering the external mass-transfer resistance as negligible, the boundary conditions are

\[
r = 0, \quad \frac{\partial C_{p,j}}{\partial r} = 0 \tag{9}
\]

\[
r = r_p, \quad C_{b,j} = C_{p,j=r_p} \tag{10}
\]

Upon introduction of the dimensionless space variable \( \rho = r/r_p \), the model equations become

\[
\frac{dC_{b,j}}{dt} = - \frac{3}{r_p^2} \varepsilon_b \frac{1}{\rho} D_j \frac{\partial C_{p,j}}{\partial \rho} \bigg|_{\rho=1} \tag{11}
\]

where \( \varepsilon_b \) is the bulk porosity.

\[
\frac{\partial C_{p,j}}{\partial t} = \frac{D_j}{r_p^2} \frac{1}{\rho^2} \varepsilon_b \left( \frac{\partial^2 C_{p,j}}{\partial \rho^2} \right) + \frac{1 - \varepsilon_b}{\varepsilon_p} v_j \rho_j \mathcal{R} \tag{12}
\]

Boundary conditions:

\[
\rho = 0, \quad \frac{\partial C_{p,j}}{\partial \rho} = 0 \tag{13}
\]

\[
\rho = 1, \quad C_{p,j} = C_{p,j=1} \tag{14}
\]

5.1. Kinetic Model. In this work, the Langmuir–Hinshelwood model equation (15) was considered, following previous experience in our laboratory with diethylacetal and dimethy lacetal synthesis.\(^{1,3,21}\) The reaction rate is

\[
\mathcal{R} = \frac{a_Aa_B - a_Ca_D}{K_{dA}a_A} \left( 1 + K_{sA}a_A + K_{sB}a_B + K_{sC}a_C + K_{sD}a_D + K_{sA}a_A + K_{sC}a_C + K_{sD}a_D \right) \tag{15}
\]

This model is based on adsorption of the reactant species (butanol and acetaldehyde), the reaction between adsorbed reactants on the catalyst surface, and desorption of the reaction products (water and DBE). The surface reaction involves three steps:

Surface reaction between the adsorbed species of butanol (A) and acetaldehyde (B) to give adsorbed hemiacetal, I\(_1\)S:

\[
AS + BS \iff I_1S + S
\]
Table 2. Estimated Model Parameters

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k_c$ (mol g$^{-1}$ min$^{-1}$)</th>
<th>$K_{c,D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>1.5761</td>
<td>16.765</td>
</tr>
<tr>
<td>303.15</td>
<td>3.0424</td>
<td>12.338</td>
</tr>
<tr>
<td>313.15</td>
<td>6.091</td>
<td>8.649</td>
</tr>
</tbody>
</table>

Surface reaction to obtain adsorbed water, DS:

$$I_1S + S \rightleftharpoons I_2S + DS$$

Surface reaction to obtain adsorbed acetal, CS:

$$I_2S + AS \rightleftharpoons CS + S$$

The reaction where water is formed (step 2) was assumed to be the rate-controlling step because formation of the intermediate $I_2$ from the protonated hemiacetal is the rate-determining step for acetalization.32,33 Because of the acidic property of Amberlyst-15, water will be the more adsorbed component; therefore, when the other adsorption constants are neglected, the kinetic model can be reduced to a three-parameter equation (eq 16):

$$\beta = k_c \frac{a_c a_{D}}{K_c a_A} \left(1 + K_{c,D} a_{D}\right)^2$$

6. Numerical Solution

The model equations were solved using the commercial software gPROMS (general PROcess Modeling System), version 3.1.5. The batch reactor model is defined by a set of partial differential equations. The radial domain was discretized using the second-order orthogonal collocation in the finite-element method (OCFEM). The system of ordinary differential equations, resulting from radial discretization, was integrated over time using DASOLV integrator implementation in gPROMS. For radial discretization, 10 finite elements with two collocation points were used in each element. For all simulations, a tolerance equal to $10^{-7}$ was fixed.

6.1. Parameter Estimation. In order to determine the parameters of the reaction rate model proposed, it is necessary to find a combination of these parameters that provide the best fit of the batch reactor model results with experimental measurements.

The parameter estimation was performed in gPROMS software34 providing the best fit of measured and predicted data using the maximum likelihood method.35

The objective function associated with the parameter estimation is described by the following equation:

$$\Phi = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min \left\{ \sum_{i=1}^{N} \sum_{j=1}^{N_V} \sum_{k=1}^{N_M} \left[ \ln(\sigma_{ijk}^2) + \frac{(z_{ijk} - \tilde{z}_{ijk})^2}{\sigma_{ijk}^2} \right] \right\}$$

(17)

where $z_{ijk}$ and $\tilde{z}_{ijk}$ are the measured and predicted data, respectively, $N$ is the total number of measurements taken during the experiments, $\theta$ is the set of parameters to be estimated ($k_c$ and $K_{c,D}$), $NE$ is the number of experiments performed, $NV_i$ is the number of variables measured in the $i$th experiment, $NM_j$ is the number of measurements of the $j$th variable, and $\sigma_{ijk}^2$ is the variance of the $i$th measurement of variable $j$ in experiment $i$.

The results of the parameter estimation for different temperatures are presented in Table 2.

![Figure 7. Representation of the experimental values of $k_c$ and $K_{c,D}$ as a function of $1/T$ and linear fitting.](image)

Table 3. Kinetic Law and Parameters Used in Batch Reactor Model Simulations

<table>
<thead>
<tr>
<th>kinetic law</th>
<th>$\beta = k_c(\sigma_{aD} - \sigma_a g_K a_A)/(1 + K_{c,D} a_{D})^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>equilibrium constant</td>
<td>$K_c = 9.59 \times 10^{-3} \exp[1755.3/(T (K))]$</td>
</tr>
<tr>
<td>kinetic constant</td>
<td>$K_{c,D} = 2.25 \times 10^{-2} \exp[3303.1/(T (K))]$</td>
</tr>
</tbody>
</table>

The predicted values of $k_c$ and $K_{c,D}$ are represented as a function of the temperature in Figure 7. By fitting of the predicted values by eq 18 and eq 19, $E_{c,c} = 51.55$ kJ mol$^{-1}$ and $\Delta H_c = -27.5$ kJ mol$^{-1}$ are obtained.

7. Model Results

The kinetic law and the parameters of the batch reactor model considered in the following simulations are presented in Table 3.

Parts a and b of Figure 8 show the time evolution of the amount (moles) of reactants (butanol and acetaldehyde) and products (acetal DBE and water) at two different temperatures (293.15 and 313.15 K); a comparison between the experimental and simulated results is also presented.

In order to validate the estimation of the mass-transfer parameters, experiments for different particle diameters were performed. Parts a and b of Figure 9 show that the model gives a good prediction of the batch reaction for both experiments and, therefore, the good agreement between the experimental and simulated results leads us to conclude that the model gives a good prediction of the effect of the internal mass-transfer resistance.

By simulation, it is possible to observe the effect of the particle diameter on the internal concentration profile. Figure 10 shows the internal concentration profile of butanol for
three particle diameters. The presence of a concentration gradient between the surface and the center of the catalyst indicates the presence of internal mass-transfer resistances. The internal concentration profile is more abrupt for greater particle diameter, indicating that the internal mass-transfer resistance increases with the particle diameter, as was expected.

In order to evaluate how much the internal mass transfer is controlling the kinetic experiments, it is possible to calculate the catalyst effectiveness factor for each experiment, which is defined by the following expression:

\[ \eta = \frac{\langle R \rangle}{R_s} = 3 \int_0^1 \frac{\rho^2 R}{R_s} d\rho \]

(20)

where \( R_s \) is the reaction rate at surface conditions and \( \langle R \rangle \) is the average reaction rate defined as

\[ \langle R \rangle = \frac{\int_0^r r^2 R \, dr}{\int_0^r r^2 \, dr} = 3 \int_0^1 \rho^2 R \, d\rho \]

(21)

The highest effectiveness factor of about 69% at equilibrium was obtained using a catalyst with an average diameter of 428 µm (Figure 11). For the largest particle diameter of 890 µm, the effectiveness factor is about 42% at equilibrium. From this, it is possible to conclude that all experiments were performed under a diffusion-controlled regime. In order to
operate under a chemical reaction-controlled regime (effectiveness factor of about 1), it would be necessary to use a particle diameter of lower than 175 μm, which is not commercially available, and it is not possible to grind the resin without affecting its catalytic properties.

In Table 4, acetalization reactions of acetaldehyde with methanol, ethanol, and 1-butanol are compared with the terms of equilibrium conversion, reaction half-life, effectiveness factors, and activation energy. These results show that both the equilibrium conversion and reaction rate decrease with an increase in the chain length of the alcohol.

### 8. Conclusions

The DBE synthesis in a liquid-phase reaction catalyzed by Amberlyst-15 was studied in a laboratory-scale batch reactor. The thermodynamic equilibrium constant was calculated based on the equilibrium compositions in the temperature range of 293.15–323.15 K and is given by the expression $K_a = 0.00959 \exp[1755.3/T (K)]$. The reaction is exothermic, and the standard properties of the reaction at 298.15 K are $\Delta H^o = -14593.6$ J mol$^{-1}$, $\Delta S^o = -38.6$ J mol$^{-1}$ K$^{-1}$, and $\Delta G^o = -3074.1$ J mol$^{-1}$.

Kinetic experiments showed that the rate of reaction increases with the temperature; however, the equilibrium conversion decreases with the temperature because of the exothermic nature of the reaction. Experiments performed at different particle diameters showed the existence of internal mass-transfer resistances for particle diameters greater than 0.5 mm.

Because of the strong nonideality of the liquid reaction mixture, both the equilibrium constant and kinetic law were expressed in terms of activities. The activation energy of 51.55 kJ mol$^{-1}$ was calculated by fitting the estimated kinetic parameters at different temperatures to the Arrhenius equation.

A comparison between the experimental and simulated results shows that the model gives a good representation of the batch reactor performance for different temperatures and particle diameters of the catalyst. The simulated results of the catalyst internal concentration profiles showed a concentration gradient between the surface and the center of catalyst because of the presence of internal mass-transfer resistances. The time evolution of the effectiveness factor, for different particle diameters, shows that the controlling mechanism is the internal diffusion.

This work is an important step for further implementation of an integrated reaction–separation process, such as a SMBR, in order to enhance the conversion of the reaction limited by chemical equilibrium.

### Acknowledgment


### Appendix A. UNIFAC Method Parameters

Tables A1 and A2 present the UNIFAC method parameters used in this work to calculate the activity coefficients ($\gamma_i$).
The viscosity of the liquid mixture was calculated by the

\[ \tau \Delta E DCi \]

where \( \tau \) is the tortuosity of an ion-exchange resin. The coefficients \( D_{j,m} \) were estimated in a way similar to that performed to the system of ethyl lactate synthesis; once one reactant (lactic acid solution) has a high viscosity, similarly to this case, where butanol is very viscous also. Different values of \( \tau \) such as 1.3, 2, and 4.9 were reported in the literature for calculation of the effective diffusivity in Amberlyst-15. Estimations of the tortuosity were made using the correlations given by Wakao and Smith \( ^{42} \) \( \tau = \epsilon_0 + 1.5(1 - \epsilon_p) \); the values obtained with \( \epsilon_0 \) were 2.78 and 1.32, respectively. In this work, the tortuosity used was 2, i.e., the mean between the estimated values.

The infinite dilution molecular diffusivities were estimated by the Scheibel correlation, which modified the Wilke–Chang equation in order to eliminate its association factor \( ^{44} \)

\[ D_{j}^0 = \frac{8.2 \times 10^{-8}}{\eta_i V_j^{1/3}} \left[ 1 + \left( \frac{3V_i V_j^{2/3}}{V_j} \right)^{2/3} \right] \]  

(23)

where \( D_{j}^0 \) is the diffusion coefficient for a dilute solute \( j \) in a solvent \( i \), \( V_j \) is the molar volume of the component \( j \), and \( \eta_i \) is the viscosity of solvent \( i \). Table A3 presents the liquid molar volume and viscosity for the pure components.

For a concentrated multicomponent system, the Perkins and Geankoplis \( ^{46} \) method was used:

\[ D_{j,m}^0 \eta_m^{0.8} = \sum_{i=1}^{n} \chi_{ij} D_{j,i}^0 \eta_i^{0.8} \]  

(24)

The viscosity of the liquid mixture was calculated by the Grunberg–Nissan approach \( ^{47} \)

\[ \ln(\eta_m) = x_i \ln(\eta_i) + x_j \ln(\eta_j) + x_k G_{1,2} \]  

(25)

where \( G_{1,2} \) is an empirical interaction parameter adjusted by the experimental data. The liquid mixture viscosity and the molar diffusivities are presented in Table A4.

### Appendix C

**Notation**

- \( a \) = liquid-phase activity
- \( A \) = external exchange area between the bulk and the particles
- \( C_i \) = concentration, mol cm\(^{-3}\)
- \( C_b \) = bulk concentration, mol cm\(^{-3}\)
- \( C_p \) = concentration inside the particle, mol min\(^{-3}\)
- \( d_p \) = average particle diameter, mm
- \( D_{i} \) = effective diffusivity, cm\(^2\) min\(^{-1}\)
- \( D_{j,m} \) = molecular diffusivity coefficient of a solute in a mixture, cm\(^2\) min\(^{-1}\)
- \( E_{act} \) = reaction activation energy, kJ mol\(^{-1}\)
- \( \Delta G^0 \) = standard Gibbs free energy, J mol\(^{-1}\)
- \( \Delta H^0 \) = standard enthalpy, J mol\(^{-1}\)
- \( \Delta H_i \) = enthalpy of adsorption, J mol\(^{-1}\)
- \( k_i \) = kinetic constant, mol g\(_{cat}\)^{-1} min\(^{-1}\)
- \( k_{oa} \) = Arrhenius constant for eq 19, mol g\(_{cat}\)^{-1} min\(^{-1}\)
- \( K_e \) = equilibrium constant based on activities
- \( K_{eq} \) = equilibrium constant based on the molar fraction
- \( K_s \) = equilibrium constant based on activity coefficients
- \( k_{p} \) = equilibrium adsorption constant
- \( n \) = number of moles, mol
- \( P \) = pressure, atm
- \( R \) = gas constant, J mol\(^{-1}\) K\(^{-1}\)
- \( r \) = radial position, cm
- \( r_{p} \) = particle radius, mm
- \( r_{AB} \) = initial molar ratio of the reactants
- \( \Delta S^0 \) = reaction rate, mol g\(_{cat}\)^{-1} min\(^{-1}\)
- \( \Delta \) = reaction at surface conditions, mol g\(_{cat}\)^{-1} min\(^{-1}\)
- \( \langle \Delta \rangle \) = average reaction rate, mol g\(_{cat}\)^{-1} min\(^{-1}\)
- \( r_{p} \) = reaction relative to the local pore concentration, mol g\(_{cat}\)^{-1} min\(^{-1}\)
- \( r \) = time coordinate, min
- \( T \) = temperature, K
- \( x \) = molar fraction
- \( X \) = conversion of the limiting reactant
- \( V \) = volume of the solution, cm\(^3\)
- \( V_{liq} \) = total volume of the reactant mixture, cm\(^3\)
- \( V_p \) = total volume of the particles, cm\(^3\)
- \( w_{cat} \) = mass of the dry catalyst, g

**Greek Letters**

- \( \gamma \) = activity coefficient
- \( \epsilon_0 \) = bulk porosity
- \( \epsilon_p \) = particle porosity
- \( \eta \) = effectiveness factor
- \( \rho \) = dimensionless radial coordinate
- \( \rho_0 \) = particle density, g cm\(^{-3}\)
- \( v \) = stoichiometric coefficient
- \( \tau_p \) = tortuosity factor

**Subscripts**

- \( A \) = butanol
- \( B \) = acetaldehyde
- \( C \) = DBE
- \( D \) = water
- \( i \) = relative to component \( i \)
- \( liq \) = liquid phase
- \( p \) = relative to the particle
- \( s \) = relative to the surface of the particle

### Literature Cited

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