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Separating 2,3-butanediol from fermentation broth using n-butylaldehyde

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Kinetic;
Reactive-extraction;
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Abstract In this paper, a complete separation process for 2,3-butanediol fermentation broth has been developed using reactive-extraction and reactive-distillation. n-Butylaldehyde can be used as both reactant and extractant in the process. Equilibrium and kinetics were studied on the reaction between 2,3-butanediol and n-butylaldehyde using different catalysts. Pseudo-Homogeneous model was used to describe the reaction behavior. The kinetic parameters were determined by analyzing experimental data. The results revealed that the reaction enthalpy $\Delta H^0 = -21.58 \pm 1.63$ kJ mol$^{-1}$. The reaction rate was found to increase with increasing reaction temperature and had a linear correlation with catalyst amount. The activity energy for H$_2$SO$_4$ system and HCl system was 57.52 ± 5.35 and 58.14 ± 5.06 kJ mol$^{-1}$, respectively. Feasible operation conditions have been obtained as follows: volume ratio of n-butylaldehyde to fermentation broth is 0.2; feed molar ratio of water and 2-propyl-4,5-dimethyl-1,3-dioxolane (n-butylaldehyde 2,3-butanediol acetal) for hydrolysis is 3.0; theoretical plate number for reactive-distillation column is 10 with concentration of HCl solution of 0.5 mol/L. With the above conditions, more than 90% of 2,3-butanediol can be recovered from fermentation broth by reactive-extraction process and the purity of final product can be over 99%.

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1. Introduction

Bio-based 2,3-butanediol (2,3-BD) is a renewable resource (Ji et al., 2011; Palsson et al., 1981; Syu, 2010) that can be applied in many fields. It can be used as a potential liquid fuel as its heating value is 27.19 kJ/g (Flickinger, 1980; Jansen et al., 1984; Yu and Levitin, 1982). Biological route of producing 2,3-BD has made a great progress in the past decades (Klebsiella et al., 1998; Garg and Jain, 1995), which makes it possible to produce 2,3-BD from fermentation broth. However, recovery of 2,3-BD from fermentation broth is an
expensive process for the special properties of fermentation broth, which limits the industrial application of bio-based 2,3-BD.

Separating 2,3-BD directly by distillation costs a large amount of energy for the low concentration of 2,3-BD in fermentation broth. So several separation processes for recovery of 2,3-BD from fermentation broth have been reported. Liquid-liquid extraction (Shao and Kumar, 2009) using n-butanol as extractant can separate 2,3-BD from fermentation broth with less energy but requires a large amount of solution. Aqueous two-phase extraction (Li et al., 2010) has its advantage in low energy and solution consuming, but it requires a large amount of salts in the process.

Reactive-extraction (Xiang et al., 2001) is one of the most effective ways to separate special material from complicated system by improving its solubility in the organic phase via reaction. In former report (Xiu and Zeng, 2008; Hao et al., 2006), reactive-extraction was used in 1,3-propanediol separation, which had mentioned 2,3-BD as a byproduct can also be separated in the method. The hydroxyl groups help 2,3-BD owning high hydrophilicity, but they can also help 2,3-BD react with aldehyde to form corresponding acetal. So Xiu (Hao et al., 2005) considered reactive-extraction using n-butylaldehyde (BA) as both reactant and extractant can be used to develop a complete 2,3-BD separation process.

In this paper, a separation process containing reactive-extraction and reactive-distillation has been developed to separate and concentrate 2,3-BD from fermentation broth. BA has been used in the process as both reactant and extractant. 2,3-BD can be effectively separated from fermentation broth in the form of 2-propyl-4,5-dimethyl-1,3-dioxolane (PDD) (Fig. 1) by reactive-extraction, and then PDD turned back to 2,3-BD, which was concentrated at the same time, by reactive-distillation. Furthermore, intrinsic reaction kinetics of 2,3-BD and BA was investigated in this paper to provide basic data for process development. The group additivity method was used to compare with experimental data.

2. Materials and methods

2.1. Materials

All the chemicals were purchased from commercial source in the study. 2,3-Butanediol (2,3-BD) was bought from the Sinopharm Chemical Reagent Co. Ltd. with a minimum mass fraction purity of 98.2%. n-Butylaldehyde (BA) was purchased from the Sinopharm Chemical Reagent Co. Ltd. with a minimum mass fraction purity of 98.5%. 2-Propyl-4,5-dimethyl-1,3-dioxolane (PDD) was provided by Chemical Engineering Research Center of East China University of Science and Technology with a minimum mass fraction purity of 98.3%. All these chemicals were measured and assured by the gas chromatography. Sulfuric acid (H₂SO₄) was provided by the Sinopharm Chemical Reagent Co. Ltd. with a mass fraction of 95–98%. Hydrochloric acid (HCl) was provided by the Sinopharm Chemical Reagent Co., Ltd. with a minimum mass fraction of 36%. Water was distilled twice before utilization. Fermentation broth was provided by the National Key Lab of Bioreactor Engineering in East China University of Science and Technology.

3. Methods

3.1. Equilibrium

The reaction between BA and 2,3-BD is reversible. The reaction equilibrium \( K \) is used to describe the reaction limit of reaction, which can be calculated by Eq. (1) (Fredenslund et al., 1975).

\[
\begin{align*}
&\text{BA} + \text{(2,3-BD)} \rightleftharpoons \text{PDD} + \text{H₂O} \\
&\text{RT}_{eq} \quad \text{time to reaction equilibrium} \\
&\text{STR} \quad \text{stirring rate} \\
&\text{W} \quad \text{water}
\end{align*}
\]

Figure 1 Reaction equation of 2,3-butanediol and n-butylaldehyde.
\[ K = \frac{[W_{\text{eq}}][PDD_{\text{eq}}]}{[BA_{\text{eq}}][BD_{\text{eq}}]} \tag{1} \]

And the reaction enthalpy \( \Delta H^0 \) can be calculated by Van’t Hoff equation (Zheng et al., 2010),

\[ \frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2} \tag{2} \]

The least square inversion method was used to analyze the experimental data.

### 3.2. Kinetic study

Kinetic study was conducted in a beaker with a water jacket connected to a thermostat using simulated broth. As owning two reactants, the reaction was assumed as a second order reaction (Zheng et al., 2010). For there were two phases in the reaction system, the reaction rate equations can be presented as follows (Eqs. (3)–(5)):

\[ r_{\text{BDor}} = -\frac{dC_{\text{BDor}}}{dt} = f_{\text{or}}(C_{\text{cat}}) \times (k_{\text{-or}} C_{\text{BAor}} \times C_{\text{BDor}} - k_{\text{-or}} C_{\text{PDDor}} \times C_{\text{Wor}}) \tag{3} \]

\[ r_{\text{BDaq}} = -\frac{dC_{\text{BDaq}}}{dt} = f_{\text{aq}}(C_{\text{cat}}) \times (k_{\text{-aq}} C_{\text{BAaq}} \times C_{\text{BDaq}} - k_{\text{-aq}} C_{\text{PDDaq}} \times C_{\text{Waq}}) \tag{4} \]

\[ r_{\text{BDsys}} = r_{\text{BDor}} + r_{\text{BDaq}} = -\frac{dC_{\text{BDsys}}}{dt} = -\frac{dC_{\text{BDor}}}{dt} - \frac{dC_{\text{BDaq}}}{dt} = f_{\text{or}}(C_{\text{cat}}) \times (k_{\text{-or}} C_{\text{BAor}} \times C_{\text{BDor}} - k_{\text{-or}} C_{\text{PDDor}} \times C_{\text{Wor}}) + f_{\text{aq}}(C_{\text{cat}}) \times (k_{\text{-aq}} C_{\text{BAaq}} \times C_{\text{BDaq}} - k_{\text{-aq}} C_{\text{PDDaq}} \times C_{\text{Waq}}) \tag{5} \]

In a uniform distributed reaction system, the organic phase and aqueous phase were evenly distributed in microspheres. The system can be considered as a pseudo-homogeneous system. In that case, pseudo-homogeneous model (Zheng et al., 2010) can be used to describe the reaction behavior, which was presented as follows (Eq. (6)):

\[ r_{\text{BDsys}} = -\frac{dC_{\text{BDsys}}}{dt} = f_{\text{sys}}(C_{\text{cat}}) \times (k_{\text{sys}} C_{\text{BAsys}} \times C_{\text{BDsys}} - k_{\text{sys}} C_{\text{PDDsys}} \times C_{\text{Wsys}}) \tag{6} \]

As

\[ K = \frac{[W_{\text{eq}}][PDD_{\text{eq}}]}{[BD_{\text{eq}}][BA_{\text{eq}}]} = \frac{k_{\text{sys}}}{k_{\text{sys}}} \frac{C_{\text{sys}}}{C_{\text{sys}}} \]

Eq. (6) can be shown as:

\[ r_{\text{BDsys}} = -\frac{dC_{\text{BDsys}}}{dt} = f_{\text{sys}}(C_{\text{cat}}) \times k_{\text{sys}} \times (C_{\text{BAsys}} \times C_{\text{BDsys}} - \frac{1}{K} C_{\text{PDDsys}} \times C_{\text{Wsys}}) \tag{7} \]

And activation energy of reaction can be calculated by Arrhenius equation (Zheng et al., 2010) (Eq. (9))

\[ \frac{d\ln k}{dT} = \frac{E_a}{RT^2} \tag{9} \]

Model parameters can be obtained by fitting experimental data.

### 3.3. Separation process

The separation process is shown in Fig. 2. Fermentation broth was pretreated to remove cells and proteins before the separation process. In the reactive-extraction unit, BA reacted with 2,3-BD to form PDD which was extracted into the organic phase in sequence, the aqueous phase was removed from the system; in the reactive-distillation column, acid solution was added into the distillation column, PDD hydrolyzed became 2,3-BD and BA again, BA was collected at the top of the column and reused in the reactive-extraction and 2,3-BD was concentrated at the bottom of the column. Unreacted PDD in the hydrolysis part went with BA from the top of the distillation column and back to the reactive-extraction unit.

Extraction rate of 2,3-BD (ERBD), hydrolysis rate of PDD (HRPDD), recovery rate of 2,3-BD (RBD) and loss of BA (LBA) were used to measure the process, which can be calculated by Eqs. (10)–(13):

\[ \text{ERBD} = \frac{r_{\text{BDor}}}{n_{\text{BDor}} + n_{\text{BDaq}}} \times 100\% \tag{10} \]

\[ \text{HRPDD} = \frac{n_{\text{PDDextraction}} - n_{\text{PDDbottom}}}{n_{\text{PDDextraction}}} \times 100\% \tag{11} \]

\[ \text{RBD} = \frac{n_{\text{BDbottom}}}{n_{\text{BDtotal}}} \times 100\% \tag{12} \]

\[ \text{LBA} = \frac{n_{\text{BAadded}}}{n_{\text{BAadded}}} \times 100\% \tag{13} \]

### 3.4. Analysis

The concentrations of 2,3-BD, PDD and BA were analyzed by GC FULLI GC9790I, FID-detector, PEG-20M 50 m × 0.32 mm × 0.5 μm capillary column and operated with N_2 as the carrier gas at a flow rate of 50 mL min^{-1}, detector temperature at 200 °C and column temperature at 140 °C.

### 4. Results and discussion

#### 4.1. Reaction equilibrium

Regression result (Fig. 3) reveals that the reaction enthalpy is \( \Delta H^0 = -21.58 \pm 1.63 \text{ kJ mol}^{-1} \), which indicates that PDD formation is an exothermic reaction. Increasing reaction temperature will benefit the counter reaction and decrease the conversion rate of 2,3-BD.

\[ \Delta H^0_{298} = \sum_i g_i \Delta H^0_i \tag{14} \]

The definition of the reaction enthalpy (Xie et al., 2009) \( \Delta H^0 \) (Eq. (14)) can be used to measure the reliability of the experimental results. In this paper, the group additivity method is used to predict the standard mole enthalpy of the chemicals’ formation which cannot be got from the literature. The calculated result shows that the reaction enthalpy of the reaction \( \Delta H^0 = -28.64 \text{ kJ mol}^{-1} \). The regression result and calculated result of the reaction enthalpy are on the same order of magnitude. It illustrates that the experimental results are reliable and the UNIFAC method can be used to assess the process. The reaction equilibrium can be presented as follows:

\[ K = 2.307 \times \exp \left( \frac{2596.176}{T} \right) \tag{15} \]
5. Kinetic study

5.1. Effect of diffusion on reaction

The results (Fig. 4) reveal diffusion has an effect on the reaction, but it can be removed by increasing the stirring rate (STR). The curve under 0 rpm is the slowest in the graph and has a big difference with others. It indicated that diffusion can control the reaction rate with no agitation. If there is agitation in the system, the diffusion can be weakened, even if the stirring rate is only 90 rpm. When the stirring rate reaches 500 rpm, the diffusion impact disappears. According to the above, intrinsic kinetic experiments should be carried out with STR over 500 rpm.
5.2. Kinetic study of sulfuric acid system

When H$_2$SO$_4$ was chosen as catalyst (Fig. 5), increasing the H$_2$SO$_4$ concentration, the reaction rate will be accelerated. When the H$_2$SO$_4$ concentration is 0.05 mol/L, it takes more than 30 min to reach the reaction equilibrium. Time to reaction equilibrium (RT$_{eq}$) for 0.2 and 0.5 mol/L is 15 and 10 min, respectively. And when the catalyst amount is 1 mol/L, the RT$_{eq}$ is less than 1 min. Regression results of the data in Fig. 4 reveal that reaction rate has a linear correlation with H$_2$SO$_4$ concentration and the square of linear correlation coefficient $R^2$ is over 0.998. That means the experimental results are reliable. And the reaction rate increases linearly with increasing catalyst amount in this system.

The results of reaction rate constant under different temperatures are listed in Table 1. The results reveal that increasing reaction temperature will accelerate the reaction rate for both positive reaction and counter reaction. Using the data in Table 1, the activity energy of the positive reaction and counter reaction is 57.52 ± 5.35 kJ mol$^{-1}$ ($R^2 = 0.974$) and 77.66 ± 5.20 kJ mol$^{-1}$ ($R^2 = 0.987$), respectively. It indicates that the positive reaction is easier to occur than the counter one. The reaction rate can be presented as

\[
r_{BDsys} = -\frac{dC_{BDsys}}{dt} = 1.735 \times 10^{10} \exp\left(-\frac{5113}{T}\right) C_{H2SO4sys} \left( C_{BAsys} C_{BDsys} - \frac{1}{K} C_{PDDsys} C_{Wsys} \right)
\] (16)

5.3. Kinetic study of hydrochloric acid system

The results (Fig. 6) reveal that HCl can be used as catalyst. Reaction rate increases with the increasing of catalyst amount in the system. When $C_{HCl} = 0.01$ mol/L, the reaction rate is slow, only 50% of 2,3-BD will react in 60 min. When $C_{HCl} = 0.1$ mol/L and $C_{HCl} = 0.2$ mol/L, their RT$_{eq}$s are almost the same at 60 min. Increasing $C_{HCl}$ to 0.5 mol/L, reaction rate will accelerate, and for RT$_{eq}$ it is 15 min. When $C_{HCl} = 1$ mol/L, it only takes 2 min to reach reaction equilibrium. Using the data in Fig. 5, it can be conducted that reaction rate has a linear correlation with HCl concentration and the square of linear correlation coefficient $R^2$ is over 0.993.

The results of reaction rate constant under different temperatures are listed in Table 2. The results reveal that increasing reaction temperature will accelerate the reaction rate for both positive reaction and counter reaction. Using the data in Table 2, the activity energy of the positive reaction and counter reaction is 58.14 ± 5.06 kJ mol$^{-1}$ ($R^2 = 0.987$) and 79.73 ± 5.20 kJ mol$^{-1}$ ($R^2 = 0.987$), respectively. It indicates that the positive reaction is easier to occur than the counter one. The reaction rate can be presented as

\[
r_{BDsys} = -\frac{dC_{BDsys}}{dt} = 1.099 \times 10^{10} \exp\left(-\frac{6993}{T}\right) C_{HClsys} (C_{BAsys} C_{BDsys} - \frac{1}{K} C_{PDDsys} C_{Wsys}).
\] (17)

![Figure 5](image50x103 to 280x276) Conversion rate of 2,3-butanediol under different concentrations of H$_2$SO$_4$ ($T = 25 \degree C$, $C_{BD} = 1.08$ mol/L, $C_{BA} = 2.23$ mol/L, STR = 500 rpm).

![Figure 6](image307x426 to 537x601) Conversion rate of 2,3-butanediol under different concentrations of HCl ($T = 25 \degree C$, $C_{BD} = 1.13$ mol/L, $C_{BA} = 2.26$ mol/L, STR = 500 rpm).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_1$ (L$^2$ mol$^{-2}$ min$^{-1}$)</th>
<th>$k_2$ (L$^2$ mol$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.234 ± 0.027</td>
<td>(2.869 ± 0.143) $10^{-5}$</td>
</tr>
<tr>
<td>20</td>
<td>0.382 ± 0.053</td>
<td>(6.684 ± 0.278) $10^{-5}$</td>
</tr>
<tr>
<td>30</td>
<td>2.662 ± 0.102</td>
<td>(2.985 ± 0.094) $10^{-4}$</td>
</tr>
<tr>
<td>40</td>
<td>3.712 ± 0.127</td>
<td>(5.368 ± 0.372) $10^{-4}$</td>
</tr>
<tr>
<td>50</td>
<td>9.875 ± 0.469</td>
<td>(1.682 ± 0.067) $10^{-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_1$ (L$^2$ mol$^{-2}$ min$^{-1}$)</th>
<th>$k_2$ (L$^2$ mol$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.124 ± 0.027</td>
<td>(1.057 ± 0.073) $10^{-5}$</td>
</tr>
<tr>
<td>20</td>
<td>0.236 ± 0.053</td>
<td>(2.358 ± 0.058) $10^{-5}$</td>
</tr>
<tr>
<td>30</td>
<td>1.242 ± 0.102</td>
<td>(1.027 ± 0.094) $10^{-4}$</td>
</tr>
<tr>
<td>40</td>
<td>1.243 ± 0.127</td>
<td>(2.026 ± 0.274) $10^{-4}$</td>
</tr>
<tr>
<td>50</td>
<td>8.409 ± 0.469</td>
<td>(6.843 ± 0.374) $10^{-4}$</td>
</tr>
</tbody>
</table>

Table 1 The calculated results of reaction rate constant catalyzed by H$_2$SO$_4$.

Table 2 The calculated results of reaction rate constant catalyzed by HCl.

*C$_{cat} = 0.05$ mol/L, STR = 500 rpm.*
5.4. Comparison of experimental results with model

The differences (Fig. 7) between experimental results and calculated results are very small (±4.0%). It indicates that Pseudo-Homogeneous model can well predict the reaction behavior. With the same catalyst concentration, H_2SO_4 system owns a faster reaction rate than HCl system. But taking H^+ as the catalyst, under same pH value, the reaction rate of H_2SO_4 system is almost the same as the HCl system.

6. Separation process

6.1. Catalyst selection for separation process

The experiment is done to compare the catalyst activity of H_2SO_4 and HCl. The pH of the reactive-extraction solution is 1 and the pH of acid solution for hydrolysis is also 1. The volume ratio of BA to fermentation broth is 1:2 and the mole ratio of water in acid solution to PDD in the organic phase is 1:1. Reactive-extraction runs under room temperature and reactive-distillation runs in the column with theoretical plate number of 5. The feed stage number is 2 (from the top), the top temperature is 78 °C and bottom temperature is 100 °C. The results are listed in Table 3.

![Figure 7 Comparison of experimental results with calculated results (T = 20 °C, C_{BD} = 1.01 mol/L, C_{BA} = 1.00 mol/L, C_{cat} = 0.1 mol/L, STR = 500 rpm).](image)

It can be conclude from Table 3 that both H_2SO_4 and HCl can be used as catalyst of the separation process. In reactive-extraction part, more than 99% of 2,3-BD can be recovered from fermentation broth for both systems. In the reactive-distillation part, with the same operation time, the hydrolysis rate of H_2SO_4 system is higher than that of HCl system. However, the loss of PDD, BA and 2,3-BD of the H_2SO_4 system is higher than those of the HCl system. As HCl system owns the lower loss of 2,3-BD and BA, HCl is chosen as the catalyst for the separation process.

6.2. The volume ratio of BA to fermentation broth

The experiments have been done under room temperature. Fig. 8a illustrates that increase in the amount of BA in reactive-extraction part can improve the conversion rate. When the volume ratio of BA to fermentation broth (V_{BA}/V_{FB}) increases from 0 to 2.0, the conversion rate of 2,3-BD goes up from 0% to more than 95%. Fig. 8b tells how the concentration of 2,3-BD and PDD in the aqueous phase changes with V_{BA}/V_{FB}. It can be concluded from the figure that the solubility of PDD in the aqueous phase is quite small, less than 3 g/L. The concentration of 2,3-BD decreases with the increasing amount of BA. When the amount of BA is 200 mL for 1 L fermentation broth, the concentration of 2,3-BD in the aqueous phase is lower than 5 g/L. According to the results, feasible V_{BA}/V_{FB} can be set at 0.2.

Using n-butylaldehyde as both reactant and extractant, reactive-extraction can separate more than 95% of 2,3-BD from fermentation broth. To treat 1 L fermentation broth, only 200 ml n-butylaldehyde is required. That means the amount of solvent required is 160 g L^{-1}. These results obtained in our study are much better than those (CBD = 80 g L^{-1} in final organic phase, the amount of solvent required is 800 g L^{-1}) by using aqueous two-phase extraction (Shao and Kumar, 2009).

6.3. Mole ratio of water to PDD for hydrolysis

Reactive-distillation runs in the column with theoretical plate number of 5. The feed stage number is 2 (from the top), the top temperature is 78 °C and bottom temperature is 100 °C. The pH of feed acid solution is 1. Fig. 9 shows how the feed mole ratio of water to PDD for hydrolysis (FR, n_{water}/n_{PDD}) affects the hydrolysis. Hydrolysis rate of PDD can be increased by increasing the use of water. When FR = 0.5, only 12% of PDD can hydrolyze, while the hydrolysis rate goes up

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Catalyst selection for 2,3-butanediol and n-butyl aldehyde system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>H_2SO_4</td>
</tr>
<tr>
<td>Extraction rate of 2,3-BD</td>
<td>99.1 ± 0.3</td>
</tr>
<tr>
<td>Hydrolysis rate of PDD</td>
<td>59.2 ± 0.1</td>
</tr>
<tr>
<td>Loss of PDD</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>Loss of BA</td>
<td>4.5 ± 0.3</td>
</tr>
<tr>
<td>Loss of 2,3-BD</td>
<td>5.4 ± 0.2</td>
</tr>
<tr>
<td>CBD = 87.2 g/L, pH = 1, V_{BA}/V_{FB} = 1:2, n_{water}/n_{PDD} = 1:1.</td>
<td></td>
</tr>
</tbody>
</table>
Figure 8 Effect of extractant ratio on reactive-extraction of 2,3-butane diol (T = 20 °C, C_{BD} = 1.26 mol/L, C_{cat} = 0.1 mol/L, STR = 500 rpm).

Figure 9 Effect of water/PDD ratio on the hydrolysis (T_{top} = 78 °C, T_{bottom} = 100 °C, C_{cat} = 0.1 mol/L).

Figure 10 Hydrolysis rate of PDD under different theoretical plate numbers (T_{top} = 78 °C, T_{bottom} = 100 °C, C_{cat} = 0.1 mol/L).

6.4. The theoretical plate number of the reactive-distillation column

The experiments are carried out in the distillation columns with different theoretical plate numbers. The feed stage number is the second plate from the top. The top temperature is 78 °C and bottom temperature is 100 °C. Fig. 10 illustrates that both the theoretical plate number and concentration of HCl solution can affect the HR_{PDD}. The effect of concentration of HCl solution is larger than the theoretical plate number. When C_{HCL} = 0.1 mol/L, HR_{PDD} increases from 53% for 4-stage-column to 56% for 14-stage-column. While in a 4-stage-column, HR_{PDD} can increase from 53% (C_{HCL} = 0.1 mol/L) to 85% (C_{HCL} = 1 mol/L). According to Fig. 10, when C_{HCL} = 0.5 mol/L in a 10-stage-column,

HR_{PDD} can reach 88%. The feasible theoretical plate number is set at 10 with concentration of HCl solution of 0.5 mol/L.

6.5. The purification

The 2,3-BD solution obtained by reactive-distillation is purified in a vacuum rectifying apparatus with a vacuum degree of 0.07 MPa. Unreacted PDD is recycled. The distillation cut between 140 and 143 °C is collected.

Distillation is used to recycle BA, which is left in the aqueous phase. The bottom temperature of the distillation column is 95 °C, and BA is collected at the top with the temperature between 75 and 78 °C. Over 85% of BA has been recovered.

With the complete separation process described above, the mass fraction of 2,3-BD as the final product is more than 99% and the total yield rate of 2,3-BD from fermentation broth by reactive-extraction process can be over 90%.
7. Conclusion

In this study, the kinetics of the reaction of 2,3-butanediol and n-butylaldehyde catalyzed by sulfuric acid and hydrochloric acid was studied. The dependence of the equilibrium constant on the reaction temperature was in line with Van’t Hoff equation. The reaction enthalpy is $-21.58 \pm 1.63 \text{ kJ mol}^{-1}$. The reaction rate was found to increase with increasing reaction temperature and has a linear correlation with catalyst amount. It was found that Pseudo-Homogeneous model was able to describe the kinetics of the reaction of 2,3-butanediol and n-butylaldehyde without high errors. The activity energy for H$_2$SO$_4$ system and HCl system was $57.52 \pm 5.35$ and $58.14 \pm 5.06 \text{ kJ mol}^{-1}$, respectively.

A complete separation process combined by reactive-extraction and reactive-distillation has been developed, in which BA acts as both reactant and extractant. The process can effectively recover 2,3-BD from fermentation broth. The yield rate of 2,3-BD is more than 90% with purity over 99%. Feasible operation conditions have been obtained as follows: volume ratio of BA to fermentation broth (VR$_{BA}$/VR$_{FB}$) is 0.2; feed mole ratio of water to PDD for hydrolysis (FR, n$_{water}$/n$_{PDD}$) is 3.0; theoretical plate number for reactive-distillation column is 10 with concentration of HCl solution of 0.5 mol/L.

Catalyst H$_2$SO$_4$ and HCl are easy to get, but hard to recycle. They should be neutralized after reactive-distillation. And the corrosion of equipment should been taken into consider, which may limit the use of the reactive-extraction process. If suitable recycle catalyst can be found, the process will have a good future.

Acknowledgement

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Reference