Design and optimization of the levulinic acid recovery process from lignocellulosic biomass

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ABSTRACT

Levulinic acid (LA), which is one of the top twelve value-added chemicals from biomass feedstock, has been recognized in a large number of applications. Nevertheless, its capability on an industrial scale has been limited by the high-cost of the raw materials and the lack of detailed process design. This paper reports the simulation, detailed design and optimization of an industrial process recovering LA from biomass, a renewable and inexpensive feedstock. The aqueous feed mixture from the acidic hydrolysis of biomass was fed to the separation process to recover LA as the main product, along with furfural and formic acid as valuable byproducts. Furfural was then used as an extracting solvent, resulting in a significant decrease in total cost. Detailed analysis was conducted to assess the feasibility of the separation method. The purification process was intensified by applying an innovative top dividing wall column with a decanter configuration (TDWC-D). The response surface methodology (RSM), which allows the interactions between variables to be identified and quantified, was used to optimize the TDWC-D structure. The predictions by the RSM showed satisfactory agreement with the rigorous simulation results. The results showed that the innovative TDWC-D configuration could save up 16.4% and 20.6% of the overall energy requirements and total annual cost, respectively, compared to the conventional sequence.

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1. Introduction

The dependence of the global economy on the utilization of mineral resources has increased in recent years, accounting for 80.9% of the total energy production in 2006 (Koh and Ghazoul, 2008). Nevertheless, these resources have many disadvantages, such as limited reserves, environmentally damaging and responsibility for global warming. Therefore, the interest of biomass, which is the only renewable resource of fixed carbon, has increased considerably. Biomass can not only produce conventional hydrocarbon liquids for transportation, but also petrochemical products (Huber et al., 2006; Petrus and Noordermeer, 2006; Corma et al., 2007). Biofuels from biomass are viewed by many policy makers as a key to reduce the reliance on foreign oil, lowering the emissions of greenhouse gases and meeting the rural development goals (Koh and Ghazoul, 2008).

Levulinic acid, which is recognized in a large number of applications, is listed as one of the top-twelve value-added chemicals from biomass in terms of its potential markets, its derivatives and the complexity of the synthetic pathways (Werpy and Petersen, 2004). This compound has frequently been suggested to be a starting material for the production of many industrial and pharmaceutical compounds, such as methyltetrahydrofuran, delta aminolevulinic acid, ethyl levulinate and diphenolic acid. In particular, with MTHF applications only, LA manufacturers could face the potential demand of more than 20,000 kilotons by 2020 (Grand View Research, 2014). Nevertheless, the capability of this process on an industrial scale has been limited by the expensive raw

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Several processes have been used to produce LA from an inexpensive feedstock, lignocellulosic biomass. Dunlop and Wells (1957) proposed the earliest continuous process for producing LA from corn cob waste. The aqueous feed mixture obtained from acidic hydrolysis is introduced to an extractor to extract LA and then fed to a distillation column to produce pure LA. Ghorpade and Hanna (1999) presented the LA process based on the reactive extrusion from corn starch. These two processes only considered LA as a product. Recently, Sadhukhan et al. (2014) presented a good example of a LA production process from corn cob, which considered both the reaction and separation stages. Seibert (2010) reported a process that uses furfural to extract LA and formic acid from the acidic hydrolysis of biomass. The advantage of this process is the use of furfural, one of the products, as a solvent. Interestingly, these reports showed that a combination of an extractor and a series of distillation columns is used to purify LA, showing great potential to improve the energy efficiency, economic performance and environmental impact. Furthermore, none of the previous processes considered the detailed design methodology and advanced techniques in the case of commercial scale production. A comprehensive design by intensified configurations with economic evaluation is needed to expand the capacity to an industrial scale as well as to reduce the LA price and environmental impact.

Many studies have examined the relative advantages of a dividing wall column (DWC) (as shown in Fig. 1) to improve the energy efficiency and reduce the consumption of utilities (Ammimudin and Smith, 2001; Long and Lee, 2013a,b). These reports have shown that DWC systems can achieve energy savings of up to 30% over conventional direct and indirect distillation sequences (Kiss and Ignat, 2012; Long et al., 2013). This is because DWCs can allow reversible splits with no part of the separation being performed twice, which is the main contributor to their superior energy efficiency over other column configurations (Pothen et al., 2004). Additional benefits arise from the fact that only one reboiler and condenser are involved instead of two reboilers and two condensers in a conventional distillation sequence (Premkumar and Rangaiah, 2009).

To design and optimize DWC, Halvorsen and Skogstad (2003) proposed the use of a minimum vapor flow, or the so-called $V_{\text{min}}$ diagram method, which is a graphical visualization of the minimum energy. On the other hand, it cannot be applied to the separation of azetotropic mixtures. Several rigorous methods have proposed, such as a sequential quadratic programming-based method implemented in Aspen Plus (Kiss and Suszwalak, 2012a), and a MILP approach based on the use of two structure levels (Caballero and Grossmann, 2014).

Recently, Lee and Long (2012) reported a practical and efficient method based on the response surface methodology (RSM). The RSM is a general technique that is used for an empirical study of the relationships between the measured responses and independent input variables (Box and Wilson, 1951). By allowing the interactions between variables to be identified and quantified, RSM can predict reliable results with a little computational effort. Therefore, it can be used to optimize the design and operation conditions of a process (Long and Lee, 2012). On the other hand, when the behavior of the function is highly nonlinear in terms of the design variables, the RSM encounters some difficulties in approximating the sufficient quality on the entire design space (Merval et al., 2006). The optimum may not be defined if the range of factors is too narrow or too wide. Furthermore, critical factors may not be defined or specified correctly. In the case of many factors, the problem becomes complex and the RSM cannot be predicted well.
This paper proposes an economical and environmental process for producing LA from an inexpensive raw material, lignocellulosic biomass, along with the detailed design variables and operating conditions. The simulation work was conducted using the commercial simulator, Aspen Plus. A range of sequences and intensified configurations applying TDWC-D are presented with respect to their energy consumption and economic performance. Furthermore, the RSM was used to optimize the structure of the proposed TDWC-D.

2. LA separation process

2.1. Separation feasibility

The feed mixture considered was obtained from the acidic hydrolysis process of biomass and was an aqueous solution containing LA, furfural, formic acid, and water. The typical concentrations of the mixture ranged from 3 to 8 wt.% LA, from 1 to 5 wt.% furfural, from 1 to 5 wt.% formic acid, and the balance being water (Reunanen et al., 2013). With this component mixture, although LA did not form an azeotrope with the other components, two azeotrope mixtures still formed. Fig. 2 shows a ternary diagram for the furfural–water–formic acid system. As shown in this figure, the water–furfural mixture has a minimum-boiling heterogeneous azeotrope with a composition of 64.5 wt.% furfural at 97.8 °C. Another maximum-boiling homogeneous azeotrope forms between formic acid and water with a higher azeotropic temperature of 106.8 °C. In that ternary map, there are two distillation regions divided by the distillation boundary.

Fig. 3 presents a simplified feasible flow sheet for producing LA from lignocellulosic biomass (Seibert, 2010). The conventional process sequence consists of one extractor and three distillation columns. The feed mixture and the furfural solvent are introduced into the extractor (EX) to generate a water-rich mixture.
phase as the top stream and a solvent-rich phase containing mainly furfural, LA and formic acid as the bottom stream. The furfural-rich stream is then fed to the first distillation column (C1) to collect LA as the bottom stream product, whereas the distillate contains furfural, formic acid and water, which are introduced into the second distillation column (C2). The function of C2 is to separate the inlet into furfural, formic acid as the bottom stream and a light boiling furfural–water azeotropic mixture as the top stream. The azeotropic mixture is then delivered to storage before being recycled back to the extractor. The bottom stream of C2 is then subjected to the third distillation column (C3) to recover the formic acid as the distillate product, and the furfural is collected as the bottom stream. The furfural solvent is recycled back to the extractor and reused as the extractant.

All processes were performed using the simulator, Aspen Plus V8.6, with the NRTL–HOC (nonrandom two-liquid–Hayden–O’Connell) fluid package. The HOC equation of state as the vapor phase model and NRTL for the liquid phase were used to predict not only the vapor–liquid equilibrium but also the vapor–liquid–liquid equilibrium of these simulations. Dimerization affects the vapor–liquid–liquid equilibrium, vapor phase properties, density, and liquid phase properties. The HOC equation reliably predicts the solvation of polar compounds and the dimerization in the vapor phase that occurs with mixtures containing carboxylic acids (Aspen Technology, 2010). The binary pairs of the interaction parameters for LA were estimated using the UNIFAC model.

### 2.2. Conventional distillation sequence (CS)

The LA production rate considered in this study was 50 kilotons per year with a commercial purity of 98 wt.% (Hayes et al., 2008). The furfural reused as a solvent was kept at 99.9 wt.% purity while the purity of the formic acid product was 85 wt.%, which is considered the industry standard and accounting for the major portion of the global demand (Burke, 2015). Table 1 lists the feed composition, temperature and pressure used in this process.

In this study, the CS was designed and optimized first for a fair comparison with the other proposed optimized sequences (Fig. 3). In this process, the component recoveries depend mainly on the efficiency of the extractor or the extraction solvent efficiency. This means that solvent selection is the key in this process. Although formic acid recovery is quite low when selecting furfural as a solvent, there is some trade-off between the total process cost and the formic acid recovery. Note that furfural is one of the products and more effective in the recovery of LA and formic acid than other solvents, such as methyl isobutyl ketone and isopropyl acetate (Seibert, 2010). In the extractor, the recovery of LA, formic acid and furfural also increase with increasing extracting solvent/feed ratio but more water appears in the furfural-rich phase. In this study, a solvent/feed ratio of 1:2.1 was selected to obtain 97 wt.% LA recovery. Table 2 lists the conditions and product specifications for each column in the conventional column sequences. Note that high pressure (HP) steam is used in the first column while medium pressure (MP) steam is used in the second and third columns. The rigorous simulation results showed that the energy requirements of C1, C2 and C3 were 22,930, 4250 and 3770 kW, respectively.

### 3. Proposed sequences

This section proposes the different configurations to separate LA and co-products. The results were then compared in terms of the energy requirement and total annual cost while obtaining the same requirements of productivity, recovery and purity. The column diameters were determined using the column flooding conditions that fix the upper limit of the vapor velocity. The operating velocity is normally between 70% and 90% of the flooding velocity (Premkumar and Rangaiah, 2009). In this study, all columns were designed with a load near 85% of the load at the flooding point to prevent flooding in the columns. The capital costs were calculated based on Guthrie’s modular method (Biegler et al., 1997). Table 3 lists the utility cost data used in this study. The 10 year-plant lifetime was used to calculate the total annual cost (TAC).

All conventional columns were optimized with the number of trays and the feed location as the main variables for maximizing total annual cost saving (Fig. 4). Fig. 5 shows one optimization case of the C3 in the conventional sequence. In TDWC-D optimization, after a preliminary design, the main variables, such as the internal vapor flow to the prefractionator (Fv), and the number of trays in the top (N1), bottom (N2) and feed rectifying (N3) sections were then optimized. The aim of the optimization was to maximize the TAC savings.

#### Table 1 – Conditions of the feed mixture.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass fraction (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>86%</td>
</tr>
<tr>
<td>Formic acid</td>
<td>3%</td>
</tr>
<tr>
<td>Furfural</td>
<td>4%</td>
</tr>
<tr>
<td>Levulinic acid (LA)</td>
<td>7%</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>2</td>
</tr>
<tr>
<td>Mass flow rate (kg/h)</td>
<td>90,000</td>
</tr>
</tbody>
</table>

#### Table 2 – Design parameters of a conventional sequence for the production of LA from biomass.

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of trays</td>
<td>22</td>
<td>27</td>
<td>28</td>
</tr>
<tr>
<td>Tray type</td>
<td>Sieve</td>
<td>Sieve</td>
<td>Sieve</td>
</tr>
<tr>
<td>Column diameter (m)</td>
<td>3.6</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Number of flow paths</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Tray spacing (mm)</td>
<td>610</td>
<td>610</td>
<td>610</td>
</tr>
<tr>
<td>Max flooding (%)</td>
<td>87.83</td>
<td>80.36</td>
<td>85.93</td>
</tr>
<tr>
<td>Condenser duty (kW)</td>
<td>17,220</td>
<td>2699</td>
<td>3694</td>
</tr>
<tr>
<td>Reboiler duty (kW)</td>
<td>22,930</td>
<td>4250</td>
<td>3770</td>
</tr>
</tbody>
</table>

#### Table 3 – Utilities cost data (Turton et al., 2012).

<table>
<thead>
<tr>
<th>Utility</th>
<th>Price ($/GJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling water</td>
<td>0.35</td>
</tr>
<tr>
<td>Medium pressure steam</td>
<td>14.19</td>
</tr>
<tr>
<td>High pressure steam</td>
<td>17.70</td>
</tr>
</tbody>
</table>
The optimization was constrained by the product purities and recoveries.

\[
\text{Max}(%\text{TAC saving}) = f(N1, N2, N3, F_2)
\]  

A Box–Behnken design was used under the response surface methodology to determine how the variables interact and to optimize the system in terms of the TAC saving. Box and Behnken (1960) proposed some three-level designs for fitting the response surfaces. These designs are formed by combining \(2^k\) factorials with incomplete block designs. The resulting designs are generally very efficient in terms of the number of required runs, and they are either rotatable or nearly rotatable. Rotatability is a very important property in the selection of the RSM. Because the purpose of the RSM is optimization and the location of the optimum is unknown prior to running the experiment or simulation, it makes sense to use a design that provides equal estimation precision in all directions (Montgomery, 2001). Note that the Box–Behnken design is a spherical design with all points lying on the sphere of the radius. In addition, the Box–Behnken design does not contain any points at the vertices of the cubic region created by the upper and lower limits for each variable. This could be advantageous when the points on the corners of the cube represent the factor-level combinations that are prohibitively expensive or impossible to test because of the physical process constraints. Moreover, the Box–Behnken designs often have fewer design points; they require less effort to run than central composite designs with the same number of factors (Minitab 16, 2010). After determining the preliminary ranges of the variables through single-factor testing, the simulation run data was fitted to a second-order polynomial model and the regression coefficients were obtained. The generalized second-order polynomial model used in the response surface analysis is as follows:

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i N_i + \sum_{i=1}^{k} \beta_i^2 N_i^2 + \sum_{i<j} \beta_{ij} N_i N_j + \epsilon
\]  

where \(Y\) is the predicted response, \(N_i\) are the uncoded or coded values of the variables, \(\beta_0\) is a constant, \(\beta_i\), \(\beta_i^2\), and \(\beta_{ij}\) are the coefficients of the linear, quadratic, and interactive terms, respectively, and \(\epsilon\) is the error term. Minitab<sup>®</sup> software was used for response surface fitting to maximize the total annual cost savings.

3.1. Improving conventional sequence by a decanter (CS-D)

In the C2 of the conventional sequence, there was an amount of furfural loss (2175 kg/h) in the C2-top due to a heterogeneous azeotrope between water and furfural (see Fig. 6). As shown in Fig. 2, a significant liquid phase split envelope is clearly shown in the ternary diagram of the furfural–water–formic acid system so that a decanter can be applied to reduce the furfural loss and make the distillation more efficient. In particular, the decanter or gravity settling tank, are the simplest form of equipment used to separate liquid–liquid mixtures. Several studies have reported the benefits of a decanter in solving a heterogeneous azeotrope (Kiss and Suszwalak, 2012; Wu et al., 2014). In this case, furfural and formic acid are collected as the bottom stream of the

Fig. 4 – Flowsheet of the optimization procedure for a single distillation column.

Fig. 5 – TAC saving plots for the C3 of the conventional sequence.
C2, while the binary heterogeneous azeotrope water–furfural is sent to the overhead of C2, which is then delivered to a condenser–decanter. Fig. 6 presents a flow sheet of the C2 integrated with a decanter. The azeotrope furfural–water on top of C2 is cooled and then split naturally into two liquid phases by the decanter, following the liquid–liquid equilibrium tie lines. The water-rich phase is designed to be totally delivered to storage while the organic phase, which contains mainly furfural, is refluxed back to C2. Fig. 7 shows the effects of temperature on the liquid–liquid separation in the decanter. In particular, the amount of furfural loss decreases with decreasing temperature of the inlet-decanter stream. Therefore, in the decanter design, the temperature of the C2-overhead is cooled to 60 °C to make the separation in the decanter more efficient. As a result, integration of the decanter can not only save the energy requirements in the reboiler duty (2.39% of the C2 and C3), but also increase the furfural recovery. The amount of furfural loss in the C2-top stream was reduced from 2175 kg/h to 336 kg/h, i.e. a decrease of 85% furfural loss compared to that in the column without a decanter.

3.2. Intensifying conventional sequence by innovative TDWC-decanter (TDWC-D)

In addition, to improve the energy efficiency in the columns, minimizing the number of columns is also crucial because it directly affects the overall economics and safety in a LA production process. DWC would be the best option to intensify the process for achieving both tasks simultaneously. In particular, an innovative TWDC-D was considered here to integrate the C2 and C3 to improve the energy efficiency and reduce the investment cost.

After a preliminary design for TDWC-D, it was then optimized using the RSM. Table 4 lists the factors and levels used in the RSM based optimization. Fifteen simulations were run to optimize 3 parameters of the TDWC-D structure. For each run, the internal vapor flow to the prefractionator was varied to maximize the TAC saving while obtaining the required product purity and recovery. Fig. 8 presents a schematic diagram illustrating the optimized TDWC-D that replaces the

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**Fig. 6 – Schematic diagram of the C2 of the CS integrated with a decanter.**

**Fig. 7 – Effect of temperature on furfural loss in the water-rich stream of the C2-decanter.**

**Fig. 8 – Schematic diagram of the innovative TDWC-D.**

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**Table 4 – Coded levels of the factors for TDWC variables of the CS sequence and PS sequence.**

<table>
<thead>
<tr>
<th>Case</th>
<th>Factor</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>Top section (N1)</td>
<td>22</td>
</tr>
<tr>
<td>sequence</td>
<td>Bottom section (N2)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Feed rectifying section (N3)</td>
<td>14</td>
</tr>
<tr>
<td>Proposed</td>
<td>Top section (N1)</td>
<td>18</td>
</tr>
<tr>
<td>sequence</td>
<td>Bottom section (N2)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Feed rectifying section (N3)</td>
<td>13</td>
</tr>
</tbody>
</table>

---

columns, C2 and C3, of the CS sequence. The rigorous simulation results show that the optimized TDWC-D can save up 30.6% and 28.1% in terms of the operating cost and TAC, respectively, compared to the two columns, C2 and C3, of the base sequence. Compared to the whole CS sequence, the innovative configuration combining TDWC and a decanter can allow operating cost and TAC savings of 7.0% and 7.2%, respectively.

3.3. Improving conventional sequence by changing sequence – proposed sequence (PS)

Multicomponent mixtures can be separated by different distillation column sequences. Many studies have examined the optimal sequence of simple columns that do not involve heat integration (Nishida et al., 1981; Smith, 2005; Westerberg, 1985). The number of possible distillation sequences increases with increasing number of products (King, 1980). Interestingly, the "rule of thumb" is the most common method used for finding the optimal sequence of simple distillation columns (King, 1980). The sequences that remove the lightest components alone one by one in the column overheads should be favored (Smith, 2005), i.e., favor the direct sequence. In addition, in the base case, the first distillation column C1 requires the largest amount of energy and highest level of steam (high pressure steam) compared to the other columns. This column is used to vaporize a large number of furfural and light components as well as purify LA, which has the highest boiling point (257 °C) compared to the other components, furfural (162 °C), formic acid (101 °C), water (100 °C). Based on the well-known heuristics for separation sequence synthesis, a proposed sequence for producing LA was used to enhance the energy efficiency (see Fig. 9).

An aqueous mixture from the acidic hydrolysis reaction of biomass and the furfural solvent was fed to the extractor (P-EX) to generate a water-rich phase as the top stream and solvent-rich phase containing mainly furfural, LA and formic acid as the bottom stream. In contrast to the CS sequence, the bottom stream of P-EX was fed to the proposed C1 (P-C1), which delivered a light boiling azeotrope of furfural and water as the top stream, whereas the bottom stream contained formic acid, furfural and LA. The bottom of P-C1 was then introduced to the proposed C2 (P-C2) to collect formic acid as the distillate and the bottom stream comprising furfural and LA, which was subjected to the proposed C3 (P-C3). The role of P-C3 is to separate levulinic acid as the bottom product and furfural as the top product. Here, LA is recovered at the third column so the proposed sequence is called the direct sequence.

Note that medium pressure steam was used on P-C1 and P-C2, whereas P-C3 used high pressure steam. The simulation results showed that the energy requirement in the reboiler using HP columns is reduced from 22,930 kW in C1 of the CS sequence to 13,850 kW in C3 of the PS sequence. As a result, the PS sequence that changes the order of the distillation columns can reduce the annual operating cost and TAC by up to 16.4% and 16.0%, respectively, compared to the base case. Note that these heuristics are not novel but they can be applied easily and efficiently, which leads to significant TAC savings in the LA process. This process is particularly interesting to many companies that prefer to use conventional columns.

3.4. Improving the proposed sequence by decanter (PS-D)

In the PS sequence, the main role of the first column (P-C1) is to remove water as much as possible. On the other hand, the minimum-boiling heterogeneous azeotrope mixture between furfural and water forms, causing a furfural loss of 3196 kg/h in the top of this column. Therefore, a decanter, which can split the liquid-liquid mixture naturally, can be integrated in this column as same as the second column in the base case to reduce the loss of furfural. Fig. 10 shows the simplified flow sheet of the P-C1 integrated with a decanter. To improve the separation efficiency in decanter, the overhead of P-C1 was cooled to 60 °C before being introduced to the decanter. Not only can the furfural loss be reduced by up to 87.9%, but also the amount of water removed increases from 2960 kg/h to 3157 kg/h, which is comparable to the column without a decanter. The simulation results showed that not only can the energy requirement in the reboiler duty in P-C1-D column be reduced slightly (1.7%), but there is also less furfural loss compared to the column without a decanter.

3.5. Intensifying proposed sequence with innovative TDWC-D (PS-TDWCD-D)

In the CS sequence, although the C1 requires most energy, however, TDWC-D can only be used to replace the C2 and C3. On the other hand, in the PS sequence, both the P-C1 and P-C3 are energy-intensive columns so that intensification either the P-C1 or P-C3 can bring more benefit. In particular, to intensify the proposed conventional sequence, the TDWC was used to integrate the first two columns. To optimize the TDWC-D, some preliminary simulation runs were carried out to determine the main optimizing variables and their levels. Corresponding to the changes in the factor value, the response
values (TAC saving) were recorded. The presence of curvature suggests that the simulation region is close to the optimum. Table 4 lists the factors and levels used in the RSM-based optimization. The TDWC-D parameters were optimized over 15 simulation runs. For each run, the internal vapor flow to the prefractionator was varied to maximize the TAC savings while obtaining the required product purity and recovery. Fig. 11 presents a contour plot of the interactions between the design variables N1, N2 and N3. In each case, the one remaining parameter was set automatically as its center point value by the software. The resulting second-order polynomial model was as follows:

$$Y = 10.3743 + 5.44663N_1 + 3.99257N_2 - 4.11248N_3$$

$$= 3.01056N_1^2 - 5.15933N_2^2 - 1.55725N_3^2 + 1.2084N_1N_2$$

$$+ 1.96654N_1N_3 - 0.582208N_2N_3$$

(3)

As shown in Fig. 12, the TAC saving was predicted to be highest (15.3%) with the coded levels of the top section (N1), bottom section (N2) and feed rectifying section (N3) of 0.6970, 0.5152 and −0.9798, respectively. The resulting determination coefficient was $R^2 = 95.7$, which indicates that the model is suitable for prediction within the range of simulated variables. The natural values of the variables can be derived from the coded levels. Recycling of the vapor was then optimized to maximize the TAC savings while achieving the product purity requirements and recovery. Fig. 13 compares the three-dimensional response surface plots of the interaction between N1 and N2 evaluated by the RSM and by rigorous simulation. The figure shows that the three-dimensional response surface plots by the RSM are similar to the actual ones. Fig. 14 shows a schematic diagram illustrating the optimal TDWC-D from the conventional sequence. The TDWC-D combining a decanter, which can increase the furfural recovery and improve the

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Fig. 10 - Schematic diagram of the proposed conventional sequence integrated a decanter.

Fig. 11 - Contour plots of the interactions between the top section (N1), bottom section (N2) and feed rectifying section (N3).
heterogeneous azeotrope separation, with a TDWC, which can reduce energy requirement and TAC, can bring many benefits in terms of energy saving and cost reduction. The simulation showed that the TDWC-D can save up to 13.2% in terms of the TAC compared to the C2 and C3 of the conventional sequence. This rigorous simulation agreed well with the predicted value (15.3%). In addition, using a TDWC-D could save 15.4% of the energy requirements in terms of the reboiler duty compared to P-C1 and P-C2 of the PS sequence.

Table 5 summarizes the key results, while Fig. 15 conveniently illustrates the annual operating cost and TAC for all configurations considered. The results suggest that the

<table>
<thead>
<tr>
<th>Structural alternative</th>
<th>CS (US $)</th>
<th>CS-D (US $)</th>
<th>CS-TDWC-D (US $)</th>
<th>PS (US $)</th>
<th>PS-D (US $)</th>
<th>PS-TDWC-D (US $)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual operating cost (US $)</td>
<td>16,332,077</td>
<td>16,234,472</td>
<td>15,151,046</td>
<td>13,646,300</td>
<td>13,729,322</td>
<td>12,812,024</td>
</tr>
<tr>
<td>Annual operating cost saving (%)</td>
<td>0.6%</td>
<td>7.2%</td>
<td>16.4%</td>
<td>15.9%</td>
<td>21.6%</td>
<td></td>
</tr>
<tr>
<td>Total annual cost (US $)</td>
<td>17,308,411</td>
<td>17,214,679</td>
<td>16,103,366</td>
<td>14,541,721</td>
<td>14,640,722</td>
<td>13,736,949</td>
</tr>
<tr>
<td>Total annual cost saving (%)</td>
<td>0.5%</td>
<td>7.0%</td>
<td>16.0%</td>
<td>15.4%</td>
<td>20.6%</td>
<td></td>
</tr>
</tbody>
</table>

TDWC-D can be applied efficiently to improve the distillation processes while requiring less TAC and energy.

4. Conclusions

A levulinic acid recovery process from abundant and inexpensive lignocellulosic biomass was designed and optimized to be more energy-efficient. This process was then intensified efficiently using an innovative TDWC-D. After a preliminary design, the TDWC-D structure was then optimized and implemented simply and efficiently by the RSM using Aspen Plus and Minitab. The simulated results were in good agreement with the predicted values. The use of innovative TDWC-D can have many benefits, such as increasing the furfural recovery, increasing the separation efficiency and decreasing the TAC significantly. The incorporation of a decanter into the TDWC is a very attractive option for improving the separation efficiency and energy savings, especially for the separation of heterogeneous azetrope mixtures. The proposed sequence including TDWC-D showed 21.6% and 20.6% decreases in the energy requirement and TAC, respectively, compared to a conventional column sequence. Based on these results, the use of TDWC-D for LA production, which has the limitations in commercial scale of existing processes currently, is technically feasible and particularly interesting in constructing a new levulinic plant. The process compactness is an additional benefit from TDWC-D applications.

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Appendix. Column cost correlations

(a) Capital cost: Guthrie’s modular method was applied (Biegler et al., 1997). The investment cost for conventional distillation is the total cost of the column and auxiliary equipment, such as reboilers and condensers. For the DWC, it includes the additional dividing wall cost. In this study, the Chemical Engineering Plant Cost Index of $85.7 (2011) was used for cost updating.

\[ \text{Tray stack} = (N - 1) \times \text{tray spacing} \] (4)

Total height = tray stack + extra feed space + disengagement + skirt height

Updated bare module cost (BMC) = \( UF \times BC \times (MPF + MF - 1) \) (5)

where

\( UF \) is the update factor : \( UF = \frac{\text{present cost index}}{\text{base cost index}} \) (7)

\( BC \) is the bare cost, for vessels : \( BC = BC_0 \times \left( \frac{L}{L_0} \right)^a \times \left( \frac{D}{D_0} \right)^b \) (8)

For the heat exchanger : \( BC = BC_0 \times \left( \frac{A}{A_0} \right)^a \) (9)

Area of the heat exchanger, \( A = \frac{Q}{UA_T} \) (10)

where MPF is the material and pressure factor; MF is the module factor (typical value), which is affected by the base cost. \( D \), \( L \) and \( A \) are the diameter, length and area, respectively.

Updated bare module cost for the tray stack (BMC) = \( UF \times BC \times MPF \) (11)

(b) Operating cost (Op):

\[ Op = C_{\text{steam}} + C_{\text{CW}} \] (13)

where \( C_{\text{steam}} \) is the cost of the steam and \( C_{\text{CW}} \) is the cost of cooling water.

(c) Total annual cost (TAC) (Smith, 2005):

\[ \text{TAC} = \text{capital cost} \times \frac{i(1 + i)^n}{(1 + i)^n - 1} + Op \] (14)

where \( i \) is the fractional interest rate per year and \( n \) is the number of years.

References


