Novel heat–integrated and intensified biorefinery process for cellulosic ethanol production from lignocellulosic biomass

Le Cao Nhien 1, Nguyen Van Duc Long 1, Moonyong Lee 1

School of Chemical Engineering, Yeungnam University, Gyeongsan 712–749, South Korea

ABSTRACT

Biofuels have the most potential as an alternative to fossil fuels and overcoming global warming, which has become one of the most serious environmental issues over the past few decades. As the world confronts food shortages due to an increase in world population, the development of biofuels from inedible lignocellulosic feedstock may be more sustainable in the long term. Inspired by the NREL conventional process, this paper proposes a novel heat–integrated and intensified biorefinery design for cellulosic ethanol production from lignocellulosic biomass. For the preconcentration section, heat pump assisted distillation and double–effect heat integration were evaluated, while a combination of heat–integrated technique and intensified technique, extractive dividing wall column (EDWC), was applied to enhance the process energy and cost efficiency for the purification section. A biosolvent, glycerol, which can be produced from biodiesel production, was used as the extracting solvent in an EDWC to obtain a high degree of integration in a biorefinery context. All configuration alternatives were simulated rigorously using Aspen Plus were based on the energy requirements, total annual costs (TAC), and total carbon dioxide emissions (TCE). In addition, the structure of the EDWC was optimized using the reliable response surface method, which was carried out using Minitab statistical software. The simulation results showed that the proposed heat–integrated and intensified process can save up to 47.6% and 56.9% of the TAC and TCE for the purification section, respectively, compared to the conventional purification process.

1. Introduction

Over the past few decades, the production of biofuels, which are more environmentally sustainable fuels, has stimulated intense interest as a substitute for fossil fuels. Among the biofuels, bioethanol is one of the most promising candidates and has attracted considerable attention. The first generation bioethanol was derived from sugar or starch produced by food crops, which are considered critical to feeding the world’s increasing population; therefore, its production may create a food–versus–fuel scenario. On the other hand, the abundant and relatively low–cost lignocellulosic materials make them attractive as a feedstock for the production of sufficient amounts of bioethanol from renewable resources at a reasonable cost [1]. The production of cellulosic ethanol (CE) from lignocellulose, which was estimated to produce approximately 86% less CO2 emissions than oil sources [2], might be more sustainable.

Basically, the production of CE has three main steps: pretreatment of raw materials, bioethanol fermentation, and separation. Among them, the energy–intensive separation process comprises a major proportion of the overall production cost [3]. Consequently, improvements of the separation process may have a dominant effect on the bioethanol market price. The function of the separation process is to produce a commercially pure CE product from a fermentation broth composed of 5–12 wt.% of CE with the balance being many other components. Note that most studies of the bioethanol separation process assumed that the feed from the fermentation broth was comprised of only bioethanol and water; hence, the separation of a homogeneous azeotropic mixture of ethanol and water (95.63 wt.% ethanol) was investigated. Obviously, this assumed feed leads to a simpler process but so far from the real biomass–based feed composition. In fact, breaking down the cellulose–hemicellulose–lignin structure of lignocellulosic biomass leads to the presence of more compounds in the output of the fermentation step, resulting in a more complex separation step. Therefore, a study of the CE separation process from lignocellulosic biomass should consider a real fermentation broth feed, which usually consists of water, CE, gases, soluble solids, and insoluble solids to reliably reflect the lignocellulosic–based process.

Owing to the presence of an azeotrope between ethanol and water, the separation process is usually divided two parts:
The selection of a suitable solvent plays an important role in ED design and optimization. Currently, ethylene glycol (EG) is the most common solvent applied in industry to separate ethanol–water mixtures [11]. On the other hand, it has serious environmental issues, such as fatal intoxication by ED poisoning [12]; and can also cause some health effects, e.g., central nervous system depression, cardiopulmonary effects, and renal damage [13]. As a result, a green solvent is needed as a substitute for EG. Bioglycerol, which is available as a byproduct in biodiesel production, is a promising solvent alternative. The use of bioglycerol as an extractive solvent can achieve a high degree of integration in a biorefinery context, leading to a more sustainable ED process in the long term.

In recent years, several commercial scale processes for CE production have been constructed in the US, Brazil, and Europe. The first commercial scale CE plant producing 75 million liters of CE per year, which is currently the largest advanced biofuels refinery in the world, was opened in 2013 at Crencentino, Italy. Another plant using Beta Renewables technology began production in 2014 at Alagoas, Brazil. In the US, a 30 MMgy CE plant in Imperial Valley, California will also begin production in 2016. In addition, a number of demonstration plants and pilot plants are also under development. Nevertheless, due to the complexities of lignocellulose feedstock and biorefinery technology, more intense research and advanced designs are needed to make CE more cost–competitive with petroleum–based fuels and corn ethanol.

An innovative solution to overcome the disadvantages of an energy–intensive separation process is to apply advanced heat–integrated and intensified techniques, such as heat pump assisted distillation, double–effect heat integration, thermally coupled distillation, and dividing wall columns (DWC) [14–17]. Remarkably, DWC is one of the best examples of a proven intensified technique in distillation because it can reduce the operating and investment costs significantly while also achieving a great reduction of CO₂ emissions [15–17]. Recent studies reported the use of a DWC to enhance the bioethanol dehydration process [7,9], but they did not consider the most energy–intensive step, the preconcentration process. To the best of the authors’ knowledge, none of the studies used advanced process intensification and integration techniques for the whole bioethanol separation process from an actual fermentation broth, particularly with those processes using lignocellulosic feedstock as the raw material.

This paper proposes a novel heat–integrated and intensified biorefinery design for CE production from actual lignocellulosic biomass. For the preconcentration section, heat pump assisted distillation and double–effect heat integration were evaluated. For the dehydration section, in addition to heat integration, process intensification, which is an extractive dividing wall column (EDWC), was applied to enhance the energy and cost efficiency of the purification process. Furthermore, a biosolvent, bioglycerol, which may be produced from biodiesel production was used as an extracting solvent in EDWC to obtain a high degree of integration in a biorefinery context. The structure of the EDWC was optimized using the reliable response surface method (RSM), which was carried out in Minitab statistic software. All configuration alternatives were simulated rigorously using Aspen Plus and evaluated based on the energy requirements, total annual costs (TAC), and total carbon dioxide emissions (TCE). Moreover, the contribution of proposed process on the absolute production cost for CE that can be used to assess its competitiveness and market potential with corn ethanol and petroleum–based fuels was explored.

2. Methodologies

2.1. Design

In this study, inspired from the CE production process developed at NREL (National Renewable Energy Laboratory in the US) [8], several alternatives for the separation process of CE were proposed and simulated using Aspen Plus V8.8. The lignocellulosic biomass type used in this process was corn stover, which is the most abundant agriculture residue in the US. This feedstock was comprised of 17.9 wt.% soluble material (ethanol, sucrose, extractable inorganics, and other water extractable material), 31.9 wt.% glucan, 18.9 wt.% xylan, 13.3 wt.% lignin, and the balance being other components [18]. Fig. 1 illustrates the cost contribution details from each process area (per gallon CE) in the NREL process [8]. The distillation and solids recovery section, which is the motivation of this study, accounts for 5.6% of the CE selling price ($2.14/gallon in 2007$).

In this purification process, the feed mixture with detailed composition listed in Table 1 is the fermentation broth obtained from the CE fermentation process. This complex broth stream contains a large number of compounds in three phases, resulting in a more complicated separation process.

Fig. 2 presents a systematic procedure to improve the CE purification process. First, the CE base case was designed and optimized based on the NREL reference case [8]. In particular, the pre-concentration part was kept same as the NREL case while the dehydration part was designed using extractive distillation with bioglycerol solvent. After achieving the optimal base case, the CE process was then explored for heat integration opportunities. Two common heat integration techniques such as heat pump and double–effect were applied and evaluated in detail. In the next step, process intensification techniques were assessed to improve process performance further. Two columns in the traditional ED configuration were combined into one compact column, EDWC. Subsequently, the feasibility of combining both process intensification and heat integration techniques was carried to maximize the process efficiency. In addition to energy–saving comparison, all alternatives were also compared in terms of process economics and environmental impact. Through this framework, a promising process for CE purification from actual fermentation broth was proposed with detailed design and operating condition.
2.2. Simulation

Physical property data for all insoluble solid components are not available in the native Aspen database. Therefore, these data were taken from the NREL database [8], which was developed specially for simulating biofuel components in Aspen Plus. Meanwhile, physical property data of other components were taken from Aspen V8.8’s native databanks. Basically, the need to distill ethanol and to handle dissolved gases, NRTL (Non–Random Two–Liquid) was used for the liquid activity coefficient model and Henry’s law for dissolved gases. In addition, because the feed mixture composed carboxylic acids such as acetic acid, HOC (Hayden–O’Connell) equation of state, which can predict the solvation of polar compounds and dimerization was used for the vapor phase model [19]. In Aspen Plus, insoluble solid components were defined as “solid” components, which were not performed using the vapor–liquid equilibrium, whereas other components such as gases, soluble solids and liquid were defined as “conventional” components.

All distillation columns were simulated using Radfrac model in Aspen Plus. The column diameter was determined using a column flooding condition that fixes the upper limit of the vapor velocity. As the normal operating velocity from 70 to 90% of the flooding velocity [20], a load of approximately 85% of the load at the flooding point was designed for all distillation columns. The design of the preconcentration process was taken from the NREL as the base case.

### Table 1

Feed mixture conditions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Flowrate (kg/h)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>552</td>
<td>Gas (0.12 wt.% )</td>
</tr>
<tr>
<td>Ethanol</td>
<td>21,944</td>
<td>Ethanol (4.86 wt.% )</td>
</tr>
<tr>
<td>Water</td>
<td>378,966</td>
<td>Water (84.01 wt.% )</td>
</tr>
<tr>
<td>Glucose</td>
<td>3842</td>
<td>Soluble solids (5.74 wt.% )</td>
</tr>
<tr>
<td>Xylose</td>
<td>1384</td>
<td></td>
</tr>
<tr>
<td>Extractive</td>
<td>12,200</td>
<td></td>
</tr>
<tr>
<td>Soluble lignin</td>
<td>657</td>
<td></td>
</tr>
<tr>
<td>Hydroxymethylfurfural</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>Furfural</td>
<td>336</td>
<td></td>
</tr>
<tr>
<td>Lactic acid</td>
<td>1695</td>
<td></td>
</tr>
<tr>
<td>Xyritol</td>
<td>814</td>
<td></td>
</tr>
<tr>
<td>Glycerol</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Succinic acid</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>2482</td>
<td></td>
</tr>
<tr>
<td>Ammonium acetate</td>
<td>1861</td>
<td></td>
</tr>
<tr>
<td>Diannmonium phosphate</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Oleic acid</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>1351</td>
<td>Insoluble solids (5.26 wt.% )</td>
</tr>
<tr>
<td>Xylan</td>
<td>913</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>12,477</td>
<td></td>
</tr>
<tr>
<td>Protein</td>
<td>2865</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>4108</td>
<td></td>
</tr>
<tr>
<td>Microorganisms</td>
<td>1535</td>
<td></td>
</tr>
<tr>
<td>Tar</td>
<td>474</td>
<td></td>
</tr>
<tr>
<td>Total flowrate (kg/h)</td>
<td>451,071</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>6.1</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Cost contribution details from each process area (per gallon CE).

Fig. 2. Systematic approach for improvement of CE purification process.
while the dehydration process was designed. It is worth noting that all distillation columns designed by NREL can tolerate solids well and have a good efficiency. In particular, C1 and C2 operated at 48% and 76% tray efficiency, respectively while the effect of solid presence in auxiliary equipment was ignored. First, the initial structures of the columns in dehydration step were obtained using the Shortcut Distillation modules. All design parameters, such as the total number of trays, feed tray location, solvent tray location, and solvent–to–feed ratio were manipulated to reduce the energy requirements while maintaining the product purities and recoveries. According to the two popular standards, ethanol for blending with gasoline allows a maximum water content of 0.3 wt.% (prEN 15376 in Europe) and 1.3 wt.% (ASTM D 4806 in USA) [21]. Therefore, in this study the CE product was concentrated to a purity of 99.7 wt.% to satisfy all bioethanol standards.

2.3. Economic assessment

To determine the economics of CE production, the total investment cost (TIC), operating costs (TOC), and TAC of all process alternatives were estimated using the correlations from the Smith textbook [22]. For preliminary design purpose, an order–of–magnitude estimate with 25–40% error level is sufficient [23]. Therefore, of all the works related to equipment cost calculation, Guthrie’s modular method described in [23,24] was applied. The Tray Sizing function in Aspen plus was used to estimate the column diameters, tray spacing, and column heights. All reboilers, condensers, heat exchangers, column vessels, and tray stacks were considered in the TIC. The Chemical Engineering Index of 556.8 in 2015 was used to update the TIC estimation. The utility prices listed in Appendix A were used for the TOC calculation [24]. A plant lifetime of 10 years and a fixed rate of interest (8%) were assumed for TAC estimation.

2.4. Environmental impact

In addition to an economic evaluation, the carbon footprint of all processes was calculated to make a fair comparison of the environmental impact. Note that as a process uses different energy sources, such as a heat source (i.e. steam reboilers) and an electricity source (i.e. compressor), the paradigm of a lower energy being directly proportional to lower CO₂ emissions is not necessarily correct [25]. For example, the compressor always produces more CO₂ than the reboiler for the same energy requirement. In reality, electricity production fuel varies from fossil fuels to renewable energy; however, for a fair comparison, the electricity was considered to have been produced from natural gas, similar to steam generation. For steam reboilers, the Gadalla’s modular method was applied to calculate the CO₂ emissions [26]:

\[
[\text{CO}_2]_{\text{emiss}} = \left( \frac{Q_{\text{fuel}}}{\text{NHV}} \right) \left( \frac{C\%}{100} \right) \alpha
\]

where NHV is the net heating value of the fuel and C% is the carbon content. For natural gas, the NHV is 48,900 kJ/kg and C% is 0.41 kg/kg. The molar mass ratio of CO₂ and C was \( \alpha = 3.67 \). In addition, \( Q_{\text{fuel}} \) denotes the amount of fuel used, which was calculated as follows:

\[
Q_{\text{fuel}} = \left( \frac{Q_{\text{proc}}}{\lambda_{\text{proc}}} \right) \left( h_{\text{proc}} - 419 \right) \left( \frac{T_{\text{FTB}} - T_0}{T_{\text{FTB}} - T_{\text{stack}}} \right)
\]

where \( Q_{\text{proc}} \) is the heat duty requirement of the system, and \( \lambda_{\text{proc}} \) (kJ/kg) and \( h_{\text{proc}} \) (kJ/kg) are the latent heat and enthalpy of the steam, respectively. The flame, stack, and ambient temperatures were \( T_{\text{FTB}} \) (1800 °C), \( T_{\text{stack}} \) (160 °C), and \( T_0 \) (25 °C), respectively.

For the electricity power delivered by a gas turbine, \( Q_{\text{fuel}} \) can be calculated from the efficiency of a gas turbine (\( \eta_{\text{GT}} \)) and the Carnot factor (\( \eta_{\text{C}} \)) [26]:

\[
Q_{\text{fuel}} = \left( \frac{Q_{\text{proc}}}{\lambda_{\text{proc}}} \right) \left( \frac{1}{1 - \eta_{\text{GT}}} - \eta_{\text{C}} \right)
\]

3. Results and discussion

3.1. Conventional process

The process of CE production in this study was developed from the NREL process [8] with a production capacity of 180 kilotons annually. The feed mixture considered is the actual fermentation broth obtained from the fermentation process of biomass and consists of a number of components in three phases, as listed in Table 1. This feed is introduced to a series of distillation columns to achieve an anhydrous CE. Fig. 3 presents a simplified flowsheet.
of the conventional separation process of CE. In this sequence, the preconcentration section (C1 and C2) is kept the same as the NREL case [8] and the dehydration section (C3 and C4), which employs an extractive distillation process using a bioglycerol solvent, was optimized and designed. Initially, the fermentation broth was fed to the first distillation column to remove CO$_2$ in the overhead while insoluble solids and approximately 90 wt.% of water was delivered in the bottom stream. A forced–circulation reboiler was used in the C1 to accommodate solids in the bottom. The C1 bottom then preheats the feed stream before being sent to a centrifuge filter to carry out a liquid-solid separation. A liquid stream called stillage is delivered to the wastewater treatment section while the solid stream is sent to a lignin combustor to produce electricity and steam. The side vapor stream that recovers most of CE in the feed (99 wt.%) is then introduced to the second distillation column (C2) to produce water at bottom and the close azeotropic composition mixture between water and ethanol as the top vapor stream.

Extractive distillation is then employed to break the azeotrope to achieve anhydrous ethanol (99.7 wt.%). Currently, EG is the most common extractive solvent used in industry for the separation of ethanol–water azeotrope [11]. On the other hand, a green solvent should be used as a substitute for EG because of its adverse effects on the environment and human health. Interestingly, bioglycerol, which is a major by-product from biodiesel production is a promising solvent alternative not only because it is a green solvent, but also the use of bioglycerol can obtain a high degree of integration in a biorefinery context.

As shown in Fig. 4, no distillation boundary divides the composition profiles in different regions on both residue curve maps of water–ethanol–EG and water–ethanol–glycerol mixtures. Accordingly, bioglycerol can alter the relative volatility of the ethanol–water azeotrope, resulting in its possible use as a solvent in extractive distillation. In this study, the C2 top and bioglycerol were fed to the extractive distillation column (C3) to separate pure CE as the top, whereas a mixture of bioglycerol and water was delivered at the bottom before being introducing to the fourth distillation column (C4). The function of the C4 column is to separate water as the top stream and bioglycerol in the bottom stream. The solvent is then cooled before being recycled back to the C1 for reuse. Note that a small amount of makeup solvent stream is required because of the small losses of bioglycerol in the water and CE streams.

Because the CE composition in the C2 top is a key design variable for the bioethanol separation process [27], sensitivity analysis was carried out to determine its optimal value. Because of the azeotropic composition of 95.63 wt.% CE, the preconcentrated composition of CE was varied from 89 to 94 wt.%, while the product recoveries and purities of CE and bioglycerol in C2, C3, and C4 were kept the same in the conventional process. The process was optimized with the objective being the total energy of the C2, C3, and C4 columns. Fig. 5 shows that the minimum total energy use can be achieved when the CE preconcentrated composition is 93 wt.%. Note that if this composition is higher than the optimum, the energy of C2 increases significantly as it reaches close to the azeotropic composition, whereas the C3 and C4 require a lower energy considering the small amount of water that needs to be removed. On the other hand, if the CE preconcentrated composition is lower than the optimal value, a high CE concentration results in a decrease in C1 duty while the energy requirements of C3 and C4 increase considering the large amount of water that needs to be removed.
3.2. Heat integration of preconcentration process

Basically, all distillation processes could be explored for heat integration opportunities and a significant decrease in energy requirements can be obtained by applying the appropriate heat integration systems. In the following section, two types of heat integrated techniques were considered and are described in detail. The discussion and evaluation will focus on comparing the process economic and environmental performance.

3.2.1. Heat pump assisted distillation (HP)

Distillation is still the most common separation technology despite consuming approximately half of the operating costs of the chemical plants. This is because distillation has low thermodynamic efficiency that requires high energy at high temperatures in the reboiler, whereas a similar amount of energy is released at low temperature in the condenser [28]. The heat pump (HP) is a state-of-the-art system that can overcome this distillation drawback by pumping heat from a lower temperature to a higher temperature to improve overall energy efficiency. Recently, a simple equation for the feasibility of HP use in distillation was proposed [29]:

$$\frac{Q}{W} = \frac{1}{\eta} = \frac{T_c}{(T_h - T_c)}$$

where $T_c$ and $T_h$ (°C) are the condenser and reboiler temperatures, $\eta$ is the Carnot efficiency, and $Q$ (kW) and $W$ (kW) are the reboiler duty and work provided, respectively. If the $Q/W$ ratio is greater than 10, HP is strongly recommended, whereas HP use is not suggested if the $Q/W$ ratio lower than 5. Further evaluation is necessary in the case of the ratio between 5 and 10.

With a $Q/W$ ratio of 4, the use of a HP to pump heat from the C2 top to the C2 bottom is not attractive, whereas the use of a heat pump to pump heat from the C1 side stream to the C1 bottom is economically feasible with a $Q/W$ ratio of approximately 14. Fig. 6 presents a simplified flowsheet of HP use on the preconcentration process. On the other hand, the latent heat of the C2 side stream is also used to reduce the energy requirements in the C2. If the HP uses that latent heat to supply the C1 reboiler, the energy required in the C2 reboiler would certainly increase. Sensitivity analysis was carried out for a further evaluation. In particular, the compressor ratio was varied from 1 to 2.8 corresponding to the discharge temperature from 117 to 226 °C, in which the higher discharge temperature may cause compressor overheating problem. Note that the feed tray location of C2 was optimized by minimizing the reboiler duty while maintaining the product purity and recovery.

Table 3 lists the primary results of sensitivity analysis, including the energy requirements and total CO2 emissions. Basically, only a portion of the thermal energy given to the feed stream can reduce the energy required in the reboiler [30]. Thus, the amount of latent heat of the C2 side stream could not transfer totally to the heat sink of C2. In particular, as the compressor ratio increased, the C1 reboiler duty decreased significantly, whereas the C2 reboiler duty decreased gradually, leading to more energy benefit of HP use.

On the other hand, on a sustainability development point of view, the HP process can save up to 36.0% and 29.9% in terms of the TOC and TIC compared to the conventional preconcentration process. Remarkably, the HP process can save up to 36.0% and 29.9% in terms of the TOC and TAC, respectively, while increasing 107.8% of the TIC compared to the conventional preconcentration process. The high investment cost and process complexity related to using compression equipment are the disadvantages of using HP, which limit the use of HP in industry.

3.2.2. Double-effect heat integration (DHI)

The traditional HI of distillation column is based on the appropriate placement of the column in the temperature/pressure domain to make the best use of the process cold stream in the reboiler and process hot stream in the condenser [31]. Double-effect
heat integration (DHI), which is a common HI technique to improve the energy and cost efficiency of a distillation process, was investigated as the preconcentration process in this study. As shown in Fig. 3, the temperature and pressure of the C1 bottom (125°C and 2.3 atm, respectively) and C2 top (91°C and 1.6 atm), and a large amount of heat rejected in the C2 condenser can provide a promising opportunity to apply the DHI to the preconcentration process.

Table 3
Results of sensitivity analysis: key performance indicators as function of the compressor ratio.

<table>
<thead>
<tr>
<th>Pressure ratio</th>
<th>1</th>
<th>1.3</th>
<th>1.6</th>
<th>1.9</th>
<th>2.2</th>
<th>2.5</th>
<th>2.8</th>
</tr>
</thead>
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<tr>
<td>Compressor outlet temperature (°C)</td>
<td>117</td>
<td>143</td>
<td>165</td>
<td>184</td>
<td>200</td>
<td>214</td>
<td>226</td>
</tr>
<tr>
<td>Compressor duty (kW)</td>
<td>–</td>
<td>812</td>
<td>1484</td>
<td>2060</td>
<td>2567</td>
<td>3019</td>
<td>3297</td>
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<tr>
<td>C1 reboiler duty (kW)</td>
<td>38,429</td>
<td>38,177</td>
<td>37,508</td>
<td>28,875</td>
<td>18,707</td>
<td>10,974</td>
<td>9438</td>
</tr>
<tr>
<td>C2 reboiler duty (kW)</td>
<td>3487</td>
<td>3498</td>
<td>3510</td>
<td>4010</td>
<td>7918</td>
<td>14,810</td>
<td>15,913</td>
</tr>
<tr>
<td>Total reboiler duty (kW)</td>
<td>41,916</td>
<td>41,675</td>
<td>41,018</td>
<td>32,885</td>
<td>26,625</td>
<td>25,784</td>
<td>25,351</td>
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<tr>
<td>CO₂ emissions from compressor (ton/y)</td>
<td>–</td>
<td>3594</td>
<td>6570</td>
<td>9120</td>
<td>11,364</td>
<td>13,365</td>
<td>14,596</td>
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<tr>
<td>CO₂ emissions from reboilers (ton/y)</td>
<td>85,499</td>
<td>85,008</td>
<td>83,669</td>
<td>67,079</td>
<td>54,310</td>
<td>52,594</td>
<td>51,712</td>
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<td>Total CO₂ emissions (ton/y)</td>
<td>85,499</td>
<td>88,602</td>
<td>90,239</td>
<td>76,198</td>
<td>63,674</td>
<td>63,960</td>
<td>66,308</td>
</tr>
</tbody>
</table>

Fig. 7. Economic assessments of the HP and conventional preconcentration configurations.

Fig. 8 shows a simplified flowsheet of applying DHI of the preconcentration process with the key design parameters. The C1 pressure was decreased slightly from 2.3 to 1.5 atm at the bottom to reduce the temperature of the C1 bottom to 113°C, while the C2 pressure was increased from 1.6 to 4.6 atm at the top to achieve a temperature of the C1 top of 123°C. Accordingly, the heat source of C2 was used to supply the heat sink of C1 through a heat exchanger with the minimum temperature approach of 10°C. Changing the pressures of the two columns also leads to a change in the energy requirement of these columns. The reboiler duty of C1 is reduced from 38,429 to 8013 kW while the energy required in the C2 reboiler is increased from 3541 to 4866 kW.

Fig. 9. Comparison of key results between the HP and DHI alternatives for dehydration section.
Note that as the latent heat of the C2 top stream is totally transferred to the heat sink of C1, the feed to the ED process changes to a liquid phase. This means that amount of thermal energy given to this feed is reduced, leading to an increase in the energy requirements in the ED process. Nevertheless, only a portion of the thermal energy given to the feed stream can reduce proportionally the energy requirement in the reboiler [30]. In fact, the total energy requirement that was increased in the ED process (4836 kW) was much lower than the amount of energy that was reduced in the C1 (30,417 kW). Consequently, the simulation results showed that the DHI process can achieve energy savings of up to 52.3% compared to the entire conventional process. Fig. 9 shows the comparisons of key results between the HP and DHI configurations. Obviously, the DHI case can achieve much more benefits of energy requirements, costs and environmental sustainability than the HP case. This is because in DHI case, with only little changes of C1–C2 pressures, a large amount of latent heat of the C2 top was fully utilized; meanwhile in HP case, purchase of a costly compressor increased significantly the TIC and a large amount of heat in the C2 condenser was still rejected. Therefore, the DHI technology was proposed for improving the preconcentration process.

3.3. Heat integration and intensification of dehydration process

In the preceding section, the green conventional process of ED using bioglycerol was designed for the dehydration process. The use of advanced integrated and intensified techniques to improve the process further was explored. In this case, the EDWC (extractive dividing wall column) was applied to combine two conventional columns.

Designing DWCs is much more complex than conventional arrangements because of the greater number of degrees of freedom [32]. These degrees of freedom interact with each other and need to be optimized simultaneously for optimal column design. A common difficulty associated with DWC design is estimating the number of stages in each section [33]. Since the number of stages is an integer variable, column optimization is a mixed integer non-linear programming problem (MINLP). However, this method cannot be solved with commercially available process simulators, and solving the MINLP does not guarantee the global optimum in a non–convex problem. Meanwhile, the response surface methodology (RSM), which is simple and efficient to implement using Aspen Plus and Minitab software, has been used to optimize a complex column structure and bioprocess parameters. It allowed interactions between variables to be identified and quantified, thus the column structure was practically optimized with a minimum of simulation runs [34]. Consequently, the RSM was used to optimize the structure of the EDWC. Fig. 10 presents the detailed optimization procedure with the optimization target of the TAC minimum, which performs the optimal trade–off between the TIC and total energy requirements.

First, the initial structure of the DWC, key optimization variables, and variable ranges were determined by conducting several preliminary simulation runs. The solvent tray location input to the second stage of EDWC was found to be optimal in any case; then, the feed section (N1), wall section (N2), and bottom section (N3) were selected as the optimization variables, as shown conveniently in Fig. 11. Next, the Box–Behnken design was used under the RSM to design the simulation runs. Box–Behnken design that has three coded levels as $-1, 0, +1$ (low, medium, and high) derived from natural variables as listed in Table 4 can perform how variables interact and optimize the system with regard to TAC. In particular, 15 simulation runs were carried out and the TAC of each case was calculated. For each run, the internal vapor flow to the prefraction-
ator was adjusted to achieve the TAC minimum while maintaining the product purities and recoveries. Subsequently, the RSM then performed to fit the TAC results to a second-order polynomial model, and the following regression coefficients were obtained:

$$Y = 4,587,630 + 3550N_1 + 9724M_2 + 33,048N_3 + 5852N_1^2$$
$$+ 27,555N_2^2 + 18,782N_3^2 - 16,684N_1N_2 + 7589N_1N_3 - 5811N_2N_3$$

According to the RSM, a TAC minimum of $4,571,000 was predicted with the coded levels of the feed section (N1), wall section (N2), and bottom section (N3) of −0.2121, −0.3333, and −0.8788, respectively as shown in Fig. 12a. The resulting determination coefficient was $R^2 = 95.1$, which indicates that the model is suitable for the prediction within the range of simulated variables. Fig. 12b depicts the interactions between the optimization variables on the TAC. The optimal natural values of the variables were then derived from the coded variables and a rigorous simulation was then conducted. The rigorous simulation result of $4,513,700 showed good agreement with the value predicted from the RSM with a deviation of 1.2%. Eventually, the optimal structure of the TDWC with the key design parameters was obtained, as illustrated in Fig. 13. It is worth noting that as DHI was applied in the preconcentration section, the phase of feed–to–C3 changed to liquid instead of vapor in the original ED process (see Fig. 3). The latter reboiler duties of C3 and C4 were 6948 and 2300 kW, respectively. The results show that the EDWC configuration (8354 kW) can reduce the energy

<table>
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<tr>
<th>Case</th>
<th>Factor</th>
<th>Levels</th>
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<tbody>
<tr>
<td></td>
<td>Feed section (N1)</td>
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</tr>
<tr>
<td></td>
<td>Wall section (N2)</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Bottom section (N3)</td>
<td>2</td>
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**Table 4**

<table>
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<tr>
<th>Case</th>
<th>Factor</th>
<th>Levels</th>
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<tbody>
<tr>
<td></td>
<td>Feed section (N1)</td>
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</tr>
<tr>
<td></td>
<td>Wall section (N2)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Bottom section (N3)</td>
<td>10</td>
</tr>
</tbody>
</table>

**Fig. 12.** (a) Optimization plot by the RSM from Minitab, (b) contour plots of the interactions between the feed section (N1), wall section (N2) and bottom section (N3).
requirement by 11.1% compared to the conventional dehydration process. In particular, the temperature difference between the two sides of the wall is approximately 27 °C; thus, the EDWC can be implemented easily in the practical applications.

In addition to process intensification, heat integration was also evaluated to improve the energy efficiency of the dehydration process. The high temperature level on the bottom stream of EDWC allows to be utilized to preheat the feed stream, resulting in a reduction in its reboiler duty. The simulation results showed that the heat integration of the EDWC can save 10.0% of the energy requirements compared to the conventional EDWC.

3.4. Novel proposed CE process

Overall, both heat integration and process intensification were simultaneously applied to maximize process efficiency. In particular, DHI was suggested to the preconcentration section while EDWC was proposed for the dehydration section. Fig. 13 presents the novel proposed separation process of CE with the key design parameters from the actual fermentation broth stream. In addition, Fig. 14 compares the key results of the proposed process and conventional process including the TOC, TAC, and TCE. The results show that the proposed process can save up to 52.7% and 47.6% in terms of the TOC and TAC, respectively, while reducing 56.9% of the total carbon footprint compared to the conventional process. Furthermore, the use of bioglycerol as an extracting solvent for the dehydration step can provide a great opportunity to integrate the production process of the CE with the biodiesel production process, resulting in a high degree of integration in a biorefinery context. As compared to the NREL process, a slight change in operating pressure of C1 and C2 to apply DHI, and the EDWC was used for the dehydration section. As the distillation and solids recovery area accounts for 5.6% of the CE price (see Fig. 1), the TAC of the proposed process reduces 47.6% compared to the conventional purification section, resulting in a decrease of 2.7% of the bioethanol price from $2.15/gal to $2.09/gal in 2007. The proposed design for CE production using corn stover as a feedstock can be also considered for improving the CE production using other lignocellulosic feedstock.

Fig. 13. Schematic diagram of the proposed alternative for separation process of CE.

Fig. 14. Economic and environmental evaluations of the proposed process for CE production.
4. Conclusions

In this study, a novel heat–integrated and intensified biorefinery process for cellulosic ethanol production from actual lignocellulosic biomass was designed and optimized to be more energy–efficient. Heat pump assisted distillation and double–effect heat integration were explored and assessed for the preconcentration step while a combination of a heat–integrated technique and intensified technique, EDWC, was proposed for the dehydration step. The structure of the EDWC was optimized efficiently by the RSM using Aspen Plus and Minitab software. The use of bioglycerol as an extracting solvent leads to a high degree of integration in a biorefinery context, making the production process of CE more sustainable in the long term. All configuration alternatives were simulated rigorously using Aspen Plus based on the energy requirements, TAC, and TCE. Furthermore, the structure of the EDWC was optimized effectively using the reliable response surface method (RSM), which was carried out in Minitab. As a result, the proposed heat–integrated and intensified process can save on the TAC and TCE up to 47.6% and 56.9%, respectively, with respect to the conventional purification section. As the distillation and solids recovery part accounts for 5.6% of the CE selling price ($2.14/gallon in 2007$), the proposed process in contrast to NREL’s process can perform better the cost competitiveness and market penetration potential of CE in comparison with oil-based fuels and corn ethanol. Moreover, the proposed design of the CE separation process from corn stover feedstock can be also considered for improving the CE process from other lignocellulosic feedstock.

Acknowledgments

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Appendix A. Utility cost [24]

The cost of low pressure steam, medium pressure steam, and high pressure steam are 13.28, 14.19, 17.70 USD/GJ, respectively. The cost of cooling water is 0.354 $/GJ while electricity cost is 16.80 $/GJ.

References