Turning waste into value: eco-efficient recovery of by-products from biomass pretreatment in lignocellulosic biorefineries

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Abstract: This original research contributes to enhancing the viability of biorefineries through recovering valuable by-products from the liquid remaining after the biomass pretreatment by hot liquid water. A novel downstream processing method is developed for the recovery of acetic acid, formic acid, furfural and 5-hydroxymethylfurfural (HMF) by enhanced distillation. The major challenge in this research is the processing of the highly diluted initial solution (>96 wt% water) and the thermodynamic limitations owing to possible formation of several azeotropes. This new process recovers 78.7% of the acetic acid (99.8 wt%), while the rest of it is recycled back to the biomass pretreatment step together with most of the separated water from the initial solution. Over 99.5% of formic acid, furfural and HMF is also recovered, at purities of 74.7, 98.0 and 100 wt%, respectively. Vapor recompression and heat integration are implemented to decrease the energy use. The results demonstrate a 77.4% decrease in total annual costs (from $3.44 to 0.78/kgproduct), a 75.0% reduction in minimum average selling price (from $3.50 to 0.87/kgproduct), an 81.1% reduction in energy requirements (from 77.41 to 14.66 kWth/h/kgproduct) and an up to 99.7% decrease in CO2 emissions (from 11.17 to 0.03 kgCO2/kgproduct). © 2023 The Authors. Biofuels, Bioproducts and Biorefining published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

Key words: lignocellulosic biomass; biorefineries; biomass pretreatment; downstream processing; by-products recovery

Introduction

The long-term use of fossil fuels for energy and chemicals has resulted in significant environmental pollution and climate change. The need for sustainable development, as well as increasing concerns on reduced availability of fossil carbon sources, inevitably lead to the transition toward biofuels and bio-based chemicals.1 Biofuels produced from renewable sources have the potential to decrease dependence on fossil fuels and significantly reduce CO2 emissions.2 First-generation biofuels are produced from biomass that can also be used for nutritional purposes. Therefore, even though...
Lignocellulosic biomass is mainly composed of three polymers: 40–50% cellulose, 25–30% hemicellulose and 15–20% lignin, which are organized into a complex non-uniform matrix. Cellulose, the major constituent of lignocellulosic biomass, is a linear polymer of glucose. Hemicellulose is composed of several different amorphous polysaccharides. It can easily be decomposed to different monosaccharides, such as xylose, arabinose, glucose, galactose and mannose. Unlike cellulose, hemicellulose chains are usually branches. Lastly, lignin is a complex polymeric structure that provides sufficient strength and mechanical resistance to plant tissue. It is mainly composed of three phenylpropane units: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Owing to the complex and diverse structure of lignocellulosic biomass, it is recalcitrant to enzymatic hydrolysis and a pretreatment step is needed in order to enable conversion into fermentable sugars. Since this step can significantly contribute to the total cost in biorefineries (up to 30–40%), its enhancement has the potential to drastically increase the economic viability and competitiveness of biorefineries. One possible approach to this is to recover and valorize the by-products that are generated during the biomass pretreatment step (Fig. 1). To the best of our knowledge, there are no process designs proposed in the literature for the by-product recovery. Thus, this study investigates in more detail the opportunity to enhance the lignocellulosic biorefineries by recovering valuable by-products after biomass pretreatment.

Numerous different methods have been proposed for treating lignocellulosic biomass before the enzymatic hydrolysis step. These methods can be divided into physical pretreatments, chemical pretreatments, biological pretreatments and their combinations. The limitation of physical pretreatment methods is high cost owing to extensive energy usage. A common problem with chemical pretreatment methods is the usage of additional chemicals, which might facilitate the pretreatment step but can significantly complicate the downstream processing. Lastly, for biological pretreatment methods, which often result in low yield and long reaction time, more efficient processes need to be developed.

Due to the lack of additional chemicals, hot liquid water and steam explosion pretreatment methods are potentially eco-efficient solutions. The hot liquid water pretreatment method implies treating biomass with hot liquid water at temperatures between 160 and 190°C in order to increase its digestibility. During this process, water removes most of hemicellulose and part of lignin, leaving cellulose more accessible for enzymatic hydrolysis. This biomass pretreatment process does not require additional catalysts, as hydronium ions, which are formed by autoionization of water, act as catalysts. Pretreatment by steam explosion consists of short exposure of biomass to high pressure and temperature, followed by rapid depressurization. The result is disruption of the biomass matrix that increases the accessibility of cellulose for enzymatic hydrolysis. Even though both described methods are proved to effectively pretreat lignocellulosic biomass, the hot liquid water method offers several advantages compared with steam explosion: milder operating conditions, lower energy requirements since high-pressure steam does not have to be generated, reduced equipment complexity without the need for high-pressure reactors, and the absence of the risk of soluble lignin.

Figure 1. Simplified scheme of biomass pretreatment with by-product recovery (designing the by-product recovery process is the focus of this research study).
component precipitation. Additionally, it offers the possibility to recover and valorize generated by-products.

After pretreating the biomass using hot liquid water method, the solid fraction is processed further in enzymatic hydrolysis and fermentation steps. The monosaccharides in the remaining liquid may also be fermentable, but owing to the presence of by-products that act as fermentation inhibitors, the value of the remaining liquid is relatively low. Therefore, the main focus of this research is downstream processing of this liquid, which might otherwise become a waste stream. The major challenge in the analyzed process is to recover the generated by-products from a very dilute solution remaining after biomass pretreatment by hot liquid water. Correspondingly, improved separation techniques need to be implemented in order to obtain by-products in forms that satisfy market purity requirements.

The original contribution of this research is novel process design for recovery of valuable by-products generated during the industrial biomass pretreatment step. The proposed processing sequence, consisting of several distillation steps, is designed for the large industrial operational scale. Advanced heat pumping and heat integration techniques are used to improve overall process performance. Acetic acid, formic acid, furfural and 5-hydroxymethylfurfural are recovered in forms that satisfy the market requirements. Implementing the results of this study at an industrial scale would not only eliminate expenses associated with disposing or treating the waste water stream that remains after the biomass pretreatment step, but also result in an additional profit since all the recovered by-products can be valorized on the market.

Methods

The main objective of this original research is to develop an optimal process design for the recovery of generated by-products after hot liquid water pretreatment of poplar biomass. Poplar biomass has been widely studied for this pretreatment, and can lead to a dilute solution (>96 wt% water) of different valuable by-products. Hydrolysis of acetyl groups in the hemicellulose chain results in the formation of acetic acid. Degradation of pentoses from hemicellulose, mainly xylose and arabinose, leads to formation of furfural. On the other hand, 5-hydroxymethyl furfural (HMF) is the result of the degradation of hexoses, mainly glucose, galactose and mannose. Decomposition of furfural can result in the formation of formic acid, while decomposition of HMF can result in the formation of formic acid and levulinic acid. Besides being economically valuable, these components are known to inhibit fermentation reactions, as mentioned previously. Accordingly, their removal offers a possibility to obtain higher bioethanol yields. In addition to the mentioned components, the liquid remaining after the biomass pretreatment by hot liquid water might also contain dissolved sugars and different solubilized lignin components. The composition of this liquid, which is also the feed stream for the designed by-products recovery process, is taken from the experimental data reported by our research group at TU Delft and presented in Table 1.

Different methods have been studied in the literature for the recovery of the involved components from dilute solutions, such as precipitation, membrane separation, chromatography and liquid–liquid extraction. However, common drawbacks of these recovery methods are insufficiently high recovery yields and the use of additional chemicals, which complicates further processing. Additionally, scale-up is often not considered as research is only done at lab-scale. Therefore, distillation is chosen as the main fluid separation technique for this process. Since it does not require additional chemicals, it can potentially present an eco-friendly solution with the possibility of recovering all generated by-products. To design recovery by distillation, rigorous simulations for every process operation are developed in Aspen Plus.

Components present in the feed stream are specified according to the recommendations from the literature. Since the initial solution contains different carboxylic acids, the thermodynamic properties are specified using the NRTL property method coupled with Hayden-O’Connell correction model for vapor phase association.

There are several challenges for by-product recovery from the defined solution. A very dilute solution remaining after the biomass pretreatment step (>96 wt% water) complicates the recovery process. Additionally, the components present in the feed stream can potentially form three azeotropes: water–furfural, water–acetic acid–formic acid and water–formic acid. Lastly, the separation of acetic acid from aqueous solution is complex owing to the tangent pinch at high water concentrations. Properties of the components present in the feed stream, as well as potential azeotropes, are presented in Table 2.

Considering the thermodynamic properties of the components present in the feed stream, a specific order of separations is proposed. Owing to the highly dilute initial solution used, it is necessary to concentrate it by separating as much water as possible. Since furfural forms a light heterogeneous azeotrope with water (Fig. 2), furfural will be separated with water in the first separation step. The resulting water–furfural mixture is further treated by an additional distillation, while pure furfural can be recovered by simple liquid phase separation in a decanter owing to the heterogeneity of the mixture. From the remaining
components, the lowest boiling points are those of formic acid and acetic acid. Recovery of these components from the aqueous mixture is complex owing to the presence of four distillation regions (Fig. 2) and the possible formation of two azeotropes (water–acetic acid–formic acid and water–formic acid). Since the concentration of acetic acid in the feed stream is the highest of all by-products, its recovery is crucial. Therefore, in order to avoid the separation of formic acid, together with acetic acid and most of the remaining water, the next distillation step is performed at a temperature below the one required for the formation of the ternary azeotrope. Additional purification of the separated water–acetic acid mixture is required to obtain high-purity acetic acid, but this step is rather complex owing to the tangent pinch at high water concentrations. The remaining stream after the separation of acetic acid and most of the water contains mainly formic acid and heavier components. Owing to the large temperature difference, formic acid, with small amounts of remaining acetic acid and water, can easily be separated from HMF and other heavier components by distillation. If needed, this mixture can further be treated to obtain high-purity formic acid. In the final distillation step, HMF is separated from the dissolved sugars and solubilized lignin components, which can be sent to the enzymatic hydrolysis or fermentation depending on the state of hydrolysis of the present sugars.

Results and discussion

Process design

This section focuses on the optimal design for recovery of valuable by-products generated by the pretreatment of poplar biomass by hot liquid water. The processing capacity is designed for an industrial level application, assuming 8000 operating hours per year. The recovered by-products are acetic acid, formic acid, furfural and HMF, and all of them are obtained in forms that can be valorized in the market. The proposed process (Fig. 3) is composed of seven distillation columns and one decanter. The first step is to separate the

<table>
<thead>
<tr>
<th>Table 1. Condition and composition of feed stream and product streams.</th>
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<tbody>
<tr>
<td><strong>Stream</strong></td>
</tr>
<tr>
<td>Temperature (°C)</td>
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<tr>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>Mass flow (kg/h)</td>
</tr>
<tr>
<td>Mass fraction</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Acetic acid</td>
</tr>
<tr>
<td>Formic acid</td>
</tr>
<tr>
<td>Furfural</td>
</tr>
<tr>
<td>HMF</td>
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<tr>
<td>Levulinic acid</td>
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<tr>
<td>Glucose, xylose and other high-boiling components</td>
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Abbreviation: HMF, 5-Hydroxymethylfurfural.

<table>
<thead>
<tr>
<th>Table 2. List of components and azeotropes (boiling points at 1 atm).</th>
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<tbody>
<tr>
<td><strong>Pure components</strong></td>
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<tr>
<td><strong>Component</strong></td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Formic acid</td>
</tr>
<tr>
<td>Acetic acid</td>
</tr>
<tr>
<td>Furfural</td>
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<tr>
<td>Levulinic acid</td>
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<tr>
<td>HMF</td>
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<tr>
<td>Glucose</td>
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water–furfural light heterogeneous azeotrope as the top product in column C1. The high-purity furfural product is obtained by additional distillation in column C2 and phase separation in decanter DEC1. The proposed sequence results in 100% furfural recovery, while the purity of the obtained product is 98.0 wt%. The bottom product from column C2 is water, which is not a waste stream since it can be recycled to the biomass pretreatment step. Even after the separation of the water–furfural azeotrope, the remaining solution is still very dilute and the next step is to concentrate it in column C3. The top product of this column is mostly water, with 0.6 wt% acetic acid. About 15.9% of the initially present acetic acid is separated together with the water. This stream can be recycled to the biomass pretreatment step, as diluted acetic acid can increase the digestibility of biomass by providing the mild low pH required for the pretreatment step.28,33–35 Furthermore, recycling acetic acid to the pretreatment step leads to the enhancement of this step without using any

Figure 2. (a) Residue curve map for system water (W)–formic acid (FA)–acetic acid (AA), mole basis; (b) ternary diagram for system water (W)–furfural (FUR)–acetic acid (AA).

Figure 3. Conceptual design of the by-product recovery process.
additional chemicals. The effects of recycling this stream with diluted acetic acid is beyond the scope of this research, but it is proposed based on published results proving that this procedure does improve the outcome of the pretreatment step.28 However, the accumulation of acetic acid might also increase degradation in this step. Therefore, an additional experimental investigation would be needed before the implementation of the proposed recycling to a real industrial-scale biorefinery. The bottom product of column C3 is a less dilute solution of all components present in the feed stream, except for furfural. This stream is further distilled in column C4. Acetic acid, together with most of the remaining water, is separated as the top product. To obtain high-purity acetic acid, additional purification in column C5 is needed. In this way, 78.6% of the initially present acetic acid is recovered as the bottom product stream, at a purity of 99.8 wt%. Approximately 3.2% of acetic acid from the feed stream is separated with water as the top product of this column. This stream contains less than 0.2 wt% acetic acid and can also be recycled to the biomass pretreatment step. The bottom product from column C4 is mainly composed of formic acid and heavier components. The next step is to separate formic acid, with small amounts of the remaining acetic acid and water, as the top product in column C6. In this way, about 99.5% of formic acid is recovered in a stream that contains 74.7 wt% formic acid. Such composition (distillation area 3 in Fig. 2(a)) disables the high recovery of pure formic acid by simple distillation owing to the formation of the water–formic acid azeotrope. Additional purification of this stream might not be necessary as there are already applications36 and hence a market for 70 wt% formic acid solution. Alternatively, one potential solution is to apply reactive distillation with methanol, to overcome the thermodynamic constraints of azeotrope formation and recover the formic acid as methyl formate.37 The last separation is the recovery of HMF from other heavy components in column C7. With a recovery of about 99.9%, HMF is obtained as the 100 wt% top product of this column. The bottom product is composed of the remaining heavy components, mainly dissolved sugars and solubilized lignin components. Depending on the degree of hydrolysis, this stream can be sent either to the enzymatic hydrolysis or to the fermentation step. The stream conditions and compositions of the recovered by-products are shown in Table 1.

Summing up, this fluid separation process recovers acetic acid, formic acid, furfural and HMF in forms that satisfy market requirements in terms of purity. Notably, maximal amounts of all the generated by-products are achieved and nothing is wasted. The non-product streams containing mostly water, with small fraction of acetic acid, can be recycled to the biomass pretreatment step. Additionally, the stream with dissolved sugars and solubilized lignin components might still be useful within the bioethanol production process, although this needs testing. In a state-of-the-art process, without by-product recovery, the fermentable components present in this stream might be wasted and not used for biofuel production. Therefore, this original recovery process adds value without producing actually any additional waste stream.

### Design of the distillation sequence

Seven distillation columns are needed for the described by-product recovery process. The design parameters for each of these columns are presented in Table 3. Owing to the highly diluted feed stream, it is necessary to evaporate large amounts of water. Consequently, columns C1, C3, C4 and C5 have relatively large numbers of stages and high reboiler duties. On the other hand, these columns are separating close boiling components, which offers an excellent opportunity to use heat pumps.6 More precisely, mechanical vapor recompression (MVR) can be implemented on these columns to decrease their primary energy use. This solution implies compressing the top vapor from the column and then using it to evaporate the bottom liquid. However, in order to obtain an optimal heat exchange between the compressed top vapor and the bottom liquid, an appropriate pressure ratio for compressor discharge has

<table>
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<th>Table 3. Design parameters for distillation columns.</th>
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<tr>
<td><strong>Column</strong></td>
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<tr>
<td>No. of stages</td>
</tr>
<tr>
<td>Feed stage</td>
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<tr>
<td>Condenser pressure (bar)</td>
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<tr>
<td>Reboiler duty (MW)</td>
</tr>
<tr>
<td>Condenser duty (MW)</td>
</tr>
<tr>
<td>Reflux ratio, mole/mol</td>
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<tr>
<td>Column diameter (m)</td>
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</table>
to be chosen. In order to achieve a larger pressure ratio, a higher compressor duty is needed. This results in an increase in both equipment costs, owing to the need for larger compressors, and operating costs, owing to higher electricity usage. Conversely, a larger pressure ratio means a higher log-mean temperature difference (LMTD) in the reboiler, thus a lower 1/LMTD. Therefore, since the driving force for the heat exchange is higher, a smaller heat exchange area of the reboiler is needed. Furthermore, some physical constraints have to be taken into account when defining a pressure ratio of a compressor. Firstly, the discharge temperature of compressed vapor must not exceed a certain limit for safety reasons. Secondly, the LMTD for the reboiler has to be above a certain value in order to insure an efficient heat exchange. The schematic representation of the MVR system, as well as the dependence of compressor duty and LMTD of the reboiler on the pressure ratio of a compressor, is given in Fig. 4.

In the proposed optimal recovery process, MVR is applied to columns C1, C3, C4 and C5. Thus, the total need for utility usage is drastically decreased, which results in reduction of the operating cost, energy requirements and CO2 emission, making the whole process more sustainable. Mechanical vapor recompression is not implemented on column C2, which has a relatively low reboiler duty. The additional cost for the compressor for this column would be greater than the savings owing to the decreased usage of external heating and cooling. Mechanical vapor recompression is also not applied to columns C6 and C7, which apart from having low reboiler duties, also separate far boiling components.

Columns C1–C5 are operated at atmospheric pressure. Sieve trays are with a pressure drop of 8 mbar per stage are assumed for these distillation columns. However, in order to avoid thermal degradation, it is preferable for columns C6 and C7 to be operated at lower pressures. The operating conditions are chosen in such a way that it is possible to use cooling water for the condensing top vapor and steam for the evaporating bottom liquid in these columns. In this way, the requirement for more expensive utilities is avoided. The structured packing type Sulzer Mellapak 250, with a pressure drop of 0.225 mbar per theoretical stage, is assumed for internals for these columns. All the associated costs owing to the usage of vacuum pumps are included in the economic assessment.

Apart from implementing MVR, it is possible to obtain additional energy savings using heat integration or other process intensification options for fluid separations, such as cyclic distillation. In the proposed by-product recovery process, heat integration is implemented by using the heat content of the top product from the column C4 to evaporate the bottom liquid from the column C2. In this way, the need for external heating and cooling is decreased even more, resulting in lower total energy requirements, CO2 emission and operating costs. The complete flowsheet with implemented MVR and heat integration is presented in Fig. 5, along with key design and operation parameters.

**Economic analysis**

**Cost analysis**

A detailed economic analysis of both the base case (process without implementation of MVR and heat integration) and the enhanced process (with both MVR and heat integration) is performed. A comparison of different project costs before and after the implementation of MVR and heat integration is presented in Table 4. Total annual production costs are

![Figure 4. (a) Mechanical vapor recompression (MVR) heat pump design; (b) and dependence of the compressor duty and log-mean temperature difference (LMTD) on the pressure ratio.](https://onlinelibrary.wiley.com/doi/10.1002/bbb.2532)
calculated following the published national renewable energy laboratory (NREL) methodology\textsuperscript{43} that takes into account both total capital (CAPEX) and operating (OPEX) costs. Expenses related to the installation of process equipment are calculated using cost estimation correlations.\textsuperscript{44} The value used for the Marshall and Swift cost index in the equipment cost calculations is 1638.2 end of 2018.\textsuperscript{45} The total cost for expenses related to the installation of process equipment for the enhanced case is $13 288 000, whereby about 63% is the cost for the distillation columns (shells and internals), 15% for heat exchangers and 1% is the cost for decanter and pumps. However, the total equipment cost for the enhanced process is $33 274 000. This increase in the total equipment cost after installing all equipment units for the base case process is $13 288 000, whereby about 63% is the cost for the distillation columns (shells and internals), 15% for heat exchangers and 1% is the cost for decanter and pumps. Distribution of the costs for specific types of equipment for the enhanced case process is presented in Fig. 6.

The CAPEX includes the installed equipment cost, site development, additional piping, field and prorateable expenses, warehouse, home office and construction, project contingency, working capital and other costs. It is calculated according to the published methodology,\textsuperscript{43} leading to the cost contributions shown in Fig. 6. The CAPEX calculated in this way equals $240 001 000 for the base case process and $612 350 000 for the enhanced process. The increase in the total equipment cost after implementing MVR and heat integration is the main reason for the increase in CAPEX by about 155.1%.

The OPEX is calculated following the same published procedure as for CAPEX.\textsuperscript{46} In this calculation, not only the utility cost, but also the cost for feedstock, additional chemicals, waste disposal, operating labor, maintenance and property insurance are also taken into account. Expenses owing to utilities usage are determined following the recommendations from the literature. The following utilities cost are considered: $16.8/GJ for electricity, $7.78/GJ for low-pressure steam, $8.22/GJ for medium-pressure steam, $9.88/GJ for high-pressure steam, $4.43/GJ for chilled water and $0.35/GJ for cooling water.\textsuperscript{46} This leads to $69 616 000/year of total OPEX for the base case process, and only $10 166 000/year for the enhanced process. This drastic decrease of about 85.4% in the total OPEX is a result of implementing MVR and heat integration. More precisely, the maximized recovery of heat contained in the process results in minimization of requirements for external heating or cooling. Therefore, the much lower amount of utilities needed leads to a lower OPEX.
In the base case process, by far the largest part of the OPEX (about 94%) is the cost for low-pressure steam, which is used to evaporate bottom liquid from columns C1–C5. After the implementation of MVR, the need for external heating for columns C1 and C3–C5 is avoided. By integrating the top stream from column C4 and bottom stream from column C2, there is also no need for external heating for column C2. Hence, after enhancing the base case process, the use of low-pressure steam is completely avoided. The requirements for external cooling for these columns are also minimized.

The distribution of costs for specific parts of OPEX for the enhanced process is presented in Fig. 6. Owing to the use of four compressors, OPEX is mainly determined by the cost for electricity (72%). The total operating labor cost is also significant (16%), while the other parts of OPEX have a lower share.

Total annual costs (TAC) were calculated using 10 years of payback time. The value of TAC for the base case process is equal to $72,016,000/year, while for the enhanced process this cost is reduced to $16,289,000/year. Since OPEX is dominant over CAPEX in the calculation of TAC, even though CAPEX is increased after the implementation of MVR and heat integration, significant reduction in OPEX results in about 77.4% decrease in TAC.

The benefits of applying MVR and heat integration are even more obvious if the costs are expressed per kg product as the basis. The OPEX and TAC per kilogram of product are $3.33 and 3.44/kgproduct respectively for the base case process and only $0.49 and 0.78/kgproduct for the enhanced process. Therefore, the implementation of MVR and heat integration significantly lowers the total costs, resulting in a better economic viability of the process.

**Minimum average selling price analysis**

In addition to the cost estimation, the already mentioned calculation methodology is used to determine the minimum average selling price (MASP) of recovered products both for the base case process and for the enhanced process. The obtained values are compared with the weighted average price that can be realized on the market ($1.07/kg). The calculated MASP for the base case is $3.50/kg which is much higher than the average market selling price, leading to an unprofitable process. On the other hand, the implementation of MVR and heat integration decreased the MASP by about 75.0%, to a competitive value of $0.87/kg. In order to evaluate the obtained MASP, a comparison with previously reported values was performed. The literature MASP is calculated using minimum selling prices for specific products reported in the literature and the production capacity analyzed in this research study. A MASP value of $1.06/kgproduct was obtained by this procedure. Therefore, the proposed novel recovery process is highly competitive and presents an economically viable and profitable process.

### Table 4. Key performance indicators.

<table>
<thead>
<tr>
<th>Key performance indicators</th>
<th>Base case process</th>
<th>Enhanced process</th>
<th>Reduction (%)</th>
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<tr>
<td><strong>Economic indicators</strong></td>
<td></td>
<td></td>
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<tr>
<td>CAPEX (k$)</td>
<td>24,001</td>
<td>61,235</td>
<td>n/a</td>
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<tr>
<td>OPEX (k$/year)</td>
<td>69,616</td>
<td>10,166</td>
<td>85.4</td>
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<tr>
<td>OPEX ($/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>3.33</td>
<td>0.49</td>
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<tr>
<td>TAC (k$/year)</td>
<td>72,016</td>
<td>16,289</td>
<td>77.4</td>
</tr>
<tr>
<td>TAC ($/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>3.44</td>
<td>0.78</td>
<td></td>
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<tr>
<td>MASP ($/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>3.50</td>
<td>0.87</td>
<td>75.0</td>
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<tr>
<td><strong>Sustainability metrics</strong></td>
<td></td>
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</tr>
<tr>
<td>Thermal energy requirements (kW&lt;sub&gt;th&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>77.41</td>
<td>0.17</td>
<td>99.8</td>
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<tr>
<td>Electrical energy requirements (kW&lt;sub&gt;el&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>n/a</td>
<td>5.80</td>
<td>n/a</td>
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<tr>
<td>Primary energy requirements (kW&lt;sub&gt;el&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>77.41</td>
<td>14.66</td>
<td>81.1</td>
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<tr>
<td>Material intensity (kg&lt;sub&gt;material&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fresh water requirements (m&lt;sub&gt;water&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>13.44</td>
<td>0.73</td>
<td>94.6</td>
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<tr>
<td>Fresh water loss (m&lt;sub&gt;water&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>0.99</td>
<td>0.05</td>
<td>94.9</td>
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<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; emissions (kgCO&lt;sub&gt;2&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>11.17</td>
<td>3.06 (0.03)</td>
<td>72.6/99.7</td>
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<tr>
<td>Toxic emissions (kg&lt;sub&gt;toxic&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pollutant emissions (kg&lt;sub&gt;pollutant&lt;/sub&gt;/kg&lt;sub&gt;product&lt;/sub&gt;)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Electricity from non-renewable sources/green electricity.*
Figure 6. Cost contribution to the installed equipment cost, capital costs (CAPEX) and operating costs (OPEX).
Sensitivity analysis

Since cost and MASP estimation are subject to uncertainty,\(^43\) sensitivity analysis is performed to further investigate the profitability of the proposed process design. The influence of changes in different cost contributors on the MASP is given in Fig. 7. The purchase cost of the equipment has the highest impact on the MASP, whereby with about 50% increase in the equipment cost the MASP becomes higher than the average market selling price (assuming that the average market selling price does not change). The second highest impact on the MASP is that of the electricity. The analyzed process would still be profitable up to an increase of almost 60% in the electricity cost. The impact of the total labor cost on the MASP is significantly lower and even with a 100% increase in labor costs the process is still profitable. Lastly, the costs of cooling water and high-pressure steam have an extremely small impact on the MASP. This is due to the low cost of cooling water relative to the cost of other utilities and the low consumption of high-pressure steam.

Moreover, an additional analysis showed that the MASP is lower than the average market selling price even if concentration of acetic acid in the feed stream is reduced from 1.75 to only 1 wt%. However, an increase in acetic acid concentration in the feed stream would result in a more profitable process.

Sustainability metrics

Process sustainability analysis is done using the following metrics from published methodology:\(^49,50\) energy intensity, material intensity, water consumption, toxic emissions, pollutant emissions and greenhouse gas emissions. Lower values of these metrics indicate better performance.

- **Energy intensity** is expressed as ratio between used energy and the total product flowrate.\(^49,50\) Thermal energy requirement for the base case is 77.41 kW\(_\text{th}h/\text{kg}_{\text{product}}\), while for the enhanced process it is 0.17 kW\(_\text{th}h/\text{kg}_{\text{product}}\). The drastic reduction of about 99.8% is due to decreased need for external heating after the implementation of MVR and heat integration. The electrical energy requirement for the base case process is negligible, but for the enhanced case it is 5.80 kW\(_e\text{h/ kg}_{\text{product}}\) (as a result of the compressor usage). For the calculation of the total energy requirements an electric
to thermal conversion factor of 2.5 is used to take into account the inefficiencies in power generation. As a result, the total energy requirement of 14.66 kWth/h/kg_{product} for the enhanced case process is much lower than 77.41 kWth/h/kg_{product} for the base case process. Hence, the implementation of MVR and heat integration results in about 81.1% total energy savings.

- **Material intensity** represents the mass of produced waste per unit of output. The amount of waste can be calculated as the difference between inputs and outputs for the by-product recovery process. Since both the base case and the enhanced case have same inputs and outputs, there is no difference in material intensity. The only input is the feed stream, with a flowrate of 110 000 kg/h. The outputs are: acetic acid (1514.5 kg/h), furfural (333.8 kg/h), formic acid (626.0 kg/h), HMF (141.1 kg/h), three streams containing water and small amounts of acetic acid (106 475.5 kg/h in total) and a stream with dissolved sugars (909.1 kg/h), being in total 110 000 kg/h. Therefore, there is no waste produced and material intensity is equal to zero.

- **Water consumption** is an indicator that presents the ratio of water amount consumed per unit output. The defined temperature range for cooling water is from 20 to 25°C. Since the total (condenser) cooling duties for the base case and the enhanced process are −203.3 and −11.1 MW_{th} respectively, the required water flowrates are 35 000 and 1904 m\(^3\)/h, respectively. Expressed per kilogram of product as the basis, the amount of cooling water used is 13.38 m\(^3\)/kg_{product} in the base case and 0.73 m\(^3\)/kg_{product} in the enhanced process. Losses of cooling water caused by evaporation have to be compensated by fresh water. According to the calculation methodology, about 7% of cooling water is lost. Thus, the amount of lost water is 2450 m\(^3\)/h, for the enhanced case. Additionally, about 70% of steam condensate recovery is assumed to include potential steam leaks, condensate losses, steam trap failures and other possible inefficiencies in the steam generation and usage.

Taking this into account, the total fresh water requirements are 13.44 and 0.73 m\(^3\)/kg_{product} for base case and enhanced process respectively. Therefore, apart from drastically decreasing the energy requirements, the use of MVR and heat integration also results in a 94.6% reduction in water consumption. Additionally, the total specific loss of fresh water is decreased by about 94.9%, from 0.99 to only 0.05 m\(^3\)/kg_{product}.

- The **GHS emission** indicator represents the amount of carbon dioxide (CO\(_2\)) emitted per product unit and it is calculated as described in the literature. Since the use of electricity in the base case process is negligible compared with the thermal energy requirements, the CO\(_2\) emission in this case is 11.17 kg_{CO2}/kg_{product} regardless of the electricity source. After the implementation of MVR and heat integration, the usage of electricity becomes significant owing to the compressors needed for the MVR heat pump systems. Therefore, the source of electricity notably affects the CO\(_2\) emission. If grey electricity (sourced from fossil fuels) is used for supplying power to compressors, the CO\(_2\) emission is reduced to 3.06 kg_{CO2}/kg_{product} (72.6% savings relative to the base case). However, if green electricity is used, the total emission of CO\(_2\) is only 0.03 kg_{CO2}/kg_{product} (99.7% savings relative to the base case).

- **Toxic materials and pollutants.** Since the designed process does not emit toxic materials or pollutants, the metrics describing these factors are equal to zero.

A comparison of the analyzed sustainability metrics before and after implementing MVR and heat integration is given in Table 4. Material intensity, toxic emission and pollutant emission indicators are the same for both the base case and the enhanced case since no waste, toxic materials or pollutants are produced. However, enhancing the base case process leads to a drastic decrease in energy requirements, water consumption and CO\(_2\) emissions. This is the result of changing the initial process flowsheet in a way that maximizes the use of energy already contained in the process and that minimizes the use of external energy sources. Consequently, the obtained result is more environmentally friendly process design.

### Conclusions

The novelty of this original research has been proved by a feasible optimal process design for the recovery of valuable by-products from the liquid remaining after the hot liquid water pretreatment of lignocellulosic biomass. The newly designed process can recover acetic acid, formic acid, furfural and HMF in forms that can be valorized on the market. Improved separation methods have to be used in order to recover these components from a very dilute initial solution (>96 wt% water) and overcome thermodynamic limitations owing to the possible formation of three azeotropes (water–furfural, water–acetic acid–formic acid and water–formic acid), as well as the tangent pinch in water–acetic acid mixtures. About 78.6% of acetic acid is recovered as the high-purity product stream (99.8 wt%), while the rest of it is in forms of diluted aqueous solutions that can be recycled to the biomass pretreatment step in order to increase biomass digestibility. Recoveries of all the other components are higher than 99.5%, whereby the purities of the product streams are 74.7 wt% for formic acid, 98.0 wt% for furfural and 100 wt% for HMF. This process does not have any waste streams, as the separated water can be recycled back to the biomass pretreatment step, while the dissolved sugars and solubilized lignin components may be kept in the bioethanol production process.
In order to get more environmentally friendly process by decreasing energy use, MVR and heat integration were successfully applied. The main results of this enhancement are: a 155.1% increase in CAPEX (from $24001,000 to 61,235,000), an 85.4% reduction in OPEX (from $3.33 to 0.49/kg_product), a 77.4% reduction in TAC (from $3.44 to 0.78/kg_product), with a payback time of 10 years, an about 75.0% reduction in MASP (from $3.50 to 0.87/kg_product), an 81.1% reduction in the primary energy requirements (from 77.41 to 14.66 kWh/kg_product), a 94.6% reduction in fresh water requirements (from 13.44 to 0.73 m³/kg_product), and a 72.6% reduction in CO₂ emission if grey electricity is used (from 11.17 to 3.06 kg CO₂/kg_product) or a 99.7% reduction in the CO₂ emission if green electricity is used (from 11.17 to 0.03 kg CO₂/kg_product). Hence, the implementation of MVR and heat integration drastically increases the economic viability and sustainability of the proposed process, despite an initially larger CAPEX requirement.

References

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Original Article: Eco-efficient recovery of by-products from biomass pretreatment


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