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**DOI**

[10.1016/B978-0-443-15274-0.50336-X](https://doi.org/10.1016/B978-0-443-15274-0.50336-X)

**Publication date**

2023

**Document Version**

Final published version

**Published in**

Computer Aided Chemical Engineering

**Citation (APA)**

Janković, T., Straathof, A. J. J., & Kiss, A. A. (2023). Enhanced hot-liquid water pretreatment of biomass with recovery and valorization of side products. In A. Kokossis, M. C. Georgiadis, & E. N. Pistikopoulos (Eds.), *Computer Aided Chemical Engineering* (pp. 2113-2118). (Computer Aided Chemical Engineering; Vol. 52). Elsevier. <https://doi.org/10.1016/B978-0-443-15274-0.50336-X>

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## Enhanced hot-liquid water pretreatment of biomass with recovery and valorization of side products

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### Abstract

Lignocellulosic biomass potentially represents a great feedstock for biofuel production, but its' pretreatment needs to be enhanced in order to make biorefineries competitive with fossil fuel based alternatives. One way to make biorefineries more economically viable is to recover and valorize all generated by-products during the biomass pretreatment step. The main goal of this original research is to design an optimal process for recovering valuable by-products after hot-liquid water pretreatment of poplar biomass. Rigorous models for all operations included in the recovery process are developed using Aspen Plus as a CAPE tool. An optimal downstream processing sequence, consisting of multiple distillation steps, is designed to recover several valuable components, such as acetic acid, formic acid, furfural and 5-hydroxymethyl-furfural (HMF).

**Keywords:** biorefineries, lignocellulosic biomass, valorization, distillation

### 1. Introduction

The increasing concerns on environmental pollution and reduction of available fossil carbon sources lead to a need for a transition towards biofuels and bio-based chemicals from renewable sources. Technologies for the production of the first generation biofuels are already well established. On the other hand, their implementation directly competes with global food production as the first generation biomass can also be used for food supply. The potential solution is usage of lignocellulosic biomass as a source for biorefineries. As the second generation feedstock, it is a non-food crop that can be easily grown on land not suitable for food production. Therefore, the production of biofuel and biochemicals from lignocellulosic biomass does not threaten the food production process (Chiaromonti et al., 2013).

However, technologies and markets for conversion of the second generation feedstocks are still not well established. In order to become competitive with fossil-based production, biorefineries need to be more economically viable (Kiss & Infante Ferreira, 2016). Due to the complexity of the lignocellulosic biomass structure, the pretreatment step is needed to facilitate further conversion of lignocellulosic components to fermentable sugars. Since this process step significantly contributes to the total costs (up to 30-40%) (Ramaswamy et al., 2013), its' enhancement can drastically increase the viability of biorefineries. One way to improve the competitiveness of biorefineries is to recover and valorize valuable by-products generated during the biomass pretreatment step, which has not been the subject of many studies so far. This research gap is covered in this study.

## 2. Problem statement

### 2.1. Enhanced biomass pretreatment step

A common problem with different pretreatment methods is usage of additional chemicals. These chemicals might facilitate the pretreatment step but complicate downstream processing, as well as valorization of generated by-products. In that context, hot-liquid water pretreatment potentially presents an eco-friendly solution due to relatively mild process conditions, lack of additional chemicals, low process costs and a possibility to recover and valorize formed by-products (Chen et al., 2022).

### 2.2. Recovery of valuable by-products from the pretreatment step

After the biomass pretreatment step by hot-liquid water, the solid fraction is sent to enzymatic hydrolysis while the potential value of the liquid fraction is usually neglected. This research focuses on downstream processing of the liquid fraction after hot-liquid water pretreatment of poplar biomass. The main goal is to fully recover valuable by-products (e.g. acetic acid, formic acid, furfural, HMF). These components are not only economically valuable, but they can also inhibit fermentation reactions. Therefore, their removal will result in higher bioethanol yields. A crucial problem regarding by-product recovery is a very dilute solution after the pretreatment step (Kiss et al., 2016). Consequently, improved fluid separation processes are needed in order to recover by-products in a high-purity form that can be valorized on the market.

## 3. Methodology/Approach

The main objective of this research is to develop an optimal way to recover by-products from the liquid obtained after hot-liquid water pretreatment. The composition of the liquid, which is the feed stream for the designed downstream processing sequence, is obtained from literature (Jiminez-Gutierrez, 2023) and is presented in Table 1. This stream is diluted solution of different products generated by pretreatment of poplar biomass. Acetic acid is formed by hydrolysis of acetyl groups in the hemicellulose chain. C-5 sugars (mainly xylose and arabinose) from hemicellulose can degrade to furfural, while C-6 sugars (mainly glucose, mannose and galactose) from both cellulose and hemicellulose can degrade to HMF. Formic acid can be generated from both furfural and HMF, while levulinic acid can be formed by degradation of HMF. Rigorous Aspen Plus simulations are developed for every process operation. Components are defined in Aspen Plus according to the literature (Aspen Technology, 2021). Due to presence of different carboxylic acids in the initial mixture, NRTL property method coupled with Hayden-O'Connell model with correction for vapor phase association of carboxylic acids is used (Aspen Technology, 2020). Properties of the components and possible formation of azeotropes (Gmehling et al., 2004) are given in Table 2.

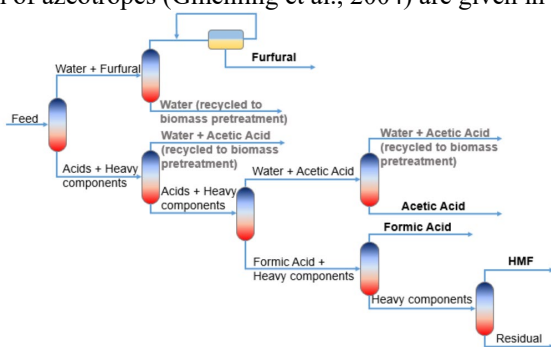


Figure 1. Simplified process flow scheme of the by-products recovery process

Table 1. Feed stream

Component	%wt
Water	96.568
Acetic acid	1.747
Formic acid	0.427
Furfural	0.297
HMF	0.128
Levulinic acid	0.005
Glucose and xylose	0.097
Other heavy components	0.730

Table 2. Components and azeotropes (1 atm)

Pure components		Azeotropes		
Component	T <sub>b</sub> (°C)	Component	Molar fraction	T (°C) / type
Water	100.02	Water	0.9066	97.79
Formic acid	100.55	Furfural	0.0934	/heterogeneous
Acetic acid	118.01	Water	0.3607	106.50
Furfural	161.35	Formic acid	0.4998	/homogenous
Levulinic acid	256.98	Acetic acid	0.1395	
HMF	281.85	Water	0.4566	106.81
Glucose	343.85	Formic acid	0.5434	/homogenous

Different methods for recovery of present components from diluted solutions are proposed in the literature (Li et al., 2016), but recovery yields are usually insufficient and the usage of additional chemicals complicates downstream processing. Research is often done on lab-scale and scale-up is not considered. To avoid adding extra chemicals, distillation is chosen and component separation is proposed in a defined order (Figure 1). Since the feed is very diluted, the first step is to concentrate it by separating as much water as possible. Due to the formation of light heterogeneous azeotrope (Figure 2), furfural is separated together with water. It can further be recovered by simple phase separation in a decanter. Recovery of acetic and formic acids from an aqueous solution is complex due to existence of four distillation areas and two azeotropes (Figure 3). As acetic acid concentration is the highest of all by-products in the feed, its' recovery is crucial. Therefore, most of acetic acid and water are separated from formic acid and heavier components (HMF, levulinic acid, dissolved sugars and solubilized lignin components) at temperature lower than needed for ternary azeotrope formation. Further recovery of acetic acid is complex due to the tangent pinch at high water concentrations. Formic acid, plus the remaining water and acetic acid, can be separated from HMF and other high boiler components by distillation. The obtained mixture can be further treated in order to obtain a high-purity formic acid product. HMF can be recovered in a high-purity form, while other components can be sent to the fermentation step.

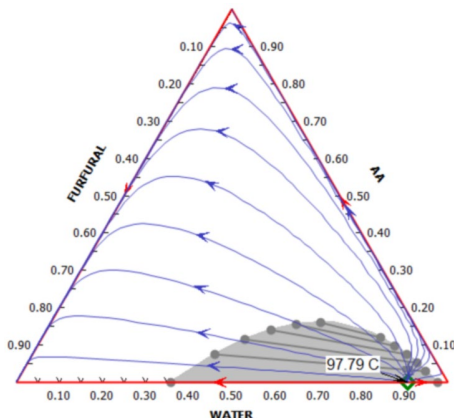


Figure 2. Ternary diagram for system water (W) - acetic acid (AA) - furfural (FURFURAL), mole basis

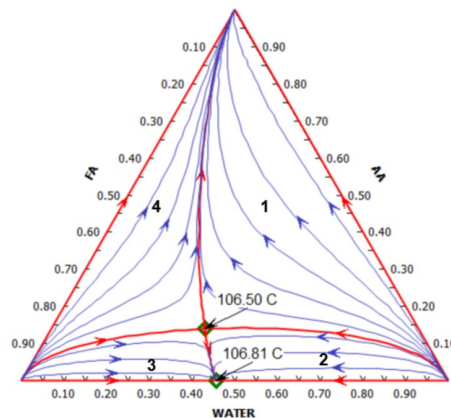


Figure 3. Residue Curve Map for system water (W) - formic acid (FA) - acetic acid (AA), mole basis

## 4. Results and discussion

### 4.1. By products recovery process design

The proposed optimal process design for recovery of valuable by-products after biomass pretreatment by hot-liquid water recovers acetic acid, furfural, HMF and formic acid. This process (Figure 4) consists of seven distillation columns and one decanter. Light azeotrope water-furfural is separated in column C-1, after which furfural is purified by additional distillation in column C-2 and phase separation in decanter DEC-1. This results in 100% furfural recovery, while purity of product stream is 97.9%wt. After separation of the water – furfural azeotrope, the solution is still very dilute and is further concentrated in column C-3. Some acetic acid is separated together with water, resulting in top product from this column with 0.5%wt of acetic acid (13.8% from acetic acid present in the feed stream). Since addition of acetic acid in pretreatment step improves digestibility of biomass by decreasing pH to mild-low values (Jiminez-Gutierrez, 2023), this stream can be recycled back to the biomass pretreatment step. Bottom product from column C-3 is further distilled in column C-4. Acetic acid, together with most of the water, is separated as a top product, while formic acid, levulinic acid, HMF and other heavy components are obtained in the bottom stream. Acetic acid is purified in column C-5 and obtained in a high purity form (99.8%wt), with total recovery of 78.8 %. HMF and heavier components are separated from formic acid, levulinic acid and remains of acetic acid and water in column C-6. HMF is further purified in column C-7 and obtained as high-purity (100%wt) top product with total recovery of 99.6 %, while heavy components that are obtained at the bottom can be recycled back to the fermentation step. Top product from column C-6 is stream with 73.6%wt of formic acid. Since composition of this stream is in distillation region 3 in Figure 3, high recovery of pure formic acid cannot be obtained by simple distillation due to the thermodynamic limitations of the water – formic acid azeotrope formation. Therefore, reactive distillation with methanol could be applied to completely recover formic acid (Painer et al., 2015). Moreover, additional purification of formic acid might not be necessary as there are applications of 70% formic acid solution (Singhal et al., 2015). Condition and composition of feed stream and product streams are given in Table 3.

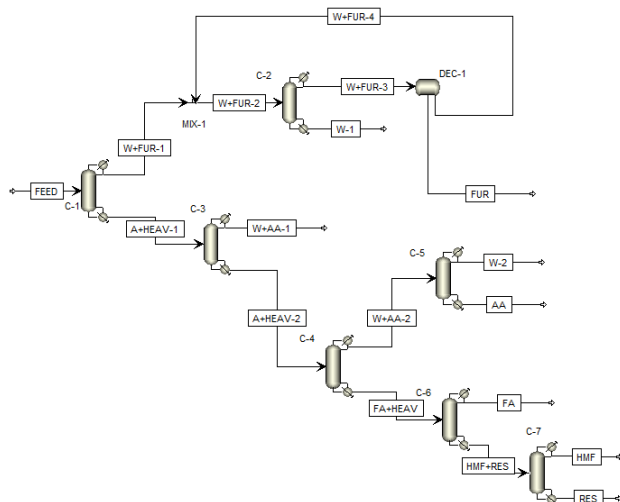


Figure 4. Flowsheet of by-products recovery process

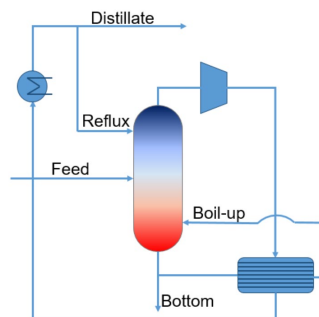


Figure 5. MVR heat pump design

Table 3. Condition and composition of feed stream and product streams for by-products recovery process

Stream	FEED	FUR	AA	FA	HMF
Temperature [°C]	99.70	27.36	26.00	34.82	26.00
Pressure [bar]	1	1	1	0.05	0.01
Mass Flow [kg/h]	110000	333.89	1517.00	635.11	140.70
Mass Fraction					
Water	0.9657	0.0206	0.0003	0.2187	0
Acetic Acid	0.0175	0	0.9982	0.0360	0
Formic Acid	0.0043	0	0.0015	0.7358	0
Furfural	0.0030	0.9794	0	0	0
HMF	0.0013	0	0	0.0003	1
Levulinic acid	0.0001	0	0	0.0091	0
Glucose, xylose and other heavy components	0.0083	0	0	0	0

Table 4. Design parameters of distillation columns in by-products recovery process

Column	C-1	C-2	C-3	C-4	C-5	C-6	C-7
No. Stages	52	30	60	48	66	20	20
Feed Stage	35	12	40	36	33	10	13
Pressure [bar]	1	1	1	1	1	0.05	0.01

#### 4.2. Distillation columns design

Design parameters (number of stages, feed stage and column pressure) for each of the columns are given in Table 4. As the feed stream is very dilute, large amounts of water need to be evaporated in C-1, C-3, C-4 and C-5. Hence these columns have larger number of stages and higher reboiler duties than the other columns. However, the top vapor from these columns can be used to evaporate bottom liquid by implementing mechanical vapor recompression as heat pump. Columns C-6 and C-7 operate at lower pressure to reduce temperatures and avoid thermal degradation.

#### 4.3. Energy analysis

Mechanical vapor recompression (MVR) and heat integration (HI) are implemented to enhance base process design. MVR is a heat pump design that can be applied to decrease energy use when separating close boiling components (Kiss & Infante Ferreira, 2016). This implies compressing top vapor and using it to evaporate bottom liquid (Figure 5). In the designed optimal recovery process, MVR is applied to the columns C-1, C-3, C-4 and C-5. Comparison of key performance indicators for processes before and after enhancing process design is given in Table 5. The inefficiencies in power generation are taken into account for calculation of the total energy requirements through an electric to thermal conversion factor of 2.5. Total investment cost (TIC), total operating cost (TOC) and total annual cost (TAC) are calculated according to a published procedure (Kiss, 2013), with a payback time of 10 years. A Marshall and Swift cost index of 1638.2 (end of 2018) is used (Mantingh & Kiss, 2021). Emissions of CO<sub>2</sub> are calculated using the equations from the literature (Mantingh & Kiss, 2021).

Table 5. Key performance indicators for processes with and without MVR

Performance indicator	Base case	Enhanced case	Savings (%)
Thermal energy requirements (kW <sub>th</sub> h/kg <sub>product</sub> )	75.13	0.18	99.8
Electrical energy requirements (kW <sub>e</sub> h/kg <sub>product</sub> )	n/a	3.53	n/a
Primary energy requirements (kW <sub>th</sub> h/kg <sub>product</sub> )	75.13	8.99	88.0
Total Investment Cost (k\$)	24923	48284	n/a
Total Operating Cost (\$/kg <sub>product</sub> )	2.29	0.33	85.5
Total Annual Cost (\$/kg <sub>product</sub> )	2.41	0.56	76.6
CO <sub>2</sub> emissions (kg <sub>CO2</sub> /kg <sub>product</sub> )	10.84	1.88/ 0.03*	82.7/ 99.7*

\*electricity from non-renewable sources / green electricity

## 5. Conclusions

This original work proposes an optimal process design for recovering by-products after biomass pretreatment by hot-liquid water. Improved fluid separation processes are used to obtain valuable products from very dilute feed stream (>96%wt water). Several biomass pretreatment products are effectively recovered, including: acetic acid, formic acid, furfural and HMF, with recoveries of around 78.8%, 99.5%, 100% and 99.6% respectively. Acetic acid, furfural and HMF are obtained in high-purity forms (99.8%wt, 97.9%wt and 100%wt respectively), while formic acid is recovered as a 73.6wt% solution. MVR and HI are efficiently implemented to further decrease the energy usage. Due to the use of additional compressors, TIC after implementation of MVR and HI is about 93.7% higher, but TOC and TAC are decreased for 85.5% and 76.6% (from 2.29 to 0.33 \$/kg<sub>product</sub> and from 2.41 to 0.56 \$/kg<sub>product</sub> respectively). Moreover, usage of MVR resulted in 88.0% energy savings and significantly lower CO<sub>2</sub> emission leading to a more environmentally friendly process.

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