Systems & Control Transactions

Research Article - Peer Reviewed Conference Proceeding
ESCAPE 35 - European Symposium on Computer Aided Process Engineering
Ghent, Belgium. 6-9 July 2025
Jan F.M. Van Impe, Grégoire Léonard, Satyajeet S. Bhonsale,
Monika E. Polańska, Filip Logist (Eds.)

PSE PRESS

Sustainable Downstream Process Design for HMF Conversion to Value-Added Chemicals

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ABSTRACT

Biomass conversion to chemical derivatives and essential intermediates is regarded as a long-term strategy for the chemical sector. Among the numerous valuable chemicals obtained from biomass, 5-hydroxymethylfurfural (HMF) is considered an industrially relevant compound due to its capacity to be converted into a variety of value-added chemicals. Compared to conventional catalytic synthesis, bio-catalysis has emerged as a potential greener substitute for HMF conversion to value-added compounds. HMF conversion through bio-catalysis, although more sustainable, seldom leads to the production of a single derivative. Thus, the development of efficient purification and separation processes of several products are crucial to scalability. The downstream process for the novel enzymatic conversion of HMF to high value-added chemicals (i.e., 1-phenylethylamine, 2,5-bis(hydroxymethyl)furan, 1-phenylethylalcohol, and 5-(aminomethyl)-2-furanmethanol) was designed by means of rigorous simulations in Aspen Plus®. The proposed process resulted in product streams with 97 wt% or larger for their respective component, and at least 95% product recovery is attained for each value-added HMF derivative. The global greenhouse gas emissions for the manufacture of a kg of product is 2.26 kg_{CO_2e}/ $kg_{product}$, while 0.086 $m^3_{wastewater}$/ $kg_{product}$ is generated. The proposed downstream sequence offers an overview of the feasibility for the scalability of the enzymatic process, crucial in developing sustainable bioprocesses.

Keywords: Modelling and Simulations, 5-hydroxymethylfurfural, Separation and purification, Sustainability

1. INTRODUCTION

Sustainable development is a concept that responds to the challenges posed by the needs of a rapidly growing population and rapidly increasing industry demands for petroleum-based carbon sources for energy and chemical synthesis [1].

Biomass has become an attractive carbon-neutral resource (as its emissions are of biogenic origin) due to its widespread availability (approximately 18 trillion tons on land and 4 billion tons of aquatic biomass) and renewable nature [2]. One particularly valuable chemical produced from glucose or fructose obtained from biomass is HMF [3]. Due to fructose's high cost and low availability, glucose can replace fructose as a feedstock to synthesise HMF. This process requires an additional step for the isomerisation of glucose to fructose. Current research focuses on biowaste and lignocellulosic biomass as feedstock for HMF synthesis due to their low cost, lack of impact on the food chain supply, and carbon-neutral nature. Processes starting from biowaste employ a pretreatment step followed by hydrolysis to liberate glucose from the starting polysaccharides [4,5].

HMF is an important intermediate in synthesising renewable polymers, pharmaceuticals, resins, solvents, fungicides and fuels. HMF is composed of a furan ring on which hydroxymethyl and formyl functional groups are grafted. Hence, complex chemicals can be obtained from simple chemical reactions such as oxidation, reduction, esterification or condensation [6]. As such, HMF has been evaluated in the Top 10 biobased chemicals by the U.S. Department of Energy [1].

The chemical synthesis of HMF derivatives typically involves metal-based catalysts (Pd, Ru, Pt, Mn, V and Au), elevated reaction temperatures and pressures, and organic solvents like dimethyl sulfoxide,

dimethylformamide, or toluene [5,7].

In contrast, enzymes are recognized as an alternative to chemical catalysis due to their alignment with the twelve principles of green chemistry. These biocatalysts require mild reaction conditions for temperatures and pressures and utilize water as a solvent. Additionally, enzymes demonstrate high specificity, which helps eliminate the need for protection and deprotection steps. They are also characterized by low toxicity and generate less harmful waste, primarily in the form of wastewater [8].

The oxidative products, including 5-hydroxymethyl-2-furancarboxylic acid, 2,5-diformylfuran, 5-formyl-2-furancarboxylic acid, and 2,5-furandicarboxylic acid, find applications in the polymer industry (such as polyurethanes, polyesters, copolyesters, polyamides, polyimides, and epoxy resins) [7]. Compounds such as 2,5-dihydroxymethylfuran and 2,5-bis(hydroxymethyl)furan (BHMF) are derived from HMF through hydrogenation, and both are valuable in polymer synthesis, particularly for polyurethanes, polyesters, and polycarbonates [7,9]. BHMF could also be utilized as a fuel source[9].

Various enzymatic oxidase systems, have been evaluated for their ability to produce oxidative products from HMF. These enzymatic systems showcase high conversion rates of HMF, however, in most cases several products are obtained. As such, product separation and purification play an essential role in scalability [10].

Chemical synthesis already produces value-added derivatives of MHF at an industrial scale [11]. For the feasibility of enzymatic synthesis on an industrial scale, downstream techniques that are both cost-effective and process-efficient need to be developed [9]. In conclusion, the viability of enzymatic synthesis as a green alternative is reliant on developing efficient downstream processes. The plethora of studies that aimed to develop new and effective enzymatic catalysts seldom researched or discussed the downstream processes necessary to separate and purify the obtained products.

The current study aims to bridge the mentioned gap and design a sustainable downstream process considering a novel enzymatic pathway for the conversion of HMF to value-added chemicals. The separation and purification process of a mixture of four products obtained from an enzymatic conversion of HMF to value-added products was designed in Aspen Plus®. To the best of the authors' knowledge the separation of 1-phenylethylamine (PEAM), BHMF, 1-phenylethylalcohol (PEA), and 5-(aminomethyl)-2-furanmethanol (HMFA) has yet to be discussed in the literature.

METHODOLOGY

The enzymatic conversion of HMF and 1-phenylethylamine (PEAM) was studied which results in a mixture of BHMF, 1-phenylethylalcohol (PEA), PEAM and 5-(aminomethyl)-2-furanmethanol (AMFM).

For the separation of alcohols and amines that come from the bioreactor, ion exchange was opted for. Mineral acid (i.e., HCl) solution is added to the mixture until pH of 2 is reached in order to form the salts of the amines, while the alcohols remain in a neutral state. As such, a cation exchange material can be utilized to form an ionic bond with the amines while the alcohols pass through the ion exchange separator.

The amines can then be recovered when regenerating the cation exchange material, which involved the use of a mineral bases (i.e., NaOH). As a result, NaCl would form in the mixture which was removed before continuing with other product purification processes. In order to eliminate the mineral salt from the solution, their crystallization was considered by evaporation of the mixture to obtain an oversaturated solution of higher temperature. This solution, when cooled results in the crystallization of said mineral salt that was filtered from the aqueous solution.

The next steps in the downstream process relate to the separation and purification of the products. In case of the stream containing the alcohol products, BHMF can be separated from the aqueous solution through distillation. As PEA forms a well-known azeotrope with water (Figure 1), these compounds cannot be separated in the same manner, a liquid-liquid extraction process was opted for. Hexane was utilized as the solvent, as it was demonstrated to be the most efficient in similar systems [12]. This is further separated from hexane by a distillation column.

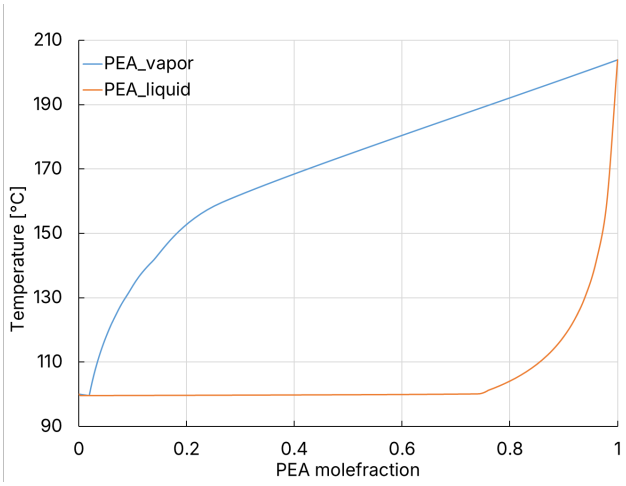

Figure 1. T-xy diagram of the PEA and water binary system.

On the other side, the aqueous solution containing the amine products goes through a crystallization process similar to the above mentioned to rid the solution of the mineral salts. In this case the separation of each

individual product from the aqueous solution can be performed by distillation. However, the intensification of these processes can be achieved through fractional distillation. The previously described downstream separation and purification processes are presented in Figure 2.

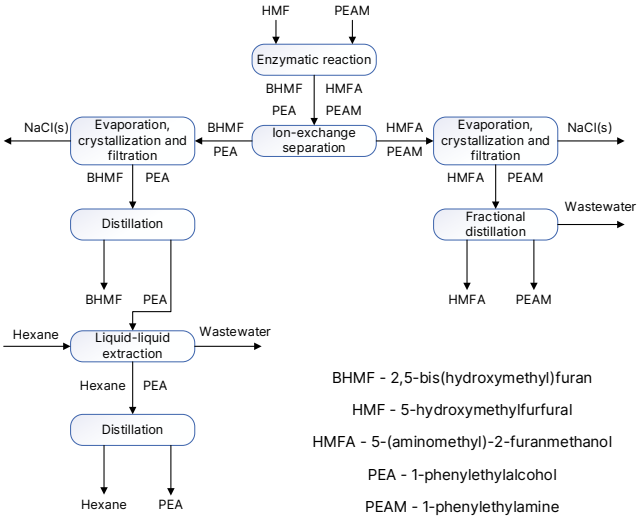

Figure 2. Simplified flowsheet of the HMF biocatalytic transformation to value-added products, their separation and purification.

The design of the separation and purification processes took into account laboratory scale experimental results, as well as the following assumptions. Firstly, full conversion of HMF is considered resulting in an equimolar mixture of BHMF, PEA, PEAM and HMFA. Secondly, the separation of amines and alcohols was assumed to be ideal in the ion exchange system. Thirdly, the solubility of the mineral salt was considered to be solely influenced by the water's mass fraction of the solution.

RESULTS AND DISCUSSION

The proposed downstream process (Figure 3) was simulated in Aspen Plus® V11 software environment. The ion-exchange separation process (IEX) is presented in a simplified form as it was not the main focus of the current study. ELECNRTL and SOLIDS property methods were utilized to model the various processes involved. ELECNRTL was used as it is the most flexible property technique since it can handle both very low and high concentrations of aqueous and mixed solvent systems. The same method cannot be used to compute the characteristics of both solids and fluid phases. Therefore, for computations involving solid components, the SOLIDS property approach was employed. The incoming, purified and other relevant material streams of the simulation are summarized in Table 1.

It can be observed that the salt (i.e., NaCl) could not be fully removed through crystallization and filtration, and it will influence the purity of the bottom product streams of the first distillation process both for the amine and alcohol products (i.e., AMFM and BHMF).

In both cases, the process occurs under vacuum

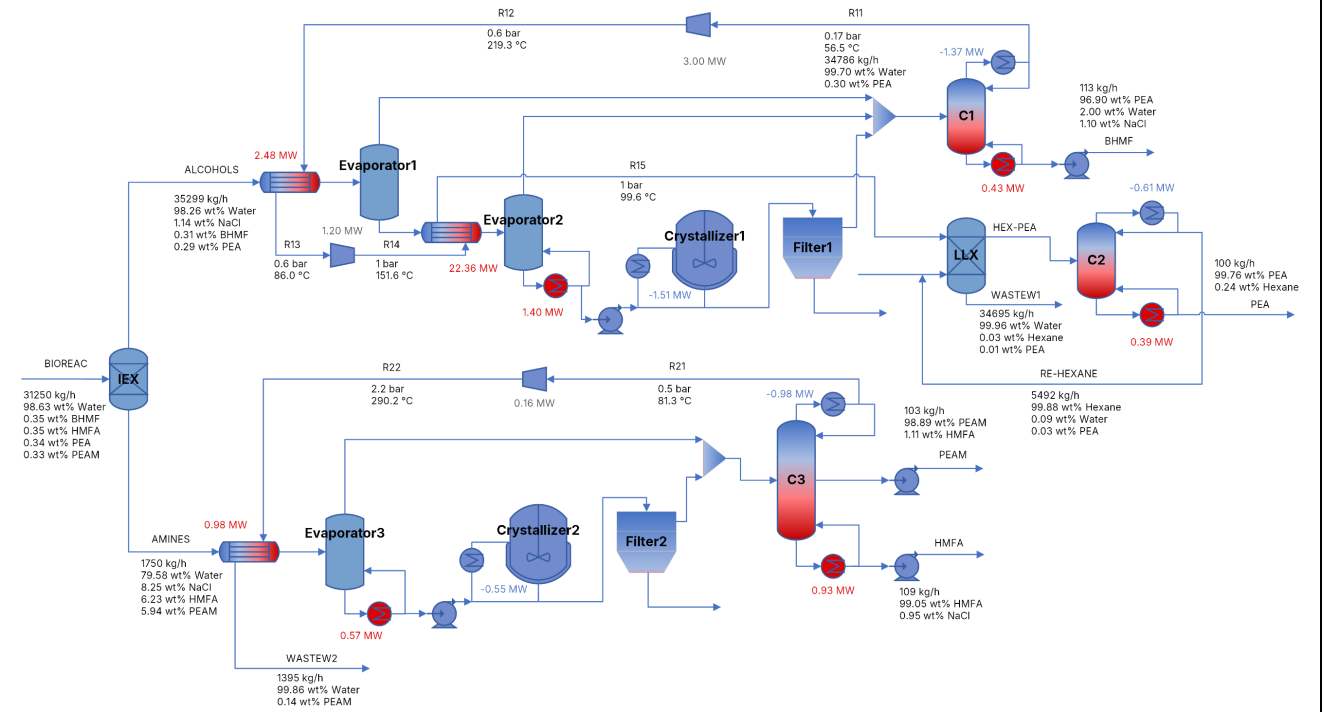

Figure 3: Schematic of product separation and purification processes implemented in the Aspen Plus® simulation

Table 1: Parameters and composition results of the most important streams from Figure 3.

Stream	BIOREAC	HMFA	BHMF	PEA	PEAM	RE-HEXANE	HEX-PEA
Temperature [°C]	30	228.2	117.3	197.1	134.7	57.2	110.9
Pressure [bar]	1	1	1	1	1	1	1
Flowrate [kg/h]	31250	109	113	100	103	5492	5592
Mass fractions							
HMFA	3.50E-03	9.91E-01	0.00E+00	0.00E+00	1.11E-02	0.00E+00	0.00E+00
BHMF	3.50E-03	0.00E+00	9.69E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Water	9.86E-01	0.00E+00	2.00E-02	0.00E+00	0.00E+00	9.00E-04	9.00E-04
PEA	3.40E-03	0.00E+00	0.00E+00	9.98E-01	0.00E+00	3.00E-04	1.81E-02
PEAM	3.30E-03	0.00E+00	0.00E+00	0.00E+00	9.89E-01	0.00E+00	0.00E+00
Hexane	0.00E+00	0.00E+00	0.00E+00	2.40E-03	0.00E+00	9.99E-01	9.81E-01
NaCl	0.00E+00	9.50E-03	1.10E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00

conditions in order to maintain the obtained products in their reported thermal stability range. In regards to BHMF, the streams containing this compound were kept at temperatures below 120 °C [13]. A partial-vapor condenser was set for both columns (i.e., C1 and C3) in order to ensure the desired reflux ratio, as well as to utilize the vapor distillate in a heat pump system to preheat the respective streams before the evaporation process. As the streams containing BHMF had to be maintained at lower temperatures, this thermal integration could only be realized in two steps, as it can be observed in Figure 2.

The optimal conditions for each unit operation were searched for by conducting sensibility analysis for each design parameter that applied to the respective unit operation (e.g.., reflux ratio, heat duty, number of stages, feed stage, by-product stage, etc.). In this manner, the desired product purity of 97 wt% or higher was obtained for all three products that could be separated in the first distillation steps (i.e., BHMF, PEAM and HMFA). Higher purity product can be obtained by evaporating a larger portion of water, thus improving the crystallization process of NaCl. However, the trade-off with the thermal energy required for the evaporation has to be considered, and the temperature constraints should also be taken into account. In case of the amine products, a single fractional distillation column was utilized for their separation and purification. The parameters of this ternary system were defined based on the study by Wen et al. 2017 [14].

The separation and purification of PEA further required a liquid-liquid extraction due to the azeotrope it forms, and a distillation process afterwards. Hexane was utilized for the extraction of PEA, based on its reported close to ideal recovery rate of PEA, also validated by the ternary diagram shown in Figure 4. The proposed process extracted more than 95% of PEA from the aqueous solution. A more efficient extraction can be achieved with a larger quantity of hexane, however that would also imply an increase in the reboiler duty of the distillation column that follows. Although the usage of an organic solvent influences the sustainability of the process, it is recovered in a high purity stream which can be recycled. In this manner, high purity PEA is obtained with a weight percent of 99.

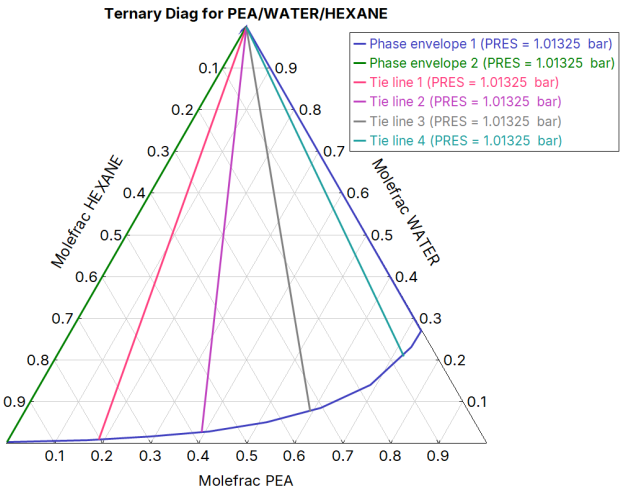

Figure 4: Ternary diagram with tie lines for the PEA-water-hexane system at atmospheric pressure.

Other than the purity of product streams, It is also important to note that the four compounds of interest are recovered from the reaction mixture in 98.9%, 99.8%, 95.3% and 96.4% for HMFA, BHMF, PEA and PEAM, respectively. To measure the sustainability of the downstream process, the specific material intensity, energy intensity, wastewater intensity, greenhouse gas (GHG) emissions, toxic emissions and pollutant emissions were calculated for a unit of output. The unit of output was

considered as a kg of product (i.e., HMFA, BHMF, PEA and PEAM).

The material intensity refers to the mass of wasted materials per unit of output. The non-recovered products were considered as wasted material resulting in a value of 0.020 $kg_{wasted}/kg_{product}$. The energy intensity criterion took into account both thermal and electric energy consumers (e.g., pumps, reboilers, etc.). The proposed process requires 4.36 MW electrical energy and 3.72 MW thermal energy. The overall energy requirement was calculated utilizing an electrical-to-thermal conversion factor of 2.5 [15] resulting in a value of 34.88 kWh/ $kg_{product}$. This value is mostly due to the low concentration of the mixture after reaction, the incoming stream containing 30.82 tonnes of water. The significant energy intensity does not thwart the feasibility of the process as the prices of the obtained products range from 0.5$/kg to 50$/kg.

In the calculation of wastewater intensity water that requires wastewater treatment per kilogram of product was considered (i.e., stream WASTEW1 and WASTEW2) resulting in 86.04 $kg_{wastewater}$/ $kg_{product}$. The large wastewater intensity can be attributed to the enzymatic process, which leads to a mixture of products from 20 to 30 mM. In addition, the usage of less concentrated solutions in the downstream process necessary to avoid the formation of Bronsted acids/bases (e.g., 2M NaOH) increases both the processes' energy and wastewater intensity.

For the calculation of GHG emissions, only off-site emissions were considered as there are no gaseous emission in the designed process. The off-site emissions considered were those related to electricity and steam generation. For calculations, the data from 2023 regarding EU-27 GHG emissions intensity for electricity generation used, i.e., 0.21 kg_{CO_2e}/kWh [16]. The emission factor for steam generation was considered as 19.46 kg_{CO_2e}/MWh [17]. The GHG emissions value per unit of output is 2.26 kg_{CO_2e}/ $kg_{product}$. These emissions could be reduced utilizing regenerable energy sources, however a more in-depth study is required to investigate the trade-off with other sustainability indices.

Toxic emissions were calculated as the mass of toxics and hazardous materials for the operating personnel present in the output streams per unit of output, other than the intended product streams. The compounds' toxicity was determined based on their material safety data sheet, as such, toxic emissions value of 0.042 kg_{toxic}/ $kg_{product}$ was obtained. Pollutants were considered as the non-toxic material present in the output streams, except the four product streams. In this manner, pollutant emissions were calculated as $2.00 \square 10^{-5}$ $kg_{pollutant}$/ $kg_{product}$. The negligible amount of pollutants is due to the toxicity of most materials present in the system, therefore special attention should be paid towards the treatment of generated wastewater.

CONCLUSIONS

The proposed downstream process concerning the four value-added HMF derivatives (HMFA, BHMF, PEA and PEAM) showed that each product can be separated with purities of at least 97 wt% comparable to those found on the market, obtained through non-enzymatic pathways. This efficient downstream configuration presents an overall recovery of over 98% of the value-added derivatives.

The studied process is suitable for production of natural chemicals, which can be essential taking into account the use of the obtained products such as food and pharmaceutical industry. Although high value-added products are obtained in the studied system, an economic assessment is required to investigate the influence of the proposed separation and purification process on the feasibility of the industrial scale from an economic standpoint, which is the scope of future work.

ACKNOWLEDGEMENTS

This study was supported from the project "Advanced (multi)-enzymatic synthesis and purification processes for bio-based furan derivatives – ASPIRE" (CF 25/14.11.2022).

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