

5-Hydroxymethylfurfural Production in a Lignocellulosic Biorefinery: Techno-economic Analysis

Bárbara L. S. Santiago*, Reginaldo Guirardello

School of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, 13083-852, Campinas-SP, Brazil
 blsilvasa@gmail.com

5-Hydroxymethylfurfural (HMF) is one of the leading versatile building blocks in the biorefinery context, and it is pointed as one of the top value-added chemicals from biomass. Its derivatives are in the main segments of the chemical industry, especially in the polymer market. One example is 2,5-furan dicarboxylic acid (FDCA), one of the twelve most promising biobased chemicals according to the US Department of Energy. It can substitute terephthalic acid in the polyethylene terephthalate (PET) production, used in huge markets that include bottles, cans, foils, cosmetics, among others. HMF has been produced using fructose as raw material. However, this feedstock represents more than 80% of the final minimum selling price. In order to make the production process economically viable and competitive, it is essential to use cheaper raw material such as lignocellulosic biomass. The aim of this research, therefore, is to address a techno-economic analysis of the 5-hydroxymethylfurfural production in a lignocellulosic biorefinery, highlighting the main obstacles to reduce the product cost and the opportunities to make it more competitive. The analysis of raw materials cost indicated a minimum production cost of 0.21 US\$/mol, and the cash flow analysis, considering the capital cost, indicated a minimum selling price of 3.18 US\$/mol. The results indicate that the HMF production process analysed is not economically feasible. The results suggest the necessity to improve the biomass hydrolysis and to increase the glucose-HMF yield.

1. Introduction

5-hydroxymethylfurfural (HMF) was described as one of the main biobased products capable of establishing a robust biorefinery that meets economic goals (Chen et al., 2017). It is a renewable product produced via carbohydrate dehydration (Li et al., 2019). HMF is considered a building block because it is a starting material used for the production of biofuels and chemicals (Hu et al., 2017). FDCA is one of the derivatives of HMF, and it could potentially replace petroleum-based chemicals used to make plastic, such as PET, competing in a well establish growing market (Wu et al. 2016). However, the high HMF production cost limits its applications, and it is related to the low selectivity reactions and the high raw material cost (Mukherjee et al., 2015).

Low selectivity occurs due to the presence of water in the medium reaction. First, the hexoses are dehydrated in HMF using different kinds of Lewis and Brønsted acid catalysts, such as CrCl_2 , producing water. In a second moment, however, it often rehydrated to levulinic acid and formic acid, lowering the total yield. In order to increase the yield, biphasic reactors have been developed, allowing the extraction of HMF as soon as it is formed in a way that it diminishes the rehydration reaction. Wang et al. (2018) evaluated seven different organic solvents on the fructose-HMF reaction concerning the conversion and selectivity. The N-methylpyrrolidone (NMP) showed the highest HMF selectivity (83%) and 2-butanol, the lowest (5%). Altway, Pujar, and de Haan (2018) studied a way to increase the HMF recovery in the biphasic system using salts with a salting-out capacity to increase HMF solubility on the organic phase. These biphasic alternatives have shown supporting/endorsing results.

The main raw material used to produce HMF is fructose, and it represents more than 80% of the total HMF cost of production (Torres, Daoutidis, and Tsapatsis, 2010). This is one of the main reason why HMF is not economically viable yet. To address this question, several experimental research has been done in order to produce HMF from biomass-derived glucose and cellulose that are much cheaper than fructose. Hou et al. (2019) develop an efficient catalyst to convert glucose into HMF with aluminum oxide in ionic liquid, reaching

an HMF yield of 50%. Wang et al. (2019) reached an HMF yield of 65% using glucose as raw material and a chromium-based ceramic and acid catalysis. Tang and Su (2019) developed a stable inexpensive solid catalyst capable of converting cellulose to HMF, using ionic liquid and DMSO as solvents. The HMF yield was 58%, with 97% cellulose conversion. Yan et al. (2019) obtained a yield of 83% with a NaCl-aqueous/butanol biphasic system on the cellulose-HMF reaction. Wu et al. (2019) obtained an HMF yield of 85% when reacting cellulose with biomass-based carbon catalysts in water as the solvent.

Although considerable experimental research has been devoted to HMF production using biphasic reactors and lignocellulosic biomass as raw material, slightly less attention has been paid to the complete economic analysis of these alternatives. In this sense, this study was designed to do the technical and economic analysis of the HMF production from lignocellulosic biomass. This paper is divided into two sections: the Aspen Plus simulation of the different configuration processes, and the economic analysis of each one of them, enabling the comparison.

2. Methodology

2.1 Process description

The hydroxymethylfurfural (HMF) production process was analyzed using three different raw materials: fructose, glucose, and sugarcane bagasse. Each of them consists of a different studied scenario (F, G, and SCB).

The base case scenario is the fructose one, and it was previously described by Torres et al. (2009). It consists of a biphasic reactor feed with fructose, water, catalyst (HCl), and the organic solvent (MIBK and 2-butanol). The HMF conversion occurs in the aqueous phase, and then it is extracted to the organic phase. This strategy has been described as a way to minimize the unwanted HMF rehydration reaction, which reduces the HMF yield and form levulinic and formic acids instead. The biphasic reactor has two product streams, the organic and the aqueous one. Both of them need to be further processed because they have a significant amount of HMF as an effect of the partition coefficient ($R=1.65$). The aqueous stream flows to an extractor fed with the same organic solvent. This operation allows the HMF to be extracted to a similar organic phase that will be joined to the organic reactor product stream in an evaporator. The evaporator is feed with solvent and HMF and then will separate the volatile organic phase and the HMF stream with 95% purity.

The main difference between fructose and glucose scenarios is the catalyst used. The fructose scenario catalyst is chloridric acid, as described by Asghari and Yoshida (2007). The glucose catalyst is $AlCl_3$ and HCl, as described by Pagán-Torres et al. (2012). All the other operations are similar.

The sugarcane bagasse scenario is peculiar. It needs two reactors before the biphasic reactor described previously. These two steps are essential to release the cellulose monomers (glucose) that will react to form HMF (Lopes et al., 2017). The first step is the pretreatment that aims to fractionate the biomass and make it more suitable for further hydrolysis. This study considers the dilute acid pretreatment, which is capable of solubilizing the hemicellulose in a liquid stream rich in xylose. The solid fraction that remains feeds the second reactor where the glucose hydrolysis occurs. This study considers the concentrated acid hydrolysis, catalyzed by sulfuric acid. The operating conditions and experimental yield considered are described by Kumar et al. (2015).

2.2 Process Simulation

The scenarios were simulated in Aspen Plus (Aspen Technology Inc., USA) v10. The thermodynamic model used to estimate a liquid-liquid equilibrium in a multi-component system (biphasic reactor) was the NRTL (Non-Random two-liquid), as previously described by Altway et al. (2018). The reactors were simulated as RStoic, which allows specifying the reaction and its conversion. The evaporator was simulated as a Flash2, and the extraction column was simulated as Extract. A decanter was included to simulate the phase separation in the biphasic reactor, but it is not mandatory in a real plant since the residence time can be adjusted to allow the separation in the reactor, as described by Torres et al. (2010).

The base case scenario was composed of a biphasic reactor, a decanter, an extractor, and an evaporator. This layout is also applied to the glucose scenario.

The sugarcane bagasse (SCB) scenario was simulated with the pretreatment and hydrolysis prior to the biphasic reactor and downstream processing. It was composed of a pretreatment reactor, a solid-liquid separator, and a hydrolysis reactor. The product of the second reactor is the glucose that feeds the biphasic reactor. The downstream processing was the same as described in the base case scenario.

Figure 1 shows that all the scenarios have in common the biphasic reactor and downstream processing. Particularly the SCB scenario has the additional pretreatment and hydrolysis reactors.

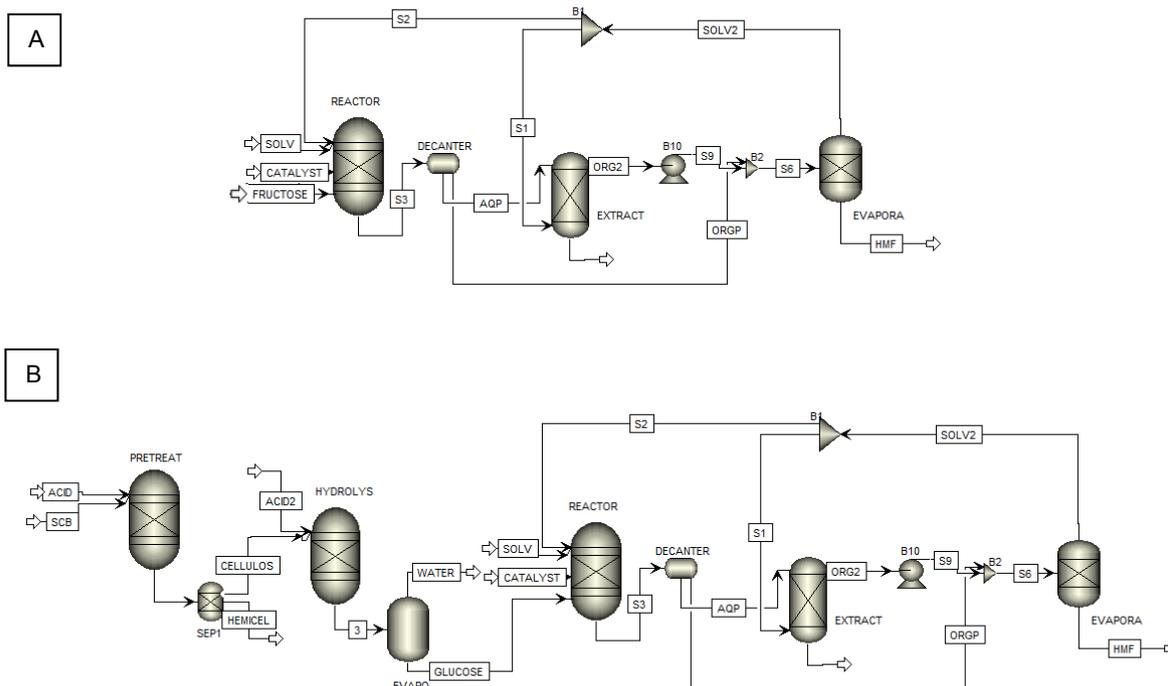


Figure 1: Process flow diagram for the 5-Hydroxymethylfurfural production (A) Base case scenario process flow diagram (fructose and glucose as raw material). (B) Process flow diagram for sugarcane bagasse as raw material.

2.3 Economic Analysis

The plant profitability was elucidate based on a discounted cash flow analysis. Aspen Plus Economic Analyzer was used to estimate the annual and capital cost, based on the mass and energy balance and equipment sizing.

The cash flow analysis was made based on some assumptions: 2 years of construction, 20 years of production length, 350 working days per year, no debt, 100% equity, 100% of nominal capacity in the first year, 34% tax rate, linear depreciation (10-year) and no scrap value. The raw material market values are 0.55 US\$/kg fructose, 0.33 US\$/kg glucose, 0.04 US\$/kg sugarcane bagasse 2.35 US\$/kg solvent (7:3 MIBK – 2-butanol)

3. Results

The present study intends to evaluate the 5-hydroxymethylfurfural production from sugarcane bagasse as raw material, in comparison with alternatives such as fructose and glucose. The base case scenario converted 340 kg/h of fructose in 106 kg/h of the desired product (HMF). The glucose scenario produced 84 kg/h of HMF from 340 kg/h of glucose, via $\text{AlCl}_3\text{-HCl}$ catalysis and the same downstream processing. The HMF production from sugarcane bagasse has its total mass balance illustrated in Figure 2. The process is feed with 2100 kg/h of biomass and produces 85 kg/h of HMF.

The biphasic reactor is feed with approximately 340 kg/h of the respective monosaccharide (fructose or glucose) in all scenarios. In this sense, the amount of sugarcane bagasse was estimated to satisfy this restriction. It was considered that this biomass has 44% (dry basis) of cellulose, which means that the system was feed with 924 kg/h of cellulose, which completely hydrolyzed represents 1026 kg/h of glucose. However, the two-step H_2SO_4 hydrolysis showed a total yield of 34%. The low yield is a consequence of the second reactor's low yield combined with losses due to partial cellulose hydrolysis in the first reactor.

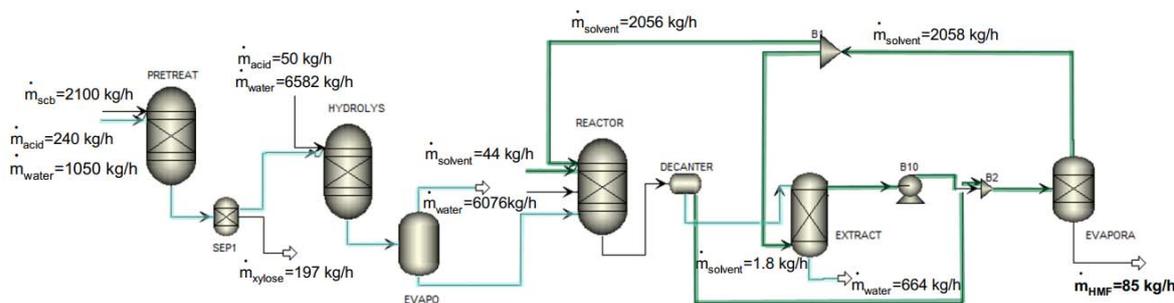


Figure 2: Mass balance of 5-Hydroxymethylfurfural production using sugarcane bagasse as raw material.

The second reactor was simulated as concentrated acid hydrolysis with H_2SO_4 , as described by Kumar et al. (2015). In this study, the authors hydrolyzed the cellulose fraction to produce ethanol, and because of that, they intend to minimize the formation of the inhibitor. This goal probably affected the glucose yield that could be higher if the process were more severe for alternative application. Unfortunately, there are limited experimental data that intends to hydrolyze the cellulose for HMF production.

Despite the hydrolysis limitations, the economic analysis shows that the sugarcane bagasse is a valid candidate as raw material for HMF production. The proposed process is not economically feasible yet, but the results suggest potential. The minimum production cost (MPC) and minimum selling price (MSP) are summarized in Table 1. The MPC intends to estimate the cost of HMF production based only on the raw materials cost (fructose, glucose or SCB, MIBK, 2-butanol, H_2SO_4 , and HCl) and energy cost. It is also used to compare the current results with the literature data. The estimated production cost using fructose as raw material was 0.25 US\$/mol HMF. This result is similar to the cost reported by Torres et al. (2010) for a production process with a comparable scale (0.273 US\$/mol).

The HMF production cost of scenario B that uses glucose as raw material was slightly smaller (0.22 US\$/mol). Since both processes are feed with monosaccharides, and glucose is cheaper than fructose, the production cost of scenario B is naturally cheaper. However, it is not as cheap as the raw material price could suggest, and one possible reason is the smaller yield of glucose-HMF conversion. The glucose goes through isomerization into fructose before reacting to form HMF, and it decreases the total yield.

The HMF production cost for the sugarcane bagasse scenario is 0.21 US\$/mol. As previously discussed, despite the low SCB price, the cost is not significantly smaller than Scenarios A and B because of the small hydrolysis yield. In order to explore the SCB potential, this study analyzed an unreal hypothetical scenario where the hydrolysis yield was 100%. In this case, the production cost would drop to 0.17 US\$/mol.

Table 1: Economic analysis results on 5-Hydroxymethylfurfural production process using alternative raw materials (MPC is Minimum production cost, and MSP is Minimum selling price).

Scenario	Raw material			HMF kg/h	MPC US\$/mol	MSP US\$/mol
	Type	Feed (kg/h)	Price (US\$/kg)			
A	Fructose	340	0.10	106	0.25	1.84
B	Glucose	340	0.06	84	0.22	2.34
C	SCB			85	0.21	3.18
D	SCB max*	2100	0.04	103	0.17	2.64

The minimum production cost does not inform about the economic feasibility of the HMF production process since there are several expenses that it does not consider. To fill this gap, the discounted cash flow analysis was made based on the assumptions described previously. The selling price that makes the net present value equals to zero in the 20 years is called the minimum selling price (MSP). The results are summarized in Table 1. In all scenarios considered, the MSP was significantly more expensive than p-xylene (0.109 US\$/mol), the compound that can be substituted by HMF in the large PET (PEF) market. Therefore, the analyzed HMF production process is not economically feasible in a competitive market.

The scenario C (SCB) minimized the minimum production cost as desired. However, analyzing the minimum selling price that considers the capital cost, this was the less profitable scenario. It is probably due to the two

additional reactors needed to release the glucose monomers from the biomass. It mainly increased capital costs without further advantages.

The minimum production cost suggests that it is essential to improve the biomass hydrolysis and develop a more efficient catalyst capable of increasing the sugar-HMF yield. The minimum selling price indicates that it is relevant to minimize the capital cost, and one way to do this is by using just one reactor for pretreatment and hydrolysis rather than two.

Another alternative to enhance the HMF proposed plant profit is to sell the xylose and lignin obtained from the sugarcane bagasse. This strategy has been described by several authors, in different contexts, as a remedy for biomass application.

4. Conclusions

Several studies demonstrated that 5-Hydroxymethylfurfural (5-HMF) production from fructose was not economically feasible on an industrial scale yet. In this context, the present study aimed to evaluate the HMF production from a cheaper renewable lignocellulosic biomass, the sugarcane bagasse (SCB). Even with a 2.5 fold cheaper raw material, the HMF production process is not economically feasible. The minimum selling price is 3.18 US\$/mol, higher than the target to enter the PEF market. This can be explained by the low yield in cellulose hydrolysis and the low yield in the glucose-HMF conversion. Efficient catalysis and process need to be developed in order to make the large-scale SCB-HMF conversion viable.

Acknowledgments

The authors acknowledge the financial support from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES - grant n. 88882.329720/2019-01) and São Paulo Research Foundation (FAPESP – grant n. 2015/20630-4).

References

- Altway S., Pujar S. C., de Haan A. B., 2018, Liquid-Liquid Equilibria of Ternary and Quaternary Systems Involving 5-Hydroxymethylfurfural, Water, Organic Solvents, and Salts at 313.15 K and Atmospheric Pressure, *Fluid Phase Equilibria*, 475, 100–110.
- Asghari F. S., Hiroyuki Y., 2007, Kinetics of the Decomposition of Fructose Catalyzed by Hydrochloric Acid in Subcritical Water: Formation of 5-Hydroxymethylfurfural, Levulinic, and Formic Acids, *Industrial and Engineering Chemistry Research*, 46, 7703–10.
- Chen S. S., Maneerung T., Tsang D.C.W., Ok Y. S., Wang C.H. Valorization of biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by heterogeneous catalysts, *Chemical Engineering Journal*, 328, 246-273.
- Hou Q., Zhen M., Li W., Liu L., Liu J., Zhang S., Nie Y., Bai C., Bai X., Ju M., 2019, Efficient Catalytic Conversion of Glucose into 5-Hydroxymethylfurfural by Aluminum Oxide in Ionic Liquid, *Applied Catalysis B: Environmental*, 253, 1–10.
- Hu L., Lin L., Wu Z., Zhou S., Liu S., 2017, Recent advances in catalytic transformation of biomass-derived 5-hydroxymethylfurfural into the innovative fuels and chemicals, *Renewable and Sustainable Energy Reviews*, 74, 230-257.
- Kumar S., Dheeran P., Singh S. P., Mishra I. M., Adhikari D. K., 2015, Kinetic Studies of Two-Stage Sulphuric Acid Hydrolysis of Sugarcane Bagasse, *Renewable Energy*, 83:850–58.
- Li X., Xu R., Yang J., Nie S., Liu D., Liu Y., Si C., 2019, Production of 5-hydroxymethylfurfural and levulinic acid from lignocellulosic biomass and catalytic upgradation, *Industrial Crops and Products*, 130, 184-197.
- Lopes E. S., Dominices K.M.C., Lopes M.S. Tovar L.P., Filho, R. M., 2017, A Green Chemical Production: Obtaining Levulinic Acid from Pretreated Sugarcane Bagasse, *Chemical Engineering Transactions*, 57, 145-150.
- Mukherjee A., Dumont M.J., Raghavan V., 2015, Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities, *Biomass and Bioenergy*, 72, 143-183.
- Pagán-Torres, Yomaira J., Tianfu Wang, Jean Marcel R. Gallo, Brent H. Shanks, and James A. Dumesic, 2012, Production of 5-Hydroxymethylfurfural from Glucose Using a Combination of Lewis and Brønsted Acid Catalysts in Water in a Biphasic Reactor with an Alkylphenol Solvent, *ACS Catalysis*, 2, 930–34.
- Tang, Zhe and Jianhui Su, 2019, Direct Conversion of Cellulose to 5-Hydroxymethylfurfural (HMF) Using an Efficient and Inexpensive Boehmite Catalyst, *Carbohydrate Research*, 481, 52–59.
- Torres A.I., Daoutidis P., Tsapatsis M., 2010, Continuous Production of 5-Hydroxymethylfurfural from Fructose: A Design Case Study, *Energy & Environmental Science*, 3, 1560.

- Wang L., Guo H., Xie Q., Wang J., Hou B., Jia L., Cui J., . Li., 2019, Conversion of Fructose into Furfural or 5-Hydroxymethylfurfural over HY Zeolites Selectively in γ -Butyrolactone, *Applied Catalysis A: General*, 572, 51–60.
- Wang Y., Ding G., Yang X., Zheng H., Zhu Y., Li Y., 2018, Selectively Convert Fructose to Furfural or Hydroxymethylfurfural on Beta Zeolite: The Manipulation of Solvent Effects, *Applied Catalysis B: Environmental*, 235, 150–57.
- Wu L., Moteki T., Gokhale A. A., Flaherty D. W., Toste D.F., 2016, Production of Fuels and Chemicals from Biomass: Condensation Reactions and Beyond, *Chem*, 1, 32–58.
- Wu Q., Zhang G., Gao M., Cao S., Li L., Liu S., Xie C., Huang L., Yu S., Ragauskas A. J., 2019, Clean Production of 5-Hydroxymethylfurfural from Cellulose Using a Hydrothermal/Biomass-Based Carbon Catalyst, *Journal of Cleaner Production*, 213, 1096–1102.
- Yan L., Ma R., Wei H., Li L., Zou B., Xu Y., 2019, Ruthenium Trichloride Catalyzed Conversion of Cellulose into 5-Hydroxymethylfurfural in Biphasic System, *Bioresource Technology*, 279, 84–91.