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MILP optimization model for 5-hydroxymethylfurfural production from fructose

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A critical strategy to sustainably satisfy the growing global demand for chemicals is to replace fuel-based products with bio-based-ones. The 5-hydroxymethylfurfural (HMF) is a bio-based versatile building block capable of substitute several chemicals; however, its production is not economically feasible yet. A promising technology is based on a biphasic reactor followed by an extractor and evaporator. It is a complex system for which it is not trivial to choose the best-operating conditions. The present study assessed the conditions that minimize the operating cost by modeling the process using a mixed-integer linear programming problem with economic objective function. The results showed that the minimum production cost (US$ 141.10) tended to minimize the reactor residence time (0.49 min) and makeup solvent (0.155 kmol/min), and maximize the total yield (0.807) and selectivity (0.871). However, technically these conditions are not feasible since they do not allow the reactor phase separation. The shortest residence time that allows this separation (2.65 min) resulted in a more expensive production cost (US$ 173.50), smaller total yield and selectivity (0.622 and 0.637) and greater makeup solvent demand (0.247 kmol/min).

1. Introduction

Bioeconomy intends to satisfy the growing global demand for chemicals while managing environmental aspects such as global warming. One critical strategy is to replace the fuel-based products with bio-based ones indulging the sustainable raw material supply (Kuo and Yu, 2020). New technical and economically viable processes need to be developed to enable this reality, which can be challenging. The 5-hydroxymethylfurfural (HMF), for example, is known as one of the top value-added bio-based chemicals because of its versatile building block characteristics (precursor of bio-based products). It is produced via fructose dehydration, and it is a precursor of several chemicals, such as 2,5-furan dicarboxylic acid, 2, 5-bis(hydroxymethyl)furan, and 2,5-di-hydroxy-methyl-tetrahydrofuran (Torres et al., 2010). However, the HMF large scale production is not economically feasible yet, and one of the main problems is the side reactions. The fructose dehydration occurs in aqueous media; however, the HMF formed can be rehydrated into levulinic acid and formic acid, reducing HMF selectivity (Roman-Leshkov et al., 2006). A promising alternative to minimize this side reaction is to use biphasic reactors that extract the HMF in an organic phase as soon as it is formed, increasing selectivity. The reactor is then followed by a solvent extractor and evaporator, in a process with recycling, purge, and high complexity. In this sense, it is difficult to define the best-operating conditions unless a mathematical model simulates the process and optimizes an economic objective function, minimizing the production cost. In the present case, the process has a nonlinear profile that results in a nonlinear programming problem hard to solve, and that does not guarantee the optimum. A more convenient model is the mixed-integer linear programming (MILP) obtained from the previous one by a linear approximation (Giuliano et al., 2016). In this context, this study intends to assess the HMF production from fructose using a MILP optimization model with an economic objective function. The results will estimate the purge, reactor residence time, yield, selectivity, efficiency, cost distribution, and how these variables interact to minimize production cost.

2. Methodology

2.1 Process description

The considered HMF production process was previous described by Roman-Leshkov et al. (2006) as a promising alternative to minimize the HMF rehydration that impacts its selectivity. The process consists of a biphasic reactor feed with fructose, catalyst, water, and solvent (Figure 1). The dehydration of fructose to produce HMF occurs in the aqueous phase, and as soon as it is formed, the HMF is extracted to the organic phase. The extraction depends on the solvent partition coefficient and the water:solvent ratio. Despite the extraction capacity, part of the HMF still remains in the aqueous phase in a way that an extractor is needed to recover the HMF_{aq}. The final HMF-rich solvent flow feeds the evaporator that separates the solvent from the HMF stream.

The purge stream is needed to avoid subproducts accumulation in the reactor, such as levulinic acid, formic acid, or humins. The makeup solvent is needed to recover the solvent lost in the product stream. The process input parameter values are summarized in Table 1.

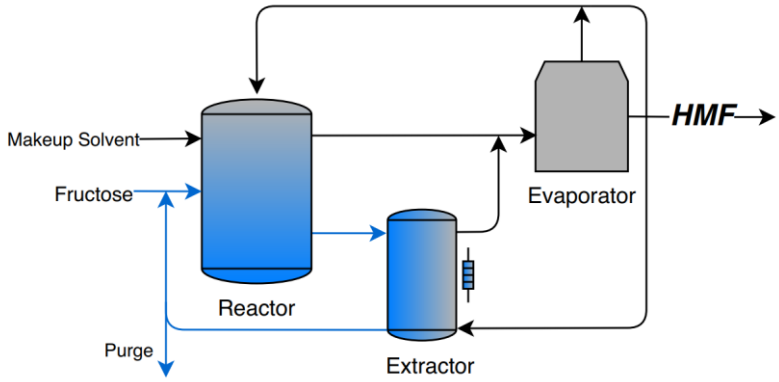

Figure 1: Process diagram (—)aqueous phase flow (—)organic phase flow.

Table 1: Input parameter values.

	Parameter	Value	Reference
Process Parameter	Reactor inlet flowrate (kmol fructose /min)	10	(Roman-Leshkov et al., 2006)
	Fructose concentration – reactor feed (w/w)	32%	
	Catalyst	HCl 0.25 M	
	Temperature (°C)	180	
	Solvent	2-butanol	
	Partition coefficient	1.6	
	Organic and aqueous phase ratio (V_{org}/V_{aq})	3.2	
	HMF purity outlet stream (molar fraction)	0.95	
Raw materials	Fructose (US$/kmol)	99.3	(Torres et al., 2010)
	Solvent 2-butanol (US$/kmol)	114	
Utilities	Steam (US$ MT^{-1})	6.61	(Kuo and Yu, 2020)
	Process water (US$ MT^{-1})	0.5	
	Cooling water (US$ MT^{-1})	0.05	
	Electricity (US$ kWh^{-1})	0.05	
	Efficiency (η_{ev} and η_{pum})	0.75	

The reaction network considered was described by Kuster and Temmink (1977). It considers the dehydration of fructose to HMF, and the unwanted rehydration of HMF into levulinc acid and formic acid. It also considers the formation of humins directly from fructose or HMF.

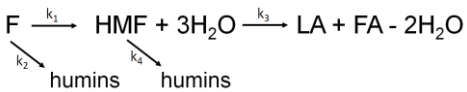

Figure 2: Reaction network of HCl catalysis to produce HMF from fructose. The kinetic constants are k_1=0.992 min^{-1}, k_2=0.992 min^{-1}, k_3=0.055 min^{-1}, k_4=0.070 min^{-1}.

2.2 Mathematical Modeling

The reactor was modeled as a steady-state continuous stirred-tank reactor (CSTR) with fast mass transfer between the aqueous and organic phases. The reaction only occurs at the aqueous phase (Eq 1 and 2), and there is continuous withdrawal of HMF defined by the partition coefficient value (Eq. 3 and 4).

$$\mathrm{F_{i,in}} - \mathrm{F_{i,out}} + \tau.\mathrm{r_i} = 0 \qquad i \neq HFM \tag{1}$$

$$\mathrm{F_{HMF,in}} - \mathrm{F_{HMF,out}} - \mathrm{N_{HMF}} + \tau.\mathrm{r_{HMF}} = 0 \tag{2}$$

$$\mathrm{N_{HMF}} - \mathrm{F^{org}_{HMF,out}} = 0 \tag{3}$$

$$\frac{\mathrm{F^{org}_{HMF,out}}}{\dot{n}_{\,org}} = \mathrm{R}\frac{\rho_{\mathrm{aq}}}{\rho_{\mathrm{org}}}\frac{\mathrm{F^{aq}_{HMF,out}}}{\dot{n}_{\,aq}} \tag{4}$$

The extractor was modeled considering ten theoretical stages since it is the upper bound for liquid-liquid extraction (Green and Southard, 2018), and the present study does not regard the capital cost. It was also assumed equilibrium at each stage, which allows the use of the correlation presented by Cussler (2009).

$$\frac{\mathrm{y_{11}}}{\mathrm{y_1}} = \frac{1 - \mathrm{A^{11}}}{1 - \mathrm{A}} \tag{5}$$

$$\mathrm{A} = \frac{\dot{n}_{\,org}\ \rho_{\mathrm{aq}}}{\dot{n}_{\,aq}\ \rho_{\mathrm{org}}\mathrm{R}} \tag{6}$$

The evaporator was modeled as a simple mass balance equation that removes HMF at 95% purity from the solvent that remains in the system. Its more significant contribution is related to the solvent evaporation's operating cost (steam, cooling water and pump electricity).

$$\dot{m}_{\,\mathrm{steam}} = \frac{\dot{n_s}\,\lambda_{\mathrm{s}}}{\eta_{\mathrm{ev}}\,\lambda_{\mathrm{steam}}} \tag{7}$$

$$\dot{m}_{\,coolingwater} = \frac{\dot{n_s}\,\lambda_{\mathrm{s}}}{c_{\mathrm{p}}\,\Delta\mathrm{T}} \tag{8}$$

$$\dot{Q_p} = \frac{\dot{n_s}(p - p_s)}{\eta_{pum}\,\rho_s} \tag{9}$$

The economic objective function is to minimize the HMF production cost:

$$\min\ \text{HMF production cost} = \frac{\text{Raw material cost (fructose and makeup solvent)} + \text{Operating cost}}{\dot{n}_{\mathrm{HMF}}} \tag{10}$$

2.3 MILP Approximation

The mathematical model obtained is a non-linear problem (NLP) that is difficult to address and does not guarantee the optimum. Thus, a variable discretization method was applied to linearize the problem, resulting in a mixed-integer linear problem (MILP) (Biegler et al., 1997). It can be mathematically expressed as follows, using as an example the stream splitter that to define the purge:

$$\mathrm{f_i^1} = \sum_{\mathrm{k=1}}^{\mathrm{N}} \mathrm{f_i^{in,k}}.\omega_{\mathrm{k}} \tag{11}$$

$$\mathrm{f_i^{in}} = \sum_{\mathrm{k=1}}^{\mathrm{N}} \mathrm{f_i^{in,k}} \tag{12}$$

$$\mathrm{f_i^{in,k}} \leq \mathrm{UB}.\mathrm{y^k} \qquad \mathrm{k} = 1,2 \ldots \mathrm{N} \tag{13}$$

$$\sum_{k=1}^{N} y^k = 1 \qquad y^k \in \{0,1\} \tag{14}$$

$$f_i^2 = f_i^{in} - f_i^1 \tag{15}$$

The method requires the introduction of y^k binary variable that represents the selection of the discrete value (split fraction ω_k) for the outlet stream (Eq 11) since all $f_i^{in,k}$will be zero except one (Eq 13 and 14). It is possible through the disaggregation of the continuous variables in terms of N discretized conditions (ω_k).
This MILP approximation was also used to select the reactor residence time and yield as discrete values, as described by Giuliano et al. (2016). The method allows for nonlinearities elimination in the cost of increasing the number of discrete and continuous variables and the number of constraints.
The objective function also needed to be adjusted to a linear form. The resulting MILP had an objective function that maximizes the profit (HMF selling revenue minus raw material cost and operating cost). A loop tests all possible selling prices, and the one that minimizes the profit (profit→0) can be called the minimum production cost (in other words, the selling price that only covers the production cost and allows no gain). Consequently, this solution also reveals the operating conditions that enable the minimum cost of production. The problem was solved by employing the General Algebraic Modelling System (GAMS) software with CPLEX optimization solver.

3. Results

5-hydroxymethylfurfural is an important versatile bio-based product for which there is no economically viable production process yet. In this context, the present work intends to mathematically model a promising alternative process aiming to highlight some barriers. Thereunto, the process was modelled as a MILP problem that maximizes the profit (HMF selling revenue minus raw material and operating cost). The minimum production cost (MPC) was accessed by varying the HMF selling price until the profit is zero. The minimum selling price was not measured since the capital cost was not forecasted.
The premature optimization results tended to minimize the reactor residence time even though this is not the condition that maximizes the HMF production. Thus, the residence time was evaluated as a strategy to understand the observed outcome. Figure 3 illustrates the results.

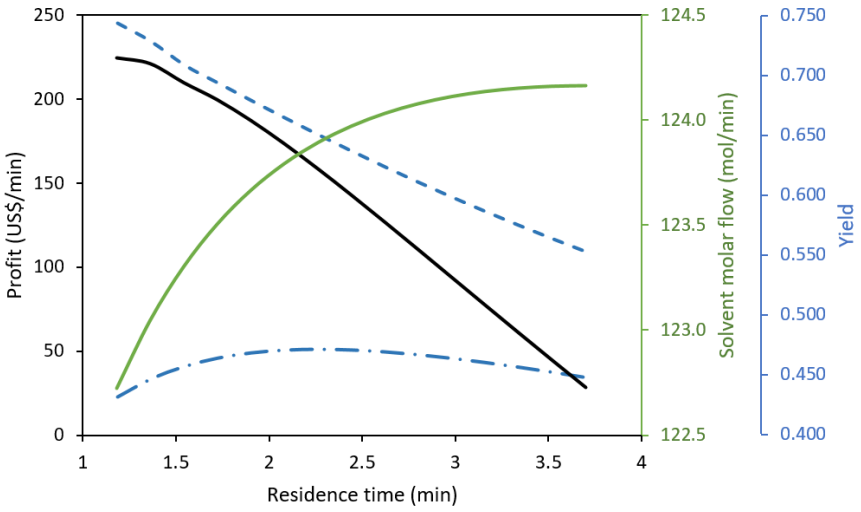

Figure 3: Effect of residence time on the solvent flow rate, reactor yield, total yield and profit (considering an HMF selling price of US$ 200) (Profit (US$/min), Reactor Yield, Process Yield, Solvent molar flow (mol/min).

Until the maximum reactor yield (τ =2.28 min), the longer the residence time, the higher the HMF production; however, the smaller the profit. Careful observation showed that it happens mainly because of the water produced in the HMF reaction. As shown in Figure 2, the HMF production from fructose occurs via dehydration reaction: for each HMF produced, 3 water molecules are released. That way, increasing HMF yield also increases the water content on the aqueous stream that feeds the extractor. More significant water flow results in more substantial solvent flow to maintain the solvent/water ratio that allows the HMF extraction. However, the

solvent flow directly impacts the evaporator energy consumption and ultimately, the operating cost in a way that bigger reactor yield is not economically attractive.
This result also goes along with the fact that a recycling system feeds the reactor with the non-reacted fructose. Thus, low reactor yield does not mean low total yield; on the contrary. Since the system was designed to consider constant reactor feeding (10 $kmol^{fructose}$/min), if the reactor yield is low, the system is feed with a small amount of fructose (to preserve the reactor feed), increasing the total yield. Moreover, when it comes to sequential reactions at CSTR, short residence time increases the HMF selectivity despite low conversion. These comparison data were summarized in Table 2. The first column shows the results of the optimization that minimizes the HMF production cost. The HMF minimum production cost is US$ 141.10, assuming the input parameters considered in Table 1, obtained with 0.49 min of reactor residence time, total production of 2.95 $kmol^{HMF}$/min, and high total yield (0.807) and selectivity (0.871). Under the same process parameters but maximizing the HMF production instead, it is obtained a minimum production cost of US$ 166.70 with 2.28 min of reactor residence time, 4.71 $kmol^{HMF}$/min and a smaller total yield (0.649), and selectivity (0.668).
Comparing the two scenarios (Min Production cost or Max HMF Production), a smaller conversion results in smaller fructose feed in the system, smaller purge, and higher total yield and selectivity.

Table 2: Optimal process conditions for different objective functions: (A) minimize the HMF MPC, (B) maximize the HMF production, (C) minimize the HMF MPC under residence time restrictions (τ>2.28).

	A Min MPC	B Max HMF	C Min MPC
Minimum production cost (MPC)	141.1	166.7	173.5
Residence time (min)	0.49	2.28	2.65
HMF (kmol/min)	2.95	4.71	4.68
Feed Fructose (kmol/min)	3.65	7.26	7.54
Reactor yield	0.295	0.471	0.468
Total yield	0.807	0.649	0.622
Conversion	0.338	0.705	0.735
Selectivity	0.871	0.668	0.637
Makeup solvent (kmol/min)	0.155	0.248	0.247
Solvent extractor feed (kmol/min)	120.3	123.9	124.0
HMF from extractor	0.170	0.173	0.173
Purge	4	7	7
Total cost (US$/min)	416	785	813
Steam (kg/min)	4208	4270	4273

As shown previously, the short residence time allows a small reactor yield that minimizes the solvent flow hence minimizing the energy consumption and HMF production cost. However, the time required to separate the organic and aqueous phases inside the reactor needs to be considered, thus impacting how small the residence time can be. According to Torres et al. (2010), the smallest residence time that allows the reactor phase separation is 2.65 min; therefore, the process is technically feasible only for residence time above this value.
The third column of Table 2 shows the HMF production cost minimization results under the lower-limit residence time restriction (τ >2.65 min). The MPC is US$ 173.50, with high conversion (0.735) but a smaller total yield (0.622) and selectivity (0.637).
The technically feasible scenario has its cost distribution illustrated in Figure 4a. The evaporation energy consumption can be optimized by altering the operating conditions; however, it represents only 4% of the production cost of HMF. The most significant contribution is given by fructose as raw material, which represents 92% of the cost of production. Similar results have been described by Torres et al. (2010) that evaluated the HMF production from fructose with MIBK:2-butanol (7:3) as the solvent. The partition coefficient is similar (1.65) even though the solvent:water ratio is smaller (1.56). The minimum HMF production cost (MPC) described by the authors was 273 US$ /kmol and some factors contributed to higher cost, such as more expensive solvent (220 US$/kmol) and smaller selectivity (0.46) despite the higher conversion (0.91). In this case, the fructose cost represents 87% of the total cost of production. According to the authors finding an alternative raw material is the only way to substantially impact the HMF final cost. Even though it could not be enough to make the large-scale HMF production economically viable yet (Santiago and Guirardello, 2020).
Figure 4b illustrates a sensitivity analysis of fructose price and how it impacts the HMF cost distribution. As expected, the smaller the fructose price, the smaller its contribution to the HMF cost of production, the more significant the makeup solvent cost contribution and the evaporation energy consumption.

The results suggest that the HMF production economic viability still depends on the raw material price. But as the fructose price cheapen or other raw materials are available, the solvent and energy consumption will become more relevant to the process improvement; thus, the residence time will have to be carefully considered to minimize the HMF production cost. Further research may regard the use of parallel decanters on the reactor outlet stream in a way that favors the phase separation even under short reactor residence time. Such analysis needs to estimate the capital cost involved in such an alternative.

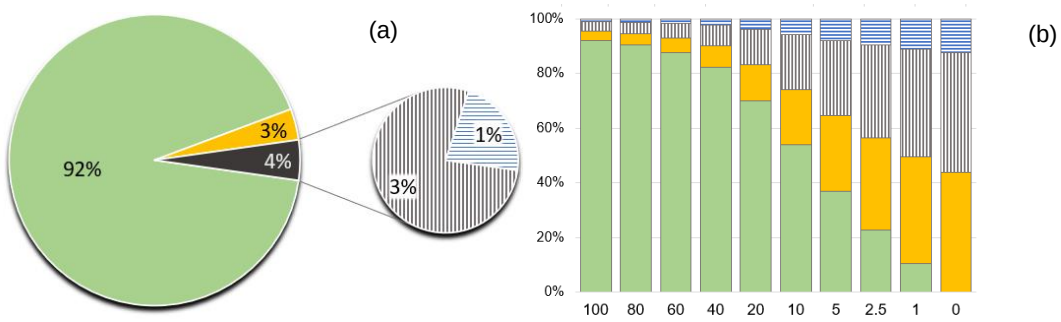

Figure 4: Cost distribution of optimized HMF minimum production cost considering (a) fixed fructose cost (99.3 US$/kmol) and (b) varying fructose cost from 0 to 100 US$/kmol (sensitivity analysis). Cost of: fructose, makeup solvent, evaporation (steam and cooling water).

4. Conclusions

The present study intended to assess the HMF production using a MILP model that minimizes the production cost (MPC). The results showed that short residence time (0.49 min) increases the total yield and selectivity (0.8 and 0.87) and decreases the production cost (MPC US$ 141.10) since it minimized the solvent demand. However, it is not technically feasible since it does not allow the reactor phase separation. Considering lower-limit residence time restriction (2.65 min) the MPC was US$ 173.50 (total yield of 0.62). The cost distribution, though, showed that fructose represents 92% of the final HMF cost of production, suggesting that the only way to substantially impact the HMF minimum production cost (MPC) is to find an alternative raw material.

Acknowledgments

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