

# Effect of the solvent on the operating cost of 5-hydroxymethylfurfural downstream processing

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The bio-based circular economy raises demand for competitive processes to produce bio-based versatile chemicals. The 5-hydroxymethylfurfural is within this demand since it is a relevant building block not economically viable yet. A promising production process is based on a biphasic reactor where the HMF is rapidly extracted to the organic phase that is further evaporated until desirable product purity. The evaporation operating cost is the second leading contributor to the HMF final price, so the present study intended to investigate the solvent's impact on energy demand and operating cost. The results showed that the solvent's physical properties impact the cost, almost doubling the utility cost among alternatives. However, a careful observation also showed that the minimum production cost is way more affected by the reaction selectivity. Thus, it is worth it to increase the solvent flow (also increasing the energy demand and utility cost) as a strategy to increase the extraction capacity and, consequently, the reaction selectivity.

## 1. Introduction

5-hydroxymethylfurfural (HMF) is a promising bio-based product. It is described as one of the top products produced from biomass mainly because it is considered a building block; therefore, it can be used to produce several sustainable chemicals (Bozell and Petersen, 2010). Nowadays, it is especially important due to social pressure for a bio-based circular economy. However, HMF production is not economically viable yet (Torres et al., 2010). HMF is produced via glucose or fructose dehydration, but it can be rapidly rehydrated to levulinic acid and formic acid. The use of biphasic reactors has been described as a promising alternative since the solvent can extract the HMF as soon as it is formed, minimizing the rehydration, and increasing the HMF selectivity. The downstream processing includes an extractor and an evaporator (Roman-Leshkov et al., 2006). The extractor recovers the HMF of the aqueous phase, and the evaporator withdraws the solvent of the HMF until it reaches the desired purity. The cost distribution reported in the literature has shown that the evaporation operating cost is the second leading contributor to the HMF high production cost (the raw material cost is the main one) (Torres et al., 2010). Although experimental research focuses on the solvent's partition coefficient, economic interests unfold to many other relevant properties. For example, the solvent heat of vaporization affects steam consumption, the solvent heat capacity affects the cooling water consumption, and the vapor pressure affects the pumping (electricity) costs. Thus, to improve the HMF production process, it is crucial to compare several solvents considering these physical properties besides their capacity to extract the HMF; however, such exploration is yet insufficient in the literature.

The present work intends to fill this gap by estimating solvent's evaporation operating costs and unfolding how its properties impact HMF production cost. Seven solvents (1-butanol, 2-butanol, 1-hexanol, MIBK, MIBK:2-butanol, Toluene:2-butanol, THF) were tested in two alternative scenarios: scenario A in which all the solvents have the same molar flow, and scenario B in which the extraction capacity was considered, resulting in greater selectivity for the solvents with higher partition coefficient. Scenario B also can be affected by the presence of NaCl salt in the aqueous phase, which causes a salting-out effect that increases the extraction. Thereby 13 settings were analysed in two alternative scenarios, lighting how the solvent's choice can impact the process.

## 2. Methodology

### 2.1 Process description

The HMF production process consists of a biphasic reactor fed with raw material (fructose or glucose), water, acid catalyst, and solvent. The reaction occurs in the aqueous phase, followed by selective extraction of HMF to the organic phase. The solvent-rich outlet stream directly feeds the evaporator, while the aqueous stream feeds the extractor. The extractor recovers the HMF that remained in the aqueous stream, and its solvent-rich outlet stream feeds the evaporator. The evaporator withdraws the solvent until the product stream is at the desired HMF purity (0.95) and recycle the solvent. Figure 1a illustrates the whole process.

This process's operating cost is highly influenced by the evaporator, representing the second leading contributor to the HMF production cost. The utilities consumed within this unit operation are illustrated in Figure 1b.

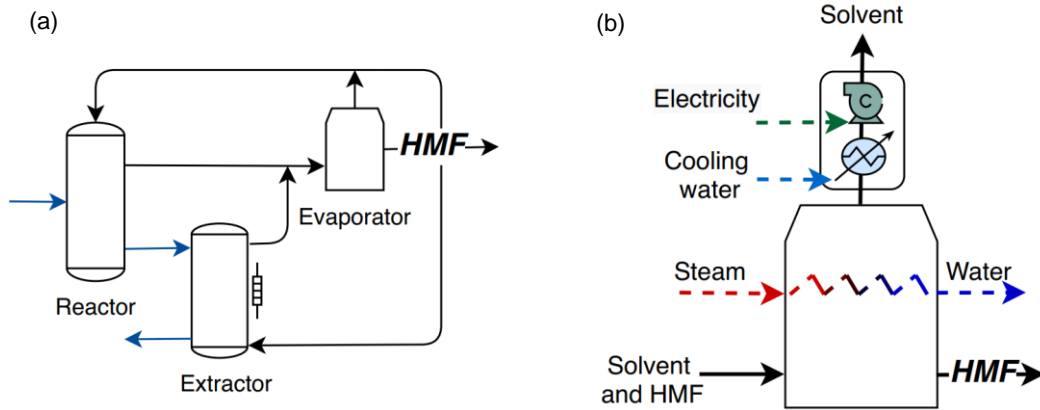


Figure 1: Process diagram (a) and evaporation diagram (b) illustrating the utility streams considered.

It was considered a single-effect evaporator fed with saturated steam that leaves as a condensate. The organic solution is considered completely mixed in equilibrium with the vapor, both in the boiling point of the solution. High temperature causes HMF thermal degradation, so it is important to keep the temperature under 343 K (Motagamwala et al., 2019). The evaporation under this condition requires the operation pressure to be smaller than each solvent's saturation pressures ( $P^{op}=0.9P^{sat}$ ) (Table 1). The solvent vapor must be condensed and fed back to the system at atmospheric pressure. The condensation is done by a surface condenser and cooling water, while a pump adjusts the pressure.

These solvent parameters (heat of vaporization, heat capacity, saturation pressure) were calculated under the operational conditions and according to standard thermophysical property formulations described by Perry's Chemical Engineers' Handbook (2018). The mixture property was calculated using a weighted average of pure solvent properties.

Table 1: Solvent properties (base case conditions): heat of vaporization, heat capacity, saturation pressure, partition coefficient, and solvent:water ratio.

| Solvent                     | $\Delta H_{vap}$<br>(MJ/kmol) | $C_p$<br>(kJ/kmol.k) | $P^{sat}$<br>(kPa) | $R^{***}$ | S:W<br>(v/v) |
|-----------------------------|-------------------------------|----------------------|--------------------|-----------|--------------|
| 1-butanol                   | 34.8                          | 332.3                | 27.2               | 1.7       | 1.6          |
| 2-butanol                   | 27.8                          | 335.8                | 11.6               | 1.6       | 3.2          |
| 1-hexanol                   | 42.1                          | 351.4                | 10.9               | 0.9       | 3.2          |
| MIBK 1                      | 29.1                          | 272.2                | 0.8                | 0.9       | 1.51         |
| MIBK3 3                     | 29.1                          | 272.2                | 19.2               | 0.96      | 3.13         |
| 7:3 MIBK:2-butanol 1        | 28.7                          | 291.3                | 16.9               | 1.65      | 1.56         |
| 7:3 MIBK:2-butanol 3        | 28.7                          | 291.3                | 16.9               | 1.73      | 3.68         |
| 5:5 Toluene:2-butanol       | 28.2                          | 274.8                | 17.8               | 1.2       | 3.2          |
| 1-butanol *NaCl             | 34.8                          | 332.3                | 27.2               | 3         | 3.2          |
| 2-butanol *NaCl             | 27.8                          | 335.8                | 11.6               | 3.6       | 3.2          |
| 1-hexanol *NaCl             | 42.1                          | 351.4                | 10.9               | 1.5       | 3.2          |
| 5:5 Toluene:2-butanol *NaCl | 28.2                          | 274.8                | 11.6               | 2.7       | 3.2          |
| THF **NaCl                  | 21.9                          | 170.3                | 104.2              | 3.51      | 3            |

\*35 wt % NaCl \*\*saturated \*\*\*Data published by experimental research under certain respective S:W ratio.

The steam, cooling water, and pump electricity demand were estimated according to Eq(1), Eq(2), and Eq(3), respectively.

$$\dot{m}_{\text{steam}} = \frac{\dot{n}_s \lambda_s}{\eta_{\text{ev}} \lambda_{\text{steam}}} \quad (1)$$

$$\dot{m}_{\text{coolingwater}} = \frac{\dot{n}_s \lambda_s}{c_p \Delta T} \quad (2)$$

$$\dot{Q}_p = \frac{\dot{n}_s (p - p_s)}{\eta_{\text{pum}} \rho_s} \quad (3)$$

The utility cost considered were 6.61 US\$ MT<sup>-1</sup> (US\$ per metric ton - 10<sup>3</sup> kg) for steam (6.2 bar;  $\lambda=2089$  kJ kg<sup>-1</sup>), 0.05 US\$ MT<sup>-1</sup> for the cooling water ( $c_p=4.17$  kJ kg<sup>-1</sup>K<sup>-1</sup>), and 0.05 US\$ kWh<sup>-1</sup> for the pump electricity (Kuo and Yu, 2020). The evaporator and pump efficiency were considered 0.75.

## 2.2 Scenario A: Fixed solvent flow

The heat of vaporization ( $\Delta H_{\text{vap}}$ ) impacts how much steam is consumed; the heat capacity ( $C_p$ ) impacts how much cooling water is consumed, and the saturation pressure ( $P^{\text{sat}}$ ) impacts how much electricity the pump consumes.

To evaluate how these properties impact the operating cost, the solvent molar flow was considered constant and the evaporation cost was estimated. This result does not consider the impact that the solvent has on the reaction selectivity or the total HMF recovered after extraction.

## 2.3 Scenario B: Reactor and extractor consideration

The solvent capacity to extract the HMF is crucial to increase the reaction selectivity, which is the main issue that the biphasic reactor intends to solve. No use in saving energy if no HMF is being produced. To evaluate this matter, the reactor and extractor were considered in the analysis, as well as the impact of different solvents on the reactor yield and extractor efficiency.

The HMF selectivity, total production, and extraction efficiency depend on the solvent capacity to extract the product from the aqueous phase and avoid undesirable rehydration, measured by the partition coefficient ( $R$ ). This property ( $R$ ) was experimentally evaluated and published by Román-Leshkov et al. (2006), Román-Leshkov et al. (2007), and Tang et al. (2016); the data is summarized in Table 1. The data shows that  $R$  depends on the solvent type, the addition of salt such as NaCl (salting-out effect), and, importantly, the solvent:water ratio. The latter is also summarized in Table 1 in agreement with the experimental conditions in which the  $R$  data were obtained.

The biphasic reactor was solved as a CSTR with fast selective continuous mass transfer between the phases as described by Torres et al. (2010). The reactor residence time was considered 2.67 min since this is the time needed to allow the organic and aqueous phase separation. The reaction network counts the fructose dehydration ( $k_1=0.992$ ), the HMF re-hydration ( $k_3=0.055$ ) and the humin formation from fructose ( $k_2=0.922$ ), and HMF ( $k_4=0.055$ ). The system of eleven equations was solved using the tool Solver on Microsoft Excel.

The conversion and selectivity were defined as:

$$\text{Conversion} = \frac{\text{moles of fructose reacted}}{\text{moles of fructose fed}} \quad (4)$$

$$\text{Selectivity} = \frac{\text{moles of HMF formed}}{\text{moles of fructose reacted}} \quad (5)$$

The extractor also considered the experimental  $R$ , and it was solved assuming ten theoretical stages and equilibrium at each stage by using the correlation presented by Cussler (2009) (Eq(6) and Eq(7)). According to Perry's Chemical Engineers' Handbook (2018) this is the upper limit for extraction efficiency.

$$\frac{y_{11}}{y_1} = \frac{1 - A^{11}}{1 - A} \quad (6)$$

$$A = \frac{\dot{n}_{\text{org}} \rho_{\text{aq}}}{\dot{n}_{\text{aq}} \rho_{\text{org}} R} \quad (7)$$

To assess the economic impact of the solvent on the HMF production cost, two outputs were calculated: the minimum production cost (MPC) and the evaporation contribution to the HMF minimum price (EC).

The minimum cost of production (US\$/kmol) is the sum of raw material, makeup solvent, steam, cooling water, and electricity costs (US\$/min) divided by the HMF total production (kmol/min). Since the raw material often represents more than 80% of the total cost, a more transparent way to evaluate the solvent impact on the production cost is to analyze only the evaporation contribution (EC - US\$/kmol). The EC is the sum of steam, cooling water, and electricity costs (US\$/min) divided by the HMF total production (kmol/min).

### 3. Results

The operating cost related to solvent evaporation's utilities (steam, cooling water, and electricity) is the second leading contributor to final HMF production cost (Torres et al., 2010). Since this critical bio-based building block production is not economically viable yet, it is essential to understand how the process variables influence this utilities' demand. To evaluate this matter, the present study simulated the evaporation process of thirteen alternative solvents (1-butanol, 2-butanol, 1-hexanol, MIBK, MIBK:2-butanol, Toluene:2-butanol, THF). It also evaluated fixed molar flow (Figure 2a) or variable molar flow (Figure 2b) depending on the HMF extraction capacity.

Solvent properties such as heat of vaporization, heat capacity, and vapor pressure directly impact the utilities' demand and, consequently, the HMF production cost. To evaluate this impact despite different extraction capacity, the analysis was made considering fixed molar flow (100 kmol/s). The main contributor to utility cost was the steam required to evaporate the solvent, affected by the heat of vaporization ( $\Delta H^{vap}$ ) (Table 1). That way, solvents with high  $\Delta H^{vap}$ , such as 1-hexanol and 1-butanol, showed the most significant utility cost (US\$22.95/s and US\$18.97/s, respectively). The second contributor was the cooling water required to condensate the solvent after evaporation, affected by its heat capacity ( $C_p$ ). Even though the cooling water cost can double within the solvents evaluated (US\$ 2.62/s for THF and US\$ 5.04/s for 1-hexanol), it averagely represents only 22% of the total utility cost. The electricity required to pump the solvent from evaporation to operating pressure was the least relevant cost representing less than 1% of the total cost for all the solvents evaluated. Hence, considering the evaporation utilities, the more expensive solvent is the 1-hexanol since it has the highest heat of vaporization and heat capacity. The less expensive solvent is the THF, with the lowest energy demand.

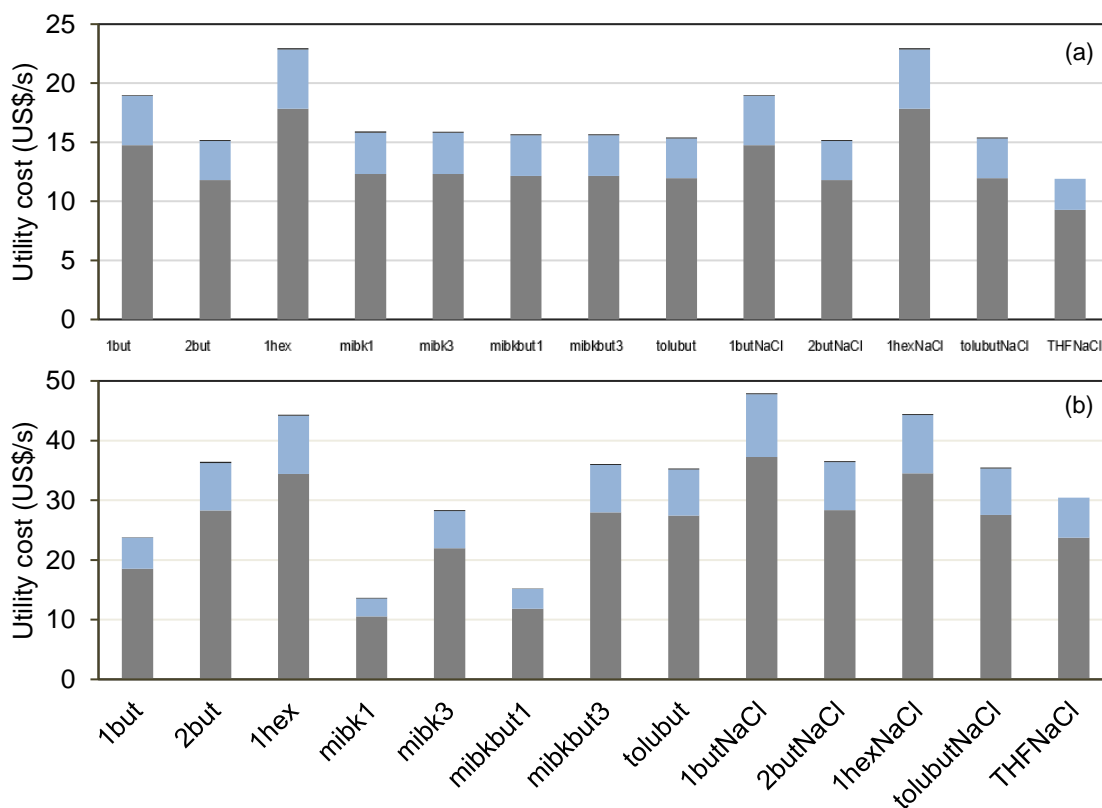


Figure 2: Utility cost distribution of evaporation process considering (a) constant solvent molar flow (100 kmol/s), and (b) different molar flow due to distinct solvent capacities to extract HMF (■ steam, ■ cooling water and ■ electricity) for all solvents evaluated.

The extraction capacity is measured by the partition coefficient (R) that depends on the solvent type and solvent:water ratio. Different solvents can be experimentally evaluated under different S:W ratios (Table 1); which directly impact the solvent molar flow and, consequently, the energy demand. That way, the impact on the evaporation utilities' demand goes beyond its physical properties and needs to also be analyzed in an extraction capacity point of view. For example, the solvents 1-hexanol and MIBK1, have the same partition coefficient (R=0.9) even under different S:W ratio (3.2 and 1.51, respectively). Analyzing just the physical properties, the MIBK can seem more interesting (Figure 2a) but taking the extraction capacity into account its advantage significantly increases (Figure 2b). Analyzing 1-butanol and 2-butanol this effect became even more apparent. Both have comparable R (1.7 and 1.6, respectively) but under highly different S:W ratios (1.6 and 3.2, respectively). That way, even though the 2-butanol can seem more attractive from a physical properties point of view when extraction capacity (R and S:W ratio) is considered, then the 1-butanol becomes highly more interesting (Figure 2a and 2b).

Among the same solvent, an attempt to increase the partition coefficient is to increase the S:W ratio, as can be seen in Table 1. For example, by doubling up the S:W ratio of MIBK solvent, it was possible to increase the R from 0.9 to 0.96. Or, by increasing in 2.3-fold the S:W ratio of MIBK-2butanol solvent, the R has risen from 1.65 to 1.75. For these two cases, increasing the S:W ratio equally increases the utility cost (2-fold for MIBK and 2.3-fold for MIBK-2-butanol) (Figure 2b). Economically the question is: is it worth it to double the utility cost (because of doubling the S:W ratio) to gain 6.7% on the partition coefficient and extraction capacity?

The understanding of this matter depends on the comprehension of the whole process. This configuration (Figure 1a) was developed to allow the HFM extraction from the aqueous phase as soon as it is formed, minimizing side reaction and selectivity lost. Thus, the biphasic reactor has two outlet streams, the aqueous and the organic streams. The organic goes direct to the evaporator, and the aqueous goes to the extractor where the HMF remained can be extracted. It is essential to highlight that the HMF formation is followed by water formation (1:3 ratio) since it is a glucose/fructose dehydration reaction. Considering that a solvent:water ratio needs to be held to guarantee the extraction capacity, the extent of reaction can increase the extraction of solvent demand, which increases the evaporation energy demand. This brief process overview shows that it is not enough to look for the utility cost without analyzing the reaction extent and its impact on solvent demand. With that in mind, the further analysis will focus on the minimum production cost (MPC) and the evaporation contribution to the HMF minimum price (EC), which reflect the HMF unit cost (US\$/kmol).

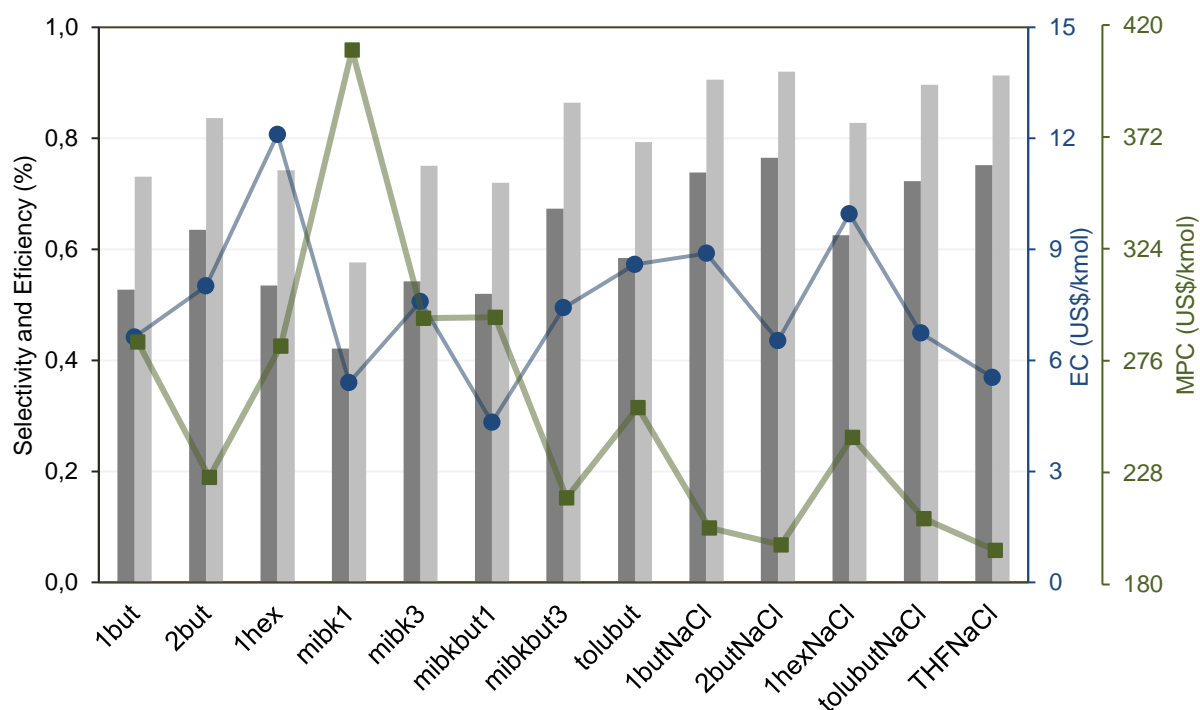


Figure 3: Peculiarities of Selectivity (■), Efficiency (■), Evaporation utility cost (●), and Minimum production cost (■) of evaporation process considering different molar flow for each solvent due to distinct capacities to extract HMF from the aqueous phase.

Proceeding the comparison between different S:W ratio (1.51 - 3.13) for the same solvent (MIBK) (Table 1), even though it allows a small gain in partition coefficient (0.9 – 0.96), it has a significant impact on the selectivity, extraction efficiency, and minimum production cost, despite the higher operating cost. The solvent molar flow more than doubled, causing the evaporation cost to double as well. But the amount of HMF produced increased by 30%, increasing the selectivity from 42% to 52%. The extraction efficiency has also risen from 58% to 75%. That way, even though the evaporation cost increased from 5.40 to 7.59 US\$/kmol, the minimum production cost decreased from 409 to 294 US\$/kmol.

A similar effect occurs when the S:W ratio of the solvent MIBK/2-butanol increases (Table 1): the selectivity increased 29%, the extraction efficiency increased 19%, the evaporation cost doubled, but the minimum production cost decreased from 294 to 217 US\$/kmol. Similar values of MPC (250 US\$/kmol) were reported by the literature for the HMF production from fructose with MIBK/2-butanol as solvent and HCl as catalyst (Santiago and Guirardello, 2020).

The more significant impact on the MPC is because, frequently, more than 85% of the total cost of production is spent on raw material (fructose or glucose) (Torres et al., 2010). That way, is more relevant to increasing selectivity and extraction efficiency than decreasing the evaporation energy demand.

An alternative to increase the partition coefficient is to add salt (NaCl) to the aqueous phase, creating salting-out effect that increases the solvent extraction capacity without changing the W:S ratio (Altway et al., 2018). This effect can be seen within three pairs of solvents evaluated: 2but and 2butNaCl, 1hex and 1hexNaCl, tolobut and tolobutNaCl (Figure 3) - all have the same W:S ratio (3.2). The NaCl presence was enough to increase the HMF selectivity (20, 17, and 24%, respectively), the extraction efficiency (by around 10%), and decrease the minimum production cost (13, 14, and 19%, respectively).

#### 4. Conclusions

The present work intended to study the solvent's impact on the evaporation operating cost of HMF production; since this is the second leading cost contributor to a relevant but not yet economically viable process. Seven solvents under thirteen conditions were evaluated, and the results showed that the physical properties notably impact the energy demand, and consequently, the process's cost. However, the results also show that the solvent's impact on the reaction selectivity is even more critical. It is more beneficial to increase the solvent flow and, hence, the energy demand (and operating cost) in improving the extraction capacity and reaction selectivity. This strategy increases the HMF production and significantly decreases the minimum production cost.

#### 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).

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