

# Comparison of Extraction Solvents in the Recovery of Levulinic Acid from Biomass Hydrolysate Using a Group Contribution Method

Jean Felipe Leal Silva\*, Rubens Maciel Filho, Maria Regina Wolf Maciel

School of Chemical Engineering, University of Campinas, São Paulo, Brazil  
[jefelipe@outlook.com](mailto:jefelipe@outlook.com)

Cost-efficient production of renewable chemicals depends not only on cheap feedstocks and efficient reactor technology, but also on efficient downstream processing technologies. Levulinic acid, a product of hydrolysis of biomass, is a renewable chemical with various potential applications in several industries, such as chemical, pharmaceutical and food. However, its production in large scale is hampered because of deficient reactor and recovery technologies. Recovery of levulinic acid is a cumbersome task since degradation of biomass in high temperatures also leads to production of humins. In this work, the recovery of levulinic acid from biomass hydrolysate was evaluated using the UNIFAC group contribution method. As consequence of the dilute nature of the process and the presence of water, two scenarios with two different organic, aprotic solvents were tested to perform liquid-liquid extraction of levulinic acid: 2-methyltetrahydrofuran (MTHF) and hexane. Both scenarios were optimized considering the all process requirements for solvent recovery and recycling, and the overall process was evaluated in terms of capital and operational expenditures. Although hexane is a traditional extraction solvent option in industry, results demonstrated that the use of MTHF leads to a recovery cost 26% lower than using hexane. Therefore, this investigation using a group contribution method demonstrated the potential of using MTHF in the recovery of levulinic acid. The potential of this process needs to be validated experimentally in the future, and such approach contributes to the development of separation processes for production of renewable chemicals in biorefineries.

## 1. Introduction

Economic success in the production of biofuels depends not only on reactor technology and security of biomass supply, but also depends on reliable downstream processing technologies (Valdivia et al., 2016). One of the main hurdles when it comes to production of renewable chemicals is that the desired product is generally obtained in dilute aqueous solutions (Thompson et al., 2014). This factor has an even more negative impact in economics when the chemical is less volatile than water, as in the case of levulinic acid (LA).

Hydrolysis of biomass under appropriate conditions produces sugars such as glucose and xylose, which under more severe conditions undergo dehydration to produce 5-hydroxymethylfurfural (HMF) and furfural, respectively. HMF, in acidic aqueous media, decomposes into formic acid and LA (Lopes et al., 2017). LA is a chemical building block with potential applications in food, polymer, pharmaceutical, and fuel industries (Morone et al., 2015), being pointed out as one of the DOE's 12 top value-added chemicals from biomass. One of its main potential applications is as feedstock for production of ethyl levulinate, a biodiesel additive which improves cold flow properties (Leal Silva et al., 2018).

This mixture of furans and sugars inside the hydrolysis reactor is very reactive, and much of the selectivity in production of LA is compromised due to side reactions that lead to production of humins (van Zandvoort et al., 2013). Humins are a black, insoluble, and invaluable product of biomass hydrolysis (Puccini et al., 2016), and represent a great burden in LA production (Raspolli Galletti et al., 2012). Formation of humins occurs mostly inside the hydrolysis reactor which operates in severe conditions, and to a lesser extent in the downstream

equipment. Therefore, proper technologies must be used to recover high purity LA from hydrolysate. Since LA is less volatile than water, one option to recover LA at high purity is solvent extraction.

In this context, this work assesses the downstream processing of a biomass hydrolysate rich in LA by employing liquid-liquid extraction using 2-methyltetrahydrofuran (MTHF), a green solvent which can be obtained from LA or furfural (Silva et al., 2018). Liquid-liquid equilibrium data for all components is not available in the literature. Therefore, activity coefficients were calculated using the UNIFAC model. Results were compared to another extraction system employing hexane, a common solvent in liquid-liquid extraction (Cheng and Rosentrater, 2017). Important steps in the separation process were considered, such as the concentration step and the recovery of solvent, to demonstrate the potential to use a green solvent in the recovery of LA.

## 2. Methodology

Comparison of extraction solvents was carried out by means of process simulation using Aspen Plus 8.6 (Aspen Technology, Inc., 2014) and economic assessment. A design of experiment was used to develop a model to determine optimized operating conditions, and the results of simulations in these conditions were compared.

### 2.1 Process description and simulation

For process considerations, hydrolysate composition was based on the best case reported by Leal Silva et al. (2018) for production of LA from sugarcane bagasse in Brazil. Mass flow rate was determined supposing the use of surplus bagasse from a sugarcane mill processing 4 million tonnes of sugarcane per year (Klein et al., 2017), with an operational year of 200 days due to harvesting limitations, which averages to a capacity of 80 kt/y of LA. Hydrolysate available at 1 bar and 90 °C containing LA was fed to a concentration step, which consisted of six multiple-effect evaporators. The minimum temperature difference between hot and cold sides was fixed at the first effect, 10 °C, and the operating pressures of the other effects were adjusted to provide the same heat transfer area to all of them. Following the evaporators, the mixture was contacted with an extraction solvent at a required mass proportion to recover 99% of LA. The top stream, containing solvent and LA, was sent to a stripping column. The bottom product of this stripping column was separated in a second column to yield formic acid and LA. The raffinate was also stripped off solvent. From the remaining water in the raffinate, 5% was purged and treated as wastewater stream, whereas the rest was assumed to be reused in hydrolysis. In the case of MTHF as extraction solvent (Figure 1a), the recovered solvent from the stripping column was contaminated with water, and this last separation was performed by means of molecular sieves because of the azeotrope. Separation of MTHF and water using molecular sieves is not reported in the literature. Therefore, data for ethanol-water separation in molar basis was used (Kang et al., 2014). In the case of hexane (Figure 1b), the amount of water in the extract was neglectable (< 500 ppm), and no further purification was required.

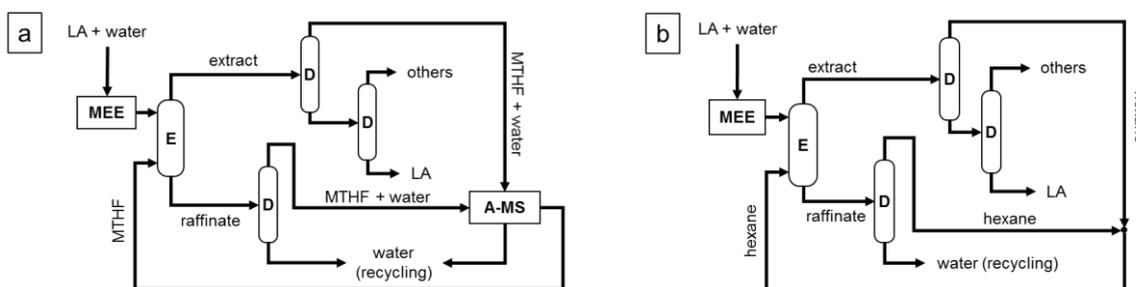


Figure 1: Block flow diagram of the extraction processes in the case of: a) MTHF and b) hexane. Abbreviations: MEE – multiple effect evaporators, E – extractor, D – distillation, A-MS – adsorption in molecular sieves.

Because of the presence of carboxylic acids, the vapor phase behavior was modeled using the Hayden-O'Connell equation of state to account for the dimerization effect. Interaction parameters not available in the Aspen Plus database of version 8.6 were added from Resk et al. (2014). As for the liquid phase, there are no liquid-liquid equilibrium data for all combinations of components, which prevents the use of more reliable activity coefficient models such as NRTL or UNIQUAC. Therefore, activity coefficients in the liquid phase were estimated using the UNIFAC group contribution model, with the appropriate dataset for liquid-liquid equilibrium. All components considered in the simulation can be described using UNIFAC's group classification.

### 2.2 Analysis and optimization

Variables considered in process optimization were concentration of LA (CLA) in the extractor feed stream and number of extractor stages (NST). Solvent to feed (S/F) ratio, an important parameter in liquid-liquid extraction,

was varied to achieve a LA recovery of 99% in all cases. Temperature of extractor feed streams were fixed at 70 °C to decrease energy requirement in re-heating. Moreover, MTHF and water present reverse solubility: the increase in temperature decreases mutual miscibility. Higher temperatures were not allowed because of volatility of solvents, and this could lead to problems regarding extractor operability.

The systems with the two extraction solvents were studied beforehand using graphical methods to determine  $S/F_{\min}$  and  $S/F_{\max}$ , and choose a suitable range of NST to be used in process optimization. Ranges for CLA were chosen considering process limitations. Since the relative volatility between water and LA is large, losses of LA in the concentration step are low, and they are balanced out by the reduction in steam requirement due to the use of multiple effect evaporators. Regarding the system using MTHF, the two-phase region occurs for feeds with solute concentrations below 40 wt%, and therefore an upper limit of 35 wt% LA concentration was imposed. As for the hexane system, the same occurs for feeds with a maximum of 90 wt%, and therefore 85% was imposed as the upper limit. As for the lower limits for CLA in both cases, several values were tested to determine a suitable range. The final variable levels are listed in Table 1.

Table 1: Variable levels used in the optimization of liquid-liquid extraction of LA for each solvent option.

Solvent	MTHF			Hexane		
	-1	0	+1	-1	0	+1
NST	4	8	12	4	8	12
CLA	0.15	0.25	0.35	0.45	0.65	0.85

A face centered composite design of experiment was applied to analyze the effects of these variables in the response, which was chosen to be the recovery cost of LA (RC), defined as the sum of capital and operational expenditures on a yearly basis divided by the amount of LA produced. Capital cost was determined using the Aspen Plus Economics module integrated to Aspen Plus 8.6, updated to June 2017 using the Chemical Engineering Plant Cost Index (CEPCI), and annualized using a life span of 10 years at a discount rate of 10% with no salvage value due to corrosion reasons. For the same reason, SS316 was chosen as material of construction. Utilities cost was estimated according to Ulrich and Vasudevan (2006). Hexane price was determined based on its average cost in 2016-2017 (AliceWeb, 2017). MTHF is not available in commercial scale and still does not have a determined market price. Yet, it has potential to be used as fuel in light vehicles (Leal Silva et al., 2018). Therefore, MTHF price was determined based on its energy equivalence to ethanol and the ethanol price in 2012-2017 (CEPEA, 2017). The results of the response variable were analyzed using the software Statistica 12.5 (StatSoft Inc., 2014), and a surrogate model was determined for each solvent option:

$$RC = C_0 + \sum_{i=1}^n C_i x_i + \sum_{i=1}^n C_{ii} x_i^2 + \sum_{i=1}^n \sum_{j \geq i}^n C_{ij} x_i x_j \quad (1)$$

where RC is the recovery cost, x represents each coded variable, and C represents the coefficients of the surrogate model. Optimized operating conditions were determined using the gradient-based optimization method of Solver in Microsoft Excel 2016. Finally, these conditions were simulated and the results were used to determine the optimized RC, which was then compared to the value predicted by the surrogate model.

### 3. Results and discussion

#### 3.1 Simulation of different scenarios and optimized case

Results of RC for each case simulated based on the design of experiment are presented in Table 2. The cases simulated according to the design of experiment are cases M01 to M09 for MTHF, and cases H01 to H09 for hexane. Cases M10 and H10 represent the optimized scenarios for MTHF and hexane, respectively, which will be discussed later in this section.

Figure 2 presents the Pareto charts of standardized effect estimates for each solvent option. The coefficients of quadratic terms demonstrated to bear no significance for a confidence interval of 95%. For both solvents, CLA demonstrated to be main parameter influencing RC. Naturally, CLA is the main parameter influencing economics of this separation process because it impacts heavily the minimum S/F ratio required to perform the extraction. NST is also important because of the relationship between  $S/F_{\min}$ , actual S/F, and actual NST:  $S/F_{\min}$  corresponds to minimum solvent use combined with an impractical infinite number of stages; on the other hand, choosing an appropriate NST is important because of the compromise between operational expenditures with solvent recycling and make-up and capital investment due to extractor dimensions.

Both models tested successfully for overall significance with the F-test, and the  $R^2$  was 0.962 for the model using MTHF as solvent and 0.993 for hexane as solvent. The response surfaces obtained from these models

are available in Figure 3. It can be noticed in Figure 3a that in the case of using MTHF, there is a clear minimum. However, as seen in Figure 3b, in the case of hexane, the minimum RC occurs for the maximum allowed CLA value of 0.85. Simulation of both optimized conditions led to values of RC that agreed with the values predicted by the models. In the case using MTHF as solvent, the predicted value was 3.9% lower than the real RC, whereas in the optimized case for hexane, the predicted value was only 0.6% lower than the real. The values presented in cases M10 and H10 in Table 1 correspond to the real values of RC for each case.

Table 2: Summary of simulated cases along with their respective response variable, RC. MTHF is the extraction solvent in cases M01 to M10, and hexane is the extraction solvent in cases H01 to H10.

Case	NST	CLA	RC (\$/kg LA)	Case	NST	CLA	RC (\$/kg LA)
M01	4	0.150	0.266	H01	4	0.450	0.372
M02	4	0.350	0.192	H02	4	0.850	0.263
M03	12	0.150	0.198	H03	12	0.450	0.332
M04	12	0.350	0.187	H04	12	0.850	0.248
M05	4	0.250	0.207	H05	4	0.650	0.312
M06	12	0.250	0.181	H06	12	0.650	0.295
M07	8	0.150	0.207	H07	8	0.450	0.333
M08	8	0.350	0.184	H08	8	0.850	0.250
M09	8	0.250	0.188	H09	8	0.650	0.296
M10	9.62*	0.293	0.184	H10	9.12*	0.850	0.247

\*values were rounded in process simulation, since they represent a discrete variable (number of stages).

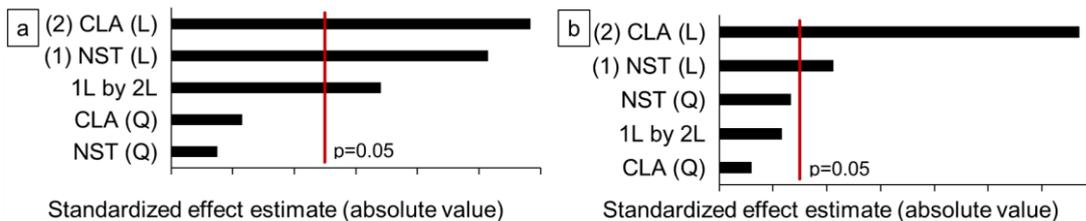


Figure 2: Pareto chart of standardized effects for a) MTHF and b) hexane as extraction solvents.

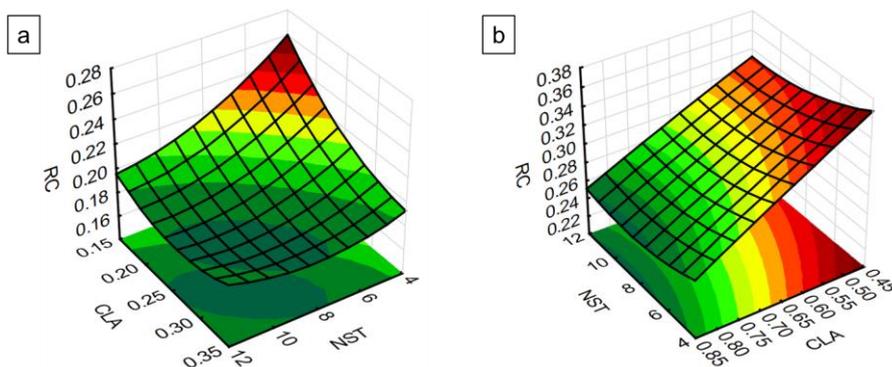


Figure 3: Response surfaces of RC in the case of a) MTHF and b) hexane as extraction solvents.

It can be noticed that the costs of using hexane are higher than those of using MTHF. In the optimized scenarios, the costs with utilities differ by only 1.2%. However, due to the higher S/F ratio used in extraction with hexane, larger equipment was required and, therefore, the capital cost was 70% higher than that of the optimized case with MTHF. Whereas the S/F ratio was 0.469 in scenario M10, it was 11.7 in scenario H10, 25 times larger. Although the difference in S/F ratios was much larger than the difference in capital cost, the use of hexane allows the extractor to operate with a feed richer in LA than in the case of MTHF, a factor that heavily impacts the RC as observed in Figure 3b. Also, the higher demand of solvent requires a larger solvent makeup, thus increasing RC because of the additional expense with more solvent purchase.

Another interesting observation is that working with a higher concentration of feed solution requires little increase in capital cost in the evaporators because of the multiple-effect setup: the six evaporators in the optimized case working with hexane have a heat exchange area only 13% higher than in the optimized case using MTHF, even though the final concentration obtained is 2.9 times larger. This more efficient use of evaporators decreases significantly the steam requirement of the process. However, this benefit is not observed in the case of hexane because of the high S/F ratio required to perform the extraction. Regarding the case of MTHF, higher CLA also means an increase in miscibility between water and MTHF and, therefore, an increase in CLA in this case also makes the recovery of solvent from extract and raffinate a more onerous task.

### 3.2 Comparison of extraction performance and impact of solvent recovery and use

The previous results demonstrated that the S/F ratio required in the case of hexane makes the use of this solvent impractical in comparison with the use of MTHF. Figure 4 presents the partition coefficient along the extractors in the case of MTHF and hexane. The partition coefficient was calculated as the ratio of solute in solvent (either MTHF or hexane) and carrier (water). Comparing the scales of the partition coefficients of Figures 4a and 4b, a clear difference in the order of magnitude between the two systems can be noticed. This difference is a consequence of the better affinity of MTHF, an oxygenate solvent, with the solutes, all oxygenated as well. Phase separation between water and MTHF is not as good as that observed between hexane and water. Consequently, the use of MTHF require more steps: raffinate must be stripped off solvent before being recycled or sent to any effluent treatment, as well as the extract will also contain water.

On top of that, recovered MTHF contains a small amount of water because of the azeotrope between these two chemicals. In this investigation, the use of 3 Å molecular sieves was suggested to perform this separation. According to the results of the thermodynamic model employed in this investigation, the azeotrope occurs for a concentration of water of 9.03 wt% (1 atm), close to the value of 10.6 wt% reported in a patent (Hangx et al., 2016). This situation is very similar to the case of hydrous ethanol, which contains about 6 wt% of water (Kang et al., 2014). The use of 3 Å molecular sieves for dehydration of MTHF is appropriate because its pore size is smaller than the size of a MTHF molecule, which was calculated to be 5.1 Å (Chem3D 15.1, PerkinElmer Informatics, Inc., 2016). However, experimental adsorption trials and a proper comparison with other techniques to circumvent an azeotrope must be conducted to determine which option is the best. For example, the fact that MTHF and water are partially immiscible liquids represents a case very similar to that of furfural and water, whose separation process is well developed (Leal Silva et al., 2018).

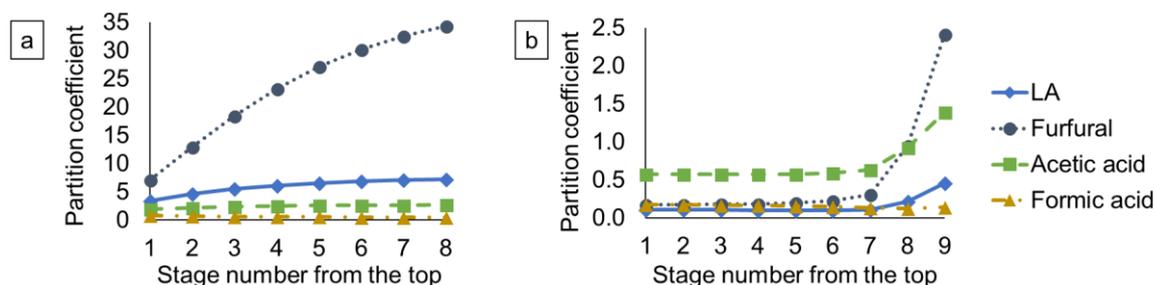


Figure 4: Partition coefficients in the optimized case using: a) MTHF (M10) and b) hexane (H10).

Regarding sustainability and safety of operation, according to the updated version of the GSK's Solvent Sustainability Guide (Alder et al., 2016), MTHF presents some issues, being biotreatment and exposure potential the more critical. However, the authors explain that this solvent is one of those with several data gaps, which may lead to incorrect score and placement in the guide. In some criteria, MTHF received low scores that does not seem reasonable. For example, based on their methodology, a score of 4 out of 10 in life cycle analysis seems low considering that MTHF can be obtained from renewable resources and solvent recovery is easy. Therefore, careful investigation of this solvent, including synthesis and handling, may elucidate this question, since part of its recovery from water was demonstrated to be performed easily in this investigation.

## 4. Conclusions

This work presented a preliminary assessment of solvents for recovery of levulinic acid using process simulation with the UNIFAC group contribution method. The results demonstrated the potential of using 2-methyltetrahydrofuran (MTHF) instead of hexane, a traditional solvent. The calculated recovery cost of levulinic acid, which included capital and operational expenditures, was 26% lower in the system using MTHF. The success of the use of this solvent was attributed to the higher affinity between MTHF and levulinic acid.

Moreover, since the potential of this process was demonstrated via a group contribution method, this work strongly supports an experimental component to obtain thermodynamic data to validate these simulation results. This is an important strategy because the frontier being explored in the development of biorefineries faces lack of appropriate thermodynamic data for process simulation. This preliminary investigation helps to narrow down possible options and avoid unnecessary experimental work to obtain accurate performance data for any solvent.

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