



## Techno-Economic Assessment of the AHP Based Selected Method for Separating Formic Acid from an Aqueous Effluent

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ARTICLE INFO	ABSTRACT
<p><b>Article History:</b> Received: 08 December 2021 Revised: 20 January 2022 Accepted: 26 January 2022</p> <p><b>Article type:</b> Research</p> <p><b>Keywords:</b> Analytic Hierarchy Process, Water Recycle, Formic Acid, Liquid-Liquid Extraction, Techno-Economic Assessment</p>	<p>Formic acid (FA) is used across the world for a wide variety of applications spanning from chemical production to textile and pharmaceutical industries. FA can be synthesized efficiently from the lignocellulosic biomass constituent carbohydrates by acid hydrolysis in a dilute aqueous reaction media. Since FA forms an azeotrope with water, its purification, water recycling, and reuse are vital to establishing a cost-competitive process. In this study, the analytic hierarchy process (AHP) was implemented to determine the desired separation method for isolating FA from a 3 wt.% aqueous solution by considering the advantages and disadvantages of each process. Four parameters named scalable, quality of the final product, repeatable, and energy consumption, were defined as criteria to perform AHP analysis. Furthermore, six alternative approaches, namely (i) azeotropic distillation, (ii) extractive distillation with a liquid solvent and (iii) solid salt, (iv) the combination of liquid solvent and solid salt, (v) pressure-swing distillation, and (vi) liquid-liquid extraction (LLE) were examined to decide the most preferred separation method concerning the goal, which is the desired separation method. The AHP results indicated that the alternative approach, the LLE, and the scalable criteria have the highest preference with 39.4% and 54% priority, respectively. The proposed process based on the alternative approach could extract 99% of FA by using diethyl ether. Moreover, an estimated minimum selling price (MSP) of 2.48 \$/kg FA with 97.4% purity was achieved by using a techno-economic assessment for a typical plant with 1715 ton/day capacity.</p>

## Introduction

Fossil-based resources (e.g., crude oil, natural gas, and coal) have been the main supply to provide energy and synthesize chemicals [1]. For an instant, formic acid (FA) is a promising compound produced from fossil feedstocks as a versatile reagent. FA is consumed in a wide range of applications, such as pesticide production, chemical synthesis, agricultural, textile,

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dyeing, leather, rubber, and pharmaceutical industries [2, 3]. On the other hand, insisting on utilizing these carbon-based resources has resulted in greenhouse gas emissions, global warming, rising water levels, and other unwanted impacts on the plant's environment.

Due to a wide variety of applications, alternative and renewable sources should be developed for FA production to mitigate environmental issues [4, 5]. FA can be synthesized from the acid hydrolysis of lignocellulosic biomass constituent carbohydrates in an aqueous media with a considerable molar yield of up to 65% [6]. The acid hydrolysis not only provides FA but also produces an important building block, levulinic acid (LA), which is a platform chemical to alternate fossil-based products in a broad range of applications [5]. Therefore, more emphasis is given to LA generation, while the treatment of water containing FA has also a great potential for FA recovery.

From an economic viewpoint, it is a cost-effective approach to use an effluent containing carboxylic acid to recover FA since the feed is a free stream. Besides, avoiding the costs associated with the treatment of acidic water and reusing water makes biomass conversion to FA and LA more promising [6, 7]. It is worth mentioning that not only FA recovery from a low-concentration aqueous solution is the main hurdle, but also FA forms an azeotrope with water (22.4 wt.% FA, 77.6 wt.% water with a boiling point of 383.5 K). Therefore, a single conventional distillation column could not isolate FA from the water to the desired purity and other methods such as azeotropic distillation, extractive distillation, or pressure-swing distillation should be exploited. Besides, liquid-liquid extraction (LLE) is considered a promising technology for carboxylic acid recovery [8].

Generally, the chemical process includes different competing criteria and most of the time are complex, as a result, their assessment is considered a decision-making task. For instant, Wang and Li [9] have proposed a model to perform the chemical process evaluation. On the other hand, a comprehensive evaluation of a process not only demands consideration of various criteria but also assessing conflicting criteria covering the issue [10]. Consequently, in such cases conducting a multi-criteria decision-making (MCDM) is inevitable. To identify the environmentally friendly and economically desirable approach among the alternative separation processes to isolate FA from the aqueous media, a systematic MCDM approach, named as analytical hierarchy process (AHP), is incorporated. AHP utilizes a hierarchy that consists of a goal, criteria, and/or sub-criteria to tackle the under-investigated problem. The application of the AHP as a useful decision-making tool in a wide range of complex issues, i.e., complex chemical process assessment [9], optimal clean technology selection [10], and hydrogen generation by biological methods evaluation [11] has been reported or reviewed. Therefore, for the first time, the AHP's ability in decision making and selecting a viable separation process is implemented to evaluate purification methods for a value-added compound. To the best of our knowledge, such a novel approach has not been utilized for choosing the FA isolation process from a dilute aqueous media. This study aims to consider various parameters with AHP assistance to select a promising approach not only for FA extraction and recovery but also to reuse water and prevent waste production. Discussion and required assumptions were made to develop the sustainable FA purification process as well. In addition, a techno-economic assessment (TEA) is conducted to determine the minimum selling price (MSP) of the FA in the established process. The detailed TEA discussions highlight the major component costs and barriers for future commercialization and pave the way for sustainable FA production.

## Methods and Procedure

### The Analytic Hierarchy Process (AHP)

Decision analysis methods have been practiced for different applications, such as energy, environmental, supply, and chain issues [12]. Among the methods, MCDM quantitatively analyzes alternatives based on the advantages and disadvantages of criteria that provide decision-makers with ranked alternatives as per several assessed criteria. This method provides opportunities for pairwise comparison of choices based on multiple criteria, then ranks them to make the final selection. Zhou and co-workers [13] studied different MCDM approaches and concluded that AHP is the most preferred approach among the existing methods for energy evaluation.

AHP analysis, which was introduced by Saaty in the late 1970s [14], has a great potential to deal with uncertainties that exist in decision-making processes. In this method, the goal, criteria, and alternatives are situated in the first, the second, and the third levels, respectively. To perform AHP multiple steps should be conducted. Briefly, this approach includes these steps. Crucial criteria are identified in the first step. In the following step, required data are collected from a panel of experts, and then measures are compared with each other considering the goal. As shown in Eq. 1, the  $A$  matrix is prepared based on the criteria score. In this matrix, each element is assigned with a value that presents the  $i^{\text{th}}$  criterion pairwise comparison to the  $j^{\text{th}}$  criterion preference result. This procedure is similar to alternatives. Saaty's 9-point scale, as illustrated in Table 1, was utilized to prepare the comparative significance of the two criteria or alternatives.

$$A = \begin{bmatrix} d_{1,1} & \cdots & d_{1,n} \\ \vdots & \ddots & \vdots \\ d_{n,1} & \cdots & d_{n,n} \end{bmatrix} \quad (1)$$

Conditions  $a_{ij} > 0$ ,  $a_{ij} = 1/a_{ji}$ , and  $a_{ii} = 1$  are considered in this matrix. The normalized principal eigenvector of matrix  $A$  is provided in the fourth step. Finally, the consistency ratio (CR) of matrix  $A$  is calculated. To do that, initially, the consistency index (CI) should be prepared. The CI can be provided utilizing Eq. 2. In this equation, the  $n$  is the number of matrix comparison sizes, and the largest eigenvalue of the matrix is  $\lambda_{\max}$ .

$$CI = \frac{\lambda_{\max} - n}{n - 1} \quad (2)$$

As shown in Eq. 3, the CR of the matrix can be provided by dividing the CI by its random reliability indicators (RI). The RI values are presented in Table 2.

$$CR = \frac{CI}{RI} \quad (3)$$

The CR values of the matrices should be less than or equivalent to 0.10 consequently, decision-making results are considered acceptable and reliable. In the case that higher amounts than 0.10 are observed, the comparison performance is not validated, and the process has to be rechecked to improve the CR value.

**Table 1.** Saaty's fundamental pairwise comparison 9-point scale, linguistic equivalents for comparison of importance/preferences [29].

Saaty's Numerical Rating	Linguistic Equivalent for Comparison of Criteria	Linguistic Equivalent for Comparison of Alternatives
1	Equally important	Equally preferred

2	Equally to moderately important	Equally to moderately preferred
3	Moderately important	Moderately preferred
4	Moderately to strongly important	Moderately to strongly preferred
5	Strongly important	Strongly preferred
6	Strongly to Very strongly important	Strongly to Very strongly preferred
7	Very strongly important	Very strongly preferred
8	Very strongly to extremely important	Very strongly to extremely preferred
9	Extremely important	Extremely preferred

**Table 2.** RI for pairwise comparison matrix

Number of Elements (n)	RI Value
1	0.00
2	0.00
3	0.52
4	0.89
5	1.11
6	1.25
7	1.35
8	1.40
9	1.45
10	1.49
11	1.51
12	1.54
13	1.56
14	1.57
15	1.58

## Research Method

As discussed earlier, the FA isolation from an aqueous solution could not be performed by a single conventional distillation column due to azeotrope formation. Therefore, different approaches have been proposed, and among them, the FA extraction by an immiscible organic solvent from the aqueous phase [15, 16] and different distillation methods are found promising [17]. To do so, selecting a suitable separation method requires performing a systematic MCDM approach, which must be conducted by logical comparison and investigating the pros and cons of the suggested separation pathways. Consequently, AHP was implemented to analyze and assess these methods. To perform AHP, six methods including azeotropic distillation, extractive distillation with a liquid solvent, extractive distillation with solid salt, and extractive distillation with the combination of liquid solvent and solid salt, pressure-swing distillation, and LLE were considered. The goal, as the first level, was set to separate FA from the aqueous solution. In the second level, the economic justification, energy consumption, environmental impacts, and types of final products were included as criteria for pairwise comparison. Selected isolation methods (the third level) were assumed as alternatives. The goal, criteria, and alternatives are presented in Fig. 1.

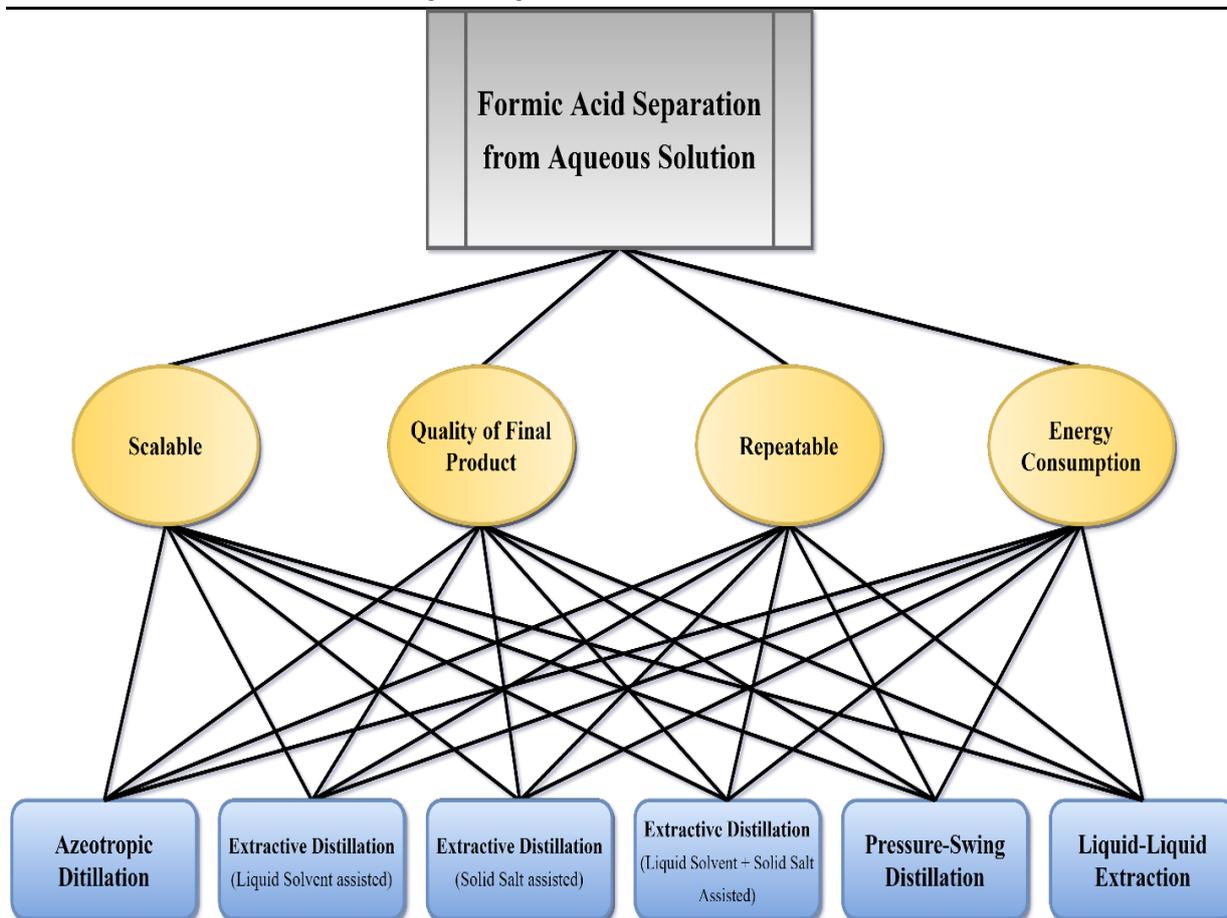


Fig. 1. The AHP flowchart for the separation of FA from the aqueous media

### Techno-Economic Assessment (TEA)

The economic evaluation of a process is a proper tool to assess the performance of the plant and facilitate the development of the process [18]. For instance, TEA has been used to evaluate the hydrocarbon fuel generation from plastic waste [19], investigate helium recovery by membrane process [20], assess small scale electricity production from the lignocellulosic biomass [21], and study the feasibility of microalgae conversion to biodiesel [22]. Here, the MSP for isolating FA from an aqueous dilute solution (i.e., 3 wt.%; FA) was estimated for a process established by AHP results. The process flow diagram of the plant with 1715 ton/day capacity is presented in Fig. 4 in the results and discussion section. Here, the plant's lifetime is 20 years, and it works for 8000 hours of operation (~330 days) each year. Since the FA purification data were provided by laboratory-scale experiments, similar to the Dumesic group's approach [23], it was assumed that separation results would not be affected during scaling up. Furthermore, as suggested by Kazi et al. [18], the economic analysis was conducted for the  $n^{\text{th}}$  plant. In other words, the  $n^{\text{th}}$  plant implies the fact that the approach has been established and operated in different plants, and it is mature not a pioneer process. In this study, total investment cost was estimated based on procured equipment costs and costs ratio [24, 25]. The equipment cost and installation cost were obtained from public databases and they were indexed to US\$2019 values [26, 27]. To estimate the operating cost of the plant, the required utilities (e.g., electricity, steam, etc.) were not included in the modeling and assumed to be available to purchase. Although recycled water in the biomass conversion to acids could be considered a credit, the revenue of the process was achieved from the sale price of FA. Lastly, one year was dedicated to plant construction/commissioning and the internal investment rate (IR) was assumed to be 10%.

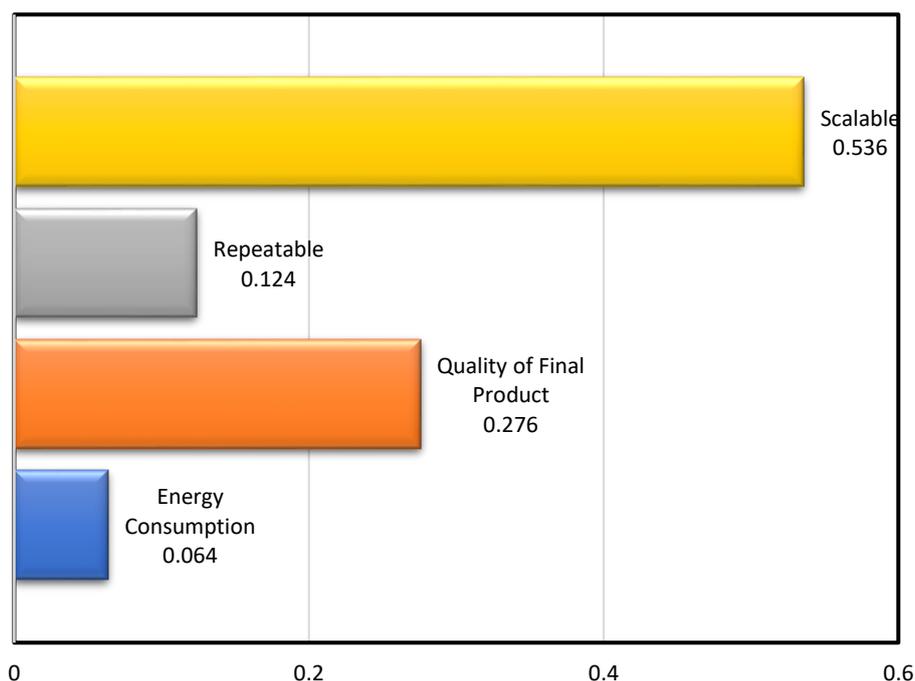
## Results and Discussion

### Decision-Making Results

To conduct AHP, the goal, criteria, and alternatives were determined. Based on the authors' experience and comments from academic researchers as well as a panel of experts from related chemical companies, four criteria, including scalable, quality of the final product, repeatable, and energy consumption, were selected. The achieved global weight of criteria is reported in Table 3. The AHP results proved that the scalable criterion with 54% importance is the most important one to the goal, as illustrated in Fig. 2. In the following priorities, the quality of the final product (28%), repeatability (12%), and energy consumption (6%) are of the greatest importance in prioritizing the methods for FA separation. The 0.00835 inconsistency, significantly less than  $<0.1$  by more than ten folds, indicates that the pairwise comparison of criteria is logical.

**Table 3.** Global weights of criteria

Criteria	Global Weight	Rank
Scalable	0.536	1
Quality of Final Product	0.276	2
Repeatable	0.124	3
Energy Consumption	0.064	4
<b>Overall Inconsistency = 0.00835</b>		



**Fig. 2.** Priorities of criteria according to importance to the goal. For a better interpretation of colored segments in this Fig., the reader is referred to the Web version of this article

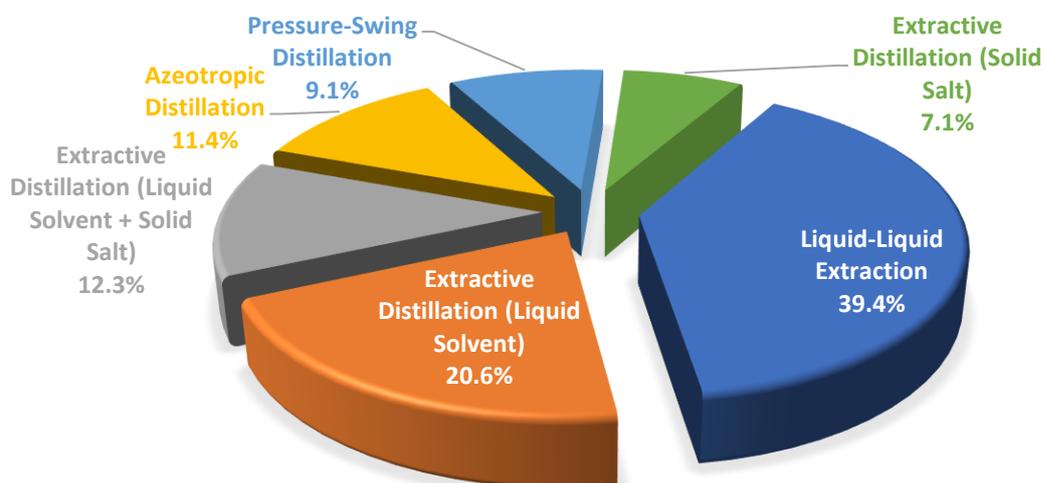
The relative weights of FA-water separation methods were calculated using Eqs. 1 to 3 according to the criteria. The criteria's weights were multiplied by the separation method's weights associated with four criteria to derive the final weights of alternatives. Table 4 lists the relative weights of each separation method in association with the criteria. Results indicated that the LLE method had the highest final score of 0.32, and both the extractive distillation with

solid salt and pressure swing distillation earned a minimum score of 0.10. The score for other methods is in the range of 0.13 to 0.21. The overall inconsistency of the approach is 0.0129, which is much less than 0.1. Therefore, the AHP results are valid and reliable.

**Table 4.** Final scores of AHP for prioritizing FA separation from the aqueous solution

Criteria	Energy Consumption (0.064)	Quality of Final Product (0.276)	Repeatable (0.124)	Scalable (0.536)	Total Weight	Rank
<b>Alternative</b>						
<b>Liquid-Liquid Extraction</b>	0.033	0.112	0.031	0.217	0.393	1
<b>Extractive Distillation (Liquid Solvent)</b>	0.007	0.043	0.019	0.136	0.205	2
<b>Extractive Distillation (Liquid Solvent + Solid Salt)</b>	0.007	0.025	0.007	0.084	0.123	3
<b>Azeotropic Distillation</b>	0.003	0.070	0.011	0.030	0.114	4
<b>Pressure-Swing Distillation</b>	0.012	0.010	0.050	0.019	0.091	5
<b>Extractive Distillation (Solid Salt)</b>	0.002	0.016	0.004	0.049	0.071	6
<b>Overall Inconsistency= 0.0144</b>						

Fig. 3 shows the absolute priority of FA–water separation methods to the goal of the AHP approach. According to Fig. 3, the LLE is the most preferred method with 39.4% priority for separating FA from the aqueous solution. The LLE process has unique specifications, such as simplicity, no need for special and complex equipment, ease of operation, operation at low temperatures and pressures, and almost complete recovery of solvent and reuse. The next priorities are assigned to be extractive distillation with liquid solvent assisted by 20.6% preference compared to other methods. The third priority is the extractive distillation by assisting liquid solvent and solid salt as entrainer (12.3%), while the obtained weight for azeotropic distillation, pressure-swing distillation, and extractive distillation with solid salt entrainer is 11.4, 9.1 and 7.1%, respectively.



**Fig. 3.** Priorities of alternatives to the goal. For a better interpretation of colored segments in this Fig, the reader is referred to the Web version of this article

## Process Design

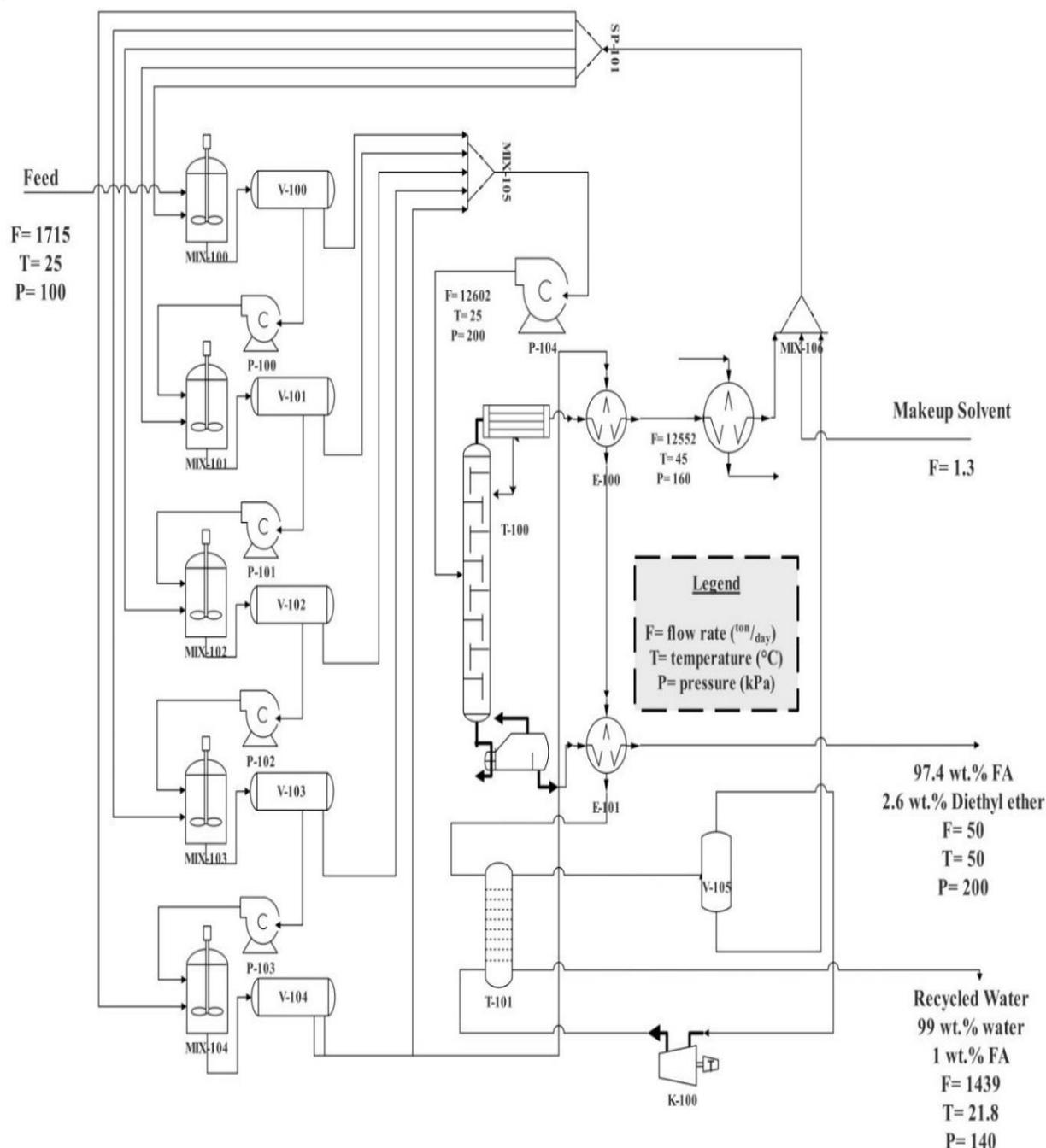
The analysis by the AHP indicated that the LLE method is a promising process for isolating FA from the aqueous media. As per the literature review summarized in Table 5, various

organic solvents were examined to extract FA from the FA-water mixture. Among them, aliphatic alcohols, ethers, and esters have received more attention and have been investigated in detail due to their performance efficiency. For a cost-effective process, the important factor during the selection is not only solvent selectivity but also the boiling point. This is since a solvent with a high boiling point requires a considerable amount of energy for the recycling process. The literature review implied that a single-stage LLE system could not completely isolate FA from an aqueous solution. This is attributed to the high solubility of FA in both organic solvents and water. Consequently, Wang et al. [28] proposed a multistep approach to overcome this hurdle, which could extract 99% of FA in a five-stage LLE unit by using diethyl-ether from the aqueous media. The boiling point of diethyl ether, 35 °C, is significantly low compared to FA, 100.8 °C, which not only makes the organic solvent recovery less energy-intensive but also offers a wide range of temperature differences for easy separation.

**Table 5.** Distribution coefficients ( $d_i$ ) of water ( $i = 1$ ), carboxylic acid ( $i = 2$ ) and separation factors ( $S$ ). The  $d_i$  is the ratio of FA concentrations in a mixture of two immiscible solvents at equilibrium, while  $S$  is equal to the ratio of the  $d_2$  to  $d_1$

Solvent	T= 298.2 °K			Normal Boiling Point [°C]	Ref
	$d_1$	$d_2$	$S$		
Ethyl acetate	0.042	0.653	15.37	77.1	[30]
1-Butanol	0.240	1.180	4.90	117.7	[31, 32]
Diethyl carbonate	0.125	1.190	9.47	126.8	[33]
1-Pentanol	0.140	1.031	7.50	138.0	[32]
Isoamyl alcohol	0.098	1.351	13.74	132.1	[30]
Diethyl fumarate	0.138	1.380	9.96	205.0	[33]
Butyl acetate	0.015	0.015	23.46	126.1	[28, 30]
1-Hexanol	0.080	0.890	11.00	157.1	[32]
Diethyl malonate	0.456	1.620	3.55	198.8	[33]
1-Heptanol	0.060	0.780	13.30	176.6	[32]
2-Ethyl-1-hexanol	0.040	0.510	14.50	184.6	[34]
Ethyl heptanoate	0.120	0.796	6.63	188.0	[35]

The schematic diagram of the FA isolation from the aqueous phase is presented in Fig. 4. In order to establish the process, the inlet feed is an aqueous stream containing 3 wt.% FA, which can be an effluent of LA production from fructose. Based on the suggested plant size (i.e., 2000 metric tons/day of lignocellulosic biomass or 300 metric ton of fructose/day) [18] and one molar fructose stream conversion yield to FA (65%; molar base) [7], the inlet rate of the aqueous stream containing FA is 1715 ton/day. The process flow diagram and operating conditions are shown in Fig. 4.



**Fig. 4.** The schematic process flow diagram and operating conditions of the FA-Water separation plant

In this process, the recovery unit consists of two major sections, namely extraction and purification. Initially, in the five mixer settler stages in cross current mode (MIX-100 and V-100 to MIX-104 and V-104), the FA is extracted from aqueous media by diethyl ether. The volumetric ratio of organic solvents to the aqueous phase in each section is adjusted to be 2 to maximize the FA extraction (99%) as described by Wang et al. [28]. The FA-rich organic solvent streams are pressurized by P-104 to overcome pressure drops in down streams. This stream is transferred to a distillation column (T-100) to separate FA from diethyl ether. The process provides 50 tons/day of FA with 97.4 wt.% purity. The organic solvent exits the distillation column (T-100) is mixed with other diethyl ether streams in a mixer (M-107) and recycled back to the extraction section. Due to the solubility of the organic solvent (6 gr diethyl ether in 100 ml water), a nitrogen stream is contacted with the acid lean aqueous phase in the gas absorption column (T-101) to extract the remaining diethyl ether completely. After separating diethyl ether from nitrogen in the separator vessel (V-101), the recycled diethyl ether



is added to the makeup stream, mixed in a mixer (M-107), and sent to the first extraction unit (M-101). Finally, the striped aqueous stream is transferred to the carbohydrate conversion section to be reused.

### Techno-Economic Assessment (TEA)

The MSP associated with FA through the proposed process can be estimated by implementing TEA, in which total capital investment and operating costs are the main contributors. The total capital investment can be determined based on the purchased equipment cost (PEC). In the first step of this method, PEC was obtained, as mentioned, based on 2019 indexed values and presented in Table 6. Comparing different equipment prices indicates that the cost of the distillation column (T-100) is the main component with the highest price tag among other equipment. This can be attributed to a considerable amount of surface area and energy required to recover the organic solvent. Total direct plant cost (TDPC) and total indirect plant cost (TIPC) were calculated and illustrated in Table 7. The costs presented in Table 7 show that TDPC and TIPC are \$25,459,920 and \$10,183,968, respectively. The purchase value of the organic solvent (\$1,557,420), which is used for the startup, is also considered to determine the required capital investment. Finally, considering 10% IR, the total capital investment with profit per year is determined to be \$15,327,527.

**Table 6.** List of PEC indexed to US\$2019 values

Name	PEC	Name	PEC
E-100	\$31,400	T-100	\$2,697,200
E-101	\$9,600	T-101	\$136,700
E-102	\$840,600	V-100	\$41,100
K-100	\$3,007,500	V-101	\$42,500
P-100	\$6,800	V-102	\$42,500
P-101	\$6,700	V-103	\$41,100
P-102	\$6,600	V-104	\$32,500
P-103	\$6,700	V-105	\$100,600
P-104	\$22,100		
<b>Total Equipment Cost</b>		<b>\$7,072,200</b>	

**Table 7.** Capital Investment cost based on which are indexed to US\$2019 values

Cost Category	Value	Reference	Price
	[%]	cost	[USD]
<b>Direct Costs</b>			
Purchased equipment delivered (PEC)	100	-	\$7,072,200
Purchased equipment installation	47	PEC	\$3,323,934
Instrumentation and controls (installed)	36	PEC	\$2,545,992
Piping (installed)	68	PEC	\$4,809,096
Electrical systems (installed)	11	PEC	\$777,942
Buildings (including services)	18	PEC	\$1,272,996
Yard improvements	10	PEC	\$707,220
Service Facilities (installed)	70	PEC	\$4,950,540
<b>Total Direct Plant Cost (TDPC):</b>	<b>360</b>	<b>PEC</b>	<b>\$25,459,920</b>

<b>Indirect Costs</b>			
Engineering and Supervision	33	PEC	\$2,333,826
Construction Expenses	41	PEC	\$2,899,602
Legal Expenses	4	PEC	\$282,888
Contractor's Fee	22	PEC	\$1,555,884
Contingency	44	PEC	\$3,111,768
<b>Total indirect plant costs (TIPC):</b>	<b>144</b>	<b>PEC</b>	<b>\$10,183,968</b>
<b>Capital Investment</b>			
Fixed-Capital Investment (FCI)	504	PEC	\$35,643,888
Working Capital	89	PEC	\$6,294,258
First Cycle Solvent (FCS)			\$1,557,420
<b>Total Capital Investment:</b>	<b>593</b>	<b>FCI</b>	<b>\$43,495,566</b>
<b>Profit</b>			
Total Profit For 21 Years (10%) [USD]			<b>\$321,878,060</b>
Total Capital Investment with Profit per Year [USD/Year]			<b>\$15,327,527</b>

Besides, total operating costs (TOC) in USD per year were estimated by considering feedstocks, utilities, and other operating costs. Raw materials are generally considered the major component of the operating cost. Since water and FA mixture is assumed as an effluent stream from the LA production process, there is not a price designated to them as feedstocks. On the other hand, there is a price associated with the make-up diethyl ether stream that should be considered. The utility cost includes steam, cooling water, and electricity, whereas the main contributor is steam with 89.7% contribution. TOC also includes labor, maintenance, tax, and insurance costs. The presented results in Table 8 indicate that the total utility cost is the major contributor to TOC at 85.4%. The summation of operating cost elements provides the TOC, which is \$26,134,973.

**Table 8.** A list of different associated costs, which are composed of feedstock, utility, and other operating costs to estimate annual TOC in US\$. All prices are indexed to US\$2019 values.

<b>Operating Cost</b>		
<b>Cost Category</b>	<b>Components</b>	<b>Price [USD/Year]</b>
<b>Feedstock &amp; Makeup Cost</b>		
	Water	\$0
	Formic Acid	\$0
	Diethyl Ether	\$1,313,942
<b>Total Feedstock Cost</b>		<b>\$1,313,942</b>
<b>Utilities Cost</b>		
	Electricity	\$748,424
	Cooling Water	\$1,531,072
	Steam @100PSI	\$20,046,560
<b>Total Utilities Cost</b>		<b>\$22,326,056</b>
<b>Operating Cost</b>		
	Total Feedstock Cost	\$1,313,942
	Total Utility Cost	\$22,326,056
	Labor Cost	\$891,000
	Maintenance	\$1,603,975



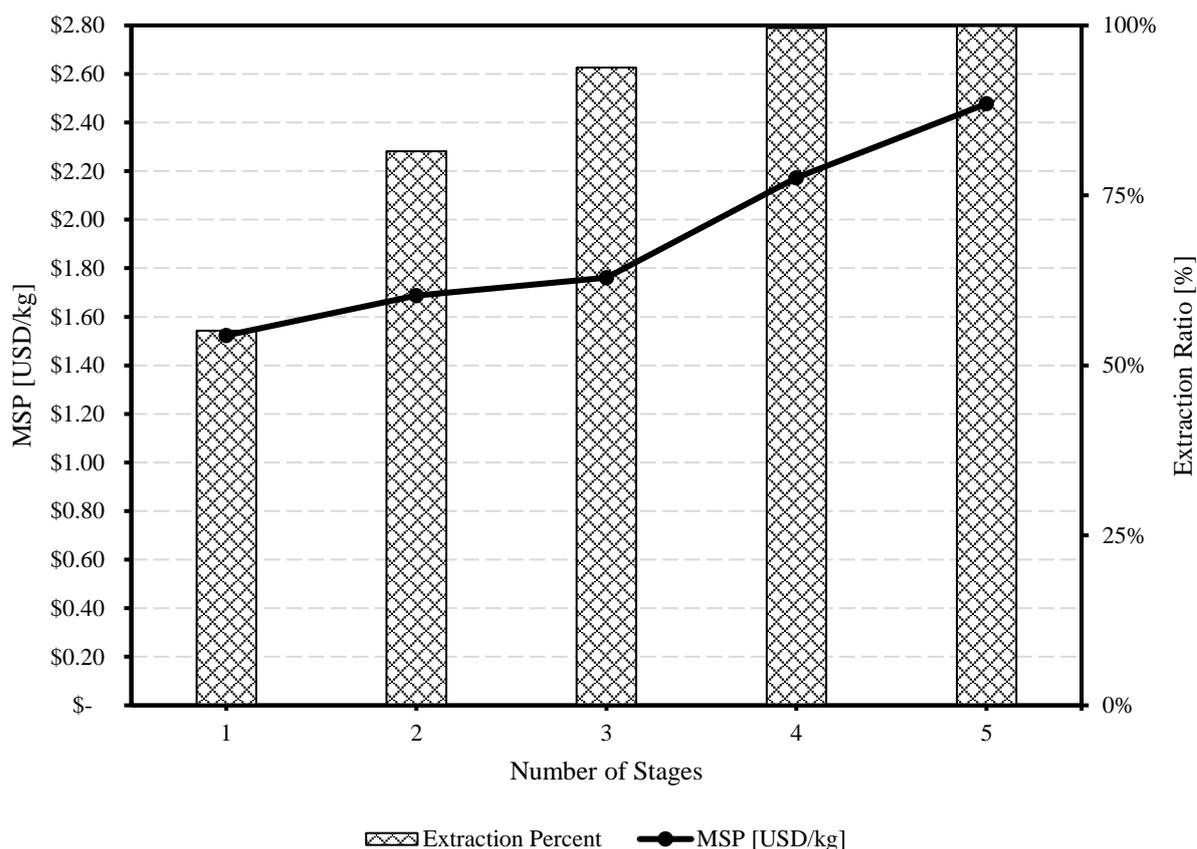
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**Total Operating Cost (TOC)****\$26,134,973**

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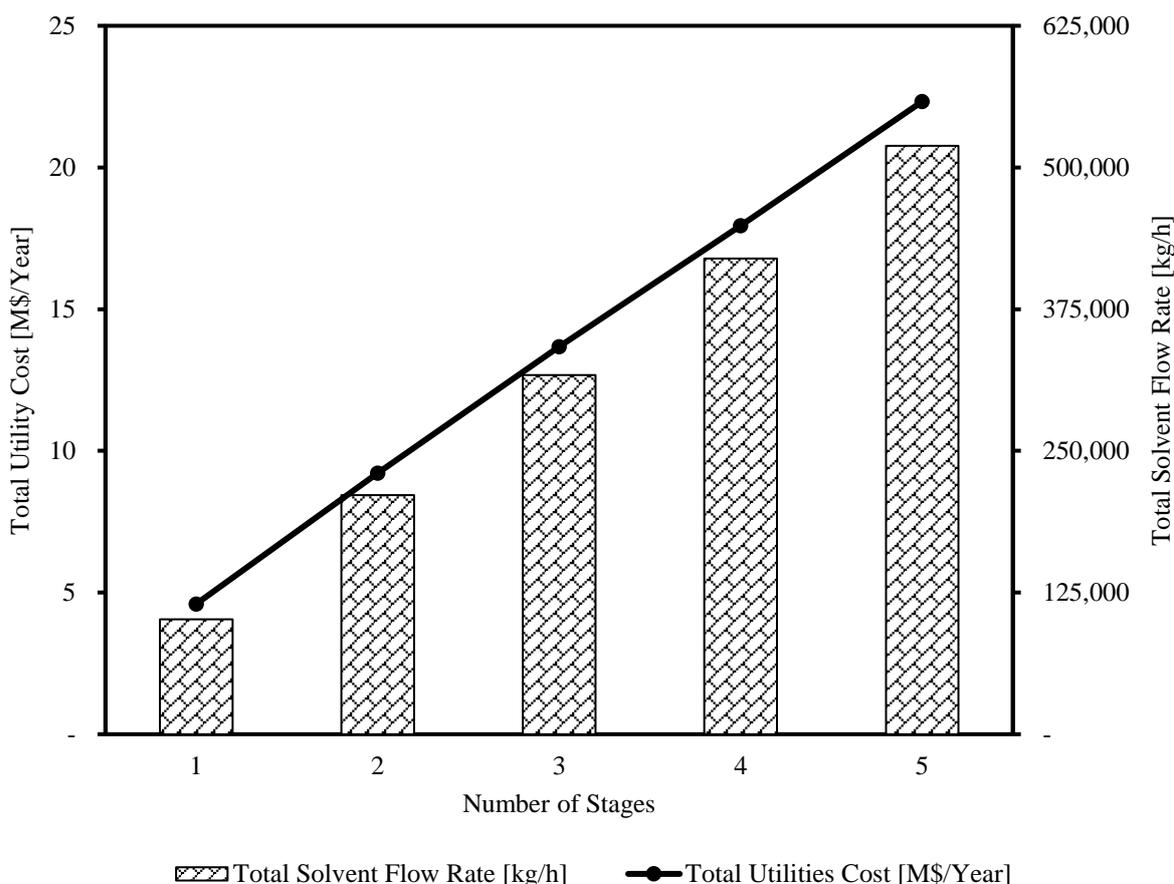
Based on the total capital investment associated with extracting 99% FA from a 1715 ton/day inlet (including 3 wt.% FA) that produces 50 tons/day with a 97.4% pure FA stream as described in Fig. 4, the MSP is estimated to be 2.48 \$/kg. As mentioned earlier, considering recycled water could be an additional benefit to this process, while it is not included and credited to this process. The recycled water can be reused in the carbohydrate conversion to carboxylic acids, FA, and LA. Besides, water recovery that prevents damage to resources and makes the process more environmentally friendly is not only considered an important advantage of this process but also agreed with Green Chemistry principles. Furthermore, TEA results indicate that the multi-stages LLE approach presents a cost-effective method for FA isolation from the aqueous phase. However, introducing a novel organic solvent that can completely extract FA in a single stage and easily separate it from FA will significantly reduce MSP and makes the process more cost-competitive. On the other hand, increasing the FA concentration in the inlet stream of this process, for instance, by improving the carbohydrate conversion yield to FA upstream, will considerably decrease the MSP. These steps seem crucial to make the process of commercialization feasible.

The results indicated that the five-stage LLE unit could extract FA from the aqueous phase. As shown in Fig. 5, the recovery per stage is not constant, and it increases as per the evolution of the stages. For example, 55% of FA can be recovered in the first stage, and then it increases to 81.5%, 94%, 99%, and over 99%, accordingly. Most of the FA can be recovered in the first three stages, while the MSP decreases significantly from 2.48 \$/kg for a five-stage process to 1.76 \$/kg for a three-stage process, as presented in Fig. 5. It is also possible to further reduce stage numbers to two as the MSP of a two-stage process is 1.69 \$/kg which is only 4% less than the MSP of the process with three stages. In addition, it should be considered that 18.5% and 12.5% of FA will remain in the aqueous phase and cannot be extracted compared to the process with five and three stages LLE units, respectively. Lowering down the extraction unit to a single-stage process will intensify the portion of unextracted FA to 45% in the aqueous phase. Although, the MSP will be lowered to 1.52 \$/kg. Comparing stage number effect on MSP for the processes with five and three stages LLE units illustrate a 5% loss of FA. On the other hand, the MSP is decreasing dramatically by 29%. Besides, in the case that four stages of LLE were applied, the loss is negligible (less than 1%) but the MSP reduction is not considerably sharp (almost 12% reduction), and the MSP, which is 2.17\$/kg remains above 2 \$/kg.



**Fig. 5.** The number of stages affects MSP and extraction ratio

Reduction in the MSP is proportionally attributed to the decreased organic solvent flow rate and total utility cost, as illustrated in Fig. 6. For an instant, the diethyl ether flow rate in the five stages LLE unit decreases dramatically from 519,140 to 317,000 kg/h in the process with the three stages LLE unit. Besides, comparing these two cases show that the total utility costs reduced significantly from 22.33 to 13.68 M\$/year. Lowering down the MSP highlights the fact that the required surface area and consumed energy for organic solvent recovery are both reduced.



**Fig. 6.** The number of stages affects the total utility cost and organic solvent flow rate

## Conclusion

FA has been synthesized from the lignocellulosic biomass constituent carbohydrates by the acid hydrolysis method. In the typical production process, an aqueous phase is the desired reaction media, which results in FA at a low concentration of <3 wt.%. Due to the azeotrope formation, the FA isolation from water by a single conventional distillation column is impossible. Thus, different separation approaches were examined with the support of AHP to investigate their advantages and disadvantages. To perform the AHP analysis, scalable, quality of final product, repeatable, and energy consumption were defined as criteria. Moreover, six alternative pathways, namely azeotropic distillation, extractive distillation with a liquid solvent, extractive distillation with solid salt, extractive distillation with the combination of liquid solvent and solid salt, pressure-swing distillation, and LLE, were suggested to decide on the optimal separation method. Assessing the purification processes was conducted for an aqueous stream containing 3 wt.% FA. The AHP results indicated that the LLE and the scalable criteria have the highest preference with 39% and 53% priority, respectively. Besides, the inconsistency is significantly less than <0.1, which indicates that the pairwise comparison of criteria is logical. Hence, a process for a 1715 ton/day inlet stream was established to estimate the MSP of purified FA. In this process, the diethyl ether was used as an immiscible solvent. The LLE was conducted using diethyl ether in five stages mixer-sellers that extract 99% of FA and later, the FA was isolated from diethyl ether in a distillation column. Water and diethyl ether were recycled and reused. Based on TEA results, the MSP of 97.4% pure FA was estimated to be

2.48 \$/kg. Results indicated that it is also feasible to conduct LLE in three stages and recover 94% of inlet FA and reduce the MSP to 1.76 \$/kg. Further decreasing the LLE units will lower the MSP. However, a significant amount of FA will remain in the aqueous phase.

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## Nomenclature

<i>CI</i>	Consistency Index
$\lambda_{max}$	Largest Eigenvalue
<i>n</i>	Comparison Matrix Size
<i>CR</i>	Consistency Ratio
<i>RI</i>	Reliability Indicators

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