UNIVERSIDADE FEDERAL DE SÃO CARLOS

CENTRO DE CIÊNCIAS EXATAS E DE TECNOLOGIA

PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

ASSESMENT OF ALTERNATIVE ROUTES FOR SUGARCANE-BASED ETHANOL RECOVERY: EXERGY AND ECONOMIC ANALYSIS

William Costa e Silva

DOCTORAL THESIS

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AVALIAÇÃO DE UMA ROTA PARA O PROCESSO DE RECUPERAÇÃO DO ETANOL DE CANA-DE-AÇÚCAR: ANÁLISE EXERGÉTICA E ECONÔMICA

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Thesis submitted to Graduate Program in Chemical Engineering of Federal University of São Carlos in partial fulfillment of requirements for the Degree of Doctor of Philosophy in Chemical Engineering, area of concentration in Chemical Process Research and Development.

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PREFACE

The present thesis is submitted to accomplishment of the requirements for obtaining a PhD degree at the Federal University of São Carlos (UFSCar). This project has been performed from August 2013 to February 2018 with a financial support by FAPESP. The thesis was produced at the Department of Chemical Engineering (DEQ) under the main supervision of Professor Alberto Colli Badino Junior and co-supervision of Professor André Bernardo.

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William Costa e Silva

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ABSTRACT

The aim of this thesis was to develop a methodological approach that can systematically guide process simulation for better understanding of bioethanol production process. In the present work, the ethanol production process was studied combining liquid-liquid extraction (LLE), non-conventional process, with extractive distillation system. The designed process was based on an autonomous distillery that crushs 500 tons of cane per hour. The commercial process simulator Aspen Plus® V.8.2 was used as a computer-aided tool. In this work, isoamilic alcohol, n-octanol, n-dodecanol and oleic acid were evaluated as solvent extraction for LLE and monoethylene glycol was used as entrainer in the extractive distillation column. The results of the environmental impact of a standard distillery applying renewability analysis showed that the conventional distillation process provides worse environmental performance. Distillation with use of a reboiler as heat source has better environmental performance than other two cases. In addition, the economic evaluation showed that distillation with use of a reboiler achieved the value of US$ 115 million with respect to ethanol selling. This finding is approximately 9% and 12% higher than achieved for standard process and distillation with mechanical vapor recompression scheme. In sequence, it was carried the simulation of an alternative route combining liquid-liquid extraction-distillation system to evaluate the process downstream and its environment impact. The results have shown that among the candidates under investigation: isoamilic alcohol, n-octanol, n-dodecanol and oleic acid, the hybrid system with dodecanol reached 37.57 % reduction of liquid waste emissions when compared to conventional process. At the same time, using the concepts of exergy and renewability index, LLE with oleic acid and conventional process were considered to provide the worst environmental performance when compared to extraction system with dodecanol. The analysis of optimal entrainer agent feeding flow into the extractor column showed that LLE with oleic acid required a solvent feeding flow of 2.40e+6 kg/h which represent an increasing of 83% in solvent consumption when compared to isoamilic alcohol system the lowest solvent feeding flow (4.06e+5 kg/h). The hybrid system with dodecanol reached 35.6 m^3 of anhydrous ethanol per hour .This value is close to standard process production which is 38.8 m^3 of anhydrous ethanol per hour.

Keywords: ethanol, simulation process, solvent extraction, exergy, environment analysis

RESUMO

O objetivo da presente foi estudar uma rota alternativa do processo de produção de etanol anidro através do processo de extração líquido-líquido (ELL) conectada a destilação extrativa convencional. O processo desenvolvido foi baseado em parâmetros operacionais de uma destilaria autônoma de capacidade de moagem de 500 toneladas de cana por hora. A ferramenta computacional Aspen Plus® V.8.2 é um simulador comercial de processos e foi utilizado no desenvolvimento do trabalho por apresentar em seu banco de dados inúmeros componentes presentes na indústria sucroalcooleira. Nesse trabalho, os solventes orgânicos: álcool isoamílico, octanol, dodecanol e o ácido oleico foram escolhidos para estudar a ELL, enquanto monoetileno glicol foi utilizado para simular a destilação extrativa. O estudo ambiental utilizando os conceitos da análise exergética mostraram que a configuração de destilação tradicional apresenta maior impacto ao meio ambiente. O melhor desempenho ambiental ficou para o sistema de destilação utilizando refervedores como fonte de aquecimento das colunas. Além do mais, a análise econômica mostrou que a destilação com refervedores gerou 115 milhões de dólares com a venda do etanol anidro, este desempenho é 9% a 12% maior do que os alcançados pelo processo tradicional e a destilação com recompressão mecânica de vapor, respectivamente. Em seguida, foi estudada uma tecnologia alternativa composta de ELL e a destilação extrativa avaliando o processo de purificação e recuperação do solvente e seu impacto ao meio ambiente. De acordo com resultados obtidos, o sistema de extração utilizando n-dodecanol como agente extrator alcançou uma redução de 37,57% na emissão de resíduos líquidos. Além disso, levando em consideração os conceitos de exergia e o índice de renovabilidade o sistema de extração utilizando ácido oleico e o processo tradicional apresentaram pior desempenho ambiental comparado com o sistema com dodecanol. A análise da demanda do agente extrator na ELL mostrou que o sistema de ELL com ácido oleico consume 2.40e+6 kg/h, isto representa um aumento de 83% na demanda por solvente comparado com a ELL com álcool isoamílico. O sistema híbrido com dodecanol produziu 35,6 m^3 de etanol anidro por hora. Este valor está próximo do processo convencional de produção de etanol que é de 38,8 m^3/h.

Palavras-chave: etanol, simulação de processos, extração com solvente, exergia, análise ambiental.

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CHAPTER 1 – INTRODUCTION

1.1 Overview of bioethanol process

Ethanol is considered one of most interesting biofuels in the current world, as it is obtained from renewable feedstocks. Therefore, bioethanol contributes to reduction of greenhouse gas emissions produced through the worldwide consumption of fossil fuels (CORTES-RODRIGUES *et al*., 2018; CARDONA; SANCHES, 2007). In the last decades, a huge number of countries have been investigating the production of ethanol from various biomass resources. The United States of America (USA), Brazil, China, Canada, and some European Union (EU) members have already adopted policy commitments to produce bioethanol as a way to replace or minimize the fossil fuels dependence (ZABED *et al*., 2016).

As a result, the production of bioethanol has been increased in the last decades. In 2015, the overall bioethanol production achieved an expressive mark of 97 million m^3, where USA and Brazil were the main producers, corresponding together to approximately 85% of market share. According to the Brazilian sugarcane industrial sector, the 2017/2018 harvest is expected to generate 27 million m^3 of bioethanol (UNICA, 2017).

In this sense, sugarcane industry plays an important role in economic activities in Brazil. However, this relationship between Brazil-ethanol fuel is not from now. The large-scale production started almost 50 years ago, when the Brazilian federal government launched the national program of alcohol (Proálcool) in 1974, to face the international oil crisis (ALVES, 2014).

Nevertheless, ethanol production is a complex operation, where the bioconversion of sugarcane juice into bioethanol fuel is a sequence of multi-step processes (AGHAZADEH; ENGELBERTH, 2016). The standard Brazilian ethanol production is based on fermentation of sugarcane molasse where a fermenting organism is added to consume all the fermentable sugars in their metabolism, in which ethanol, carbon dioxide and minor components are generated as byproduct of this mechanism (AGHAZADEH; ENGELBERTH, 2016; LEMOS *et al*., 2017).

As stated by Lemos and collaborator (2017) and Cortes-Rodrigues *et al.* (2018) the alcoholic solution produced at the end of the fermentation process has an ethanol mass fraction in the range of 6-9%. This diluted fermented wine should be concentrated in a set of distillation columns to produce hydrous ethanol with an ethanol content of 93.5%wt. Later, hydrous ethanol is dehydrated by extractive distillation to obtain anhydrous ethanol with an ethanol content of 99.4% wt. (CORTES-RODRIGUES *et al*., 2018).

It is well known that distillation systems are energy intensive operations, which causes a huge impact for both economic and environmental aspects (TUTUTI-AVILA *et al*., 2016). Therefore, designing a more cost-effective process for bioethanol production has been on focus for a large number of researchers and industry (CORTES-RODRIGUES *et al*., 2018; ERRICO *et al*., 2017; TUTUTI-AVILA *et al*., 2016).

With the aim of designing new technologies or enhance already existing plants for the production of bioethanol, the implementation of process engineering tools is extremely required to obtain faster, low cost and accurate results. In this thesis, the process simulator Aspen Plus® is applied to investigate the cost-effective of a hybrid system combining liquid extraction-distillation process with distillation system to produce anhydrous ethanol. Previously, Errico *et al.* (2017) used Aspen Plus® to investigate the liquid-liquid extraction-assisted divided wall columns to separate butanol from the acetone-butanol-ethanol (ABE) mixture. Almeida *et al.* (2014) simulated the extractive fermentation process using dodecanol as the entrainer to increase the ethanol content in the fermented wine led to purification step.

1.2 Motivation

Bioethanol fuel is attracting considerable interest at academic and industrial. Because of that, there is an increasing necessity to implement a comprehensive analysis of the processes. In order to accomplish such objectives, computer simulation is extremely necessary in most cases, once they provide a faster understanding and enhance the process. For ethanol separation and purification process, the use of processes simulator brings a significant benefit to understand the relation among process design, cost-effective, and product in a sequence of columns, because a great number of simulations of the process can be conducted. In this sense, alternative technologies or different conditions should be analyzed in order to identify potential process modifications. Hence, time and cost in laboratory experiment are reduced.

There are few simulations designing liquid-liquid extraction-distillation system and no evidence or data of a systematic procedure for downstream process and its impact to environment. Therefore, the lack of further information makes it extremely hard to move forward with these kind of technologies, especially to scale the process up. Thus, the present thesis provides fruitful and interesting data to establish a methodological scheme for process designing . In this context, all the cases simulated in this work provided information, experience and insight that may be used later to improve the process.

1.3 Scope of the thesis and specific goals

The aim of this thesis is to analyze the impact of changes in the conventional industrial ethanol production process using Aspen Plus® software, a commercial process simulator, to design an alternative route and perform an extensive cost-effective and environmental analysis.

The specific goals of this work were:

i. Simulation of an autonomous standard ethanol distillery adopting operational parameters as applied in the real industrial process.

ii. Simulation of an alternative technology for distillation system, investigating indirect heat system using reboilers.

iii. Simulation and performing cost-effective and environmental analysis of the alternative route designed and compare to standard distillation system.

iv. Simulation of a hybrid system liquid-liquid extraction assisted extractive distillation to produce anhydrous ethanol, techno-economic and environmental analysis.

v. Simulation of extractive fermentation with raffinate stream recycling to fermenter, assisted distillation system to produce anhydrous ethanol, environmental impact analysis.

1.4 Thesis outline

The present thesis is structured in 4 chapters. Each chapter developed are presented as follow:

Chapter 1 is a general introduction of the thesis. The entire topics studied in this work is briefly discussed, highlighting its relevance and the contribution to academia.

Chapter 2, entitled "Environmental assessment of a standard distillery using Aspen plus®: simulation and renewability analysis", this study investigates the sustainability of the first-generation ethanol production process (ethanol 1G). Given the relevance of the distillation design and its influence on sustainability, tree alternative routes were simulated. The three cases investigated are: distillation with use of reboiler as heat source (Case I); traditional direct steam injection distillation (Case II), and distillation with mechanical vapor recompression (Case III). For all cases techno-economic and environmental impacts analysis are performed in order to identify the best design. This first part of the work is also considered as the reference to the sequence of the thesis.

Chapter 3, entitled “Simulation of an alternative route combining liquid-liquid extraction-distillation system to produce anhydrous ethanol: downstream process and its environmental impact” reports a comprehensive methodology of solvent screening to remove ethanol from the diluted fermented wine. Then, downstream process after extraction process is also evaluated. The four solvents selected are: isoamilic alcohol (C-5), n-octanol (C-8), n-dodecanol (C-12) and oleic acid (C-18). The screening of solvents is one of relevant issue in this process. Alcohols presenting 12 or fewer carbons can be considered toxic or inhibitory to yeast, but those having 14 or more carbons are considered non-toxic or inhibitory. In this way, raffinate stream containing non-biocompatible solvent are not recycled to fermenter, as a result the toxicity is not criteria for selection of the solvent. So, these processes were assessed in terms of the amount of solvent feed flow rate into extractor column, liquid waste stream generation, total annual cost, energy requirement and environmental impact.

Chapter 4, entitled “Simulation of liquid-liquid extraction of ethanol with raffinate stream recycled to fermenter assisted extractive distillation for anhydrous ethanol production” reports the utilization of n-dodecanol (the best option, see chapter 3) and oleic acid (the only biocompatible entrainer) to perform liquid-liquid extraction of alcohol from the fermented medium with raffinate stream recycling to fermenter vessel. The ethanol extracted is sent to dehydration step, and this process is performed by extractive distillation with MEG as entrainer. In this study, solvent feed flow rate into extractor column, liquid waste stream generation, total annual cost, energy requirement and environmental impact were the parameters investigated to outline the best process design.

The last part of the text, “Concluding remarks and future perspectives” (Chapter 5), this is a summary of the main results achieved in this study and some suggestions for further research.

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CHAPTER 2 – ENVIRONMENTAL ASSESSMENT OF A STANDARD DISTILLERY USING ASPEN PLUS: SIMULATION AND RENEWABILITY ANALYSIS

Abstract

This study investigates the sustainability of the first-generation ethanol production using a steam condensed stream reuse approach. In this sense, the determination of the effective water collection was made for autonomous distillery and opportunities for the reuse of water stream were identified. Given the importance of the distillation design and its impacts on sustainability, relevant problems and challenges are highlighted, and suggestions are made of ways to enhance the process. Simulations were carried out using the Aspen Plus simulator to perform mass and energy balances. Three case studies were investigated: distillation with use of a reboiler as heat source (Case I); conventional direct steam injection distillation (Case II); and distillation with mechanical vapour recompression (Case III). In all cases, environmental aspects were considered using WAR (WAste Reduction algorithm) software and exergy concepts. A technical-economic evaluation of the distillation system was performed in order to identify the best design. The results showed that the use of closed circuits and water reuse streams provided an overall consumption of 673 L water/t of cane in the mill. This value is lower than the statutory limit of 1000 L/t of cane established for distilleries in the State of Sao Paulo. Furthermore, according to the results obtained using the WAR software and the concepts of exergy and renewability index, Case II and III were considered to provide worse environmental performance, compared to Case I. In addition, Case I achieved net revenue of US$ 115 million, due to higher flowrate of anhydrous ethanol at the end of the process. This finding is approximately 9% and 12% higher than achieved for Cases II and III, respectively. Therefore, it is environmentally and economically beneficial to employ a reboiler as a heat source in distillation systems, compared to conventional systems employed to produce bioethanol.

Keywords: Ethanol; Recycled water; Exergy; Environment; TAC.

2.1 Introduction

The effects of increasing consumption of bioethanol have been studied extensively in recent years. However, less attention has been paid to sustainable production processes, from feedstock inputs to the final products and waste management (MOSQUEIRA-SALAZAR *et al.*, 2013). One of the most important issues to emerge concerns the large volumes of water consumed during the ethanol production process, which could lead to serious environmental problems in the future (CHAVES-RODRIGUES *et al.*, 2013).

The standard distilleries in Brazil became consolidated and very competitive industry worldwide. However, there are still major issues that need to be resolved, including industrial use of water, which can have an enormous impact on water bodies.

So, in the last two decades several discussions have been conducted about sustainable development, environmental impact and renewability of energy and water resource use. In this sense, a relevant issue that must be addressed is the industrial use of water in the sugarcane mill as water resources are scarce, and more stringent discharge regulations, because of sugarcane distillery itself consumes around 70% of water intake (TASNEEM; KAMIL, 2016).

As a result, the need of decreasing water consumption in ethanol production, as well as the partial or full recovery of water from sugarcane process has been increasingly investigated (CHAVES-RODRIGUES *et al.*, 2013). In this way, process integration is a powerful tool that can help industries to rise their profitability by decreasing energy, water and raw materials use, and reductions in waste productions rate. According to the Resource Nature Canada (2003), process integration (PI) can be defined as all improvements implemented to process, and their achievement to maximize the effective use of energy, water and raw material. Among PI techniques, pinch analysis is by far the most broadly applied. Because of the simplicity of its fundamental concepts and, particularly, of the fantastic results it has achieved in numerous areas.

Using the concepts of pinch analysis, water pinch is one alternative that can be applied to any industrial water scheme where there is consumption of freshwater and production of wastewater. Therefore, water pinch analysis is a systematic study to place and identify the best water reuse system (TASNEEM; KAMIL, 2016).

As mentioned previously, studies have been done for the reduction of process water in ethanol plant (GONÇALES FILHO *et al.*, 2018; MARTINEZ HERNANDEZ; NG, 2018; FITO *et al.*, 2017). Process integration can be accomplished through pinch analysis method which is based on thermal integration of hot and cold utilities streams. However, there are few works in literature regarding to detailed study and as well as simulation of water streams recycle of first-generation ethanol plant. For instance, the process water consumed in condensers and heat exchangers is normally cooled down in cooling towers and returns to the process. This water closed circuit is not included in the simulation manuscripts.

According to Dias *et al*. (2015), Yang *et al*. (2016) and Reis *et al*. (2017), some improvements into the processes should lead to significant reduction of fresh water intake. Those improvements are: (i) recovery of condensates and use as imbibition water, (ii) reuse of condensed steam from multiple-effect juice evaporation; (iii) vinasse concentration using vapour bleeding for heating processes; and (iv) production of a fermented broth with high ethanol content. In this study, the reuse of condensated steam and treated wastewater streams were investigated.

Pina and collaborators (2017) and Chaves-Rodrigues et al. (2013) studied the water use in the sugar and ethanol production and the result is presented in Table 2.1. It can be observed that condensing processes such as cooling of barometric condenser of 5th effect, fermentation vessels and condensers of distillation columns are the mainly consumers of water in the ethanol plant. According to Table 2.1 Case I showed lower water use in the barometric condenser (413 L/ton. of cane), however consumes four times more water (3741 L/ton. of cane) for cooling of molasses for fermentation process than to the Case II (1089 L/ton. of cane).

A possible explanation to this finding is that Case I is an autonomous distillery (ethanol plant without sugar production) which there is high volume of must entering to fermenter vessel that need to be cooled. Case II represent a distillery with sugar and ethanol production process in which the total reducing sugars was equally divided. For the Case I ^{TI} the total water use reduced almost to 50% as the amount of water provided to cool the must of fermentation reduced from 3741 L of H_2O/ton. of cane (Case I) to 250 L H_2O/ton. of cane (Case II ^{TI}). Pina et al. (2017) adopted thermal integration for Case I ^{TI} and Case II ^{TI} and this practice showed positive effect to decrease the water consumption in the ethanol plant owing to promote a reduction of cold utilities.

Table 2.1 – Water consumption in the distillery without closed circuits

Process	Water uses (L H_2O/t of cane)	[A]Case I	[A]Case II	[A]Case I ^{TI}	[A]Case II ^{TI}
Preparation and extraction system	Cane washing	300	300	300	300
	Imbibition	300	300	300	300
	Bearing cooling	50	50	50	50
Juice treatment	Preparation of lime mixture	8	23	8	23
	Filter cake washing	70	70	70	70
	Polymer preparation for settling	15	15	15	15
Juice concentration	Condenser of 5th effect evaporator	413	2,076	746	1,854
	Water for vacuum in the pans	-	2,431	-	2,431
Fermentation step	Cooling of must for fermentation	3,741	1,089	250	95
	Cooling of fermenter	2,000	1,747	2,000	1,747
	Carbon dioxide scrubber for fermentation	27	27	27	27
	Dilution of yeast broth	122	141	122	141
Distillation step	Condenser of distillation column	1,679	873	913	853
	Condenser of rectification column	2,274	1,111	-	758
Dehydration step	Condenser of extractive column	637	319	637	319
	Condenser of recovery column	106	87	106	87
	Solvent cooling	65	32	65	32
	Anhydrous ethanol cooling	741	370	741	370
Cogeneration step	Turbo generators cooling	200	200	200	200
	Washing scrubber (boiler)	200	200	200	200
	Boiler feeding	501	501	501	501
Others	General cleaning	50	50	50	50
	Drinkable uses	30	30	30	30
Total (L H_2O/ton of cane)		13,529	12,042	7,323	10,453

[A] Reference – Pina et al. (2017)

Therefore, in this work the ethanol distillery was simulated by Aspen Plus® adopting closed circuits for water reuse. The re-use of water may be a strategy to reduce the total amount of water intake (PINA *et al*., 2017). The average water consumption found in literature and simulated in this work are entirely described in Table 2.2.

Table 2.2 – Candidates for water stream reuse in the present study.

Candidates for water stream reuse (L/t of cane)	Simulated (this work)	Literature[d]
Condensate from juice treatment	53.5	19
[A]Condensate of multi-effect evaporator	255	143
Condensate from 5th effect evaporator	66.9	18
Condensate from distillation step	117	75
Total (L H_2O/t of cane)	492	255

[A]Condensate streams from 2st, 3nd, 4rd, and 5th effect vapor in barometric condenser
[d]Mosqueira-Salazar et al. (2013).

According to the results obtained the implementation of water closed cycle, the consumption of fresh water remained below the limit of 1,000 L H_2O/ton. of cane established for the sugarcane industry in State of Sao Paulo/Brazil. This finding is an important contribution for more sustainable process in ethanol industry. Another issue of concern is the large volume of vinasse produced. Vinasse, a dark brown waste liquid produced during the distillation process, is composed of minerals, water, and high levels of organic compounds, and is widely applied as a fertilizer in sugarcane plantations (OLIVEIRA *et al*., 2015).

As the main waste effluent from ethanol distilleries, vinasse has been extensively studied. The production of sugarcane ethanol implies the co-production of large amounts of vinasse containing potentially hazardous components. In Brazil, usually, the Typically, autonomous distillery produce from 10 to 15 L of vinasse per liter of ethanol, depending on the distillation system employed as well as the mix of product chosed (ethanol, sugar and electricity) (CHRISTOFOLETTI *et al*., 2013; FILOSO *et al*., 2015; SILVA; OLIVEIRA, 2014;).

According to the Brazilian sugarcane industrial sector (NOVACANA, 2016), in the 2015 and 2016 harvest season, over 439 million m^3 of vinasse were produced. An excess of vinasse deposited onto the soil can lead to salinization, leaching, and other negative impacts on the soil, if not managed correctly (MAYER *et al.*, 2015).

The search for suitable uses and treatments of vinasse has led to a proliferation of studies describing options such as biogas production, yeast production, use as a carbon substrate for fermentation, fertirrigation, and others (CHRISTOFOLETTI *et al.*, 2013). However, these techniques before to be implemented depend on satisfactory outcome of technical-economic feasibility studies (LAIME *et al.*, 2011).

Over the last decade, only a few studies have systematically investigated the heating system of the distillation column from the perspective of reducing the volume of vinasse produced (MAYER *et al.*, 2015; LAIME *et al.*, 2011). At the same time, concerns have been raised about the level of sustainability of the process. One of the best ways to assess the impact of a distillation process on the environment and to achieve a highly environmentally friendly procedure is to use exergy analysis (ROSEN; DINCER, 2001).

In comprehensive analyses of biofuel production, Oliveira (2013) and Velasquez-Arredondo *et al*. (2012) showed that the environmental impact of ethanol production could be reduced by improving the exergy efficiency of the process. A consequence of greater exergy efficiency is a decrease in the consumption of resources, hence reducing wastes and emissions to the environment (OLIVEIRA, 2013).

Process simulation is a powerful tool that can be used to investigate the efficiency and sustainability of different distillation heating systems. Due to its simplicity, ease of use, and the existence of a large database for sugarcane process Aspen Plus® simulator was selected in the present work.

In previous work, Albarelli *et al*. (2016) used Aspen Plus® software to simulate biorefineries for the production of 1st and 2nd generation ethanol fuel and electricity from sugarcane. There is increasing importance attached to the renewability of bioethanol production processes. The contribution of the present work is therefore to introduce a simple methodology for process analysis, which simultaneously evaluates the energetic, economic, and environmental aspects inside the sugarcane industry.

2.2 Methodology and approach

2.2.1 Process description of autonomous first-generation ethanol production

Simulation of a Brazilian sugarcane distillery was performed using the Aspen Plus v. 8.2 process simulator (ASPENTECH, 2010). Although previous studies have simulated 1st and 2nd generation ethanol production processes, few have focused on the simulation of a fully integrated sugarcane mill. This methodology is particularly useful for studying hot and cold utility demands (CHAVEZ-RODRIGUES *et al*., 2013).

In this study, simulations were made of an autonomous distillery for ethanol production evaluating the impact on fresh water withdrawn through the reuse of condensed vapour streams. Figure 2.1 illustrates the standard process considered. The simulation was carried out assuming a processing rate of 500 tons of sugarcane/hour, equivalent to 2,000,000 tons of sugarcane/year. The main operational parameters and the basic sugarcane composition adopted in the simulation of the autonomous distillery are shown in Table 2.3 and 2.4, respectively (PALACIOS-BERECHE *et al*., 2015). In addition to specifying the main parameters of the sugarcane mill, definition of the property methods to be applied is an important stage when carrying out a simulation.

Table 2.3 – Main parameters adopted for the simulated 1G ethanol mill

Operational Parameter	Value
Mill capacity (wet basis)	2,000,000 ton. cane/year
Crushing flow rate (wet basis)	500 ton. cane/hour
Efficiency of sugar extraction	96 %
Season running hours	4,000 Hour/year
Fermentation efficiency	90
Ethanol content of the wine fed into the distillation column	8.5 %v/v
Hydrated ethanol purity	92.6 % v/v
Anhydrous ethanol purity	99.6 %v/v
Steam pressure – process	2.5 bar

Font: Palacios-Bereche *et al*. (2015).

In this work, it was studied the conventional production of ethanol in the autonomous distillery. The main operational parameters adopted was described in Table 2.3 and the assumed average composition of sugarcane arriving at the distillery is shown in Table 2.4. For this simulation, it was considered the composition of sugarcane all the reducing sugars (RS) as dextrose, impurities like potassium salt (KCl), minerals as K_2O, and SiO_2, organic compounds as aconitic acid and the inorganic material dragged along with sugarcane was classified as dirt (SiO_2) (ALBARELLI *et al*., 2014). Here, property method which represent the physical property data for many of the components used in the simulation for the ethanol production was determined according to the methods and models used by the Aspen Plus simulator to predict their thermodynamic properties (ASPENTECH, 2009; WOODLEY; PUTSCHE, 1996). The property method could differ, depending on the specific operation that was to be simulated.

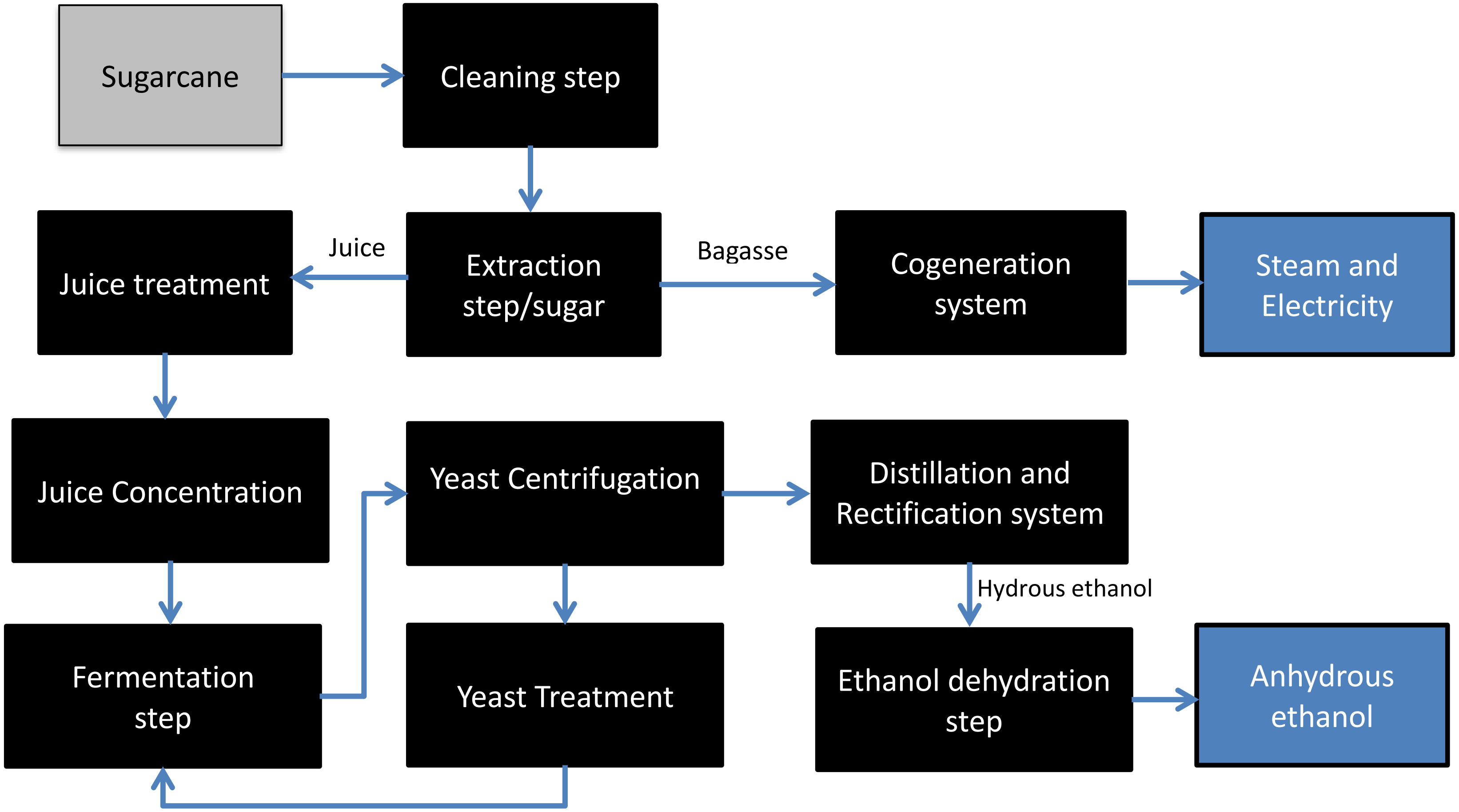
Table 2.4 – Average composition of sugarcane assumed at the beginning of the process simulation

[a]Component		[a]Composition (% mass)
Water		70.5
Fibers	Cellulose	5.8
	Hemicellulose	3.5
	Lignin	3.2
Solids	Sucrose	13.9
	Dextrose	0.6
	K_2O	0.4
	KCl	0.2
	SiO_2	0.3
	Aconitic acid	0.6
Dirt	SiO_2	1.0

[a] Data based on Albarelli et al. (2014)

For example, in the case of the juice concentration step, estimates were requested for missing binary parameters for water (i) and sucrose (j), in the Universal QUAsiChemical (UNIQUAC) model, carried out by means of the Properties Parameters Binary Interaction form presented in the simulator.This was performed because the standard binary parameter values of the process simulator did not satisfactorily describe the behaviour of the sucrose-water solution at equilibrium (PINA *et al*., 2015). For water streams in heat exchanger systems, the Steam Table method was applied. For most of the process operations, the Non-Random Two Liquid (NRTL) property method was applied. According to Dias *et al*. (2014), this model is appropriate for representing most of the unit operations. Among the components included in the simulation, some of the solid constituents of sugarcane and the fermentation process were not available in the Aspen Plus database. These components and their physical properties were therefore inserted into the program according to the database of the United States National Renewable Energy Laboratory (NREL) for biofuels components (WOOLEY; PUTSCHE, 1996).

Figure 2.1 – Schematic block diagram of a standard distillery. Cleaning step – sugarcane cleaning; Extraction step – sugar extraction; juice treatment- juice purification; Juice concentration- water remove by multi effect evaporator; Fermentation step – bioconversion of sugar into ethanol and carbon dioxide; Yeast centrifugation- separation of yeast from diluted fermented wine; Yeast treatment- acid treatment to avoid contamination; DISTILLATION/RECTIFICATION SYSTEM – hydrous ethanol production; ETHANOL DEHYDRATION STEP – anhydrous ethanol production; COGENERATION SYSTEM- steam and electricity production.



2.2.2 Water consumption analysis in the ethanol production process

A system for water reuse is the only practical way of reducing the overall water intake. This methodology can avoid the need for upstream treatment of fresh water and reduce the costs of wastewater treatment (PINA *et al*., 2015).

The sugarcane cleaning step generally consumes a large amount of water. According to Albarelli (2013), this step accounts for 15% of the overall water use in the process, and also results in a loss of 5% of the sugar. Hence, a dry-cleaning system was used for the autonomous distillery simulated in that study.

In this analysis, a closed circuit simulation was carried out according to the procedure used by Chavez-Rodrigues *et al*. (2013) and Mosqueira-Salazar *et al*. (2013). Firstly, the water requirement of a distillery without any closed circuit was determined, which varied from 13,529 to 12,042 L of H_2O/ton. of cane, as presented in Table 2.1. The industrial process water use data were obtained from previous works (ELIA NETO *et al*. 2009; PINA *et al*., 2015; PINA *et al*., 2017). The water consumption in a mill without any closed circuits is shown in Table 2.1.

The next step was to find and quantify a potential water reuse source inside the process. Table 2.2 (in section 2.1) shows the candidates water sources. Portions of these streams could be reused with or without treatment, depending on their use (MOSQUEIRA-SALAZAR *et al*., 2013).The final step included the simulation of closed circuits, enabling quantification of the effective collected water consumption. This step was required for construction of the closed system and to satisfy the requirements of the process where it was connected to the streams (PINA *et al*., 2015). The summarized data are provided in Table A.1 (see Appendix A).

Calculation was made of the net effective water consumption in the process, which was defined as the value of the total effective collected water (Table A.1) subtracted from the value of the total reused water streams (Table 2.2) (PINA *et al*., 2015; MOSQUEIRA-SALAZAR *et al*., 2013).

2.2.3 Ethanol plant - case studies

A case study approach was used to obtain a deeper insight into the distillation heating system for the autonomous distillery. This approach was particularly useful because there are little published data available concerning heating systems and their impact on liquid waste production (MAYER *et al*., 2015). In this analysis, the performances of three different distillation heating systems were simulated according to the procedure used by Silva *et al*. (2015), Albarelli (2013) and Collura and Luyben (1988).

An environmental impact assessment methodology was employed in order to understand the relationship between the heating system and the liquid waste generation, as described elsewhere (HUN *et al*., 2016; MONTOYA *et al*., 2005). In addition, thermodynamic efficiency and Total Annual Cost (TAC) analyses were used to compare the technical-economic feasibilities of the systems studied.

Three case studies were employed in order to gain a detailed understanding of the distillation process heating system. The distillation columns were modelled using the Radfrac block approach, and mass and energy balances were performed based on mesh equations (FERREIRA *et al*., 2013). The options investigated were as follows: indirect heating system using reboilers (Case I), direct steam injection (the standard process, Case II), and distillation with mechanical vapour recompression (Case III).

2.2.4 Case study process descriptions

2.2.4.1 Case I: Indirect heating system using reboilers

In the indirect heating scheme, the thermal energy input into ethanol stripping and rectification units was achieved by introducing a heat exchange device (the reboiler). In this configuration, only energy was transferred to the process, avoiding the dilution effect of condensed steam being added to the vinasse (MAYER *et al.*, 2015).

The steady-state design model for the distillation heating system using a reboiler was performed by the Aspen Plus v. 8.2 process simulator. The parameters for the simulation of stripping and rectification columns are shown in Table 2.5.

Table 2.5 – Parameters of distillation system using indirect steam injection (use of reboilers).

Column	NS	TT (ºC)	BT (ºC)	Q_R (MW)
D	6	79	84	-
A1	8	93	100	-
A	19	100	112	45
BB1	46	81.7	108	6.6

NS-number of stages; TT- top column temperature; BT-bottom column temperature; Q_R- reboiler heat duty.

The simplified flowsheet of the process is shown in Figure A.1 (see Appendix A). In this simulation, all the columns were assumed to be the Radfrac model and the kettle type of reboiler was adopted. The thermodynamic model chosen was the NRTL property method.

Aspen Plus enables the performance of material and energy balances of the process, so relevant thermodynamic properties could be obtained from the simulator. Therefore, it was possible to calculate the required steam flow rate supplied to the reboiler in order to heat the distillation columns, using Equation 2.1 (SILVA; OLIVEIRA, 2014).

$$\dot{\mathrm{m}} = \frac{\mathrm{Q}_{(\mathrm{reboiler})}}{\mathrm{H}^{(\mathrm{vaporazation})}} \tag{2.1}$$

where $\dot{m}$ represent the mass flowrate of saturated steam (kg/s), $Q_{reboiler}$ is the thermal energy applied by reboiler to distillation column (kJ/kg) and $H^{(vaporization)}$ represent the latent heat of vaporization of saturated steam (kJ/s).

2.2.4.2 Case II: Direct steam injection (standard process)

In the standard distillation process (Case II), the thermal energy inputs of the distillation columns were provided by direct injections of steam at the bottom of the columns (A and B). Direct steam injection has been a common practice in bioethanol production processes, because it provides better heat transfer. In this method, heat exchange occurs directly inside the column after injection of steam from the boiler in the cogeneration system (MAYER *et al*., 2015).

Nevertheless, a major drawback of this system is that the vinasse is diluted by the direct addition of steam, which directly increases the amount of waste that needs to be treated or disposed of (BESSA *et al*., 2012).

The steady-state design model for the distillation heating system using steam injection was performed using Aspen Plus v. 8.2. The simplified flowsheet of the process is shown in Figure A.2 (see Appendix A). In this simulation, all the columns were assumed to be the Radfrac model and reboilers were eliminated from the process. The parameters for the simulation of stripping and rectification columns are shown in Table 2.6.

The thermodynamic model selected was the NRTL property method. Details of the simulation have been reported by Palacios-Bereche *et al*. (2015), Silva and Oliveira (2014), Palacios-Bereche *et al*. (2013) and Dias *et al*. (2012).

Table 2.6 – Parameters of distillation system using saturated steam injection (Standard process).

Column	NS	TT (ºC)	BT (ºC)	SSFR (kg/h)	P (Bar)
A	19	100	112	73.000	1.39
BB1	46	81	104	4.900	1.16

Note: NS-number of stages; TT- top column temperature; BT-bottom column temperature; SSFR-Saturated Steam Flow Rate (2,5 bar); P-pressure column.

2.2.4.3 Case III: Distillation with mechanical vapour recompression (MVR)

The MVR concept is based on the principles of heat pump devices and has been extensively studied in recent years (BRUINSMA; SPOELSTRA, 2010; COLLURA *et al.*, 1988; PALACIOS-BERECHE *et al.*, 2015).

In this process, most of the thermal energy of overhead vapour is used to reboil the B column, while another part is cooled by expansion through a valve and is used in the top column condenser (COOLER-B) (COLLURA *et al.*, 1988; MODLA; LANG, 2015).

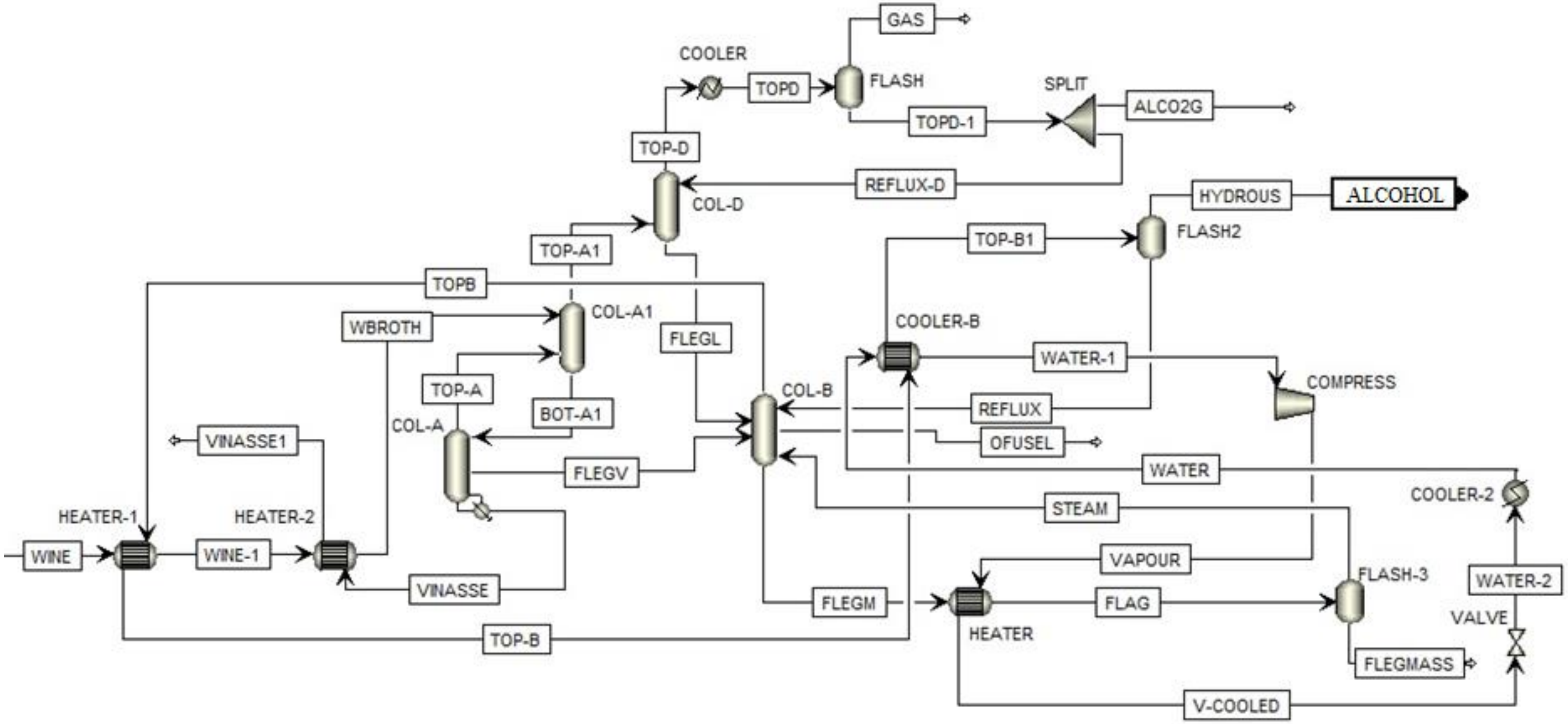
The steady-state design model for MVR distillation was performed by Aspen Plus v. 8.2. The simplified flowsheet of the process is shown in Figure 2.2. The parameters for the simulation of stripping and rectification columns are shown in Table 2.7.

Table 2.7 – Parameters for the simulation of distillation with mechanical vapour recompression scheme.

Column	NS	DF (kg/h)	Q_R (MW)
D	6	2454	-
A1	8	1861	-
A	19	291	45
BB1	46	161547	*6.6

Note: NS-number of stages; DF-distillate flow rate; Q_R-thermal energy applied; *Q_R (6.6MW) electric energy consumed by compressor to provide thermal energy to rectification column.

Figure 2.2 – Hybrid distillation heating system using reboiler and mechanical vapour recompression, simulated in Aspen Plus. COMPRESS - represents the compressor; VALVE - expansion valve; COOLER-B - condenser; HEATER - heat exchanger.



In this simulation, all the columns were assumed to be the Radfrac model and the kettle type reboiler was adopted for the first column set. For the rectification unit (column BB1), the reboiler was excluded from the process and a compressor was added, represented by the COMPRES block followed by a valve. In this scheme, the thermal energy provided by compressor to rectification column can be measured through the electricity consumed through the compressor use to recovery the energy lost in the top column stream. Table 2.7 shows the parameters adopted for the compressor.

Table 2.8 – Parameters adopted for compressor in the simulation of distillation with mechanical vapour recompression

Stream	T (ºC)	P (bar)	VF	ṁ (kg/h)	CR
Input	60	0.2	1	25.500	12.8
Output	300	2.5	1	25.500	

Note: T- temperature; P- pressure; VF- vapour fraction; ṁ- mass flow rate; CR- compression ratio which is defined as the ratio of outlet pressure by inlet pressure from compressor

The NRTL property method was the thermodynamic model selected in this simulation. The compressor was set to function at a mechanical efficiency of 80%, driven by an electric motor. The key parameters are described fully in Modla and Lang (2015).

2.2.5 Environmental analysis

An environmental assessment methodology was applied to compare the environmental impacts of the bioethanol production processes in each of the case studies described in Section 2.2.4. The environmental analysis procedure has been described in full previously (DIAS *et al.*, 2012).

This methodology not only takes into consideration the energy consumption of the process, but also environmental aspects. A very large number of indicators and methodologies, including sustainable process indices, environmental impacts, and lifecycle assessments (LCAs) have been extensively employed in the development of sustainable processes (DIAS *et al*., 2013; DIAS *et al*., 2012; MORAES *et al*., 2015; MONTOYA *et al*., 2005).

One of the available environmental indicators is the WAste Reduction (WAR) algorithm developed by the Environmental Protection Agency of the United States (USEPA). The lifecycle impact assessment method was applied in this evaluation. The WAR algorithm is based on the determination of potential environmental impacts (PEIs), by quantification of the impact that the disposal of waste material would have on the environment (CABEZAS *et al*., 1999; QUINTERO *et al*., 2008).

The environmental impacts evaluated by the WAR algorithm can be classified into two groups such as: toxicological potential effects (TPEs) and atmospheric physical potential effects (APPEs). The TPEs include human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation or dermal exposure (HTPE), terrestrial toxicity potential (TTP), and aquatic toxicity potential (ATP). The APPEs include global warming potential (GWP), ozone depletion potential (ODP), photochemical oxidation potential (PCOP), and acidification potential (AP) (QUINTERO *et al*., 2008).

2.2.5.1 Determination of vinasse application on the ground as a function of potassium concentration

For years, vinasse has been transported from alcohol distilleries to sugarcane fields in tanker trucks, followed by application to the soil using gravity or with the aid of pumps (SILVA, 2012). However, this system can be expensive and may result in a non-homogeneous vinasse application (SANTANA, 1985). More recently, various methods have been developed in attempts to identify feasible and sustainable ways of transporting vinasse and applying it to the soil. Various studies have reported the enhancement of soil properties following vinasse application (OMORI *et al*., 2016). Silva (2012) found that the application of vinasse, *in natura* or in diluted form, could improve the chemical, physical, and biological properties of the soil. However, high vinasse dosages can cause detrimental environmental effects associated mainly with its elevated temperature, high biological oxygen demand, and high salt content.

The maximum vinasse dose applied to the soil can vary greatly according to the type of sugarcane crushed and the operational conditions of the fermentation and distillation process (OLIVEIRA *et al*., 2015; SILVA, 2009). The maximum dose can be calculated using Equation 2.2, as employed in many previous studies.

$$V\left(\mathrm{m^3 vinasse}/_{\mathrm{ha}}\right) = \left[\frac{(0.05 \text{ x } \mathrm{IEC} .- \mathrm{K_{soil}}) \text{ x } 3744+185}{\mathrm{K_{vinasse}}}\right] \tag{2.2}$$

Where V represent the volume, m^3, of vinasse released on soil (per hectare); 0,05 represent the 5% of ion exchange capacity of ground given by the soil fertility analysis, IEC is the ion exchange capacity of the soil, $cmol.dm^{-3}$, K_{soil} represent the concentration of potassium in the soil, $cmol.dm^{-3}$, 3744 is the factor correction of units, 185 is the mass (kg) of K_2O extracted by culture per hectare and $K_{vinasse}$ is the concentration of potassium in the vinasse, kg of K_2O per m^3 (CETESB, 2005; DAMY *et al.*, 2008).

Here, an average value of 208 m^3 of vinasse/hectare, based on previous reports, was adopted as the maximum dose of potassium. The vinasse was assumed to be transported by tanker truck from the mill to the sugarcane crop, over an average distance of 25 km, this is considered the economic ratio to transport vinasse by truck.

2.2.6 Exergy and renewability analysis of the distillation system

Exergy of a substance or stream can be defined as the maximum obtainable work the substance can produce when it is brought reversibly to a state of thermodynamic equilibrium with the environment which is assumed to be at 298 k (T_o) and 1 bar of pressure (p_o) in this study. Exergy analysis of a process is based on the mass and energy balance with the second law of thermodynamics (KHALILI-GARAKANI *et al.*, 2016; WANG *et al.*, 2016).

In this present study, exergy calculations and analysis were conducted in Aspen Plus and Excel. It is extremely important to observer that, the exergetic study must be preceded through mass and energy balance of the system carried out in Aspen Plus simulator (DOGBE *et al.*, 2018). Aspen Plus mass and energy streams results were exported to Excel using Aspen simulation workbook in Aspen Plus V.8.2. Further, exergy analyses were finalized in the Excel® spread sheet. Exergy calculations and analysis were performed by based on the following assumptions (WANG *et al.*, 2018):

i. each of the units was assessed as a steady state flow process.
ii. variations in potential and kinetic exergy were neglected.
iii. temperature room and atmospheric pressure were assumed constants

3.2.7.1 Exergy calculations

Exergy is the maximum work obtained in a reversible process, when a stream a of mater or energy at a specific condition is brought to equilibrium with the environment which it is interacts. The total exergy transfer that across a control volume (flow exergy) is performed by material and energy (work and heat) streams as shown in Equation 2.3 (DOGBE *et al.*, 2018):

$$\dot{Ex}_{system} = \dot{Ex}_{material} + \dot{Ex}_{heat} + \dot{Ex}_{work} \tag{2.3}$$

Where the exergy of material was calculated according to Equation 2.4:

$$\dot{\mathrm{Ex}}_{\mathrm{material}} = \dot{\mathrm{Ex}}_{\mathrm{physical}} + \dot{\mathrm{Ex}}_{\mathrm{chemical}} \tag{2.4}$$

In this study, chemical exergy ($\dot{\mathrm{Ex}}_{\mathrm{chemical}}$)was neglected because there is no chemical changes or reactions in the distillation process. The physical exergies of streams ($\dot{\mathrm{Ex}}_{\mathrm{physical}}$), were calculated by Equation (2.4) obtained through Aspen Plus prop-set, EXERGYFL (exergy flow rate).

$$\dot{\mathrm{Ex}}_{\mathrm{physical}} = \dot{\mathrm{m}}\,[(\mathrm{h} - \mathrm{h_o}) - \mathrm{T_o}(\mathrm{s} - \mathrm{s_o})] \tag{2.4}$$

Where $\dot{\mathrm{m}}$ represent the mass flow rate (kg/s), h is the specific enthalpy (J/kg), $\mathrm{h_o}$ represent the specific enthalpy of a reference state, $\mathrm{T_o}$ is the environment temperature (K), s is the specific entropy (J/kg. K), and $\mathrm{s_o}$ is associated to specific entropy of the reference state (J/kg. K). The exergy transfer by work ($\dot{\mathrm{Ex}}_{\mathrm{work}}$), is calculated by equation (2.5):

$$\dot{\mathrm{Ex}}_{\mathrm{work}} = \dot{\mathrm{W}} \tag{2.5}$$

Where $\dot{W}$ either represent electrical or mechanical work. The heat exergy is calculated as shown in equation (2.6):

$$\dot{\mathrm{Ex}}_{\mathrm{heat}} = \dot{\mathrm{Q}}\left(1 - \frac{\mathrm{T_o}}{\mathrm{T}}\right) \tag{2.6}$$

Where $\dot{Q}$ is associated to heat flow rate (kW), T is the Temperature (K) at which the heat transfer occurs and T_o is the environment temperature (K).

Normally, exergy analysis is applied to assess the thermodynamic performance parameters of a process at which include process irreversibility (DOGBE *et al.*, 2018). Process irreversibility can be named as the exergy destroyed which is the difference in exergy input and output streams as demonstrated in Equation (2.7). Exergy destroyed shows how much exergy is destroyed or lost through a specific unit (DOGBE *et al.*, 2018; MABROUK *et al.*, 2016).

$$\dot{\mathrm{I}}\mathrm{rr} \;=\; \dot{\mathrm{E}}\mathrm{x}_{\mathrm{destroyed}} = \sum \dot{\mathrm{E}}\mathrm{x}_{\mathrm{in}} - \sum \dot{\mathrm{E}}\mathrm{x}_{\mathrm{out}} \tag{2.7}$$

This methodology allows to identify the local, cause, and true magnitude of waste and loss to be determined. Such information is useful for the design of new energy efficient systems and for increasing the efficiency of existing systems. There have been many recent studies that have used the concept of exergy to evaluate the sustainability of various ethanol production routes (MOSQUEIRA-SALAZAR, 2012; MOSQUEIRA-SALAZAR *et al.*, 2013; ORTIZ; OLIVEIRA, 2014; PINA *et al.*, 2015; DADAK *et al.*, 2016; KHALILI-GARAKANI *et al.*, 2016).

Ometto and Roma (2010) applied the chemical exergy concept to evaluate the atmospheric impact of the lifecycle emissions from bioethanol/electricity production at a Brazilian sugarcane mill.

However, there have been few studies focusing on the renewability analysis of ethanol production. Considering this aspect, Pellegrini and Oliveira (2011) and Oliveira (2013) presented environmental analyses employing a so-called renewability exergy index. The renewability exergy index (λ) can be calculated according to Equation 2.8 (OLIVEIRA, 2013):

$$\lambda = \frac{\Sigma \dot{Ex}_{product}}{\dot{Ex}_{fossil} + \dot{Ex}_{destroyed} + \dot{Ex}_{deactivation} + \dot{Ex}_{disposal} + \Sigma \dot{Ex}_{emissions}} \tag{2.8}$$

where $\dot{Ex}_{(product)}$ is the exergy associated with the useful product, $\dot{Ex}_{(fossil)}$ is the non-renewable exergy consumed in the production processes chain, and $\dot{Ex}_{(destroyed)}$ is the exergy destroyed inside the system, punishing the process for its thermodynamic inefficiencies. $\dot{Ex}_{(deactivation)}$ is the deactivation exergy for treating wastes, which accounts for exergy consumed in passing the streams considered as wastes out of the system, without any damage to the environment. Finally, $\dot{Ex}_{(emissions)}$ represents the exergy of wastes that are not treated or deactivated (OLIVEIRA, 2013).

In the above equation, the renewability exergy index indicates that:

✓ Processes with $0 \leq \lambda < 1$ are environmentally unfavourable;

✓ For internal and external reversible processes with non-renewable inputs, $\lambda = 1$;

✓ If $\lambda > 1$, the process is considered environmentally friendly, with a higher value of λ implying that the process is more environmentally favourable;

✓ When $\lambda \rightarrow \infty$, the process is reversible, with renewable inputs and no waste production.

In this study, the mass and energy balances were extracted from the Aspen Plus® software, which was the basis for the exergy calculations. Simulation was conducted at steady state operation, and the exergy balances for a specific control volume (MABROUK *et al.*, 2016).

Based on the above expressions, the exergy efficiency for the distillation system can be calculated according to Equation 2.9, as proposed by Oliveira (2013), Tsatsaronis and Winhold (1985):

$$\varepsilon(\%) = \frac{\sum Ex_{out}}{\sum Ex_{in}} \text{x}100 = 1\text{-} \left[\frac{Ex_{destroyed}}{\sum Ex_{in}}\right] \tag{2.9}$$

2.2.7. Economic analysis

An economic evaluation was carried out in order to compare the costs of the systems. The same operational conditions, including inputs, outputs, temperatures, pressures, and process steam conditions, were assumed for all the case studies. According to Li *et al*. (2016), the Total Annual Cost (TAC) is defined as the total operating cost added to the annualized capital investment cost, where the latter corresponds to the ratio of the capital cost and the payback period. The TAC is calculated by Equation 2.10

$$TAC\left({}^{US\$}/_{year}\right) = \left(\frac{capital\ cost}{payback\ period}\right) + operating\ cost \tag{2.10}$$

The estimated equipment cost was calculated according to the procedure used by Li *et al*. (2016) and Douglas (1989). In this study, the payback period was fixed as three years, as normal practice in sugarcane industry. The payback period is defined as the time necessary to accumulate the net revenue of the plant became equal to the value of initial investment payed for. The economic basis of the calculation was fully described by Luyben (2013) and are presented in Table A.2 and A.3 (see Appendix A). In this manuscript, we realized that the cost of vinasse transportation is relevant. Thus, it was included in the calculation of TAC of each case studied. Vinasse transportation cost calculation was based on data provided by Fermentec (2015).

2.2.7.1 Net revenue (NR) sensitivity analysis

Sensitivity analysis of the net revenue of the anhydrous ethanol production process was performed in order to determine whether there would be any substantial decrease in the net revenue (NR) of the sugarcane mill. For this analysis three scenarios was considered: (A) ethanol selling price varied in a range of 20% over the its average selling price while the surplus of electricity selling price and cost of vinasse transportation were kept fixed, (B) the selling price of surplus electricity varied in a range of 20% over the its average selling price while the ethanol selling price and cost of vinasse transportation were kept fixed and (C) the cost of vinasse transportation varied in a range of 20% over the its average selling price while the selling price of ethanol selling and surplus electricity were kept fixed.

Table 2.9 Key parameters used in the net revenue analysis.

Parameter	Value	Unit
Vinasse transport cost[a]	2.7	US$/m^3
Electricity selling price[b]	84.88	US$/MWh
Anhydrous ethanol selling price[b]	0.60	US$/L

[a]Fermentec (2015).
[b]Dias *et al*. (2015).

For all the case studies, the output parameter was the net revenue (US$), calculated according to Equation 2.11. The main parameters used in the NR sensitivity analysis are shown in Table 2.8

.

$$NR\ (US\$) = \$EtOH + \$EE - \$Vinasse \qquad (2.11)$$

2.3 Results and Discussion

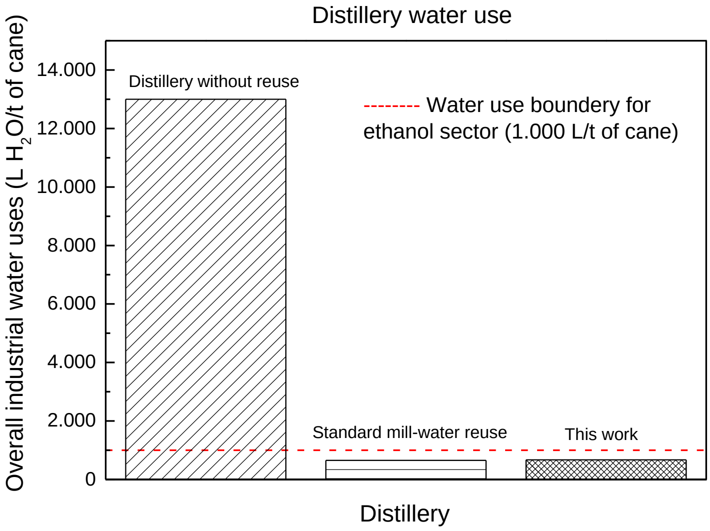
2.3.1 Water uses

A cold utilities recirculation procedure was implemented. It can be seen from Figure A.3 (see Appendix A) that the process with closed water circuits offered potential for water conservation. This methodology could assist the sugarcane plant in achieving substantial reductions in water consumption (PINA *et al.*, 2015).

Chavez-Rodriguez and collaborators (2013) studied process stream integration using closed water circuits and found that this procedure could reduce industrial water use from 15 m^3/t of crushing cane (oldest process) to less than 2 m^3/t of crushing cane. This finding is extremely important in terms of the environmental protection of water resources, because in the State of São Paulo, Brazil, the permitted rate of fresh water extraction from rivers is a maximum of 1,000 L H_2O/t of crushing cane (FILOSO *et al*., 2015).

In the present study, the net water consumption achieved in the simulated distillery was 673 L/t of crushing cane, which was well within the statutory limit (Figure 2.3).

Figure 2.3 – Overall water uses in integrated sugarcane distilleries, with and without reuse of water streams (L/t of cane).



As shown in Figure 2.5, data extracted from literature showed that the water consumption of 13,000 L H_2O/t of cane in the ethanol plant without stream reuse could be dramatically reduced by 95.5%, when the water circuits were closed. This included the reuse of water from condensate streams, enabling a reduction in external withdrawals to supply the plant water demand (PINA *et al*., 2015).

A comparison was made of the water demands of a standard distillery and a sugarcane distillery with closed circuits simulated in this study. The results obtained showed that there was a slight difference in water demand, with an estimate of 655 L/t of cane for the standard process, as reported by Mosqueira-Salazar *et al*. (2013), and 673 L/t of cane for this study, as shown in Figure 2.5. Different to the standard process, in this study the use of a dry washing system was investigated.

2.3.2 Environmental analysis of the distillation system

The mass and energy balances of the product, input, and waste streams, obtained using the Aspen Plus simulator, enabled an environmental assessment to be performed (PEREIRA *et al.*, 2015; QUINTERO *et al.*, 2008). The liquid waste output streams (formed by sugarcane vinasse and flegmass) for each configuration are presented in Table 2.9. It can be seen that there was a significant difference between the water and ethanol outflow streams for the standard process (Case II). In Case I, there was a reduction of almost 24% in vinasse production, compared to Case II.

Table 2.10 - Liquid waste outflows for each case study.

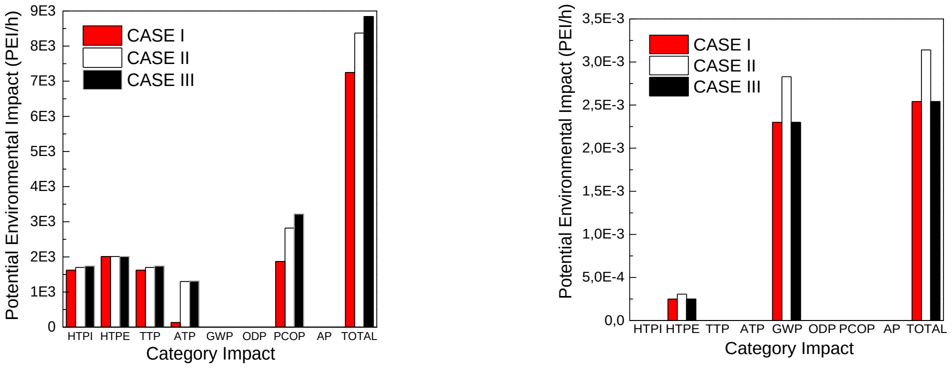
Waste stream flow rate (kg/h)	*Case I	**Case II	***Case III
Sucrose	0	0	0
Dextrose	3,820	3,820	3,820
Succinic acid	128	128	128
Acetic acid	515	514	515
Glycerol	1,771	1,771	1,771
Water	313,621	391,838	314,538
Anhydrous ethanol	0	2032	2880
Potassium chloride	0	0	0
Calcium hydroxide	985	985	985
Sulphuric acid	7,880	7,880	7,880
Total (kg/h)	334,460	414,711	338,257

* Case I - Distillation heating system using reboiler as heat source.
** Case II - Distillation heating system using direct steam injection (standard process).
*** Case III - Distillation heating system with MVR.

As expected, Case II resulted in the highest flow of waste, due to the dilution effect of condensed steam being added to the vinasse. As reported previously by Mayer *et al*. (2015) and Silva *et al*. (2015), the use of steam injection increases the production of vinasse by up to 30%, because there is an input of approximately 3-4 kg of vapour/L of ethanol distilled.

As shown in Table 2.9, Case III exhibited lower vinasse production than Case II (conventional process). However, this configuration loss a little more ethanol in the liquid waste stream (2,880 kg/h) when compared to conventional process 2,032 kg/h.

Figure 2.4 – (a) Environmental impacts caused by vinasse production for each case. The impact is expressed as the PEI leaving the system per mass of product. (b) Environmental impacts caused by CO2 emissions during vinasse transportation. The impact is expressed as the PEI leaving the system per mass of product. Category impact legend: HTPI (human toxicity potential by ingestion); HTPE (human toxicity potential by inhalation or dermal exposure); TTP (terrestrial toxicity potential); ATP (aquatic toxicity potential); GWP (global warming potential); ODP (ozone depletion potential); PCOP (photochemical oxidation potential); AP (acidification potential).



(2.4a) **(2.4b)**

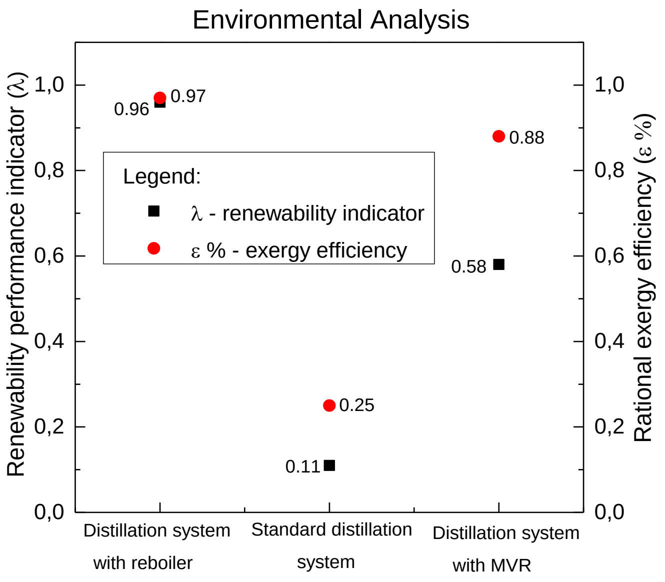
In terms of liquid waste, it is clear that the highest environmental impact was obtained for Case III (Figure 2.4a), on possible explanation for this is the high organic content of the vinasse stream (OLIVEIRA *et al*., 2015). The highest environmental impact due to CO_2 emissions was observed for Case II (Figure 2.4b). This impact was associated with transportation of the vinasse (OLIVEIRA *et al*., 2015), with CO_2 emitted to the atmosphere from diesel truck engines during transport from the plant to the field over an average distance of around 25 km (SILVA, 2009).

The single most striking observation to emerge from the data comparison was that the indirect heating system (Case I) was demonstrated to be the most environmentally friendly process, offering an interesting alternative route to produce first-generation ethanol.

2.3.3 Renewability of the distillation system

Figure 2.5 shows the renewability exergy index (λ) values for the distillation configurations evaluated, from which it can be seen that the more efficient systems provided better performance, in terms of λ (PELLEGRINI; OLIVEIRA JUNIOR, 2011). None of the systems showed a value higher than 1, indicating that the processes could be considered environmentally unfavourable, from the second law standpoint (see Section 2.6).

Figure 2.5 – Renewability performance indicator (λ) and rational exergy efficiency (ε%) for each configuration investigated



However, the most interesting aspect of the performance comparison was the better environmental performance of the distillation system that used a reboiler as heat source, compared to the standard configuration.

The values of λ for the reboiler system (Case I), the standard system (Case II), and the MVR system (Case III) were 0.97, 0.11, and 0.88, respectively. Hence, it could be argued that the Case I system provided the most sustainable process for ethanol purification.

The standard configuration presented the worst environmental performance. This could be a consequence of the inefficient operation of the distillation column heating system. According to Mayer *et al*. (2015), the use of steam injection increases the production of vinasse by up to 30%, due to the input of approximately 3-4 kg of steam per liter of ethanol distilled. The behaviour appeared to be consistent with the data presented in Table 2.9, suggesting that the standard system would require optimization in order to improve environmental performance.

2.3.4 Industrial performance of the distillation heating system

In this part of study, Case I (reboiler use) showed higher thermal energy (vapour) consumption, with values 6% and 16% higher than obtained for Case II (steam injection) and Case III (MVR), respectively (Figure 2.2). Figure 2.6 shows the thermal energy consumption of each case studied

Figure 2.6 – Thermal energy (vapour) used to heat the set of distillation columns in each case study.

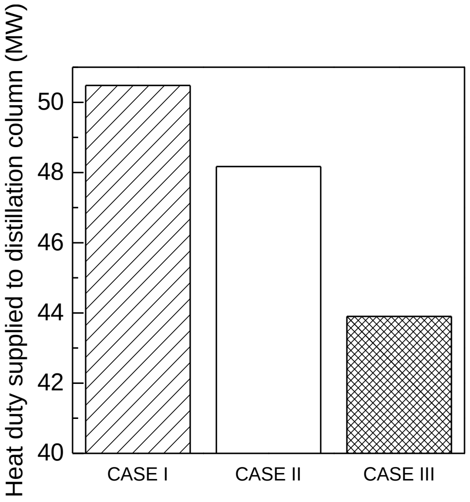
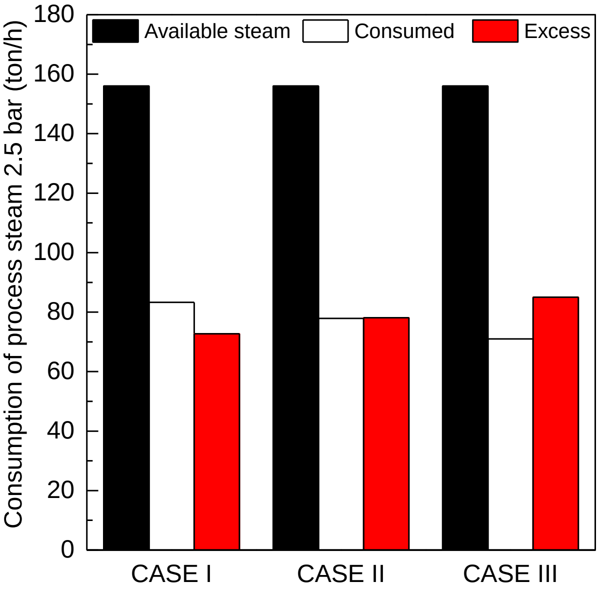


Figure 2.7 – Analysis of process steam (2.5 bar) consumption for each configuration studied.



These results were in line with the findings of Mayer *et al.* (2015) and suggested that the use of reboilers (heat exchangers) to supply heat to the distiller has low efficiency. Another drawback associated with reboiler use is the fouling caused by minerals present in the wine, because of the high temperature at the reboiler. In addition, the reboiler use has high cost of investment to buy the heat exchanger However, reboiler heat systems are simple to operate (MAYER *et al.*, 2015; SILVA *et al.*, 2015).

Case III showed lower thermal energy consumption, due to compression of the cold utility vapour to its saturation temperature, which was used to evaporate the column bottom stream. Hence, in the MVR system, there was no requirement for steam from the process to heat the column (COLLURA, 1988). The process steam consumptions of the distillation processes are presented in Figure 2.7.

2.3.5 Surplus electricity production

Table 2.11 shows the results obtained for the overall production, consumption, and surplus of electricity in each case study. In all the scenarios, the average production of electric power from the cogeneration system was taken to be 65 kWh/t of crushing cane. This value will depend on the operational parameters, including the boiler pressure and the arrangement of the turbochargers.

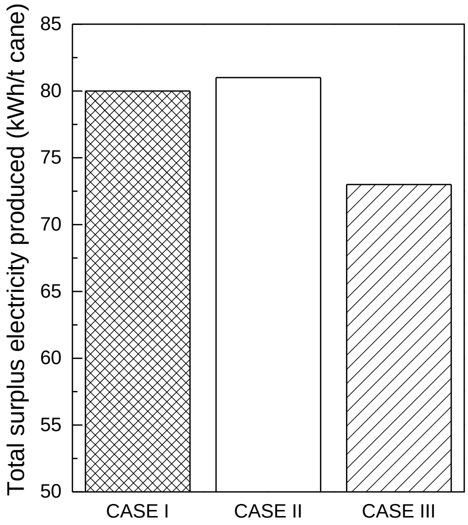
Table 2.11 - Electrical energy analysis for the ethanol production process.

Case	[a]Electricity produced (kWh/tc)	[b]Electricity produced (kWh/tc)	[c]Electricity consumed (kWh/tc)	Surplus electricity (kWh/tc)	$RE(\%) = \left[\frac{x - \bar{x}}{\bar{x}}\right] \times 100$
I	65.4	14.36	-	79.8	9.92
II	65.4	15.43	-	81	11.5
III	65.4	16.79	9.6	72.6	-

[a] Surplus electricity produced at the cogeneration stage in the condensing-extraction steam turbine system;
[b] Surplus electricity produced from the remaining process steam from the distillation system;
[c] Electricity consumed by the mechanical compressor to heat the distillation column;
RE (%) - relative error associated to surplus electricity in which case I and II are compared to case III

Case III showed higher electricity production, due to the excess steam from the distillation system, with a value of 16.79 kWh/t of cane (Table 2.11). The excess steam was converted into electricity by means of the system of extraction-condensing turbines adopted in this study (ALVES *et al.*, 2015). The global production of surplus for each case study is presented in Figure 2.8.

Figure 2.8 – Global production of surplus electricity for each case study.



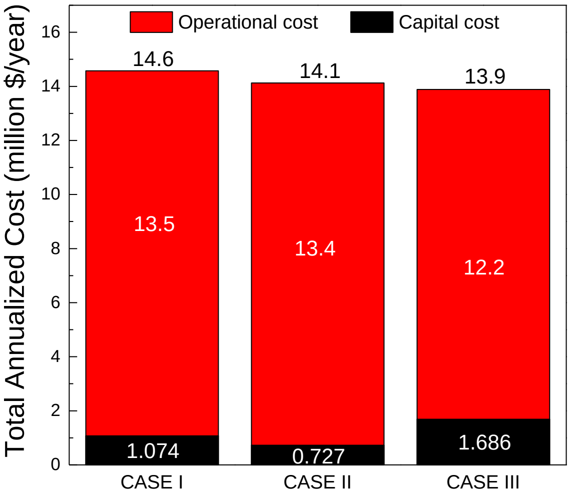
However, Case III showed the lowest surplus electricity value (72.6 kWh/t of cane), which could be explained by the high amount of electricity used by the compressor, as reported by Mayer *et al*. (2015) and Collura (1988). Hence, Case III produced 9.92% and 11.5% less surplus electricity, compared to Cases I and II, respectively. In terms of the overall surplus of electricity, no significant difference was found between the reboiler use and standard processes, with values of 81 and 79.8 kWh/t of cane, respectively.

2.3.6 Economic analysis: distillation system

Economic analysis of each distillation heating system was performed by calculating the total annual cost (TAC). Table A.2 (see Appendix A) summarizes the results of the cost calculations performed in this work. Figure 2.9 shows the TAC results for the different case studies. Compared to Cases I and III, the standard system (Case II) presented a lower capital cost, as expected because the absence of reboilers reduces capital costs (HARVIANTO *et al*., 2015).

Case III showed the TAC value of 13.9 million/year, this value is 4.7% and 1.4% lower, compared to Cases I (14.6 million/year) and II (14.1 million/year), respectively. A possible explanation for this could be that the introduction of a compressor to the rectification system produced a considerable reduction of the utility cost of the process, along with a decrease in the operational cost, as shown in Table A.4 (in Appendix A).

Figure 2.9 – Comparison of total annual costs (TAC) for the different distillation heating systems investigated.



In this study, the utilities consumed in the ethanol plant include: 2.5 bar saturated steam, 6.0 bar steam and electricity (OLIVEIRA *et al*., 2018). The steam cost was defined based on the usual conditions found in Brazilian plants. Dias et al. (2015) estimated the cost of generating steam per unit of energy as 13.89 $/GJ. The cost of steam has a substantial effect on the operational cost of all systems studied but was bigger for Case I owing to the high consumption of saturated steam in the reboilers (Figure 2.9). From Figure 2.9, the Total Annual Cost (TAC) of Case I is 15 million dollar/year. The higher cost is related to reboilers purchase as can be seen from the data in Table A.4 (see Appendix A). What is interesting about the data in this table is that the cost of vinasse transportation represent 24.8% of total cost for Case I, and 31% for Case II and 25.7% for Case III.

In this investigation, it was found that Case II (conventional process) and III were likely to be more environmentally unfavourable (see Figures 2.4 and 2.5). Therefore, considering both cost and sustainability, the distillation system using indirect saturated steam injection appeared to be most suitable.

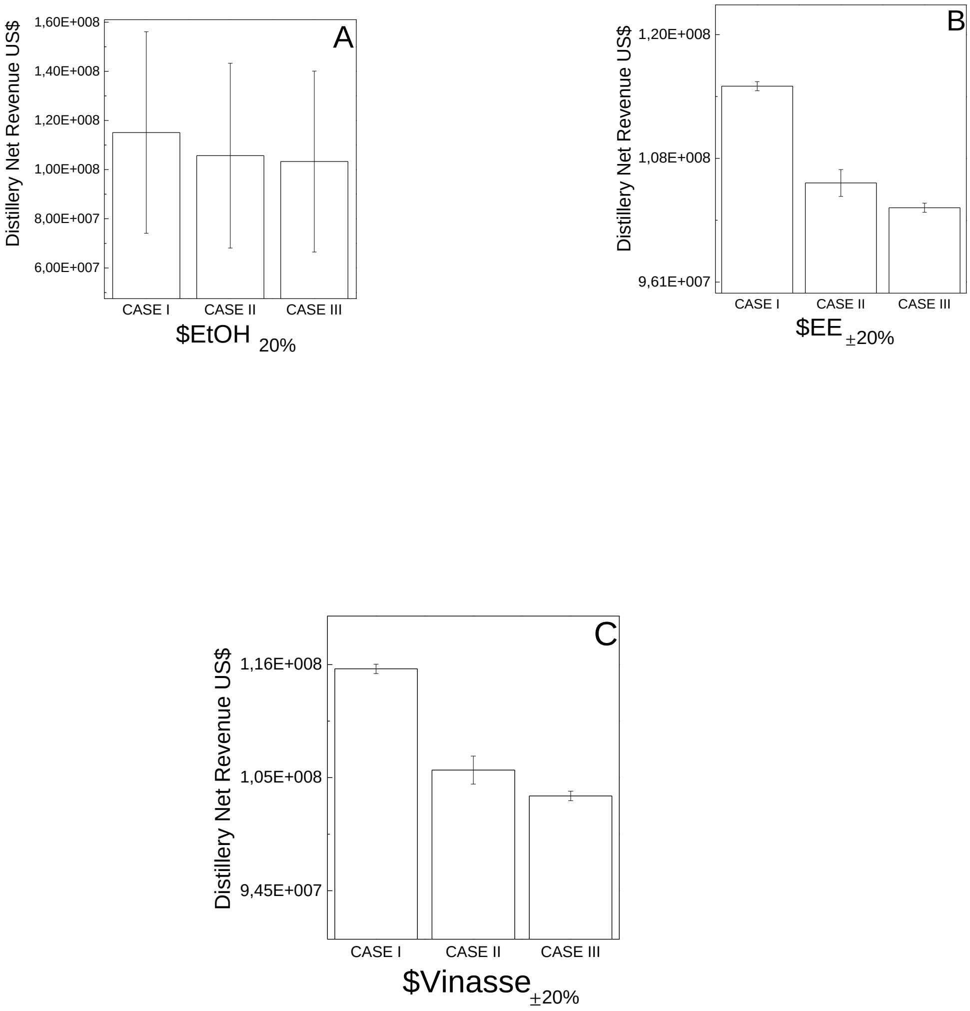
2.3.7 Sugarcane plant net revenue

The average net revenues (NR) for the distillery under investigation was calculated based on the selling price of anhydrous ethanol and surplus electricity as well as the vinasse transportation cost. The Equation 2.11 in section 2.2.7.1 describes how to calculate NR.

The values obtained in NR analysis were 115, 105.7, and 103.3 million US$ for Cases I, II, and III, respectively. The NR for Case I was 8.8% and 11.6% higher, respectively, compared to Cases II and III (Figure 2.10). This can be explained by the fact that the simulation of Case I achieved a higher anhydrous ethanol production of 611 L per tons of sugar total reducers, while Cases II and III achieved 559 L/tons L per tons of sugar total reducers and 548 L/tons L per tons of sugar total reducers.

The NR value ranged from US$ 6.7x107 to US$1.6x108 when the ethanol selling price ($EtOH) was varied by 20% (see Figure 2.10A). This contributed to a higher fluctuation of 40% cost of vinasse transportation ($Vinasse) did not substantially affect the distillery net revenue, as shown in between the minimum and maximum NR values. Changes in the surplus electricity price ($EE) and the Figures 2.10B and 2.10C.

Figure 2.10 – Sensitivity analysis of the net revenue of an autonomous distillery, considering changes in the anhydrous ethanol selling price (A), the surplus electricity selling price (B), and the cost of vinasse transportation (C).



2.4 Conclusions

This study shows that a water streams reuse methodology can be used to improve the sustainability of first generation ethanol production, and that a sustainable process can be achieved by thermal and water with better use. In the present work, application of this methodology resulted in better use of energy and water, providing a substantial surplus of electricity together with reduced water requirements that enabled the water consumption of the plant to remain below the statutory limit.

Evaluation of different types of distillation process heating systems showed that the use of reboilers (Case I) reduced vinasse production by 24% and therefore provided the greatest environmental benefits. Use of the exergy index of renewability also showed that the Case I system provided superior environmental performance, compared to the other processes. Economic evaluation showed that the TAC for Case I was slightly higher, by 1.4% and 4.7%, respectively, compared to Cases II and III.

Nevertheless, the Case I system provided advantages over Cases II and III, including improvements in anhydrous ethanol flowrate production as well as net profitability. The results demonstrated that the use of reboilers in distillation systems can contribute to the development of green sugarcane distillery processes, while at the same time being attractive from an economic perspective.

2.5 Acknowledgements

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CHAPTER 3 – SIMULATION OF AN ALTERNATIVE ROUTE COMBINING LIQUID-LIQUID EXTRACTION-DISTILLATION SYSTEM TO PRODUCE ANHYDROUS ETHANOL: DOWNSTREAM PROCESS AND ITS ENVIRONMENT IMPACT

Abstract

Bioethanol is attracting a great interest from both academic and industry, and some companies are looking for revamping their industrial unit to produce bioethanol. The recovery of ethanol from diluted fermented wine is made by distillation system, which is proved to be an energy-intensive process. In this way, hybrid processes combining liquid-liquid extraction (LLE) coupled with distillation were proposed as an alternative technology to produce anhydrous ethanol. This hybrid process has been simulated using the Aspen Plus® process simulator V.8.2. The thermodynamic model NRTL (Non-Random Two Liquid) was selected for the prediction of liquid-liquid equilibrium and also the vapor-liquid equilibrium in the distillation column sequence. In this process, solvent screening methodology is one of the most important issues, so the isoamilic alcohol, n-octanol, n-dodecanol and oleic acid were the solvents selected to be investigated. In this study, solvent feed flow rate, the liquid waste emissions, downstream process, the overall energy consumption and the Total Annual Cost (TAC) were defined as the parameters to evaluate and screen the best option of LLE. Among the candidates investigated, hybrid system with dodecanol reached 37.57% and 99% wt. reduction of liquid waste emissions and ethanol recovery rate, respectively. At the same time, using the concepts of exergy and renewability index, LLE with oleic acid and conventional process were considered to provide the worse environmental performance than extraction system with dodecanol. In addition, this last proposed purification strategy achieved 580 L of anhydrous ethanol per ton of sugar total reducers and this value is similar to standard process (560 L/ton. sugar total reducers).

Keywords: ethanol, liquid-liquid extraction, exergy, downstream process, TAC.

3.1 Introduction

In Brazil ethanol can be produced from biomass via sugarcane juice fermentation. During this process, the alcohol produced is conventionally separated from the fermented broth by distillation process. This is a robust and well-known technology applied for ethanol purification, however it is energy intensive (KURKIJARVI *et al*., 2014). According to Brito and collaborators (2016) the distillation set of columns are very energy-intensive process, once the molasses fermentation process produces a diluted fermented broth. In this sense, it important to find out alternatives technologies to increase the ethanol concentration in the fermented broth to minimize the energy consumption and as well as the operational cost of ethanol dehydration step (KURKIJARVI *et al*., 2014).

The most common methods applied for the ethanol dehydration are extractive or azeotropic distillation, pressure swing distillation, and pervaporation. Other technologies have been suggested such as supercritical fluid extraction, adsorption membranes, salt-induced phase separation and hybrid methods which include a combination of liquid-liquid extraction along with distillation process (BRITO *et al*., 2016; KURKIJARVI *et al*., 2014).

On account of the fact that the hybrid method to produce ethanol has received much attention in the last decade. The advantage of this method is related to the pre-concentration of fermented wine before the distillation step. Offeman *et al*. (2005), Offeman *et al*. (2008) and Offeman *et al*. (2010) studied many organic solvents to recover alcohol from aqueous mixtures. In particular, a common feature of this methodology is the utilization of a combination of liquid-liquid extraction with distillation to produce anhydrous ethanol (NHIEN *et al*., 2016).

In this strategy, the alcoholic wine obtained from fermentation process was introduced to an extractor column and a set of distillation columns to reach the desired concentration of anhydrous ethanol. The bigger intrinsic obstacle to this technology is related to the use of a suitable solvent for liquid-liquid extraction to maximize the recovery of compounds from the aqueous diluted fermented broth (NHIEN *et al*., 2016).

In this context, the screening of the most appropriate solvent is a challenge due to the different chemical nature of species present in the broth (NHIEN *et al*., 2016). A lot of approaches for solvent screening have been studied. One of the methodology uses traditional laboratory experiment to find out the most suitable solvent. The results obtained by this method are accurate and reliable, even though this alternative may be limited by cost and time.

Another methodology for solvent selection may be applied based on existence of powerful simulating programs. Such tools can perfectly represent the thermodynamic properties of multicomponent solutions, such as those present in alcoholic wine (BATISTA *et al*., 2012). Computer simulation has been applied as a tool for studying and evaluation of the most efficient and reliable design of candidate solvents for the bioethanol dehydration processes (BATISTA *et al*., 2012). The screening of the most suitable solvent for hybrid technology for anhydrous ethanol production has been assessed, and this process focused both on ethanol recovery rate and environmental impact (BATISTA *et al*., 2012).

In the last decades, one of the most significant current discussion in sugar-ethanol industry is about the renewability of bioethanol production processes. Thus, this study makes an interesting contribution to research on bioethanol production by presenting an integrated methodology for process analysis, which simultaneously evaluates the downstream process which is normally neglected, the economic feasibility by total annual cost analysis as well as the environmental aspects of modifications performed inside the sugarcane plant.

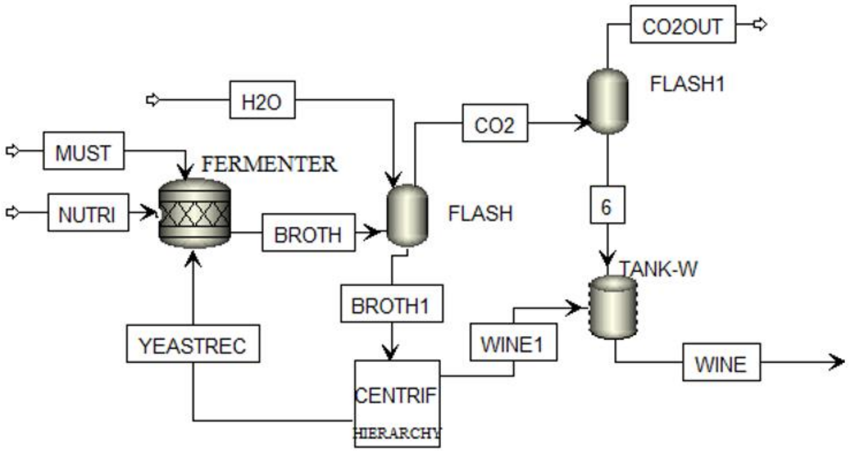
3.2 Methodology and approach

In this study, the hybrid-extraction distillation process will be investigated. The designed scheme for each solvent used in hybrid-extraction distillation process will be described, along with the strategy to minimize environmental impact and the process energy consumption. Finally, the TAC is also calculated.

3.2.1 Simulation of fermentation step

For purpose of analysis, a fermentation process for the first-generation of ethanol production was simulated using Aspen Plus®. These simulations were conducted assuming a milling rate of 500 tons of sugarcane/hour, which corresponds to a Brazilian standard size plant (PALACIOS-BERECHE *et al.*, 2014). In this study, diluted fermented broth was linked to liquid-liquid extraction process as shown in Figure 3.1.

Figure 3.1 – Flowsheet of ethanol fermentation process from molasses including ethanol LLE step. Fermenter and extractor column (B4) were operated at the same conditions (33ºC and 1.03 bar). Main streams: (MUST) molasses, (BROTH) fermented broth, (WINE1) centrifuged wine (~9% wt. ethanol) and treated yeast recycled to fermenter vessel (YEASTREC).



After the extraction and juice treatment step, molasses with a concentration of 20% by weight of fermentable sugars go directly to fermentation step (WIDJAJA *et al.*, 2014). In this proposed study, simulations have been performed using the Aspen Plus v. 8.2 process simulator (ASPENTECH, 2010). The fermentation step was simulated as a continuous mode, however the traditional real process, which is named Melle-Boinot process, is performed in a fed-batch process (PALACIOS-BERECHE *et al*., 2014).

The fermentation process was simulated as followed the hydrolysis of the sucrose into glucose and fructose followed by the bioconversion of glucose and fructose into ethanol and carbon dioxide using *Saccharomyces cerevisiae* yeast as a catalyst. In addition, some minor components such as sulphuric acid, higher alcohols like 3-methyl-1-butanol, and succinic acid, glycerol, acetic acid are contaminants in the fermented broth. At the end of process, *Saccharomyces cerevisiae* is centrifuged, treated with a diluted solution of sulphuric acid and sent back to fermenter. After the fermentation step, the alcoholic solution, without yeast, containing approximately 7 to 10% wt. of ethanol, is taken to distillation step to recover ethanol (PALACIOS-BERECHE *et al*., 2014). The simulation of fermentation process is represented by the block FERMENTER, FLASH, FLAHS1, CENTRIF and TANK-W as shown in Figure 3.1.

In recent years, there has been an increasing amount of literature focused on exploring experimental assay using organic solvents to increase ethanol content in the fermented broth (LEMOS *et al*., 2017; HABAKI *et al*., 2016; WIDJAJA *et al*., 2014).

However, there is little published data on literature regarding the use of computer simulation of fermentation process focusing on system that allows, increase the concentration of fermented broth out of the fermenter vessel. One advantage of using concentrated fermented broth is that it reduces the energy requirement in the distillation system (PALACIOS-BERECHE *et al*., 2014).

Among the alternatives, liquid-liquid extraction (LLE) emerges as a technique to preconcentrate the fermented wine before been sent to distillation process. Martinez *et al.* (2012) have investigated the dehydration of ethanol through hybrid system comprised by LLE and extractive distillation (ED), and they have found that the hybrid system presented lower energy consumption compared to conventional distillation scheme. Thus, the purpose of this study is to simulate the dehydration of ethanol by hybrid system LLE/Extractive distillation using four different extractor solvents for LLE and to compare their thermodynamic efficiency as well as waste stream generations.

3.2.2 Solvent screening approach

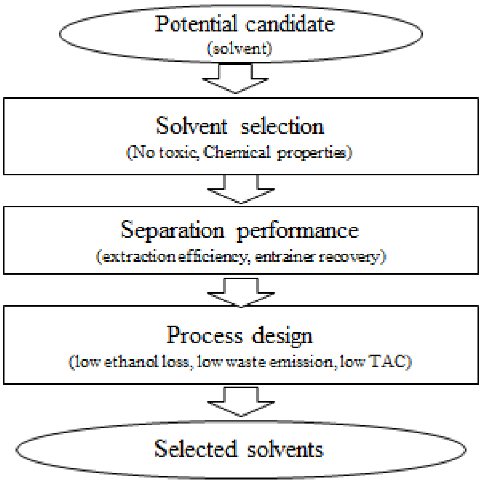
The main challenge in liquid-liquid extraction (LLE) is the screening of a desirable solvent, which presents operational and economic feasibility for separation process (BIRAJDAR *et al.*, 2014). In this sense, the solvent screening methodology is an extremely important step to the entire process design, due to LLE can cause serious damage to environment, and increase production cost.

In order to perform the separation of ethanol-water mixture from the diluted fermented broth, a careful study of the solvent has been done in literature (OFFEMAN *et al.*, 2005). The appropriate solvent must meet some requirements such as: high distribution coefficient (K_{DE}), and separation factor (α), non-toxic to microorganism, low solubility, low viscosity, low cost, ease recovery and environmental friendly. In this sense, there is a large volume of published studies describing the role of distribution coefficient and separation factor of ethanol for the purpose of solvent selection for success of liquid-liquid extraction system (NHIEN *et al.*, 2016; SCHEFFCZYK *et al.*, 2016; WIDJAJA *et al.*, 2014; OFFEMAN *et al.*, 2008; OFFEMAN *et al.*, 2005; WEILNHAMMER AND BLASS, 1994).

However, far too little attention has been paid to process downstream for liquid-liquid extraction. The downstream processing is related to regeneration and purification of a component. So, this issue makes the process design more complex which requires an accurate and efficient solvent selection study not only for solvent extraction process but also for downstream process impacts (NHIEN *et al.*, 2016).

This study attempts to show a systematic procedure of solvent screening for the removal of ethanol from the diluted fermented broth by liquid-liquid extraction process. The Figure 3.2 illustrates some of the main characteristics of the solvent selection.

Figure 3.2 – Schematic diagram of solvent screening methodology for ethanol extraction process from the diluted fermented wine



In the present study, four organic solvent were selected for liquid-liquid extraction of ethanol from diluted fermented wine. The potential candidates are: isoamilic alcohol (C-5); n-octanol (C-8), n-dodecanol (C-12) and oleic acid (C-18). The properties of the solvent under investigation are listed in the Table 3.1.

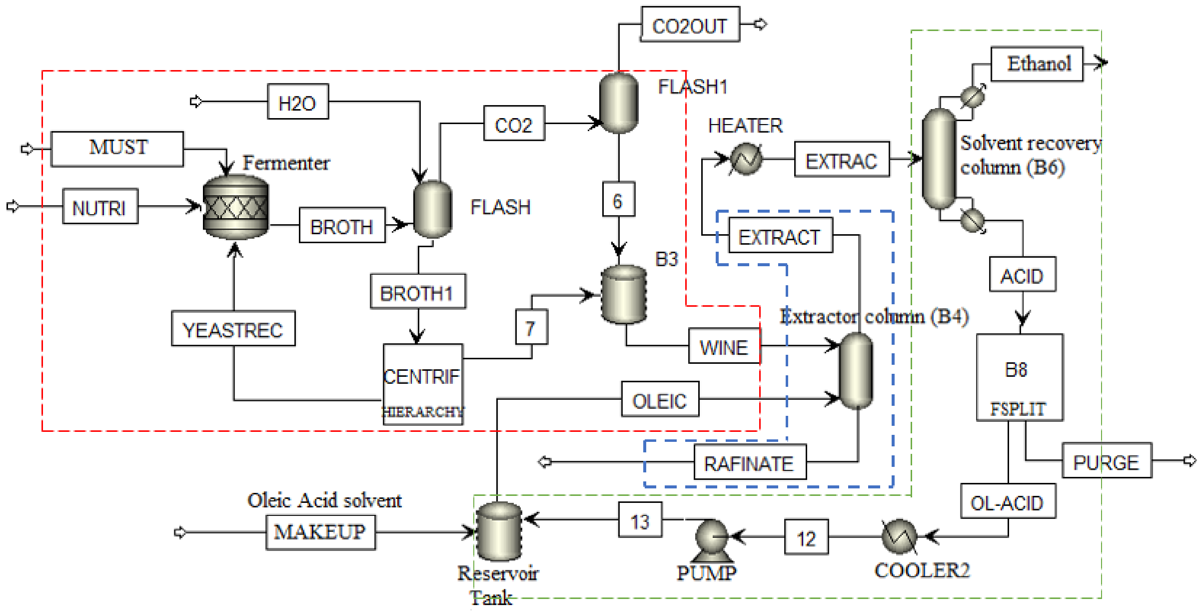
Table 3.1 – The main characteristic of the organic solvents investigated for LLE process

Solvent	[a]CAS	Density (g/cm^3)	[b]MW (g/mol)	[c]BP (°C)
isoamilic alcohol	123-51-3	0.810	88.15	131
n-octanol	111-87-5	0.826	130.23	195
n-dodecanol	112-53-8	0.831	186.34	259
oleic acid	112-80-1	0.895	282.47	360

[a]CAS – CAS NUMBER; [b]MW – Molecular Weight; [c]BP – Boiling point

The process flowsheet of the LLE with downstream process for solvent regeneration is depicted in Figure 3.3. The downstream processing was performed by an ordinary distillation column simulated using a Radfrac block.

Figure 3.3 – Process flowsheet of downstream process for LLE process. Red box is fermentation step; Blue box is LLE and Green box is solvent recovery step (downstream process).



3.2.3 Distribution coefficient analysis: solvent performance

The LLE system of ethanol from fermented media is presented. The main challenge of LLE is the screening of a desirable solvent which presents operational and economic feasibility for separation process (BIRAJDAR *et al.*, 2014). In order to perform the separation of ethanol-water mixture from fermented broth, a careful study of the solvent has done.

To prove the ability of solvent to remove ethanol from diluted broth through LLE, the ethanol distribution coefficient (K_{DE}) was calculated for each solvent investigated. The ethanol distribution coefficient is defined as the ratio of weight fraction of ethanol in the organic phase to the weight fraction of ethanol in aqueous phase. The K_{DE} was calculated by

Equation 3.1 (OFFEMAN *et al*., 2005).

$$\mathrm{K_{DE}} = \frac{[\text{ethanol flow rate}]_{\text{organic−rich phase}}}{[\text{ethanol flow rate}]_{\text{aqueous−rich phase}}} \tag{3.1}$$

For $\mathrm{K_{DE}}$ analysis it was considered a single stage extraction performed in Aspen Plus® using a Decanter block. Another important parameter to measure is $\mathrm{K_W}$, which represent the distribution coefficient of water. The distribution coefficient of water ($\mathrm{K_W}$) is calculated by Equation 3.2:

$$\mathrm{K_W} = \frac{[\text{water flow rate}]_{\text{organic−rich phase}}}{[\text{water flow rate}]_{\text{aqueous−rich phase}}} \tag{3.2}$$

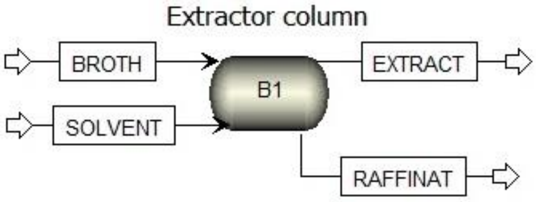
Where $\mathrm{K_W}$, it is defined as the ratio of weight fraction of water in the organic phase to the weight fraction of water in aqueous phase (OFFEMAN *et al*., 2005).

To increase the reliability of the data, separation factor (α) was calculated as well. The α represent the ratio of distribution coefficient of ethanol ($\mathrm{K_{DE}}$) to the water distribution coefficient ($\mathrm{K_W}$) and α defined as follow in Equation 3.3 (DEMESA *et al*., 2015).

$$\alpha = \frac{K_{DE}}{K_W} \tag{3.3}$$

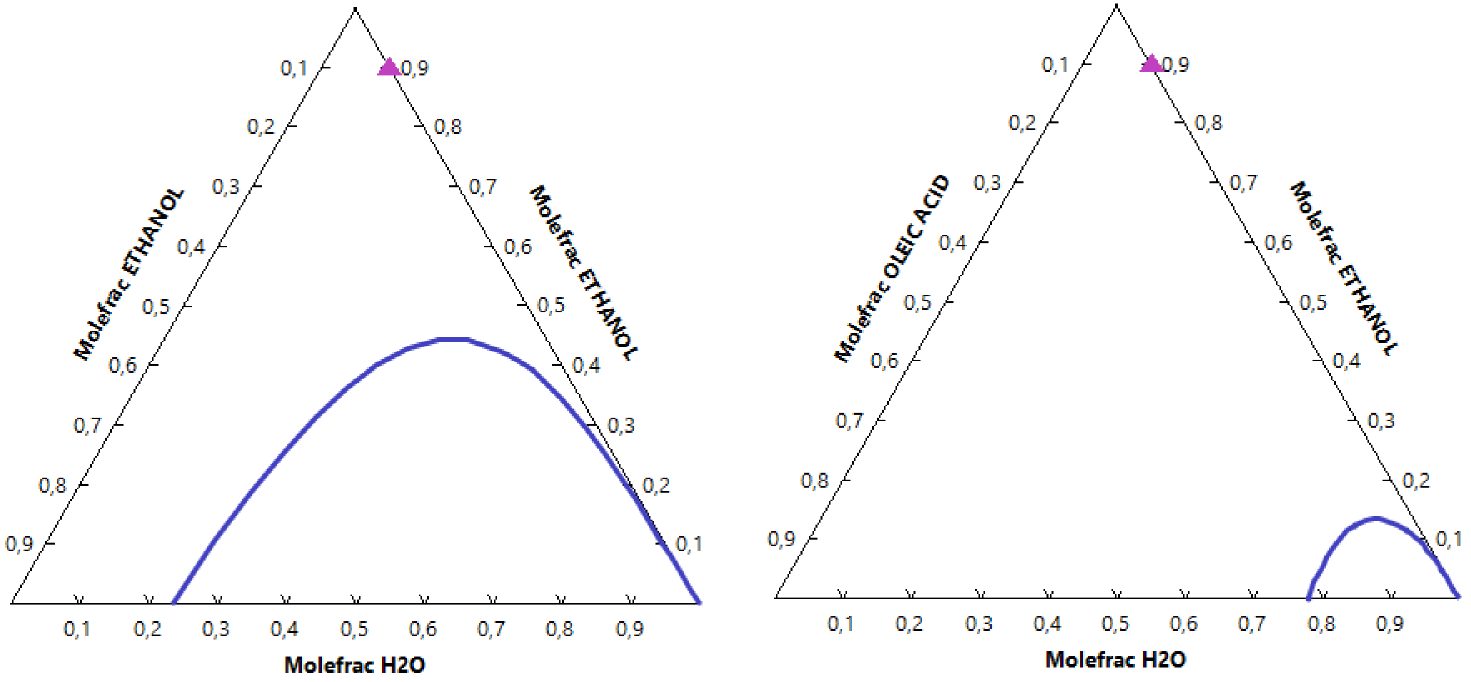
The entire procedure of how to determine $\mathrm{K_{DE}}$ and α was described by Martínez *et al*. (2013). Figure 3.4 represents the flowsheet used to determine the $\mathrm{K_{DE}}$ and α of each solvent under investigation.

Figure 3.4 – Flowsheet of single stage extraction of ethanol from fermented media (BROTH) used to calculate K_{DE} and α of each solvent investigated in this study. Block Decanter is represented by Block B1 and it was run at 1 bar and 298K.



Regarding to thermodynamic property method, the phase composition that better described the liquid-liquid extraction for K_{DE} analysis was UNIQUAC (Universal Quase Chemical) model using APV86 LLE-ASPEN parameters from the library of Aspen databank. The Figures from 3.5 to 3.6 present the liquid-liquid phase equilibria.

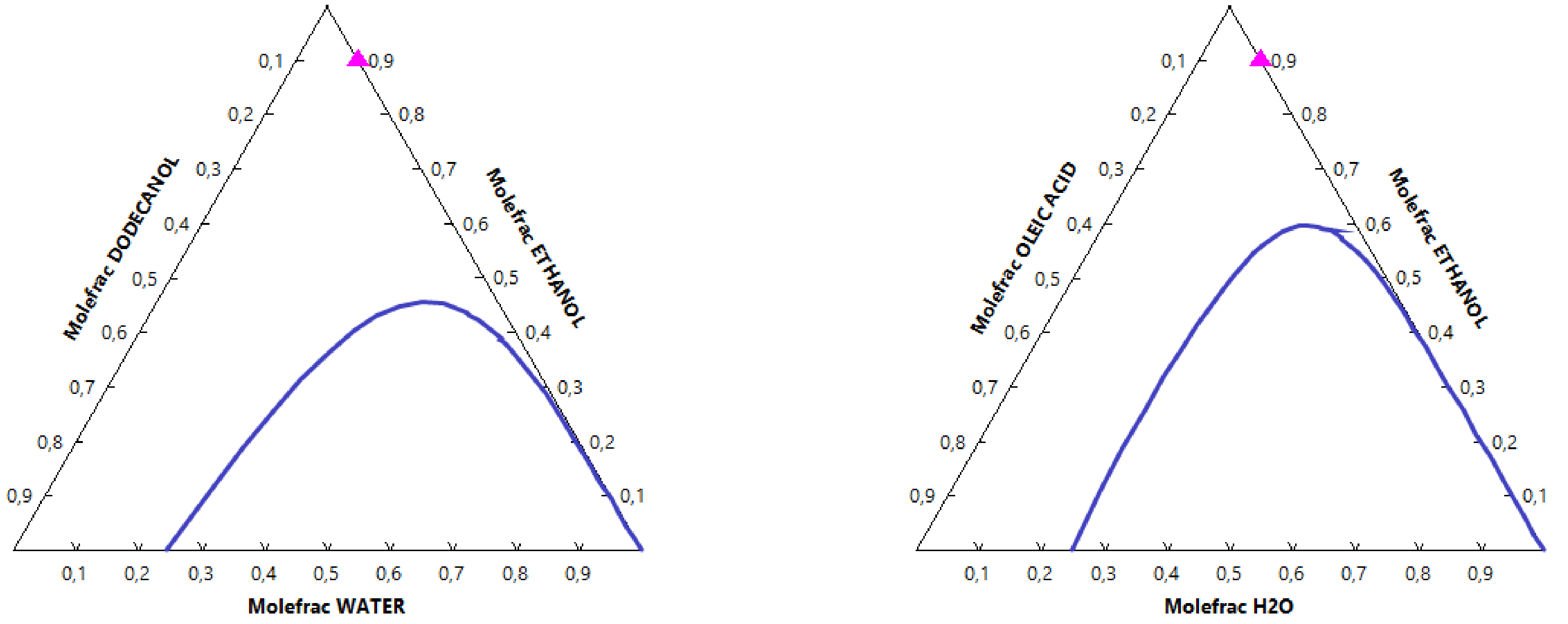
Figure 3.5 - Liquid-liquid phase equilibrium for the ternary system formed by ethanol+water+dodecanol (3.5a) and ethanol+water+oleic acid (3.5b). KDE study was performed in a block Decanter(single stage extractor column) and it was run at 1 bar and 298K. Legend: —— Phase envelope (Pressure = 1,01325 bar); ▲ Azeotrope point (Pressure = 1,01325 bar).



3.5.a) NRTL model – dodecanol

3.5.b) NRTL model – oleic acid

Figure 3.6 - Liquid-liquid phase equilibrium for the ternary system formed by ethanol+water+dodecanol (3.6a) and ethanol+water+oleic acid (3.6b). KDE study was performed in a block Decanter(single stage extractor column) and it was run at 1 bar and 298K. . Legend: —— Phase envelope (Pressure = 1,01325 bar); ▲ Azeotrope point (Pressure = 1,01325 bar).



3.6.a) UNIQUAC model - dodecanol

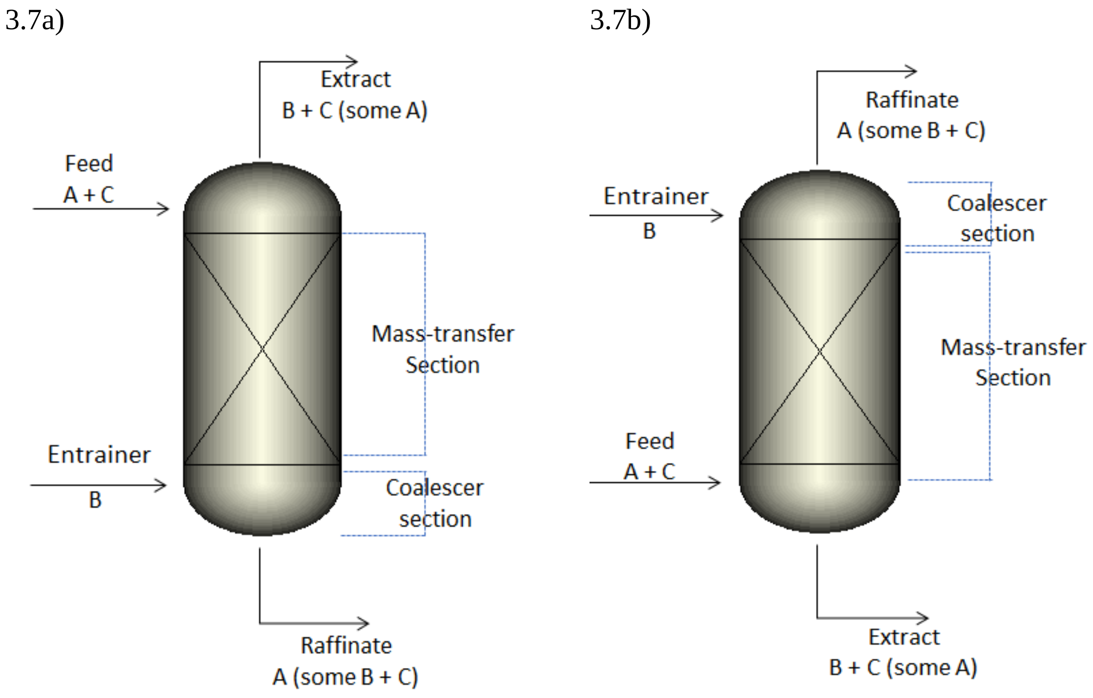
3.6.b) UNIQUAC model – oleic acid

The binary interaction parameters of UNIQUAC and NRTL models were estimated and all the missing parameters are presented in Table A4 to A7, see Appendix A.

3.2.4 Liquid-Liquid Extraction: Process design

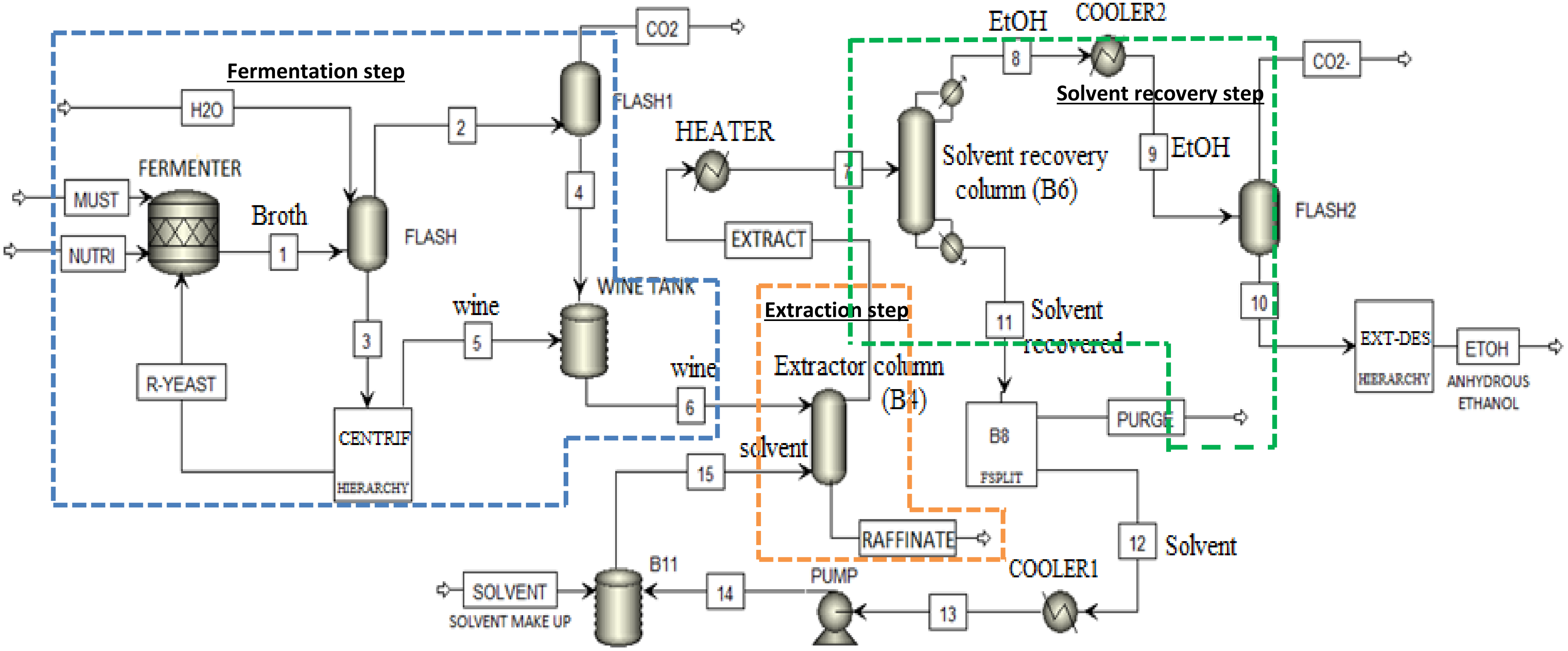
The liquid-liquid extraction unit of ethanol from the aqueous fermented wine was simulated in a counter-current multistage extractor column. All simulations were performed through process simulator Aspen Plus® V.8.2, and the extractor column was modelled by Extract block presented in Aspen Plus® library. The extraction process was conducted continuously with counter-current mixing. The solvent extraction system can be simulated in one of two forms as illustrated in Figure 3.7 (JOERG; SHIVELER, 2015).

Figure 3.7 - Schematic diagram of countercurrent extraction column using two different configuration of solvent feeding stream: 3.7a) in case of the entrainer is lighter than the carrier liquid (usually, water), so the solvent is fed at the bottom of the column, as a result, the solute is lifted toward the top of column. 3.7b) in case of the entrainer is heavier than carrier, so the entrainer agent is fed to the top extractor column, and the solute is removed downward along with the solvent at the bottom of the column.



In the present study, all simulation of LLE used the schematic diagram represented by Figure 3.7a because all the solvents studied are lighter than the carrier liquid (water), so the solvent is fed at the bottom of the column. The simulation of liquid-liquid extraction to remove ethanol from the fermented wine is illustrated in Figure 3.8.

Figure 3.8 Schematic diagram of the counter current multistage liquid-liquid extraction process simulation to remove ethanol from the diluted fermented broth. Fermentation vessel was simulated by block FERMENTER and liquid-liquid extraction by block Extractor Column. Both equipment was operated at the same conditions (303k and 1 bar). Centrifugation system is represented by HIERARCHY BLOCK (CENTRIF). The solvent recovery for LLE stage occurs at distillation column represented by block B6. The HIERARCHY BLOCK (EXT-DES) represent the extractive distillation process. Main streams: Must (molasses), (1) fermented wine, (6) centrifuged wine (~9% wt. ethanol), The threated yeast is represented by stream R-YEAST, (15) entrainer, Extract (organic rich-phase), Raffinate (aqueous rich-phase), (12) Solvent recovered for LLE.



As shown in Figure 3.8, the beer solution (stream WINE) was fed into an extractor where it contacts a solvent used as entrainer. The NRTL (non-random two liquid phase) thermodynamic model was selected for the prediction of liquid-liquid equilibrium of these simulations, but also the vapor-liquid equilibrium in the downstream process (NHIEN *et al.*, 2016).

The estimation of equilibrium conditions between two liquid phases formed by dissimilar polar species is one of the most difficult thermodynamic problems There are many correlations for activity coefficients available in the literature, however for dissimilar polar species, one of the most accurate semiempirical correlation is known to be the non-random two-liquid (NRTL) equation of Renon and Prausnitz (ZHANG; HILL, 1991).

In the NRTL model, the derivation considers the binary interactions between molecules *i* and *j* based on the local mole fraction concept. Zhang and Hill (1991) investigated the phase behaviour of alcohols, water and fatty acids focused on the influence of alcohol chain length on the liquid-liquid equilibrium of these system. These authors used the NRTL model to the system oleic acid-ethanol-water with the purpose of concentrate the ethanol produced by molasse fermentation. Ponce *et al*. (2014) also studied the solvent-liquid extraction to remove ethanol from diluted fermented wine, and the authors mentioned that the NRTL thermodynamic model was adequate for predict liquid-liquid equilibrium for multicomponent and diluted aqueous.

At the present study, the NRTL model was applied to for the liquid-liquid equilibrium study. For all the six binary system studied (see Table 3.2), the NRTL interaction parameters for the binary pair oleic acid (*i*) and water (*j*) was not present in the database of Aspen Plus®. Thus, the binary interaction parameters for oleic acid-water system was extracted from Zhang and Hill (1991) study.

Table 3.2 shows NRTL interaction parameters for each binary pair studied for the liquid-liquid extraction process. The interaction parameters of binary pair water (*i*) and ethanol (*j*) as well as ethanol (*i*) and oleic acid (*j*) were used from Aspen Plus database, represented by the source APV82VLE-IG and APV82VLE-LIT, respectively.

Table 3.2 – NRTL parameters from liquid-liquid equilibrium for water-oleic acid-ethanol system extracted from literature (ZHANG AND HILL, 1991).

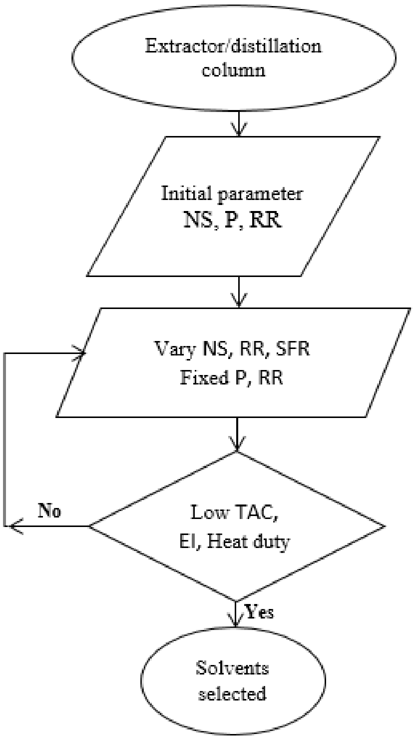
Component i	Oleic acid	Water	Ethanol
Component j	Water	Ethanol	Oleic acid
Source	USER	APV82VLE-IG	APV82VLE-LIT
AIJ	0	3.4578	0
AJI	0	-0.8009	0
BIJ	776	-586.081	490.981
BJI	2321.25	246.18	-172.878
CIJ	0.2	0.3	0.2
CJI	0	0	0
TLOWER	0	24.99	45
TUPPER	1000	100	45

For the extractor column, a rigorous simulation was performed to find out the optimal operational parameter in terms of the recovery rate of ethanol from diluted wine solution. So, the ethanol recovery rate was calculated according to Equation 3.4.

$$y = \frac{E_1 . y_{1,EtOH}}{R_0 . x_{n,EtOH}} \tag{3.4}$$

where E_1 represent the total flow rate of the extract stream, $y_{1,EtOH}$ is mass fraction of ethanol in extract stream; R_o represent the total flow rate of raffinate stream, $x_{n,EtOH}$ is mass fraction of ethanol in raffinate stream. Raffinate stream is composed basically of water with small amount of organic compounds and contaminants from fermentation process. The schematic procedure to solvent selection is presented in Figure 3.9.

Figure 3.9 - Schematic procedure to use organic solvent as entrainer to remove ethanol from the diluted fermented broth and downstream process for the entrainer regeneration: NS-number of stages; P-purity; RR-reflux ratio; SFR-solvent flow rate; TAC-total annual cost; EI-environmental impact



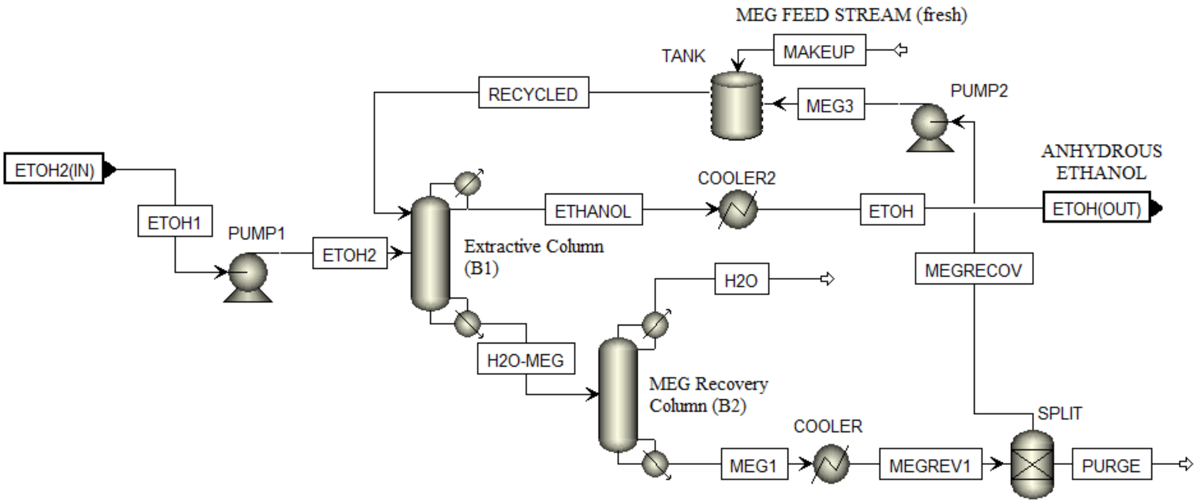
For the extractor column simulation, an ethanol mass fraction of 0.02% was assumed in raffinate stream to determine the solvent feed flow rate into the column. This value (0.02% by weight) only took into account the bottom stream of the extractor column. This assumption was necessary to accomplish a comparison to conventional distillation scheme taking into account techno-economic and environmental aspects (SILVA *et al.*, 2017).

Figure 3.9 shows how the simulation procedure was carried out for the liquid-liquid extraction system. Analysing the proposed methodology in Figure 3.9, the appropriate solvent flow rate as well as the extractor column operational parameter were obtained.

3.2.5 Simulation of conventional extractive distillation

The flowsheet of extractive distillation is shown in Figure 3.10. In the extractive column (block B1), ethanol is purified to 99.5% wt. (stream EtOH). Mono ethylene glycol (MEG) was used as entrainer agent in the extractive column (block B1). In recovery column (block MEG Recovery Column B2), MEG is purified to 99% wt. and cooled (stream MEGREV1) and recycled back (stream MEGRECOV) to extractive distillation top column.

Figure 3.10 Flowsheet of extractive distillation using MEG as entrainer. Blocks: (B1) extractive column, (B2) solvent recovery column, (B5) MEG tank. Main streams: (2) ethanol; (D) anhydrous ethanol at 333K;(4) anhydrous ethanol at 313K, (BB2) MEG removed from aqueous phase, (6) MEG recovered and sent back to extractive column.



3.2.6 Environmental analysis

An environmental assessment methodology was applied to compare the environmental impacts of the bioethanol production processes in each of the case studies described in Section 3.2.4. The environmental analysis procedure has been described in full previously (DIAS *et al*., 2012).

This methodology not only takes into consideration the energy consumption of the process, but also environmental aspects. A very large number of indicators and methodologies, including sustainable process indices, environmental impacts, and lifecycle assessments (LCAs) have been extensively employed in the development of sustainable processes (MONTOYA *et al.*, 2005; DIAS *et al.*, 2012; DIAS *et al.*, 2013; MORAES *et al.*, 2015).

One of the available environmental indicators is the WAste Reduction (WAR) Algorithm developed by the Environmental Protection Agency of the United States (USEPA). The lifecycle impact assessment method was applied in this evaluation. The WAR algorithm is based on the determination of potential environmental impacts (PEIs), by quantification of the impact that the disposal of waste material would have on the environment (CABEZAS *et al.*, 1999; QUINTERO *et al.*, 2008).

The environmental impacts evaluated by the WAR algorithm can be classified into two groups, toxicological potential effects (TPEs) and atmospheric physical potential effects (APPEs). The TPEs include human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation or dermal exposure (HTPE), terrestrial toxicity potential (TTP), and aquatic toxicity potential (ATP). The APPEs include global warming potential (GWP), ozone depletion potential (ODP), photochemical oxidation potential (PCOP), and acidification potential (AP) (QUINTERO *et al.*, 2008).

3.2.7 Exergy and renewability analysis of the distillation system

Exergy of a substance or stream can be defined as the maximum obtainable work the substance can produce when it is brought reversibly to a state of thermodynamic equilibrium with the environment which is assumed to be at 298 k (T_o) and 1 bar of pressure (p_o) in this study. Exergy analysis of a process is based on the mass and energy balance with the second law of thermodynamics (KHALILI-GARAKANI *et al.*, 2016; WANG *et al.*, 2016).

In this present study, exergy calculations and analysis were conducted in Aspen Plus and Excel. It is extremely important to observer that, the exergetic study must be preceded through mass and energy balance of the system carried out in Aspen Plus simulator (DOGBE *et al*., 2018). Aspen Plus mass and energy streams results were exported to Excel using Aspen simulation workbook in Aspen Plus V.8.2. Further, exergy analyses were finalized in the Excel® spread sheet. Exergy calculations and analysis were performed by based on the following assumptions (WANG *et al*., 2018):

i. each of the units was assessed as a steady state flow process;
ii. variations in potential and kinetic exergy were neglected;
iii. temperature room and atmospheric pressure were assumed constants.

3.2.7.1 Exergy calculations

Exergy is the maximum work obtained in a reversible process, when a stream a of mater or energy at a specific condition is brought to equilibrium with the environment which it is interacts. The total exergy transfer that across a control volume (flow exergy) is performed by material and energy (work and heat) streams as shown in Equations 3.5 (DOGBE *et al*., 2018):

$$\dot{Ex}_{\text{system}} = \dot{Ex}_{\text{material}} + \dot{Ex}_{\text{heat}} + \dot{Ex}_{\text{work}} \tag{3.5}$$

Where the exergy of material was calculated according to equation 3.6:

$$\dot{Ex}_{\text{material}} = \dot{Ex}_{\text{physical}} + \dot{Ex}_{\text{chemical}} \tag{3.6}$$

In this study, chemical exergy ($\dot{E}x_{\text{chemical}}$)was neglected because there is no chemical changes or reactions in the distillation process. The physical exergies of streams ($\dot{E}x_{\text{physical}}$), were calculated by equation (3.7) obtained trought Aspen Plus prop-set, EXERGYFL (exergy flow rate).

$$\dot{E}x_{\text{physical}} = \dot{m}\,[(h - h_o) - T_o(s - s_o)] \tag{3.7}$$

Where $\dot{m}$ represent the mass flow rate (kg/s), h is the specific enthalpy (J/kg), h_o represent the specific enthalpy of a reference state, T_o is the environment temperature (K), s is the specific entropy (J/kg. K), and s_o is associated to specific entropy of the reference state (J/kg. K). The exergy transfer by work ($\dot{E}x_{\text{work}}$), is calculated by equation (3.8):

$$\dot{E}x_{\text{work}} = \dot{W} \tag{3.8}$$

Where $\dot{W}$ either represent electrical or mechanical work. The heat exergy is calculated as shown in equation (3.9):

$$\dot{E}x_{\text{heat}} = \dot{Q}\left(1 - \frac{T_o}{T}\right) \tag{3.9}$$

Where $\dot{Q}$ is associated to heat flow rate (kW), T is the Temperature (K) at which the heat transfer occurs and T_o is the environment temperature (K).

Normally, exergy analysis is applied to assess the thermodynamic performance parameters of a process at which include process irreversibility (DOGBE *et al.*, 2018). Process irreversibility can be named as the exergy destroyed which is the difference in exergy input and output streams as demonstrated in Equation (3.10). Exergy destroyed shows how much exergy is destroyed or lost through a specific unit (DOGBE *et al*., 2018; MABROUK *et al*., 2016).

$$\dot{\mathrm{I}}\mathrm{rr} = \dot{\mathrm{E}}\mathrm{x}_{\mathrm{destroyed}} = \sum \dot{\mathrm{E}}\mathrm{x}_{\mathrm{in}} - \sum \dot{\mathrm{E}}\mathrm{x}_{\mathrm{out}} \tag{3.10}$$

This methodology allows to identify the local, cause, and true magnitude of waste and loss to be determined. Such information is useful for the design of new energy efficient systems and for increasing the efficiency of existing systems. There have been many recent studies that have used the concept of exergy to evaluate the sustainability of various ethanol production routes (MOSQUEIRA-SALAZAR, 2012; MOSQUEIRA-SALAZAR *et al*., 2013; ORTIZ; OLIVEIRA, 2014; PINA *et al*., 2015; DADAK *et al*., 2016; KHALILI-GARAKANI *et al*., 2016).

Ometto and Roma (2010) applied the chemical exergy concept to evaluate the atmospheric impact of the lifecycle emissions from bioethanol/electricity production at a Brazilian sugarcane mill.

However, there have been few studies focusing on the renewability analysis of ethanol production. Considering this aspect, Pellegrini and Oliveira (2011) and Oliveira (2013) presented environmental analyses employing a so-called renewability exergy index. The renewability exergy index (λ) can be calculated according to Equation 3.11 (OLIVEIRA, 2013):

$$\lambda = \frac{\Sigma \dot{Ex}_{product}}{\dot{Ex}_{fossil} + \dot{Ex}_{destroyed} + \dot{Ex}_{deactivation} + \dot{Ex}_{disposal} + \Sigma \dot{Ex}_{emissions}} \tag{3.11}$$

where $\dot{\mathrm{E}}\mathrm{x}_{(\mathrm{product})}$ is the exergy associated with the useful product, $\dot{\mathrm{E}}\mathrm{x}_{(\mathrm{fossil})}$ is the non-renewable exergy consumed in the production processes chain, and $\dot{\mathrm{E}}\mathrm{x}_{(\mathrm{destroyed})}$ is the exergy destroyed inside the system, punishing the process for its thermodynamic inefficiencies. $\dot{E}x_{(deactivation)}$ is the deactivation exergy for treating wastes, which accounts for exergy consumed in passing the streams considered as wastes out of the system, without any damage to the environment. Finally, $\dot{E}x_{(emissions)}$ represents the exergy of wastes that are not treated or deactivated (OLIVEIRA, 2013).

In the above equation, the renewability exergy index indicates that:

✓ Processes with $0 \leq \lambda < 1$ are environmentally unfavourable;

✓ For internal and external reversible processes with non-renewable inputs, $\lambda = 1$;

✓ If $\lambda > 1$, the process is considered environmentally friendly, with a higher value of λ implying that the process is more environmentally favourable;

✓ When $\lambda \rightarrow \infty$, the process is reversible, with renewable inputs and no waste production.

In this study, the mass and energy balances were extracted from the Aspen Plus® software, which was the basis for the exergy calculations. Simulation was conducted at steady state operation, and the exergy balances for a specific control volume (MABROUK *et al.*, 2016).

3.2.8 Economic analysis

Economic evaluation methodology differs according to investor purposes, so there are a variety of expressions which are used to estimate the economic investment. Some of these expressions are extremely elegant and adopt the concept of the time value of money. One interesting example are the net value present (NVP) and discounter cash flow (DCF). These procedures are preferred by business majors, accounts and economists because they provide a reliable data on measures profitability, over an extended time period (LUYBEN, 2013).

However, a lot of assumptions must be made in adopting these strategies and the accuracy of these methods is usually quite limited. The estimation of future sales, prices of raw material and product, and construction schedule is normally a guessing game made by marketing and business managed. Thus, the use of simple economic expression or function usually serves the purpose of optimization or just carry out economic performance (LUYBEN, 2013). In this study the Total Annual Cost (TAC) will be used to accomplish a simple economic analysis. This methodology incorporates both energy cost and the annual cost of capital, which is obtained by dividing the cost of capital through adequate payback period. Payback period compares the incomes with cost to determine the period of time to take back all the investment applied for. This economic indicator is usually used to study investment opportunities that offers incremental benefits.

In order to compare the costs of the systems. The same operational conditions, including inputs, outputs, temperatures, and pressures were assumed for all the case studies. According to Douglas (1989), Luyben (2013) and Li *et al*. (2016), the TAC is defined as the total operating cost added to the annualized capital investment cost, where the latter corresponds to the ratio of the capital cost and the payback period. The economic basis of the calculation was fully described by Luyben (2013) and is presented in Table A.3 (see Appendix A). The TAC is calculated by Equation 3.12.

$$TAC\left({}^{US\$}/_{year}\right) = \left(\frac{capital\ cost}{payback\ period}\right) + operating\ cost \qquad (3.12)$$

3.3 Results and Discussion

3.3.1 Fermentation step

The continuous ethanol fermentation process was simulated (see Figure 3.1). Table 3.3 shows the results in terms of ethanol produced and minor components present in the diluted fermented broth.

Table 3.3 – Main results obtained in the fermenter vessel running at 1.0 bar and 303K.

Stream / Component	Must	Nutrient	Wine	*Yeast_R	Unit
Water	263.5		301.9	42.1	ton/h
Carbon dioxide			32.96		ton/h
Sucrose	67.3				ton/h
Isoamilic alcohol			737ppm		ton/h
Hydrogen			6.4e-3		ton/h
Ethanol			34.2		ton/h
Glycerol			1.7		ton/h
Sulphuric Acid			2.6	2.5	ton/h
Succinic Acid			0.127		ton/h
**Ammonia		0.081	4.93e-3		ton/h
Dextrose	3.0		3.64		ton/h
Acetic Acid			0.49		ton/h
Yeast (zymo)			1.3	0.35	ton/h

*Yeast_R: yeast threated and recycled to fermenter vessel; **Ammonium was used as nutrient for yeast growth

As can be seen in Table 3.3, the ethanol mass flow in the alcoholic wine stream is 34.2 ton/h, which represents 8% of ethanol by weight. After fermentation step, the diluted wine goes through solvent extraction process to the pre-concentration of fermented wine before distillation process.

3.3.2 Entrainer screening

Solvent screening analysis was based on ethanol extraction yield, inlet solvent consumption in the extractor column, and alcohol composition in raffinate stream. It was assumed the use of raffinate as fertirrigation of sugarcane crops in this study.

3.3.2.1 Solvent performance analysis

Distribution coefficient (K_{DE}) and selectivity of ethanol (α) are important parameters for solvent selection due to K_{DE} is used to estimate the components distribution in the equilibrium phase and (α) represents the extraction ability of the solvent. Table 3.4 shows the ethanol distribution coefficient and selectivity between the two phases: organic-rich phase (Extract) and aqueous-rich phase (Raffinate) for all solvents investigated in this study (GAO *et al*., 2015). The expression to calculate K_{DE} and α were presented in section 3.2.3.

Table 3.4 – Ethanol distribution coefficient and selectivity for each selected solvent at the composition of 10 %wt. of ethanol, simulated in this study compared with the value obtained experimentally.

Solvent	^{A}Model	$^{\rho}K_{DE}$	$^{EXP}K_{DE}$	**RE (%)
*isoamilic alc	Uniquac	1.07	1.04	2.9
*isoamilic alc	NRTL	0.89		14
octanol	Uniquac	0.66	0.61	8.2
octanol	NRTL	0.73		19.7
dodecanol	Uniquac	0.42	-	-
dodecanol	NRTL	0.41		
oleic acid	Uniquac	0.22	0.24	8.3
oleic acid	NRTL	0.20		16.7

^{A} Thermodynamic property model;
$^{\rho}K_{DE}$ (distribution coefficient) – K_{DE} (mass/volume);
$^{EXP}K_{DE}$ (distribution coefficient) – K_{DE} (mass/volume) obtained experimentally (Lemos *et al.*, 2015);
^{d} selectivity of ethanol simulated in this paper;
*isoamilic alc - Isoamilic alcohol
**Relative error - $RE(\%) = \frac{|xi| - |x|}{xi}.100$

As can be observed in Table 3.4 for the NRTL thermodynamic model, the K_{DE} simulated in this study varied from 0.2 to 0.89. These values are different from experimental data of K_{DE} obtained by Lemos *et al*. (2015), presenting an average relative error between K_{DE} simulated and experimental of 16.8%. The simulated K_{DE} using UNIQUAC model varied from 0.22 to 1.07, presenting a lower relative error (an average value of 6.5%). These finding can be attributed to experimental conditions of LLE, the purity of species as well as the not appropriate binary interaction parameters selected to conduct the analysis. Furthermore, the K_{DE} analysis was performed in a single stage extractor column represented by bock DECANTER (see Figure 3.4) and LLE process will be simulated in a multistage extractor column.

From both simulated and experimental data obtained in this study (see Table 3.4) it can be observed that the length of the alcohol chain has a direct effect on its solubility in aqueous and organic phases. This finding is in line with Santos *et al*. (2015), the authors observed in their studies that as the chain length of alcohols is improved, the hydrophobicity of the alcohols is also increased. Boonmen *et al.* (2015) achieved the same observation that the extraction of alcohol is affected by the size of carbons length chains.

Comparing the Isoamilic alcohol (C-5) and n-octanol (C-8), they resulted in a higher K_{DE} (1.07) and (0.66), respectively, than dodecanol (C-12) (K_{DE}=0.42) and oleic acid (C-18) (K_{DE}=0.22). So, according to Offeman *et al*. (2005) the K_{DE} for ethanol and water is expected to reduce as the mass concentration hydroxyl group (-OH) in the solvent of fall down due to the growth of alkyl chain length.

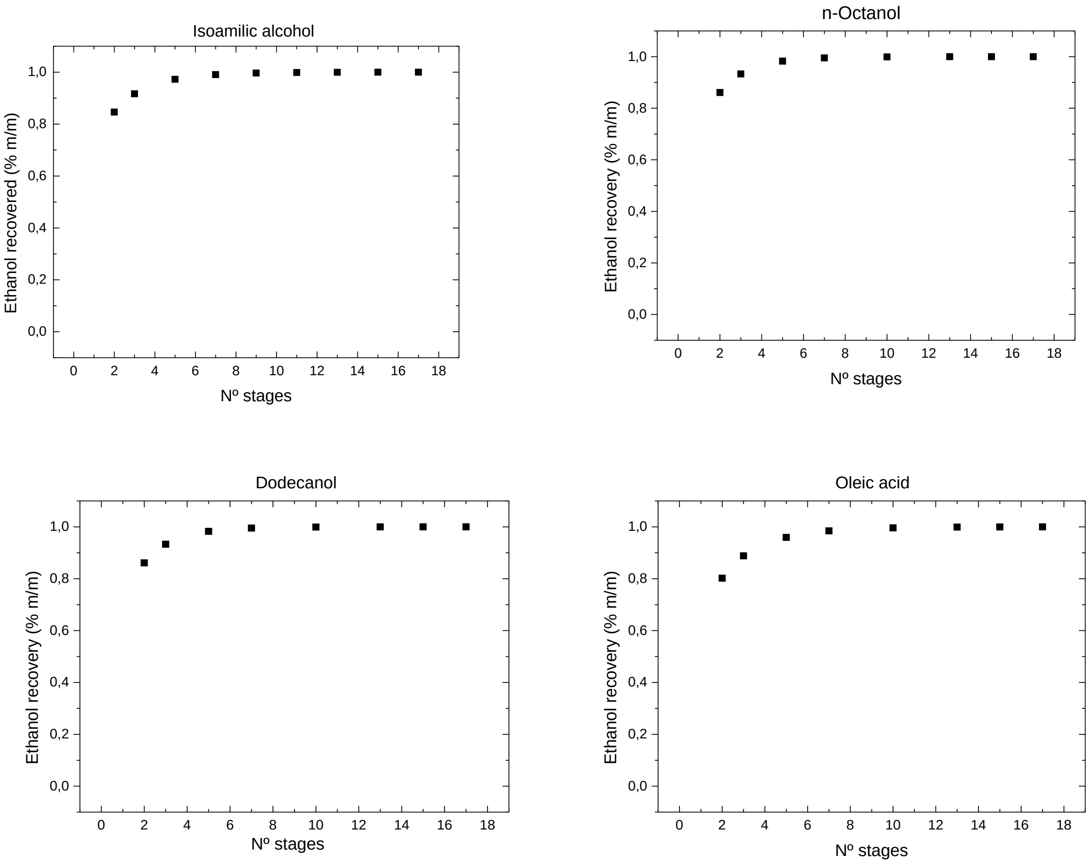
Results from this simulation were validated with those obtained experimentally as can be seen in Table 3.4, the exception was the dodecanol which was not carried out an experiment. For the solvent IA, n-octanol, and oleic acid the relative error (RE%) for K_{DE} value was 2.9%, 8.2% and 8.3, respectively. Based on the results achieved in the validation test, the UNIQUAC thermodynamic model achieved lower relative error than to NRTL model, as a result UNIQUAC model was selected to describe the liquid-liquid behaviour in the Decanter block for the K_{DE} analysis.

3.3.2.2 Liquid-Liquid extractor column: process design

The current study has investigated how the extractor column number of stages affects the efficiency extraction of ethanol at organic phase. To perform this test, the sensitivity analysis tool presented in Aspen Plus database was applied. The sensitivity analysis was carried for all the four solvents with the extractor column operating in a continuous and counter-current mode. The ethanol recovery rate ($\mathrm{EtOH_{recovery}}$) leaving the extractor column at top column can be calculated according to Equation 3.13 (FERREIRA *et al.*, 2013).

$$\mathrm{EtOH_{(recovery)}}\ (\%) = 100 \text{ x } \left(\frac{\text{ethanol mass flow in the top stream extractor column}}{\text{ethanol massl flow in the extractor feed stream}}\right) \qquad (3.13)$$

Figure 3.11 - Analysis of ethanol recovery efficiency versus number of stages from extractor column for each solvent investigated in this study.

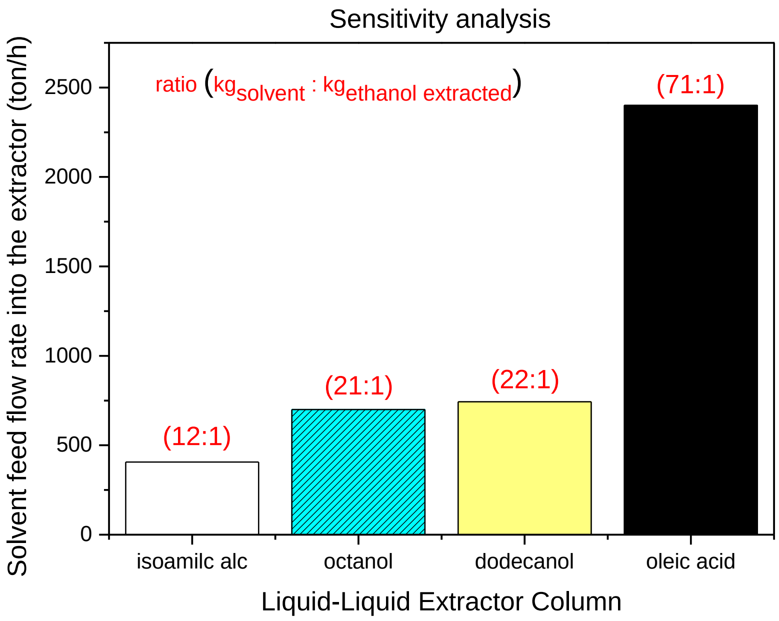


The results obtained from the sensitivity analysis of ethanol extraction efficiency versus number of stages are shown in Figure 3.9. According to Figure 3.13 all solvents applied to LLE process achieved the same ethanol recovery rate at 10th stage demonstrating an efficiency of 99.99% of extraction. After this analysis all columns will be designed with 10 stages.

3.3.2.3 Solvent feed stream analysis

After the number of stages of extractor column was selected, it was evaluated the optimal solvent flowrate through analysis of working mass flow between the solvent feed stream and ethanol at organic rich-phase (kg $_{solvent}$:kg $_{ethanol}$). To assess the effect of extractant feeding flow, the sensitivity analysis was used for all solvents applied in this study. Figure 3.12 illustrate the sensitivity analysis result.

Figure 3.12 - Result of the sensitivity analysis for solvent:ethanol ratio effect over the overall recovery rate of ethanol in the liquid-liquid extractor column.

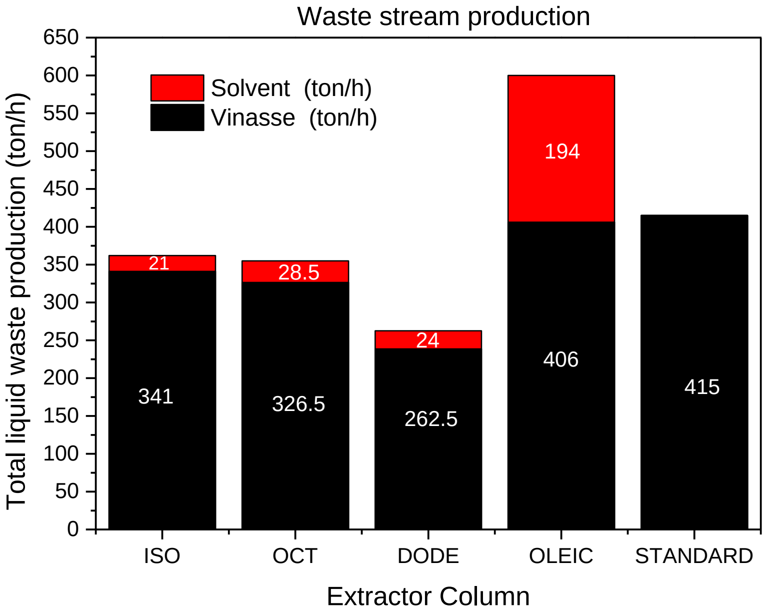


What is interesting in this data is that ethanol in the extract increase with rising (kg $_{solvent}$:kg $_{ethanol}$) ratio for each solvent studied. In the proposed study, the recovery of ethanol and organic solvent follows a trend as vinasse composition stream as in standard distillery. So, the amount of ethanol and solvent present in raffinate must be less than 0.02% (m/m), minimizing its impact to environment when disposed in the field (SILVA *et al.*, 2017).

In this sense, from Isoamilic alcohol sensitivity analysis, we can see that the maximum removal of ethanol is reached at ($kg_{solvent}$:$kg_{ethanol}$) ratio of (12:1) with solvent feeding flow of 4.06×10^5 kg/h. For n-octanol the maximum removal of ethanol is reached at ($kg_{solvent}$:$kg_{ethanol}$) ratio of (21:1) with solvent feeding flow of 7.0×10^5 kg/h. The performance analysis for dodecanol is quite similar to n-octanol where maximum removal of ethanol is reached at ($kg_{solvent}$:$kg_{ethanol}$) ratio of (22:1) with solvent feeding flow of 7.43×10^5 kg/h.

The most surprising aspect of the data is the oleic acid performance where maximum removal of ethanol is reached at ($kg_{solvent}$:$kg_{ethanol}$) ratio of (71:1) with solvent feeding flow of 2.40×10^6 kg/h. From these data, we can see that IA resulted in the lowest value of solvent flowrate fed to extractor column and oleic acid is the greatest value.

Figure 3.13 - Outflow liquid waste generated for each evaluated process and the conventional distillation process: ISO-isoamilic alcohol; OCT-octanol; DODE-dodecanol; OLEIC-oleic acid; STANDARD- Standard ethanol production process.



These findings suggest that LLE process using oleic acid produce a huge amount of waste stream. Figure 3.13 compares the results obtained from the analysis of waste stream production of each case to the conventional distillation system. The output liquid waste is comprised by Raffinate stream and purge stream after solvent recovery column.

It can be seen from the Figure 3.13 that extraction process with dodecanol produced 262.504 kg/h of liquid waste, this value represents a reduction of 57% and 37.5% when compared to oleic acid process (406 ton/h) and standard distillery (415 ton/h), respectively. However, the vinasse generated in the dodecanol process is more toxic when compared to vinasse generated in the standard process.

3.3.2.4 Downstream process: solvent regeneration after LLE

The following step is the solvent recovering from extract stream. Solvent regeneration unit is strongly important for verifying the economic feasibility of LLE process, and also liquid waste emissions (AGHAZADEH; ENGELBERTH, 2016). The downstream unit was simulated by an ordinary distillation column (see Figure 3.1).

In this unit, we want to separate all the solvent in bottom stage and send back to extractor column. One of the issues that emerges from this unit is related to energy consumption. The energy requirements of the reboiler are industrially expressed through the specific steam consumption (SSC), which is the mass of steam consumed in the heat exchanger per kg of final product produced. The SSC was calculated by Equation 3.14 (FERREIRA *et al.*, 2013). Table 3.5 to 3.8 shows the results obtained from the energy consumption analysis of recovery unit.

$$\mathrm{SSC}\left(\frac{\mathrm{kg_{steam}}}{\mathrm{kg_{product}}}\right) = \left[\frac{\dot{\mathrm{Q}}}{\mathrm{H}^{(\mathrm{vap.})}\ \mathrm{x}\ \ \dot{\mathrm{m}}}\right] \tag{3.14}$$

where SSC represent the specific steam consumption (kg$_{steam}$/kg$_{product}$) of the process, $\dot{Q}$ is the thermal energy required per hour (kcal/h), $H^{(vap.)}$ is the latent heat of vaporization (kcal/kg$_{vapor}$) and $\dot{m}$ is the product mass flow (kcal/h).

The product mass flow ($\dot{m}$) assume the values of each column under investigation (FERREIRA *et al.*, 2013). By analysing the results from the Table 3.5, it can be thus observed that the recovery unit for Isoamilic alcohol consumed 1210 GJ/h. One possible explanation for that result is related to the number of stage as well as a high reflux ratio, which make this process impracticable (FERREIRA *et al.*, 2013).

Table 3.5 – Energy consumption analysis of solvent recovery unit (Isoamilic alcohol) – column B6

Column Parameters	B6
Number of stages	15
Reflux rate	25.7
Distillate flowrate (ton/h)	38.9
**EtOH recovery (%m/m)	94.41
Solvent recovery (%)	99.97
Reboiler (GJ/h)	1209.9
*SSC (kg $_{steam}$/kg $_{product}$)	13.2

*SSC-specific steam consumption (kg $_{steam}$ / kg $_{product}$); **EtOH - ethanol

Table 3.6 – Energy consumption analysis of solvent recovery unit (n-octanol) – column B6

Column Parameters	B6
Number of stages	15
Reflux rate	0.31
Distillate flowrate (ton/h)	61.2
**EtOH recovery (%m/m)	97.72
Solvent recovery (%)	99.55
Reboiler (GJ/h)	52.3
*SSC (kg $_{steam}$/kg $_{product}$)	1.64

*SSC-specific steam consumption (kg $_{steam}$ / kg $_{product}$); **EtOH – ethanol

Table 3.7 – Energy consumption analysis of solvent recovery unit (dodecanol) – column B6

Column Parameters	B6
Number of stages	15
Reflux rate	0.36
Distillate flowrate (ton/h)	117.3
**EtOH recovery (%m/m)	94.32
Solvent recovery (%m/m)	99.98
Reboiler (GJ/h)	369.5
*SSC (kg $_{steam}$/kg $_{product}$)	1.34

*SSC-specific steam consumption (kg $_{steam}$ / kg $_{product}$); **EtOH - ethanol

Table 3.8 – Energy consumption analysis of solvent recovery unit (oleic acid) – column B6

Column Parameters	B6
Number of stages	15
Reflux rate	0.87
Distillate flowrate (kg/h)	37.3
**EtOH recovery (%m/m)	61.42
Solvent recovery (%)	99.999
Reboiler (GJ/h)	282.8
*SSC (kg $_{steam}$/kg $_{product}$)	14.7

*SSC-specific steam consumption (kg $_{steam}$ / kg $_{product}$); **EtOH - ethanol

In all cases investigated, the solvent recovery unit was run in the same operational condition (number of stage). Comparing the four results obtained in the Table 3.5 to 3.8, it can be seen that the recovering of dodecanol consumed less process steam (1.34 kg steam/kg product) when compared to other three solvents.

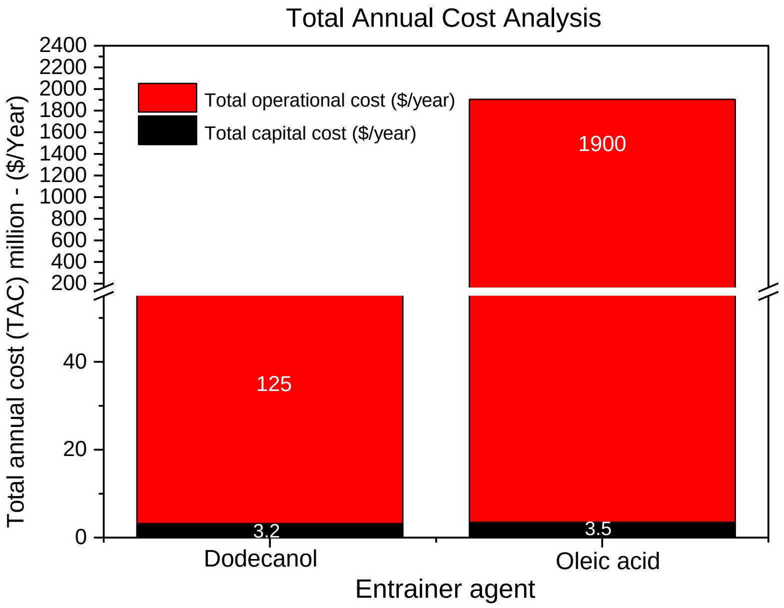
Downstream process such as distillation can have influence in the cost, as a result this must be taken into consideration when designing a process. In this sense, n-dodecanol and oleic acid were chosen to accomplish the economic evaluation of the designed process.

3.3.3 Economic evaluation

3.3.3.1 Liquid-Liquid extractor column

An economic analysis of the LLE system was carried out through calculating the total annual cost (TAC). Table A.8 (Appendix A) summarizes the results of the cost calculations performed in this work. Figure 3.14 presents the TAC results for the liquid-liquid extractor column performance for the two systems chosen after downstream analysis.

Figure 3.14 - Comparison of total annual costs (TAC) for the different extractor column operation investigated.



Extractor column operated with n-dodecanol showed the lowest TAC, with a value of 93.2% lower when compared to extraction system using oleic acid.

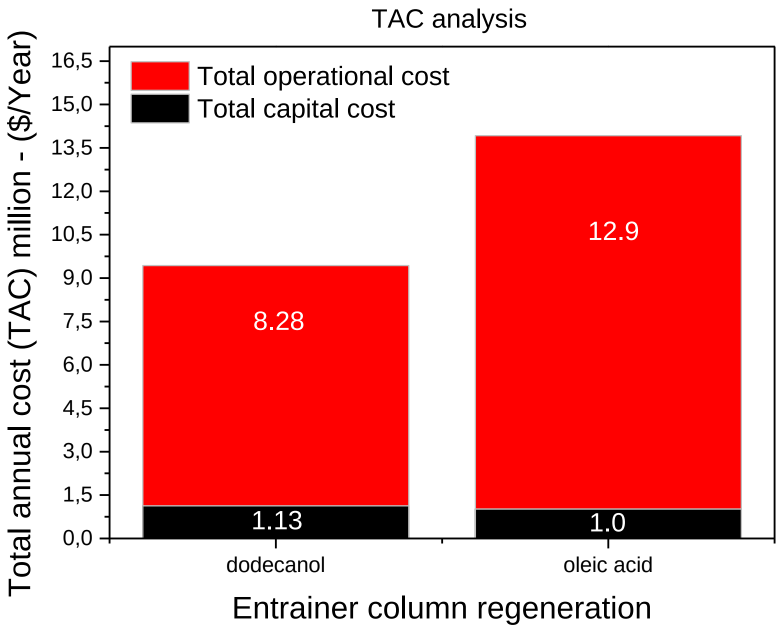
This finding may be explained by the fact that the operational cost of LLE with oleic acid showed an enormous makeup cost of US$ 1900 million/year, while for the n-dodecanol scheme was US$ 125 million/year. This result is in line with those presented in Figure 3.12, where the liquid waste stream produced was much higher for the oleic acid case.

This difference can be explained in part by the solvent stream entering in the extractor column is $7.43x10^5$ kg/h, which provides a (kg $_{solvent}$:kg $_{ethanol}$) ratio of 22:1, for dodecanol system, while the (kg $_{solvent}$:kg $_{ethanol}$) ratio for oleic acid system is 71:1. At this condition, the waste of entrainer is significantly lower in dodecanol case than in the oleic acid scheme as previously depicted in Figure 3.12.

3.3.3.2 Downstream process: solvent regeneration

As shown in Figure 3.15, the total annual cost of the solvent recovery unit was $ 9.41 million/year for dodecanol case, while the TAC for oleic acid case was $ 13.9 million/year. A possible explanation for this might be that the operational cost for dodecanol downstream process is 32.4% lower than oleic acid recovery unit. For both cases steam cost (SC) presented a significant effect on the operational costs. The steam cost in the solvent recovery stage in the oleic acid system was11437413 US$/year, while for the dodecanol system the value was 6523251 US$/year. One possible explanation for this finding is that for oleic acid case has great amount of entrainer added at the beginning of the process that must be recovery (see Figure 3.13). The detailed TAC analysis for the two-alternative designed can be found in Table A.8, in the Appendix A.

Figure 3.15 - TAC results for the downstream process in the regeneration of solvent extraction.

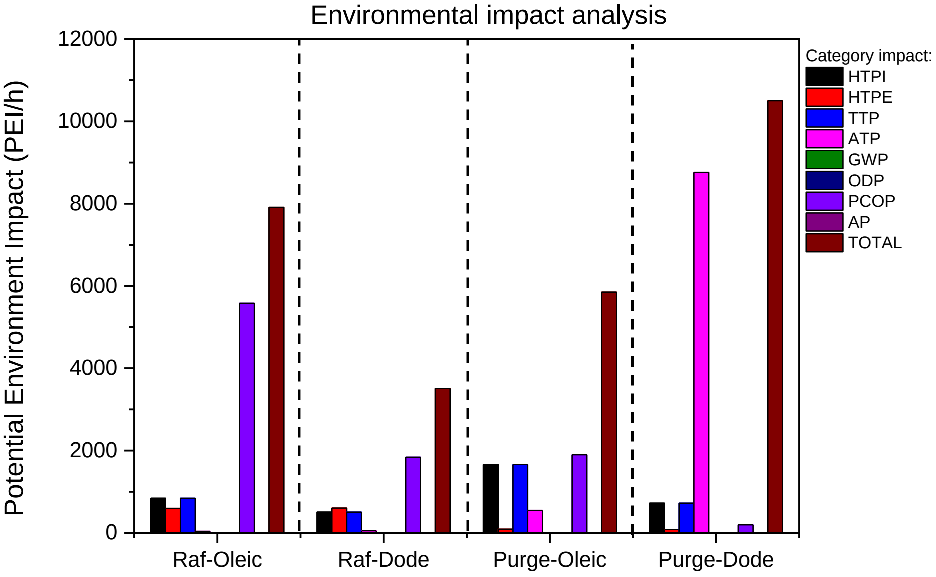


3.3.4 Environmental impact evaluation by WAR algorithm

The mass and energy balances of the product, input, and waste streams, obtained using the Aspen Plus simulator, enabled an environmental assessment to be performed (QUINTERO *et al.*, 2008; PEREIRA *et al.*, 2015). In this proposed study, the liquid waste production is formed by raffinate and purge streams as previously shown in Figure 3.12. As shown in Figure 3.16, n-dodecanol case reported significantly less liquid waste emission (286 ton/h) than oleic acid case (600 ton/h).

Interestingly, dodecanol case would have a higher environmental impact, then oleic acid system. The results obtained for the potential environmental impacts (PEIs) associated with the liquid waste is illustrated in Figure 3.16 for the two alternatives route under investigation. The most striking result noticed from the data in Figure 3.14 is that despite of the lower liquid waste emission for dodecanol system, its PEI value was little higher than oleic acid case. One possible explanation for this might be that the component dodecanol is more toxic component comparing to oleic acid, so this may cause a greater impact to environment (SILVA *et al.*, 2017). Observing the data in Figure 3.16, the aquatic toxicity potential (ATP) was the most parameter affected by dodecanol emissions.

Figure 3.16 - Environmental impact analysis through liquid waste emissions for dodecanol and oleic acid case studied. The impact is calculated like the PEI exiting the scheme per mass of product. In this work the main liquid waste stream is: raffinate and purge streams presents in LLE system. Category impact lengend: HTPI (human toxicity potential ingestion); HTPE (human toxicity potential by inhalation or dermal exposure; TTP (terrestrial toxicity potential); ATP (aquatic toxicity potential); GWP (global warming potential); ODP (ozone depletion potential); PCOP (photochemical oxidation potential); AP (acidification potential).



3.3.5 Renewability exergy index analysis for LLE process

The renewability exergy index (λ) performance of the LLE system was assessed. The results obtained from the exergy and renewability evaluation are presented in Table 3.9 (PELLEGRINI; OLIVEIRA, 2011). From the two cases studied, neither of them showed a value higher than 1, this means that all the processes should be considered environmentally unfavourable, from the second law standpoint (see Section 2.6).

What is interesting about the data in the Table 3.9 is the better environmental performance of liquid-liquid extraction system using dodecanol as entrainer, compared to traditional configuration. The renewability exergy index (λ) performance for the LLE with dodecanol, the standard distillation, and the LLE with oleic acid obtained were 0.18, 0.11, and 0.015, respectively. According to exergy and renewability analysis concepts, theses processes simulated are not considered environmentally friendly owing to process is considered environmentally friendly, with a higher value of λ implying that the process is more environmentally favourable (OLIVEIRA, 2013).

Table 3.9 – Exergy renewability performance index (λ) of each system under investigation.LLE= Liquid-Liqui Extraction process.

Configuration	Renewability performance indicator index	Ideal Renewability performance indicator
LLE with dodecanol	0.18	>1.00
LLE with oleic acid	0.015	
Standard distillation system	0.11	

What stands out from this analysis is that among the alternative studied, LLE designed with dodecanol provided the most suitable route for ethanol purification. The worst renewability exergy performance was the LLE designed with oleic acid. This outcome is likely to be associate to the huge amount of solvent feed flow rate into the extractor column. These results are in line with those of previous studies at Offeman *et al*. (2005), according to the authors the ratio of mass fraction of alcohol in organic rich-phase to mass fraction of alcohol in aqueous rich-phase is expected to reduce. Due to the mass concentration of hydroxyl groups (-OH) in the solvent decrease caused by the growth of alkyl chain length.

The behaviour seems to be consistent with the data presented in Table 3.9 suggesting that for both LLE systems using oleic acid and dodecanol would require a further analysis in order to improve environmental performance.

3.3.6 Ethanol dehydration using extractive distillation: comparison between n-dodecanol and oleic acid process design

In order to complete the solvent screening process, the conventional extractive distillation sequence was simulated to obtain the anhydrous ethanol. Once the ethanol solution has been separated in the entrainer downstream unit, the stream goes directly to extractive distillation column (MARTINEZ *et al*., 2012).

The evaluation of the ethanol dehydration process was carried out considering the specific steam consumption (SSC) as well as the final anhydrous ethanol production (kg/h) of each process. Table 3.10 compare the results obtained. According to these data, we can see that the higher production of anhydrous ethanol with lower value of SSC ($kg_{steam}/kg_{product}$) occurred for the dodecanol process design. The performance of oleic acid as extractor in LLE process provided the worst result obtaining 28.000 kg/h of ethanol with SSC of 2.29 ($kg_{steam}/kg_{product}$), which represent an increasing of 89% when compared to dodecanol process. This result may be explained by the fact that the reboiler heat duty for oleic acid case (133 KW) is extremely higher than the reboiler heat duty (21.94 KW) for dodecanol case designed, as shown in Table 3.10 (Chen *et al*., 2016).

Close inspection of the Table 3.9 below, shows that the low flow rate of MEG is required to carry out the ethanol dehydration (50.000 ton/h), this fact may have direct effect in the low heat duty (25.5 MW) in the extractive distillation for dodecanol case. These finding has important implications for developing future research.

Table 3.10 - The specific steam consumption analysis, anhydrous ethanol production and reboiler heat duty consumption analysis in the extractive distillation column for the two designed cases (n-dodecanol and oleic acid).

Parameter \ Column	Extractive distillation with MEG	
	Dodecanol case	Oleic acid case
Number of stage	35	35
MEG feed flow rate (kg/h)	51.000	222.000
Ethanol production (kg/h)	32.000	28.000
Ethanol concentration (%wt.)	99.4	99.7
Reboiler heat duty (MW)	25.5	37
SSC (kg $_{steam}$/kg $_{product}$)	1.21	2.29

3.3.5. Mono ethylene glycol (MEG) regeneration analysis

Table 3.11 shows the summary results for SSC analysis for downstream processing of MEG after extractive distillation column. By analysing the results from the Table 3.11, it can be thus noticed that the recovery of MEG with lower SSC (0.86 kg steam/kg product) occurred to the process that used dodecanol as solvent to LLE process. This result is almost two times lower when compared to oleic acid case (SSC 1.52 kg $_{steam}$/kg $_{product}$).

Table 3.11 – The specific steam consumption analysis, the recovery rate of MEG and reboiler heat duty consumption analysis in the recovery column for the two designed cases (n-dodecanol and oleic acid).

Parameter \ Column	Recovery column of MEG	
	Dodecanol case	Oleic acid case
Number of stages	20	20
Reflux rate	0.1	1.47
*MEG recovery rate (%wt.)	99	99.7
Reboiler heat duty (MW)	41.7	7.5
SSC (kg $_{steam}$/kg $_{product}$)	0.86	1.52

*Mono ethylene glycol (MEG) purified and recycled to extractive column

According to Batista and collaborator (2012) reflux ratio is one of the main parameters with considerable influence on the absolute steam consumption. The reflux ratio (RR) represents the ratio of liquid stream fed back to distillation column with the distillate stream. So, when the RR is higher it means that more liquid return to column, thus higher flows will be in the column and greater energy need is required to reboil the liquid inside the column, as consequence the distillation column ideal number of stages is reduced.

However, the number of stages (NS) for both extractive distillation column and MEG recovery column were kept the same as is used in the conventional process. The aim of this strategy is to evaluate the performance of the alternative technologies and the conventional process at the same operational conditions. This fact may explain 82% higher heat duty in the MEG recovery column for dodecanol process designing. For this process the NS could be decreased. The finding obtained in the Table 3.11 means that is still necessary to continue searching for other types of solvents for LLE process (PALACIOS-BERECHE et al., 2014).

3.4 Conclusion

In the present study, a hybrid scheme combining LLE with extractive distillation was proposed to produce anhydrous ethanol. This alternative route involved the use of four different organic solvents as entrainer in LLE unit to preconcentrate ethanol from the diluted fermented wine, being sent to extractive distillation with MEG as dehydrating agent. This strategy was expected to reduce the specific steam consumption in the ethanol purification step, since LLE unit allows to remove a considerable amount of water from process. According to the results, among the potential candidates under investigation, the best performance was the hybrid system using dodecanol as entrainer for LLE. This alternative route required less specific steam consumption than others process and has lower liquid waste emissions when compared to conventional ethanol purification sequence. The key strength of the present study was to provide a framework for investigation of liquid extraction-distillation sequence taking into account the solvent extraction performance, energy requirement, liquid waste emissions, and also economic analysis of the designed process. Thus, these finding have an important implication for developing of an alternative route for sugarcane distillery for anhydrous ethanol process production.

3.5 Acknowledgements

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Chapter 4 – Simulation Of Liquid-Liquid Extraction Of Ethanol With Raffinate Stream Reclyced To Fermenter Assisted Extractive Distillation For Anhydrous Ethanol Production

Abstract

This study aimed to investigate a hybrid system combining liquid-liquid extraction with recycled of raffinate stream to fermenter associated with dehydration process to produce ethanol fuel from sugarcane as the feedstock. The effectiveness of the system relies on the selection of the most appropriate extraction solvent. A comprehensive approach of solvent screening for the extraction process was designed using Aspen Plus process simulator. NRTL thermodynamic model was selected for achieving physical properties. Oleic acid and n-dodecanol were used as entrainer agents for in situ extraction of ethanol from the fermented medium. This hybrid system was assessed taking into account the solvent extraction consumption, ethanol recovery rate, and environmental impact. As a result, n-dodecanol presented a better result for extractive fermentation performance, due to the higher ethanol recovery (95%) than oleic acid (90%). In addition, extraction system with n-dodecanol consumed 75.3% less solvent than oleic acid and showed the greatest renewability index when compared to oleic acid system and standard process. This proposed purification strategy obtained 621 L of anhydrous ethanol per tons of sugar total reducers, this value is approximately 10% higher than conventional process which is 559 L of anhydrous ethanol per tons of sugar total reducers.

Keywords: extractive fermentation, ethanol, renewability, downstream, simulation

4.1 Introduction

In Brazil, sugarcane ethanol industry stands out as one of most relevant productive activities. This industrial segment has been expanded since the internal and external market began for the search and production of renewable energy (GUERRA *et al.*, 2018). According to the Brazilian sugarcane industrial sector in the 2016/2017 harvest season, over 27.3 billion liters of ethanol were produced in Brazil (NOVACANA, 2016; LEMOS *et al.*, 2017). In this sense, sugarcane distillery has been looking for increasing competitiveness by improving ethanol productivity, and industrial profit by designing alternatives for separation and purification techniques in bioethanol production (GUERRA *et al.*, 2018).

The Brazilian ethanol production is based mainly on the fermentation of sugarcane molasses and the composition of ethanol in fermented broth at the end of process is around 8-10 %wt. According to standard requirement for ethanol fuel, the ethanol is used in internal combustion engines with spark ignition as an additive to gasoline. The concentration of ethanol must be higher than 99.3% by weight (ANP, 2018).

However, one of the main obstacles is that the ethanol-water aqueous solution forms azeotropic point at 96% wt. From the single distillation column is impossible to increase the ethanol mass fraction of the diluted solution higher than the azeotropic point from the fermented wine (HABAKI *et al.*, 2016). In addition, there is another issue that must be addressed in the ethanol production for industrial fuel purpose which is the high energy requirement for final product recovery (PONCE *et al.*,2014).

In the last decades, there has been some enormous research focusing on variety of separation technologies in recovery and dehydration of ethanol, as well as increasing industrial product yield (HABAKI *et al.*, 2016). Thus, a great number of purification techniques have been studied, such as membrane pervaporation, adsorption, azeotropic distillation, extractive distillation, supercritical fluid extraction and liquid-liquid extraction (CHEN *et al.*, 2016; HABAKI *et al*., 2016; ZHAO et al., 2018).

An alternative route that could be applied is the use of in-situ liquid extraction of ethanol from fermentation medium. Liquid-liquid extraction-fermentation is an operation which is based on the transfer of a solute between two immiscible or partially miscible components (WEILNHAMMER; BLASS, 1994). In this technique, in situ extraction is carried out to remove the ethanol and some inhibitory components during the fermentation process, and reduce the inhibitory compounds caused by ethanol formation avoiding end product inhibition. This technique may increase the ethanol concentration of the diluted fermented solution (LEMOS *et al*., 2017; HABAKI *et al*., 2016).

According to literature the two main methods applied for simultaneous fermentation-separation schemes are membrane and solvent based (FU *et al*., 2016; JASSAL; HILL, 1994). Taking this into account, a great number of organic solvent have been studied and tested as entrainer agent to remove the ethanol from the fermented medium, such as hydrocarbons of alkanes and aromatics, higher carboxylic acids, and higher alcohols (HABAKI *et al*., 2016, LEMOS *et al*., 2017; OFFEMAN *et al*., 2005; OFFEMAN *et al*., 2008). The main purpose of simultaneous fermentation-separation technique is to reach high concentration of ethanol. This fact is extremely important parameter to reduce the consumption of energy in the ethanol downstream processes (VANE, 2008).

Thus, a plenty of paper have been published in literature investigating solvent fermentation-extraction process (BHOWNATH *et al*., 2008; OFFEMAN *et al*., 2010; KOLLERUP; DAUGULIS, 1986; MINIER; GOMA, 1982). So far, however, there has been little discussion about solvent extraction recovery techniques as well as the environmental impacts associated with wastes and emissions to the environment.

It is extremely important the search for suitable solvents that rely on the satisfactory outcome of techno-economic and environmental impact assessments. In the last decades, computer simulation is a powerful tool that has been used a lot for investigating the improvement and sustainability of bioethanol production process through the study of alternative designing (SILVA *et al*., 2017; BATISTA; MEIRELLES, 2011). In the present work, the Aspen Plus® simulator was selected to accomplish the analysis of improvement in the ethanol plant, owing to its simplicity, ease of use, and the existence of a large number of components from sugarcane industry in its library (JORGE *et al*., 2010).

The present study fills a gap in the literature by investigating the environmental consequences of in situ solvent extraction of ethanol from fermented wine for pre-concentration of alcoholic wine. Hence, the contribution of the present work is therefore to describe an integrated methodology for process analysis, which simultaneously evaluates the solvent extraction efficiency, and environmental aspects of modifications performed inside the sugarcane industry.

4.2 Methodology and approach

In this study, the hybrid-system composed by extractive fermentation coupled to distillation process will be investigated. Firstly, an aqueous mixture of treated juice containing 20 %wt. of sucrose was fed to the fermenter. The simulation of fermentation process was carried out at 30ºC and 1.0 atmosphere. The chosen solvents for the study of extractive process were n-dodecanol and oleic acid. Those selected solvents were chosen due to their different polarities and the scarcity of result available in the literature.

The designed scheme for each solvent used in hybrid-system will be described, along with the strategy to minimize environmental impact and the process energy consumption. Finally, the Total Annual Cost (TAC) is also calculated.

4.2.1 Process simulation: extractive fermentation step

In the present study, the fermentation process simulation with in situ liquid-liquid extraction was performed by Aspen Plus® process simulator V.8.2. The conversion of fermentable sugars into ethanol, carbon dioxide (CO_2) and minor compounds takes place in the fermenter vessel, which was represented in the simulation by Rstoic block. In this process, the main reactions are the hydrolysis of the sucrose into glucose and fructose followed by the conversion of glucose and fructose into ethanol and carbon dioxide using *Saccharomyces cerevisiae* yeast as a catalyst. The small quantities of other products are presented as succinic acid, glycerol, acetic acid and others components. At the end of the process, *S. cerevisiae* is centrifuged, treated and sent back to fermenting vessel (PONCE *et al.*, 2014). In this simulation, bioconversion of sugars, stoichiometric equations for reagents and products are illustrated in Table 4.1.

The traditional real fermentation process, which is named Melle-Boinot process, fermentation is performed in a fed-batch mode. In this process the cell yeast (*S. cerevisiae*) are recycled back to fermenter vessel after the sterilization process. However, the fermentation step was simulated as a continuous mode (PALACIOS-BERECHE *et al.*, 2014). Among the components inserted in the simulation, some of the solid constituents of the fermentation process as the *Saccharomyces cerevisiae* yeast was not available in the Aspen Plus® database. Those components and their physical properties were therefore inserted into the program according to the database of the United States National Renewable Energy Laboratory (NREL) for biofuels components (WOOLEY AND PUTSCHE, 1996).

In this way, in order to simulate the cell growth of the yeast and the bioconversion of fermentable sugar into ethanol it was needed to insert the yeast as solid type with the properties of Zymo component. Table 4.1 provides stoichiometric equations for reagents and products, yeast cell growth from sucrose, and the reaction yield according to Ponce and collaborators (2014). The reaction yield (%) presented in Table 4.1 represent the convertion of substrate into the main product of each reaction.

Table 4.1 – Parameters of conversion, stoichiometric equations for reagents and products formation adopted from sucrose (PONCE *et al.*, 2014).

Product	Stoichiometric reaction	Yield (%)
Dextrose	$C_{12}H_{22}O_{11}+H_2O \rightarrow 2C_6H_{12}O_6$	100
Ethanol	$C_6H_{12}O_6 \rightarrow 2CO_2+2C_2H_6O$	90.48
Glycerol	$C_6H_{12}O_6+2H_2 \rightarrow 2C_3H_8O_3$	26.99
^{a}SA	$C_6H_{12}O_6+2H_2O \rightarrow 1C_4H_6O_4+2CO_2+5H_2$	2.64
Acetic acid	$C_6H_{12}O_6+2H_2O \rightarrow 2C_2H_4O_2+2CO_2+4H_2$	10.74
^{b}IA	$C_6H_{12}O_6 \rightarrow 0.795C_5H_{12}O+2.05CO_2+1.155H_2O+0.075H_2$	$3.1\text{x}10^{-2}$
^{c}Zymo	$0.1485C_6H_{12}O_6+0.145NH_3+0.1087CO_2 \rightarrow \text{Zymo}+0.2088H_2O$	18.48

^{a}SA – Succinic Acid; ^{b}IA – isoamilic alcohol; ^{c}Zymo yeast – molecular formula – $CH_{1.8}O_{0.5}N_{0.2}$

This component and its physical properties was therefore extracted from the program according to the database of the United States National Renewable Energy Laboratory (NREL) for biofuels components (WOOLEY AND PUTSCHE, 1996). The physical property database for component Zymo and Saccharomyces c. are described at Table 4.2.

Table 4.2 – The physical property of component Zymo and Saccharomyces c. (ALMEIDA *et al.*, 2014).

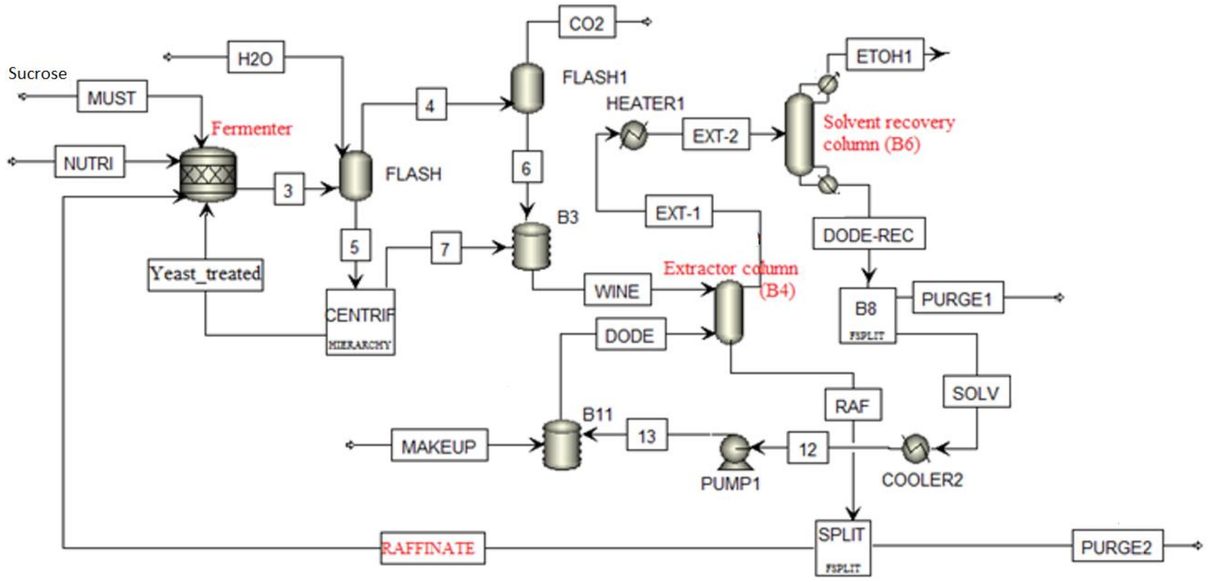
Parameter	*Saccharomyces c.*	Zymo
Heat capacity	-	0.45
Density	62.43	80.00
Molecular weight	30.23	25.2
Molecular formula	$CH_{1.8}O_{0.9}N_{0.145}$	$CH_{1.8}O_{0.5}N_{0.2}$

Font: Almeida *et al.* (2014).

This extractive fermentation process was simulated based on PONCE et al. (2014) study. The flowsheet of in situ liquid-liquid fermentation process is presented in Figure 4.1. However, the in-situ liquid-liquid extraction model is not available in Aspen Plus database, so an assumption to simulate in situ removal of ethanol from broth was adopted.

In this sense, the liquid-liquid extraction process was adopted using an extract block (Extractor column B4) at the same operational conditions of the fermenter vessel (Fermenter). The extractor bottom product stream is the raffinate (RAF) of the LLE. The raffinate stream is composed by water, glycerol, succinic acid, acetic acid, isoamilic alcohol, not converted sugars and a low composition of solvent and alcohol. While, the top extractor column stream is formed mostly by ethanol and extracted solvent (PONCE *et al*., 2014). The schematic diagram of the fermentation step is presented in Figure 4.1.

Figure 4.1 – Flowsheet of extractive fermentation from molasses with downstream process (solvent regeneration unit).



In this process, it is necessary to purge part of the raffinate stream to avoid accumulation of sub-product in the system as well as make sure that the recycled broth concentration was kept at 9.0 % by weight of ethanol, this is the same operational conditions inside the fermenter (PONCE *et al*., 2014).

One drawback of this type of process is that the extracted stream (organic rich-phase) contains one or more additional components that need to be removed from the aqueous mixture. In the present study, it was applied the distillation process for downstream purification method for the recovery of extracted solvent. Thus, this represents that additional distillation column will be required (KURKIJARVI *et al*., 2014).

The thermodynamic model NRTL (non-random two liquid) was selected to calculate thermodynamic properties for both fermentation and liquid-liquid extraction process.

4.2.2 Downstream process: solvent extraction recovery

A single distillation column was used for the solvent recovery from the extractive process. In the bottom column stream more than 95%mass of solvent is recovered from the feed stream with water, while in the top of column come out most the ethanol to be purified (PONCE *et al*., 2014). In Figure 4.1 (see section 4.2.2) is shown the solvent regeneration unit (block B6). In this part of the process it is necessary to purge part of the bottom column stream (streams PURGE1 and PURGE2) to avoid accumulation of sub-product in the system as well as make sure that do not return to much water with the regenerated solvent to fermenter.

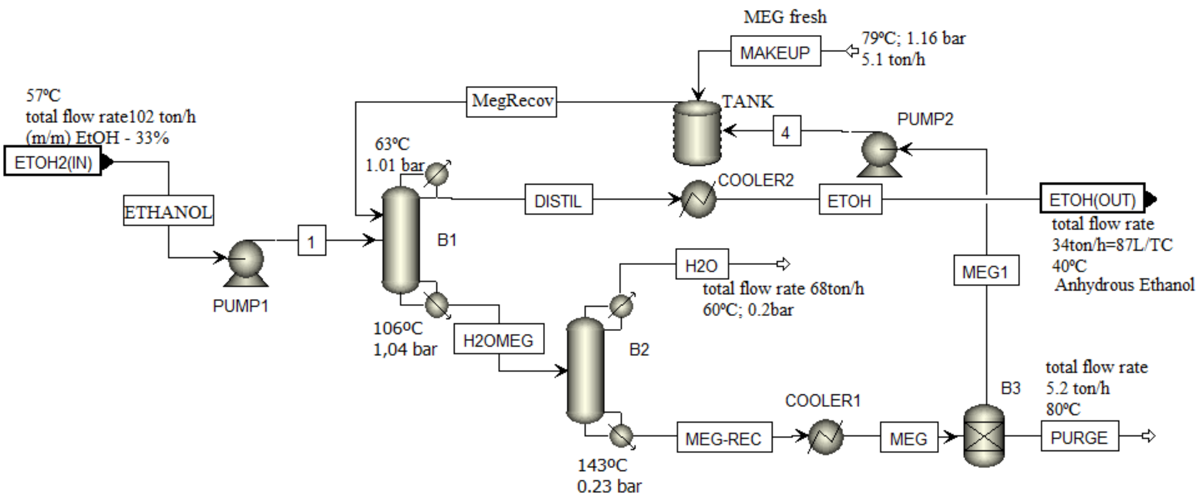
4.2.3 Ethanol dehydration step

A conventional method to produce anhydrous bioethanol was simulated to generate a comparison point for productivity of ethanol and energy requirement (KURKIJARVI *et al*., 2014). In the industrial process, extractive distillation uses mono ethylene glycol (MEG) as entrainer to break down the azeotrope between water and ethanol and remove the remaining water (BRITO *et al*., 2016). The traditional ethanol dehydration stage is presented in Figure 4.2.

According to data extracted from real process, most of pure ethanol and water exits at the top of columns B1 and B2, respectively. While the 99%mass of MEG is recovered in the bottom of column B2 and it was recycled back to extractive column(B1) (BRITO *et al*., 2016).

All the design and operational parameters were based on data extracted from the industrial real process and literature (SILVA *et al*., 2017; BRITO *et al*., 2016). The thermodynamic model NRTL was used due to it is appropriate model to non-ideal mixture with polar components. The distillation column sequence was simulated using the Radfrac block. The ethanol dehydration step is presented in Figure 4.2.

Figure 4.2 - Traditional extractive distillation set up for anhydrous ethanol production.



4.2.4 Environmental analysis using Waste Reduction Algorithm (WAR) software

An environmental assessment methodology was applied to compare the environmental impacts of the bioethanol production processes in each of the case studies described in Section 4.2.2. The environmental analysis procedure has been described in full previously (DIAS *et al*., 2012).

This methodology not only takes into consideration the energy consumption of the process, but also environmental aspects. A very large number of indicators and methodologies, including sustainable process indices, environmental impacts, and lifecycle assessments (LCAs) have been extensively employed in the development of sustainable processes (MONTOYA *et al.*, 2005; DIAS *et al.*, 2012; DIAS *et al.*, 2013; MORAES *et al.*, 2015).

One of the available environmental indicators is the WAste Reduction (WAR) algorithm developed by the Environmental Protection Agency of the United States (USEPA). The lifecycle impact assessment method was applied in this evaluation. The WAR algorithm is based on the determination of potential environmental impacts (PEIs), by quantification of the impact that the disposal of waste material would have on the environment (CABEZAS *et al.*, 1999; QUINTERO *et al.*, 2008).

The environmental impacts evaluated by the WAR algorithm can be classified into two groups, toxicological potential effects (TPEs) and atmospheric physical potential effects (APPEs). The TPEs include human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation or dermal exposure (HTPE), terrestrial toxicity potential (TTP), and aquatic toxicity potential (ATP). The APPEs include global warming potential (GWP), ozone depletion potential (ODP), photochemical oxidation potential (PCOP), and acidification potential (AP) (QUINTERO *et al.*, 2008).

4.2.5 Exergy renewability index analysis: LLE process

Exergy of a substance or stream can be defined as the maximum obtainable work the substance can produce when it is brought reversibly to a state of thermodynamic equilibrium with the environment which is assumed to be at 298 k (T_o) and 1 bar of pressure (p_o) in this study. Exergy analysis of a process is based on the mass and energy balance with the second law of thermodynamics (KHALILI-GARAKANI *et al.*, 2016; WANG *et al.*, 2016).

In this present study, exergy calculations and analysis were conducted in Aspen Plus and Excel. It is extremely important to observer that, the exergetic study must be preceded through mass and energy balance of the system carried out in Aspen Plus simulator (DOGBE *et al*., 2018). Aspen Plus mass and energy streams results were exported to Excel using Aspen simulation workbook in Aspen Plus V.8.2. Further, exergy analyses were finalized in the Excel® spread sheet. Exergy calculations and analysis were performed by based on the following assumptions (WANG *et al*., 2018):

i. each of the units was assessed as a steady state flow process.
ii. variations in potential and kinetic exergy were neglected.
iii. temperature room and atmospheric pressure were assumed constants

3.2.7.1 Exergy calculations

Exergy is the maximum work obtained in a reversible process, when a stream a of mater or energy at a specific condition is brought to equilibrium with the environment which it is interacts. The total exergy transfer that across a control volume (flow exergy) is performed by material and energy (work and heat) streams as shown in Equation 4.1 (DOGBE *et al*., 2018):

$$\dot{\mathrm{E}}\mathrm{x}_{\mathrm{system}} = \dot{\mathrm{E}}\mathrm{x}_{\mathrm{material}} + \dot{\mathrm{E}}\mathrm{x}_{\mathrm{heat}} + \dot{\mathrm{E}}\mathrm{x}_{\mathrm{work}} \tag{4.1}$$

Where the exergy of material was calculated according to Equation 4.2:

$$\dot{\mathrm{E}}\mathrm{x}_{\mathrm{material}} = \dot{\mathrm{E}}\mathrm{x}_{\mathrm{physical}} + \dot{\mathrm{E}}\mathrm{x}_{\mathrm{chemical}} \tag{4.2}$$

In this study, chemical exergy ($\dot{\mathrm{E}}\mathrm{x}_{\mathrm{chemical}}$)was neglected because there is no chemical changes or reactions in the distillation process. The physical exergies of streams

($\dot{E}x_{\text{physical}}$), were calculated by equation (4.3) obtained trought Aspen Plus prop-set, EXERGYFL (exergy flow rate).

$$\dot{E}x_{\text{physical}} = \dot{m}\,[(h - h_o) - T_o(s - s_o)] \tag{4.3}$$

Where $\dot{m}$ represent the mass flow rate (kg/s), h is the specific enthalpy (J/kg), h_o represent the specific enthalpy of a reference state, T_o is the environment temperature (K), s is the specific entropy (J/kg. K), and s_o is associated to specific entropy of the reference state (J/kg. K). The exergy transfer by work ($\dot{E}x_{work}$), is calculated by equation (4.4):

$$\dot{E}x_{\text{work}} = \dot{W} \tag{4.4}$$

Where $\dot{W}$ either represent electrical or mechanical work. The heat exergy is calculated as shown in equation (4.5):

$$\dot{E}x_{\text{heat}} = \dot{Q}\left(1 - \frac{T_o}{T}\right) \tag{4.5}$$

Where $\dot{Q}$ is associated to heat flow rate (kW), T is the Temperature (K) at which the heat transfer occurs and T_o is the environment temperature (K).

Normally, exergy analysis is applied to assess the thermodynamic performance parameters of a process at which include process irreversibility (DOGBE *et al*., 2018). Process irreversibility can be named as the exergy destroyed which is the difference in exergy input and output streams as demonstrated in equation (4.6). Exergy destroyed shows how much exergy is destroyed or lost through a specific unit (DOGBE *et al*., 2018; MABROUK *et al*., 2016).

$$\dot{\mathrm{I}}\mathrm{rr} = \dot{\mathrm{E}}\mathrm{x}_{\mathrm{destroyed}} = \sum \dot{\mathrm{E}}\mathrm{x}_{\mathrm{in}} - \sum \dot{\mathrm{E}}\mathrm{x}_{\mathrm{out}} \qquad (4.6)$$

This methodology allows to identify the local, cause, and true magnitude of waste and loss to be determined. Such information is useful for the design of new energy efficient systems and for increasing the efficiency of existing systems. There have been many recent studies that have used the concept of exergy to evaluate the sustainability of various ethanol production routes (MOSQUEIRA-SALAZAR, 2012; MOSQUEIRA-SALAZAR *et al.*, 2013; ORTIZ; OLIVEIRA, 2014; PINA *et al.*, 2015; DADAK *et al.*, 2016; KHALILI-GARAKANI *et al.*, 2016).

Ometto and Roma (2010) applied the chemical exergy concept to evaluate the atmospheric impact of the lifecycle emissions from bioethanol/electricity production at a Brazilian sugarcane mill.

However, there have been few studies focusing on the renewability analysis of ethanol production. Considering this aspect, Pellegrini and Oliveira (2011) and Oliveira (2013) presented environmental analyses employing a so-called renewability exergy index. The renewability exergy index (λ) can be calculated according to Equation 4.7 (OLIVEIRA, 2013):

$$\lambda = \frac{\Sigma \dot{Ex}_{product}}{\dot{Ex}_{fossil} + \dot{Ex}_{destroyed} + \dot{Ex}_{deactivation} + \dot{Ex}_{disposal} + \Sigma \dot{Ex}_{emissions}} \qquad (4.7)$$

where $\dot{\mathrm{E}}\mathrm{x}_{(\mathrm{product})}$ is the exergy associated with the useful product, $\dot{\mathrm{E}}\mathrm{x}_{(\mathrm{fossil})}$ is the non-renewable exergy consumed in the production processes chain, and $\dot{\mathrm{E}}\mathrm{x}_{(\mathrm{destroyed})}$ is the exergy destroyed inside the system, punishing the process for its thermodynamic inefficiencies. $\dot{\mathrm{E}}\mathrm{x}_{(\mathrm{deactivation})}$ is the deactivation exergy for treating wastes, which accounts for exergy consumed in passing the streams considered as wastes out of the system, without any damage to the environment. Finally, $\dot{E}x_{(emissions)}$ represents the exergy of wastes that are not treated or deactivated (OLIVEIRA, 2013).

In the above equation, the renewability exergy index indicates that:

✓ Processes with $0 \leq \lambda < 1$ are environmentally unfavourable;

✓ For internal and external reversible processes with non-renewable inputs, $\lambda = 1$;

✓ If $\lambda > 1$, the process is considered environmentally friendly, with a higher value of λ implying that the process is more environmentally favourable;

✓ When $\lambda \rightarrow \infty$, the process is reversible, with renewable inputs and no waste production.

In this study, the mass and energy balances were extracted from the Aspen Plus® software, which was the basis for the exergy calculations. Simulation was conducted at steady state operation, and the exergy balances for a specific control volume (MABROUK *et al.*, 2016).

4.2.6 Economic evaluation

An economic evaluation was carried out in order to compare the costs of the systems. The same operational conditions, including inputs, outputs, temperatures, pressures, and process steam conditions, were assumed for all the case studies (NHIEN *et al.*, 2016). According to Li *et al.* (2016), the TAC is defined as the total operating cost added to the annualized capital investment cost, where the latter corresponds to the ratio of the capital cost and the payback period. The TAC analysis is conducted by the Equation 4.8.

$$TAC\left({}^{US\$}/_{year}\right) = \left(\frac{capital\ cost}{payback\ period}\right) + operating\ cost \tag{4.8}$$

The estimated equipment cost was calculated according to the procedure used by Douglas (1989) and Li *et al*. (2016)). The economic basis of the calculation was fully described by Luyben (2013) and is presented in Table A.9 (see Appendix A).

4.3 Results and Discussion

4.3.1 Extractive fermentation: process design

The extractive fermentation process with raffinate stream recycling was simulated such an industrial process, as previously shown in Figure 4.1. This study was performed under different conditions of extractor solvent. Firstly, n-dodecanol was investigated as extractor solvent. The results are provided in Table 4.3.

Table 4.3 – Main streams in the liquid-liquid extractive fermentation process simulated using n-dodecanol as extractor agent, 30ºC and 1 bar.

Stream / Component	Must	FW	Wine	Solv	Ext	Raff	RS
Sucrose ton/h	67.3						
Water ton/h	263.4	997	847	139	210	803	695
Dextrose ton/h	3.0	3.80	3.79	4.05	4.13	3.71	3.2
Ethanol ton/h		40.2	39.45	1.40	36.14	5.2	4.5
CO_2 ton/h		34.4	1.48	trace	1.41	0.068	0.059
Glycerol ton/h		12	11.9	8.57	8.74	11.7	10.1
*SA ton/h		0.85	0.846	0.721	0.736	0.831	0.72
**AA ton/h		2.151	2.15	2.49	2.74	1.89	1.63
***Iso alc ton/h		0.000945	0.00094	0.0056	0.0064	0.0002	0.00018
H_2SO_4 ton/h		16.75	16.75	14.29	14.58	16.46	14.24
Yeast ton/h		1.08					
Dodecanol ton/h		0.278	0.278	1117.7	1117.68	0.321	0.278

*SA – succinic acid; **AA – acetic acid; ***Iso alc – isoamilic alcohol; FW- alcoholic solution exiting fermenter; Wine – alcoholic solution without yeast; Solv – solvent feed flow rate into extractor; EXT – extract stream (organic rich-phase); Raff – raffinate stream; RS – raffinate stream recycled to fermenter

After, oleic acid was investigated as extractor solvent. The results are provided in Table 4.4. For all two-case studied, the extractive fermentation process was carried out continuously at 30ºC. The concentration of the must of sugarcane juice fed to fermenter vessel was fixed at 20% by weight of sugars, according to standard process (SILVA *et al.*, 2017). According to results from Table 4.4, the extractive method with n-dodecanol presented higher recovery of ethanol leaving the extractor column (Extract stream) with lower consumption of solvent as well as lower recycled flow rate of solvent to fermenter as can be seen in Figure 4.3.

Table 4.4 – Main streams in the liquid-liquid extractive fermentation process simulated using oleic acid as extractor agent, 30ºC and 1 bar.

Component \ Stream	Must	FW	Wine	Solv	Ext	Raff	RS
Sucrose ton/h	67.3						
Water ton/h	263.4	1167.3	1011.4	0.00003	11	1000.3	865
Dextrose ton/h	3.0	3.798	3.79	0.235	0.248	3.785	3.27
Ethanol ton/h		89	88.6	69.7	96.67	61.69	53.3
CO_2 ton/h		34.4	1.91	trace	1.91	trace	Trace
Glycerol ton/h		12.1	12.1	2.82	2.97	11.93	10.3
*SA ton/h		0.827	0.827	0.338	0.355	0.809	0.699
**AA ton/h		2.64	2.64	2.56	2.74	2.46	2.13
***Iso alc ton/h		0.00099	0.00099	0.0116	0.0123	0.00026	0.00023
H_2SO_4 ton/h		16.36	16.36	6.68	7.03	16.00	13.84
Yeast ton/h		1.07					
Oleic acid ton/h		2.82	2.82	5594	5593.7	3.26	2.81

*SA – succinic acid; **AA – acetic acid; ***Iso alc – isoamilic alcohol; FW- alcoholic solution exiting fermenter; Wine – alcoholic solution without yeast; Solv – solvent feed flow rate into extractor; EXT – extract stream (organic rich-phase); Raff – raffinate stream; RS – raffinate stream recycled to fermenter

Figure 4.3 – The effect of solvent feed stream in the ethanol recovery rate for the two entrainer studied in this study. LL extractor column= Liquid-Liquid Extractor Column.

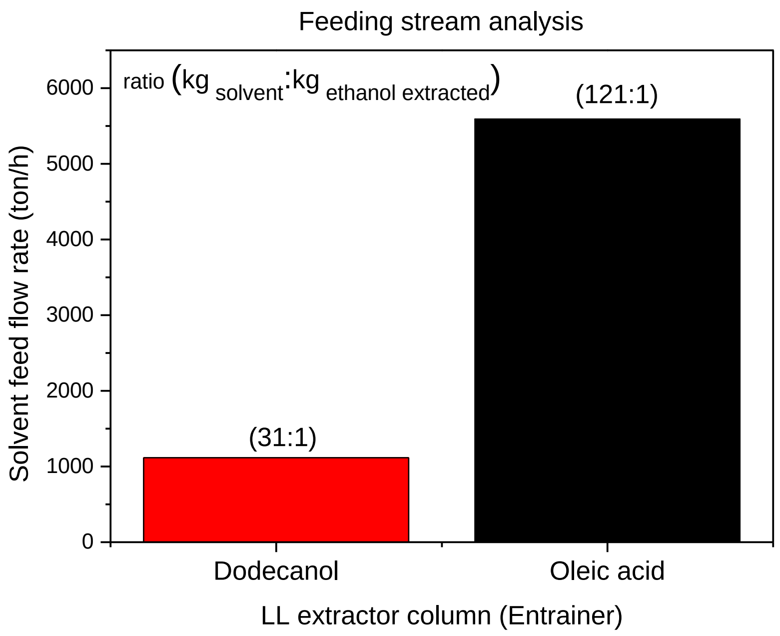
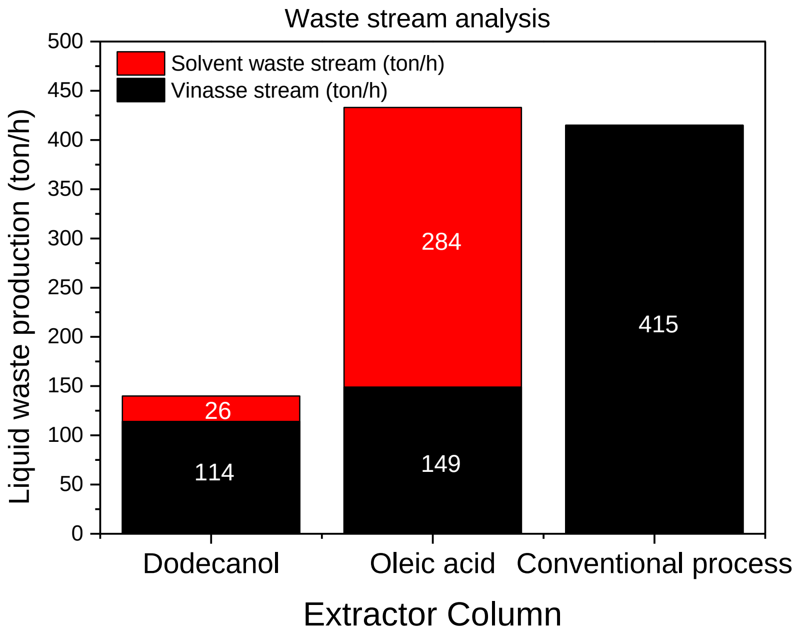


Figure 4.4 - Waste stream production for the extractive fermentation with raffinate stream recycled to fermenter.



Such technology allowed to remove most of the water from the fermented wine. It can be seen from the data in Figure 4.3 that the extraction process with oleic acid as extractor agent consumes 4.0 times more entrainer comparing to n-dodecanol system. This result may be explained by the fact that increasing the carbon chain length reduce the polarity, so that the reduced polarity affects the extraction efficiency of the solvent according to Kurkijarvi and collaborators (2014). Boonmen *et al.* (2015) achieved the same observation that the extraction of alcohol is affected by the size of carbons length chains. According to Offeman *et al*. (2005) this finding can be explained by fact that the mass concentration of hydroxyl group (-OH) in the solvent fall down due to the growth of alkyl chain length.

Further analysis showed that the oleic acid system generated a total of 433 ton of waste stream/hour which correspond to 66%mass of solvent, while n-dodecanol system produce a total of 140 ton of waste stream/hour, corresponding to 18.6% mass of solvent.

This finding is quite revealing owing to the great amount of solvent in the waste stream is not recycled to the fermenter. This result means that the separation and purification of solvent in pure component in the downstream units would increase additional cost to the process (BRITO *et al*., 2016; KURKIJARVI *et al*., 2014). Figure 4.4 shows the amount of liquid waste produced in the extraction system.

4.3.2 Environmental assessment: renewability analysis

Table 4.5 shows the renewability exergy index (λ) values for the hybrid system under investigation, from which it can be seen that the more efficient systems provided better performance, in terms of λ (PELLEGRINI; OLIVEIRA, 2011). None of the systems showed a value higher than 1, indicating that the processes could be considered environmentally unfavourable, from the second law standpoint (see Section 4.2.6).

The most interesting aspect of the performance comparison was the better environmental performance of the hybrid system using n-dodecanol as extractor solvent, compared with oleic acid system, as well as the standard configuration. The values of λ for the n-dodecanol extraction process, the oleic acid and the conventional system were 0.14, 0.025, and 0.11, respectively.

Table 4.5 - Exergy renewability analysis of extractive fermentation with the recycled raffinate stream for both selected solvent under investigation

Configuration	Renewability performance indicator index	Ideal Renewability performance indicator
***EF with dodecanol**	0.14	>1.00
****EF with oleic acid**	0.025	
Standard process	0.11	

*EF – Extractive Fermentation with dodecanol as entrainer; **EF-Extractive Fermentation with oleic acid as entrainer.

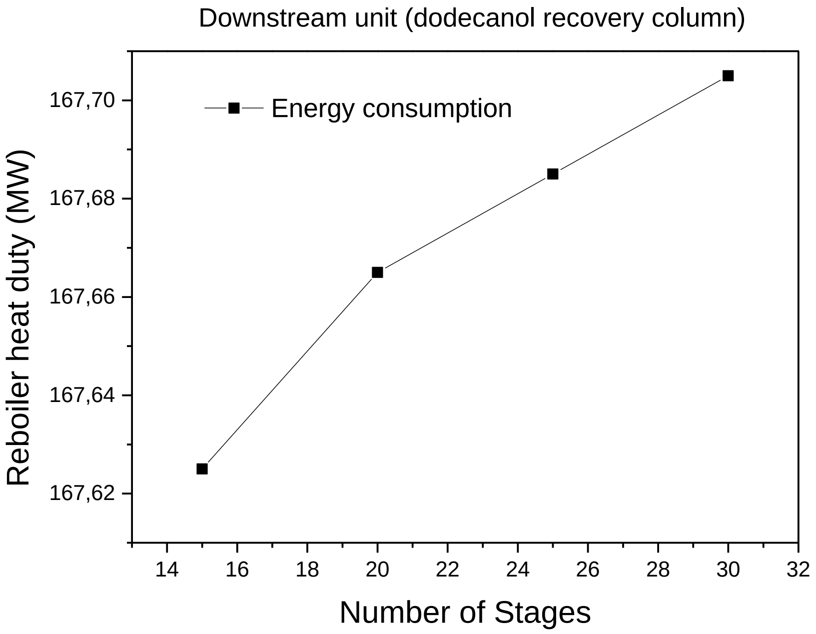
The hybrid system with oleic acid showed the worst environmental performance. This can be a result of the low ethanol extraction efficiency of the liquid-liquid extractor column. Based on prior study of Widjaja *et al*. (2014) the lighter molecular-weight solvent has high value of ethanol recovery. This behaviour appeared to be consistent with the data presented in Figure 4.3, and as well as the fact that increasing the carbon chain length reduce the polarity, so that the reduced polarity affects the extraction efficiency of the solvent as stated by Kurkijarvi and collaborators (2014).

Thus, the data presented in Figure 4.5, suggested that the extraction system with oleic acid is not a good alternative to LLE process taking into account environmental aspects.

4.3.3 Solvent regeneration – downstream process

In this part of study, only n-dodecanol entrainer was considered to investigate the distillation column performance for the solvent extraction regeneration. The rigorous simulation of n-dodecanol recovery indicates that the reboiler heat duty increases when the total number of stage increases, (see Figure 4.6). Another important aspect to be considered is the extract stream feed stage. The sensitivity analysis was accomplished to identify the optimal feed stage of extract in the distillation column. Figure 4.7 shows the results of the sensitivity analysis performance.

Figure 4.5 – Sensitivity analysis of distillation number of stages versus reboiler heat duty of the dodecanol recovery column (downstream processing).



As it shown in Figure 4.6, the increase of number of stages improves as wel the thermal energy need required (reboiler heat duty) by distillation column to recover the solvent of LLE. However, this increasing is not quite significant because from stage 14th to 32nd the reboiler heat duty varied from 167.62 MW to 167.70 MW. The sensitivity study shown that the optimum feed stream into the column is the stage 10th. At this stage the energy consumption was low compared to other stages as presented in Figure 4.7.

The flowsheet of the solvent recovery scheme after extractive fermentation step is depicted in Figure 4.8. In column B6, almost pure n-dodecanol is regenerated in bottom stream column. Part of the solvent recovered must be disposed in order to avoid accumulation in the system and the remaining solvent is recycled back to the fermentation step (PONCE *et al.*, 2014). In top column B6, ethanol comes out with 82% by weight, following to next step that is the ethanol dehydration process. The main value of downstream processing is presented in Table 4.5.

Figure 4.6 – Sensitivity analysis of distillation feed stage versus reboiler heat duty of the dodecanol recovery column (downstream processing)

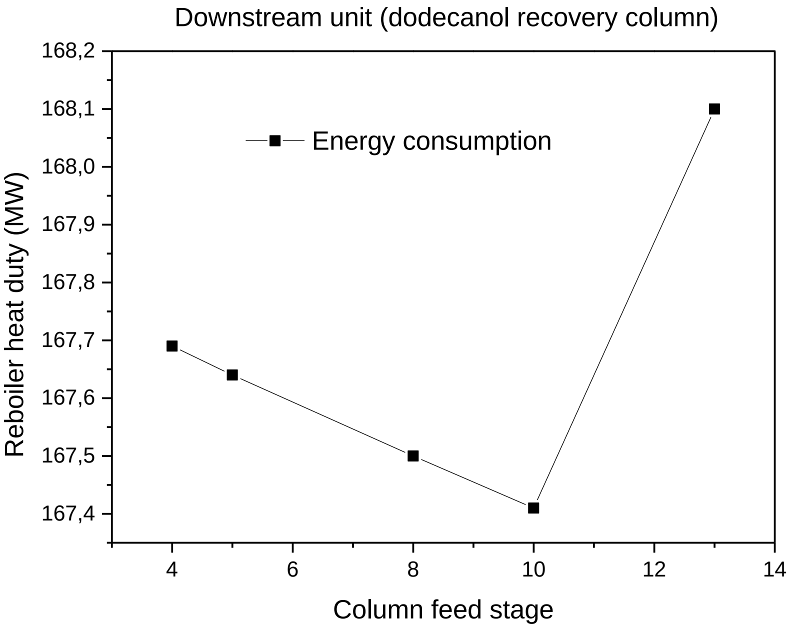
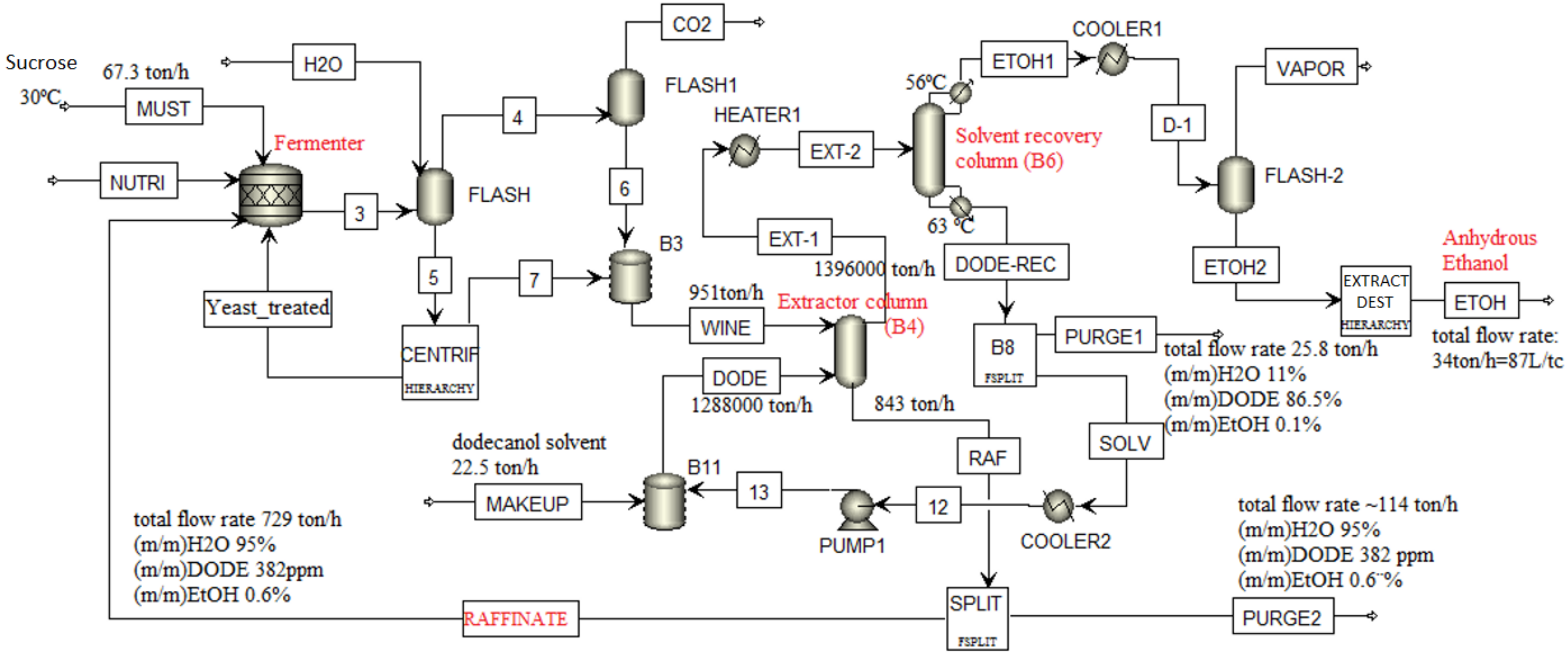


Table 4.6 – Downstream process for dodecanol regeneration performed by an ordinary distillation column

Parameter	Recovery column (B6)	Unit
Number of stages	15	-
Extract feed flow rate	1396.3	ton/h
Reflux ratio	0.41	-
Temperature -top column	56.4	ºC
*EtOH recovery	0.332	m/m
**Dode recovery	0.865	m/m
***$Q_{reboiler}$	95.61	(MW)

*EtOH recovery – ethanol content in top column stream; **Dode recovery –dodecanol content in bottom stream; ***$Q_{reboiler}$ – column heat duty

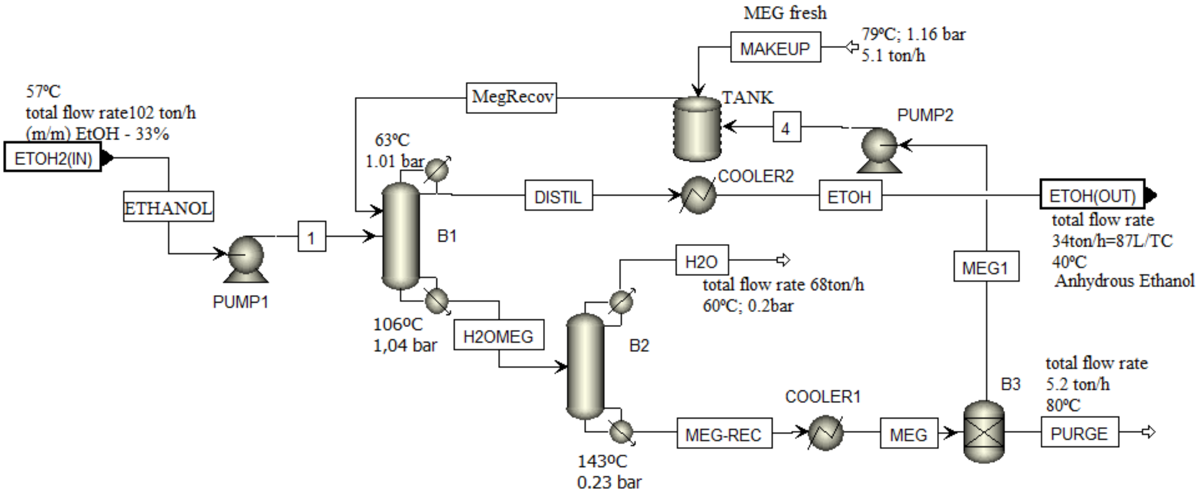
Figure 4.7 – Flowsheet of hybrid system composed by continuous extractive fermentation and distillation column for solvent recovery after liquid-liquid extraction process. Yeast cell treatment step (Hierarchy block CENTRIF); Fermented wine without yeast cell reservoir tank (B3); Liquid-Liquid extractor column (B4); Process downstream – solvent recovery column (B6); Ethanol dehydration step (Hierarchy block EXTRACT DES).



4.3.4 Ethanol dehydration: simulation of extractive distillation with MEG

The flowsheet of extractive distillation (B1) is presented in Figure 4.9. In the top column B1, ethanol is purified to 99.5% wt. (stream DISTIL). In this configuration, the alternative route achieved almost 621 L of anhydrous ethanol per ton of total reducers sugars, this value is greater than to traditional sugarcane distillery (557 L of anhydrous ethanol per ton of total reducers sugars). In column B2, MEG (stream MEG-REC) is purified to 97.3% wt. and cooled down and recycled to top extractive column (B1).

Figure 4.8 – Extractive distillation with MEG as entrainer to produce anhydrous ethanol: extractive column (B1); solvent recovery column (B2); reservoir tank of MEG (TANK).



4.3.5 Economic analysis: anhydrous ethanol selling

In this work, the anhydrous ethanol production (kg/h) and industrial profit performance was accomplished to compare and analyse to the conventional process. What is interesting about the data in the Table 4.6 is that hybrid system with n-dodecanol achieved the production of 621 L of anhydrous ethanol per ton of total reducers sugars, the standard process obtained 557 L of anhydrous ethanol per ton of total reducers sugars).

Between the two bioethanol production process, the alternative route showed high value of the profitability of anhydrous ethanol selling, 103.5 x 10^6 \$/year than the standard process that achieved 93.9 x 10^6 \$/year. The standard process achieved a reduction of 10.2% of the profit when compared to alternative process. Table 4.6 displays the results commented.

Table 4.7 - Overall sugarcane crushed, ethanol productivity and the profitability of anhydrous ethanol selling for extractive process with n-dodecanol compared to standard process.

Parameter \ Process	Dodecanol	Conventional
Total sugarcane crushed ton/h	500	500
*EtOH mass fraction %wt.	99.4	99.4
**EtOH production (L/ton of cane)	86	78
EtOH selling price	0.60	0.60
EtOH revenue production (\$/year) 1x10^6	103.5	93.9

*EtOH – ethanol; ** EtOH L/TC – volumetric flow rate of ethanol per ton of crushed cane

These finding further support the idea of pre-concentration of fermented wine to distillation stage as this have positive contribution over energy consumption and ethanol production (kg/h).

4.4. Conclusions

The system combining liquid-liquid extractive fermentation assisted with conventional extractive distillation for anhydrous ethanol production was investigated with the solvents n-dodecanol and oleic acid for the aim of ethanol concentration in the fermented wine lead to dehydration process. The detailed designs of the two processes using the investigated solvents such as n-dodecanol and oleic acid were compared. The hybrid system with oleic acid requires a large consumption of solvent. This process showed the worst environmental performance followed by the standard process. N-dodecanol presented the most favourable result to respect to anhydrous ethanol selling revenue, however it was unfavourable for environment impact in terms of the organic waste send to field. For the entire processes producing anhydrous bioethanol, the simulation suggested that the hybrid system using n-dodecanol shows an interesting result based on environmental performance and industrial profit, but a further study focused on solvent consumption and the solvent recovery methods are needed.

The findings obtained for study showed that the use of LLE system contribute to the enhancement of ethanol production of sugarcane distillery, however the techno-economic and environmental performance of LLE is quite similar to conventional process, which does not justify the investment and the implementation of LLE technology to ethanol plant.

4.5 Acknowledgements

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CHAPTER 5 – CONCLUDING REMARKS AND FUTURE PERSPECTIVES

The main purpose of this thesis was to study the liquid-liquid extraction process assisted extractive distillation to produce anhydrous ethanol. In each stage of the project the aim was to improve the understanding of the sugarcane-based ethanol production process.

In Chapter 2 – distillation with direct steam injection (standard autonomous distillery) was simulated and compared to indirect heating system using reboilers and distillation with mechanical vapour recompression. The simulation was based on literature and industrial performance which provided the parameters for the first part of this thesis. The purpose was to obtain all the information necessary to perform a simulation of ethanol plant to be used as base-case. From this study, it was possible to identify that the use of reboilers as distillation column heat source can significantly reduce the amount of vinasse, as a result decrease the total annual cost.

The second part of this thesis was Chapter 3 - simulation of an alternative route combining liquid-liquid extraction-distillation system to produce anhydrous ethanol: downstream process and its environment impact, allowed to acquire information and make progress in terms of i) process downstream for solvent extraction; ii) environmental analysis using exergy and renewability index, iii) energy consumption in solvent regeneration unit, and vi) the total annual cost for each solvent studied. The results obtained in this study showed that process downstream is extremely important point to identify the techno-economic feasibility of the new process.

The last part of this thesis is Chapter 4 – simulation of liquid-liquid extraction (LLE) of ethanol with raffinate stream recycled to fermenter assisted extractive distillation for anhydrous ethanol production. All knowledge acquired in the previous chapters could be implemented here. It was possible to conduct a simulation of extractive fermentation using n-dodecanol and oleic acid as the entrainer agent, exploring the process downstream in terms of techno-economic and environmental index, not yet described in literature. Taking into account the consumption of solvent into extractor column, the LLE process with oleic acid consumes 4 times more than the n-dodecanol system. A result this process generated a total of 433 tons of liquid waste stream/hour, which correspond to 66% mass of solvent, while for dodecanol system produces a total of 140 ton of liquid waste stream/hour, corresponding to 18.6 %mass of solvent. This finding is quite revealing which illustrate the relevance of downstream unit in LLE process. Therefore, the simulation designed herein in this Chapter, may certainly be applied for design more economical and environmental processes. Considering that, the liquid waste emissions, the process downstream, and solvent makeup costs are still high and a further study must be accomplished.

5.1 Suggestions for future works

✓ The study of energy consumption, investment cost and process optimization in ethanol separation and purification step applying the use of reboilers as distillation heat source for comparison with this work;

✓ The study of further technique for vinasse concentration which allows the re-use of water in other part of the plant and reduce the transport cost of vinasse;

✓ The study of potential biocompatible solvents for liquid-liquid extraction-fermentation process to remove the product ethanol from fermentation medium, thus to improve the ethanol yield. In this way, alcohols in the 14-20 carbons range are not considered toxic and can be used to enhance extractive performance;

✓ The study of extractive fermentation process coupled to downstream process and its energy consumption, the total annual cost and the environmental impacts;

✓ The study of continuous extractive fermentation with CO_2 stripping could be a promising alternative route to enhance the ethanol content in the fermented broth and analysis its impact to ethanol productivity.

CHAPTER 6 – LIST OF PUBLICATIONS

SILVA, W. C.; ARAUJO, E.C.C.; CALMANOVICI, C.E. ; BERNARDO, A.; GIULIETTI, M. Environmental assessment of a standard distillery using aspen plus: Simulation and renewability analysis. *Journal of Cleaner Production*, v. 162, p. 1442-1454, 2017.

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CHAPTER 7 – APPENDIX A

Table A.1 Effective collected water uses during ethanol production.

Effective water uses (L/t of cane)	This work	Ref.[e]
Cane washing	0	0
Imbibition	95	300
Bearing cooling	50	1.5
Preparation of lime mixture	10	8
Filter cake washing	29	70
Polymer preparation for settling	15	15
Condenser of 5th effect evaporator	418	30
Cooling of must for fermentation	34	7
Cooling of fermenter	53	60
Carbon dioxide scrubber for fermentation	43	27
Dilution of yeast broth	116	141
Condenser of distillation column	3	37
Condenser of rectification column	52	0
Condenser of extractive column	60	25
Condenser of recovery column	1	4
Solvent cooling	4	3
Anhydrous ethanol cooling	22	22
Turbo generators cooling	10	6
Washing scrubber (boiler)	50	50
Boiler feeding	20	25
General cleaning	50	50
Drinkable uses	30	30
Total (L H_2O/t cane)	1,165	910

[e] Mosqueira-Salazar et al. (2013).

Figure A.1. Distillation heating system using reboiler, simulated in Aspen Plus.

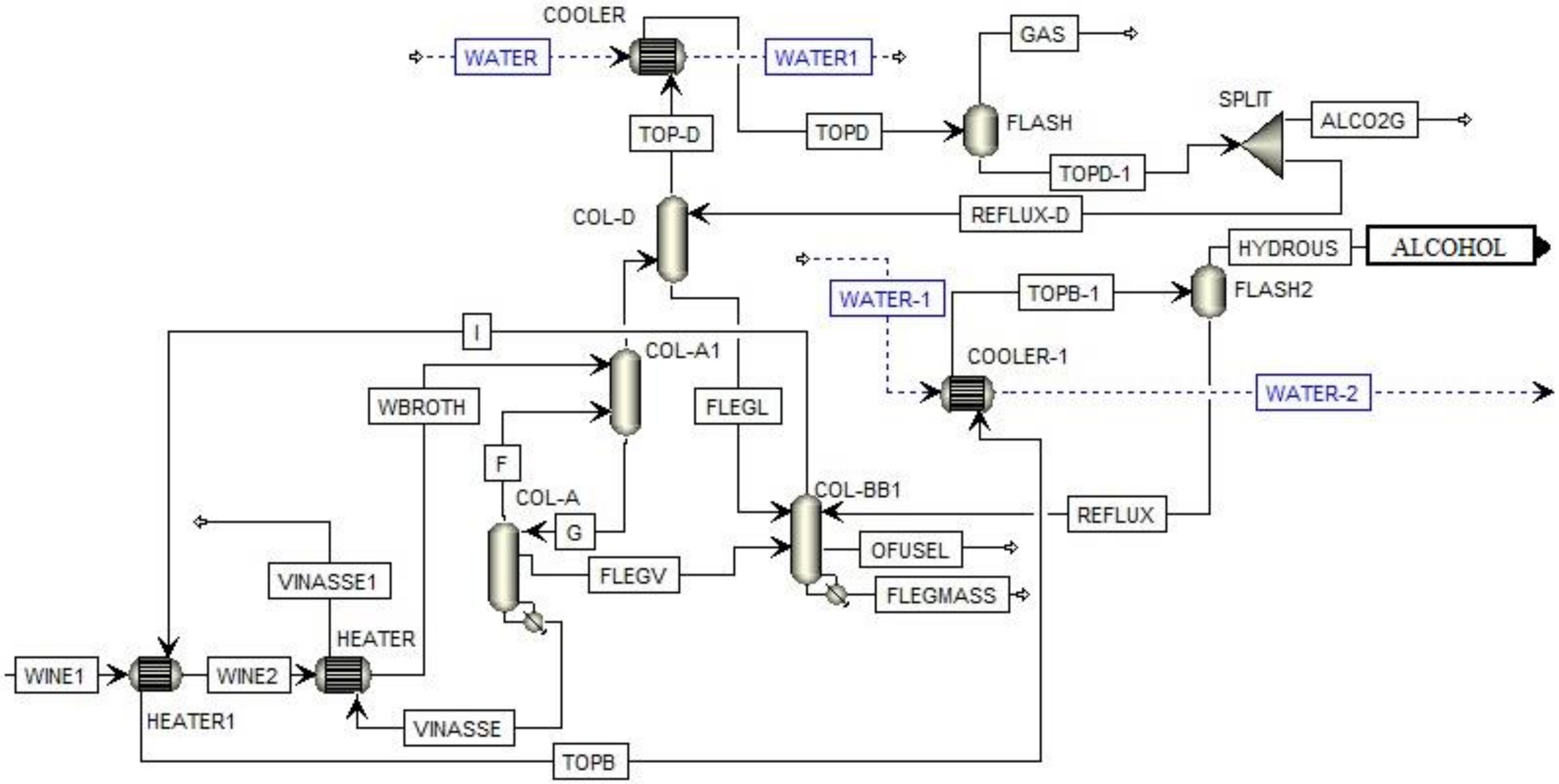

Figure A.2. Distillation heating system using direct steam injection, simulated in Aspen Plus (standard configuration commonly used in most autonomous Brazilian distilleries).

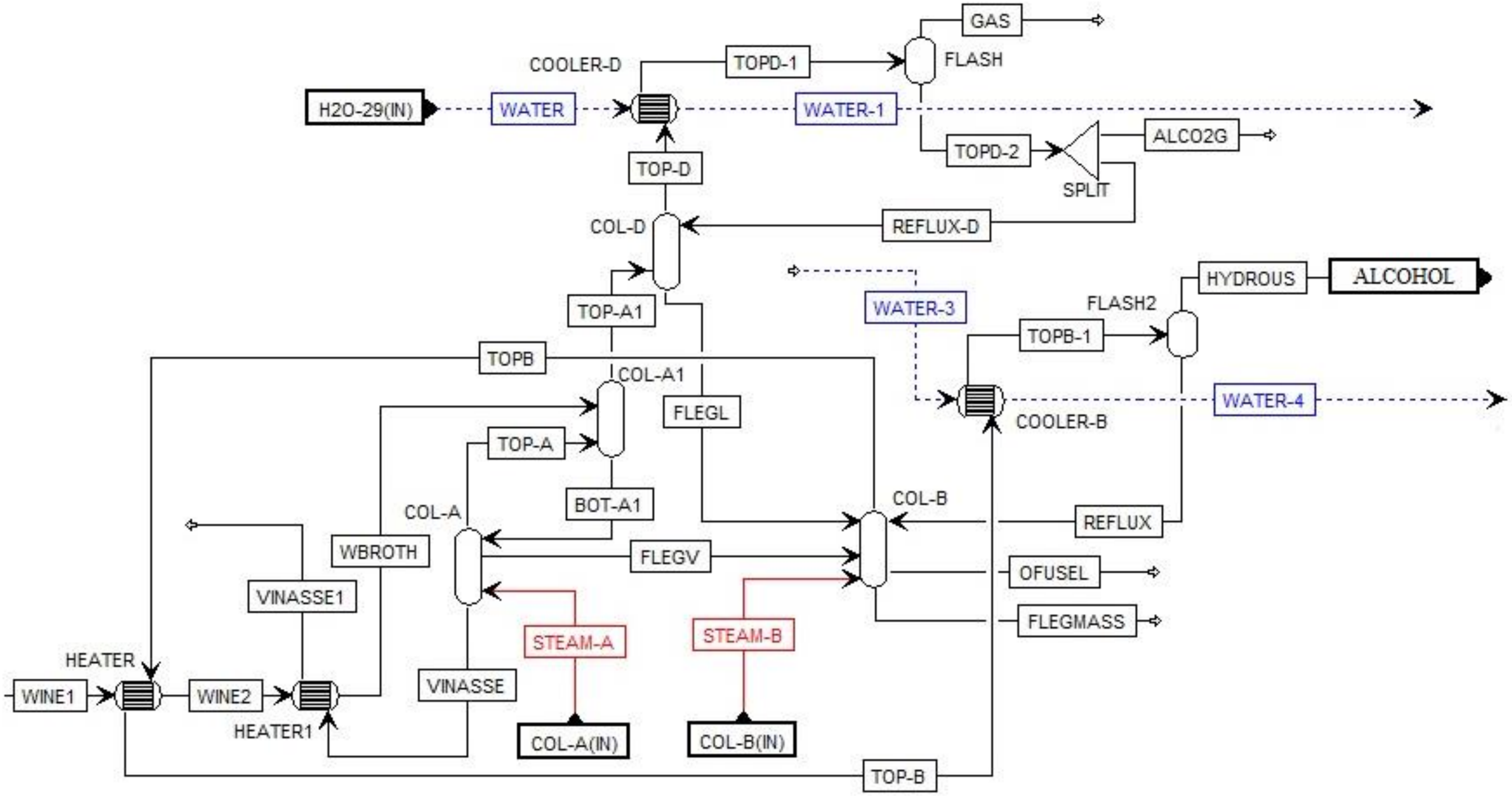

Figure A.3 – Flowsheet of the full simulated standard distillery. EXTRACT - cleaning and extraction step; TREATMEN - juice treatment; MEE - multi effect evaporator; FERMENT - fermentation step; DISTILL - distillation step; DEHYDRAT - dehydration step; COGENER - cogeneration step.

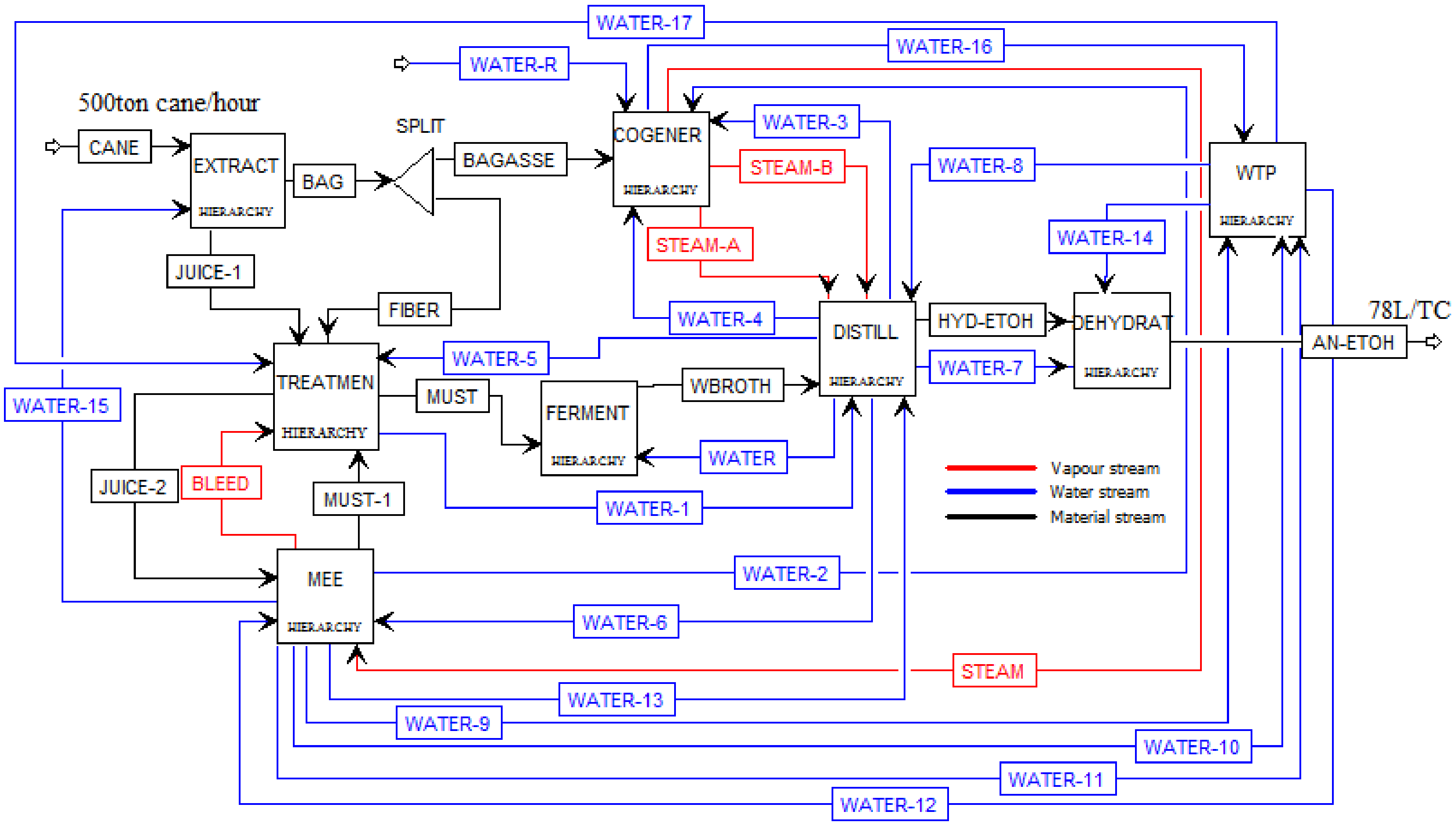

Table A.2. Binary interaction parameters of NRTL model for the system H2O(i)+Ethanol(j); H2O(i)+Dodecanol(j); Ethanol(i)+Dodecanol(j), for the LLE carried out at 1 bar and 298 K.

Component i	H2O	H2O	ETHANOL
Component j	ETHANOL	DODEC-01	DODEC-01
Temperature	ºC	ºC	ºC
Source	APV86 VLE-IG	APV86 LLE-ASPEN	R-PCES
Property units			
AIJ	3,4578	2,2353	0
AJI	-0,8009	-0,9927	0
BIJ	-586,0809	2215,7415	494,426747
BJI	246,18	389,1094	-235,589288
CIJ	0,3	0,2	0,3
DIJ	0	0	0
EIJ	0	0	0
EJI	0	0	0
FIJ	0	0	0
FJI	0	0	0
TLOWER	24,99	28,85	25
TUPPER	100	89,85	25

Table A.3. Binary interaction parameters of NRTL model for the system H2O(i)+Ethanol(j); H2O(i)+oleic acid(j); Ethanol(i)+oleic acid(j), for the LLE carried out at 1 bar and 298 K

Component i	ETHANOL	ETHANOL	H2O
Component j	H2O	OLEIC-01	OLEIC-01
Temperature	ºC	ºC	ºC
Source	APV86 VLE-IG	APV86 VLE-LIT	R-PCES
Property units			
AIJ	-0,8009	0	0
AJI	3,4578	0	0
BIJ	246,18	490,9806	4978,8569
BJI	-586,0809	-172,8778	537,273753
CIJ	0,3	0,2988	0,3
DIJ	0	0	0
EIJ	0	0	0
EJI	0	0	0
FIJ	0	0	0
FJI	0	0	0
TLOWER	24,99	45	25
TUPPER	100	45	25

Table A.4. Binary interaction parameters of UNIQUAC model for the system H2O(i)+Ethanol(j); H2O(i)+Dodecanol(j); Ethanol(i)+Dodecanol(j), for the LLE carried out at 1 bar and 298 K.

Component i	WATER	WATER	ETHANOL
Component j	ETHANOL	DODEC-01	DODEC-01
Temperature	ºC	ºC	ºC
Source	APV86 VLE-IG	APV86 LLE-ASPEN	R-PCES
Property units			
AIJ	-2,4936	1,1087	0
AJI	2,0046	-2,294	0
BIJ	756,9477	-462,1516	42,6558871
BJI	-728,9705	371,1795	-170,878556
CIJ	0	0	0
CJI	0	0	0
DIJ	0	0	0
DJI	0	0	0
TLOWER	24,99	28,85	25
TUPPER	100	89,85	25
EIJ	0	0	0
EJI	0	0	0

Table A.5. Binary interaction parameters of UNIQUAC model for the system H2O(i)+Ethanol(j); H2O(i)+oleic acid(j); Ethanol(i)+oleic acid(j), for the LLE carried out at 1 bar and 298 K

Component i	ETHANOL	ETHANOL	H2O
Component j	H2O	OLEIC-01	OLEIC-01
Temperature	C	C	C
Source	APV86 VLE-IG	APV86 VLE-LIT	R-PCES
Property units			
AIJ	2,0046	0	0
AJI	-2,4936	0	0
BIJ	-728,9705	90,9619	-232,04474
BJI	756,9477	-316,0042	-377,085922
CIJ	0	0	0
CJI	0	0	0
DIJ	0	0	0
DJI	0	0	0
TLOWER	24,99	45	25
TUPPER	100	45	25
EIJ	0	0	0
EJI	0	0	0

Table A.6 Comparison of the estimated TAC of each column for the three case studies.

Parameter	Case I				Case II				Case III			
	col.A	col.A1	col.D	col.BB1	col.A	col.A1	col.D	col.BB1	col.A	col.A1	col.D	col.BB1
CSC ($) 10e5	1.5	0.33	0.25	12.3	1.64	0.46	0.35	11.89	1.5	0.33	0.26	11.44
CTC ($) 10e3	5.27	0.59	0.43	85.3	5.27	0.95	0.67	80.80	4.6	0.59	0.42	76.4
CC_a ($) 10e6	0	0	0	0	0	0	0	0	0	0	0	2.6
CC_b ($) 10e3	0	0	103.6	524.5	0	0	190	486.6	0	0	49.6	118.2
RC ($) 10e5	8.54	0	0	2.05	0	0	0	0	8.5	0	0	0
SC ($/year) 10e6	8.61	0	0	1.26	8.46	0	0	0.57	8.6	0	0	0
CWC ($/year) 10e4	0	0	0	3.56	0	0	0	3.2	0	0	0	0.24
VC ($/year) 10e6	3.63	0	0	0	4.37	0	0	0	3.57	0	0	0
TAC_C ($/year) 10e5	3.37	0.11	0.43	6.83	0.56	0.16	0.75	5.85	3.36	0.11	0.25	13.12
TAO_C ($/year) 10e6	12.24	0	0	1.3	12.8	0	0	0.6	12.17	0	0	0.00024
TAC 10e6 ($/year)	15				14.16				13.86			

CSC: column shell cost; CTC: column trays cost; CC_a: compressor cost; CC_b: condenser cost; RC: reboiler cost; SC: steam cost; CWC: cooling water cost; VC: vinasse cost; TAC_C: total annualized capital cost; TAO_C: total annualized operating cost; Stripping stage (columns A/A1/D); Rectification stage (columns BB1).

Table A.7. Economic basis and sizing of the different process configurations.

Column
$Diameter(D) = 0.01735x\left(MWx\dfrac{T}{P}\right)xV_{NT}$
$Height(H) = Nx2x\dfrac{1.2}{3.281}$
$Column\_shell\_\cos t = 17640x\,D^{1.066}\,x\,H^{0.802}$
$Tray\_\cos t = 229x\,D^{1.55}\,x\,N$
Condenser area
$C_A = \dfrac{Q_C}{U_C x \Delta T_C}$
Reboiler area
$R_A = \dfrac{Q_R}{U_R x \Delta T_R}$
$Total\_heat\_exchange\_\cos t = 7296x\,C_A^{0.65}\,x\,R_A^{0.65}$
Utility cost
Low pressure steam \$13.28/GJ
Payback period
3 years
Vinasse transport cost
\$2.7/m^3 of vinasse

T: temperature of column; P: pressure of column; MW: heavier component molecular weight; V_{NT}: maximum vapour flow rate (mol/s); D: diameter of column (m); H: height of column (m); C_A: condenser area (m^2); Q_C: condenser heat duty (m^2); U_C: thermal coefficient of condenser; R_A: reboiler area; Q_R: reboiler heat duty; U_R: heat transfer coefficient of reboiler (kW/K.m^2).

Table A.8 Comparison of the estimated TAC of each solvent used in the LLE process.

PARAMETER / SOLVENT		**Liquid-liquid extractor column (B4)**	
		dodecanol	**oleic acid**
Capital cost	CSC ($)	9490000	10400000
	CTC ($)	78193	111281
	CC ($)	0	0
	RC ($)	0	0
Operating cost	SC ($/year)	0	0
	CWC ($/year)	0	0
	Makeup ($/year)	125000000	1900000000
	VC ($/year)	0	0
TACC ($/year)		3189397.7	3503760.3
TAOC ($/year)		125000000	1900000000
TAC (\$/year) $1\mathrm{x}10^{6}$		**128.2**	**1903.5**

CSC: column shell cost; CTC: column trays cost; CC: condenser cost; RC: reboiler cost; SC: steam cost; CWC: cooling water cost; MAKEUP cost: cost associated to make up of fresh solvent VC: vinasse cost; TAC$_{\mathrm{C}}$: total annualized capital cost; TAO$_{\mathrm{C}}$: total annualized operating cost; TAC: total annual cost (TACC+TAOC).

Table A.9 Comparison of the estimated TAC of each solvent for the LLE simulated in this study.

PARAMETER / SOLVENT		**Distillation column (B6) – solvent recovery**	
		dodecanol	**oleic acid**
Capital cost	CSC ($)	546194	270973.5
	CTC ($)	30949	11170.4
	CC ($)	1811031	1330000
	RC ($)	1005197	1444320.7
Operating cost	SC ($/year)	6523250.9	11437413.4
	CWC ($/year)	141803	88567
	Makeup ($/year)	0	0
	VC ($/year)	1616895.7	1361606.5
TACC ($/year)		1131123.67	1018821.53
TAOC ($/year)		8281949.6	12887586.9
TAC (\$/year) $1\mathrm{x}10^{6}$		**9.41**	**13.91**

CSC: column shell cost; CTC: column trays cost; CC: condenser cost; RC: reboiler cost; SC: steam cost; CWC: cooling water cost; MAKEUP cost: cost associated to make up of fresh solvent VC: vinasse cost; TAC$_{\mathrm{C}}$: total annualized capital cost; TAO$_{\mathrm{C}}$: total annualized operating cost; TAC: total annual cost (TACC+TAOC).