

FEDERAL UNIVERSITY OF PARANA

BRUNA RICETTI MARGARIDA

ESTERIFICATION OF FATTY ACIDS ANALYSIS USING DIFFERENT CONTENTS OF  
WATER: SIMULATION AND ECONOMIC EVALUATION OF BIODIESEL PRODUCTION  
FROM WASTE OIL

CURITIBA

2021

BRUNA RICETTI MARGARIDA

ESTERIFICATION OF FATTY ACIDS ANALYSIS USING DIFFERENT CONTENTS OF  
WATER: SIMULATION AND ECONOMIC EVALUATION OF BIODIESEL PRODUCTION  
FROM WASTE OIL

Dissertação apresentada ao curso de Pós-Graduação em Engenharia Química, Setor de Tecnologia, Universidade Federal do Paraná, como requisito parcial à obtenção do título de Mestre em Engenharia Química.

Orientador: Prof. Dr. Luiz Fernando de Lima Luz Jr.

CURITIBA

2021

Catálogo na Fonte: Sistema de Bibliotecas, UFPR  
Biblioteca de Ciência e Tecnologia

M327e Margarida, Bruna Ricetti  
Esterification of fatty acids analysis using different contents of water: Simulation and economic evaluation of biodiesel production from waste oil [recurso eletrônico] / Bruna Ricetti Margarida. – Curitiba, 2021.

Dissertação - Universidade Federal do Paraná, Setor de Tecnologia, Programa de Pós-Graduação em Engenharia Química, 2021.  
Orientador: Luiz Fernando de Lima Luz Junior.

1. Biodiesel. 2. Ácidos graxos. 3. Esterificação. I. Universidade Federal do Paraná. II. Luz Junior, Luiz Fernando de Lima. III. Título.

CDD: 665.37

Bibliotecária: Vanusa Maciel CRB- 9/1928

## APPROVAL TERM

BRUNA RICETTI MARGARIDA

ESTERIFICATION OF FATTY ACIDS ANALYSIS USING DIFFERENT CONTENTS OF WATER: SIMULATION AND ECONOMIC EVALUATION OF BIODIESEL PRODUCTION FROM WASTE OIL

The dissertation presented in the Post-Graduate Program in Chemical Engineering, Technology Sector, Federal University of Paraná, as a partial requirement to obtain a Master's degree in Chemical Engineering.

Advisor: Prof. Dr. Luiz Fernando de Lima Luz Jr.  
Department of Chemical Engineering, UFPR

Curitiba, January 17<sup>th</sup>, 2021



MINISTÉRIO DA EDUCAÇÃO  
SETOR DE TECNOLOGIA  
UNIVERSIDADE FEDERAL DO PARANÁ  
PRÓ-REITORIA DE PESQUISA E PÓS-GRADUAÇÃO  
PROGRAMA DE PÓS-GRADUAÇÃO ENGENHARIA QUÍMICA  
- 40001016056P9

## TERMO DE APROVAÇÃO

Os membros da Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação em ENGENHARIA QUÍMICA da Universidade Federal do Paraná foram convocados para realizar a arguição da dissertação de Mestrado de **BRUNA RICETTI MARGARIDA** intitulada: **Esterification of fatty acids analysis using different contents of water: Simulation and economic evaluation of biodiesel production from waste oil**, sob orientação do Prof. Dr. LUIZ FERNANDO DE LIMA LUZ JUNIOR, que após terem inquirido a aluna e realizada a avaliação do trabalho, são de parecer pela sua APROVAÇÃO no rito de defesa. A outorga do título de mestre está sujeita à homologação pelo colegiado, ao atendimento de todas as indicações e correções solicitadas pela banca e ao pleno atendimento das demandas regimentais do Programa de Pós-Graduação.

CURITIBA, 28 de Janeiro de 2021.

Assinatura Eletrônica

28/01/2021 11:15:02.0

LUIZ FERNANDO DE LIMA LUZ JUNIOR

Presidente da Banca Examinadora (UNIVERSIDADE FEDERAL DO PARANÁ)

Assinatura Eletrônica

28/01/2021 11:15:17.0

ALEXANDRE FERREIRA SANTOS

Avaliador Interno (UNIVERSIDADE FEDERAL DO PARANÁ)

Assinatura Eletrônica

28/01/2021 12:16:40.0

MARIA JOSE JERONIMO DE SANTANA PONTE

Avaliador Externo (UNIVERSIDADE FEDERAL DO PARANÁ)

---

Rua Cel. Francisco Heráclito dos Santos, s/nº - CURITIBA - Paraná - Brasil

CEP 81531-980 - Tel: (41) 3361-3590 - E-mail: ppgeq@ufpr.br

Documento assinado eletronicamente de acordo com o disposto na legislação federal Decreto 8539 de 08 de outubro de 2015.

Gerado e autenticado pelo SIGA-UFPR, com a seguinte identificação única: 70834

Para autenticar este documento/assinatura, acesse <https://www.prppg.ufpr.br/siga/visitante/autenticacaoassinaturas.jsp>  
e insira o código 70834

## **ACKNOWLEDGMENTS**

In the first place, I want to thank God for giving me the strength to finish my Master's dissertation and the courage to keep me moving forward.

I would also like to thank my parents, João Luiz e Ivana Silvia, for always being by my side, supporting me, and believing in my choices.

Special thanks to my supervisor Prof. Luiz Fernando de Lima Luz Junior, for all the advice and guidance, and Prof. Fernando Pedersen Voll, for the great support.

To all the professors that helped me to reach this point in my life, giving me the knowledge and guidance necessary.

Also to the Separation Process Engineering Laboratory (LES) and the Federal University of Parana for the installations, and the Chemical Engineering Graduate Program for the opportunity.

To Luana Flores, Wanderson Giacomin, and to all the people who contributed to this and other works and helped me achieve results.

And to CAPES/CNPq for financial support.

Everything is possible. The impossible  
just takes longer.

(DAN BROWN.)

## RESUMO

A crescente demanda por biodiesel é altamente importante e necessária, uma vez que os combustíveis provindos do petróleo não são ambientalmente favoráveis, podem ter flutuações de preço e não são renováveis. Embora o preço do diesel no Brasil seja 14% mais barato que o preço médio mundial, ele ainda é mais caro que nos Estados Unidos, Bolívia e Rússia, por exemplo, alcançando apenas o 57º lugar no ranking de preço do diesel (Neder, 2019). Além disso, verificou-se que, recentemente, a gasolina vendida no Brasil era a segunda mais cara do mundo, onde o primeiro lugar pertencia ao Reino Unido (Fontes, 2018). Por esses motivos, os mercados que utilizam combustíveis renováveis estão sendo constantemente estudados e aprimorados para poder entrar no mercado de maneira competitiva. Observando a situação no Brasil, a maioria das indústrias produtoras de biodiesel está na região centro-oeste, que detém 39% da capacidade instalada do país, seguida pela região sul, com 38%. Levando em consideração as várias questões sobre sustentabilidade, meio ambiente e economia de combustível, a ênfase crescente no biodiesel é notória. Essa importância pode ser percebida pelos incentivos ao seu uso no diesel, como na aprovação pela ANP para aumentar de 11 para 12% a mistura de biodiesel no diesel a partir de março de 2020, e com a intenção de aumentar esse valor nos próximos anos. Com uma demanda constante por combustíveis alternativos e ecológicos, o biodiesel aparece como uma boa opção de uso. Embora o biodiesel seja obtido a partir de óleos vegetais ou gordura animal, outra fonte está se tornando muito promissora na indústria; o uso de óleo residual. Como essa nova fonte geralmente inclui uma quantidade considerável de ácidos graxos livres (AGLs), o processo de produção de biodiesel deve ser adaptado para atingir as especificações necessárias. Neste trabalho, diferentes condições de reação de esterificação, como tipo de óleo, temperatura (50 a 70°C), concentração de catalisador (0,33% a 0,66% em relação à massa reacional), razão etanol/água (7:3 a 9:1) e a razão etanol/ácido (1:1 a 12:1) foram variadas para analisar a melhor condição a ser definida e, com os dados, encontrar os parâmetros corretos para a cinética da reação. A equação regredida foi obtida utilizando todos os pontos experimentais, a exceção do conjunto com razão etanol/água de 7:3 e quatro experimentos com razão etanol/água de 9:1, sendo utilizadas posteriormente para validação dos parâmetros regredidos. Uma vez definida a equação da cinética, ela foi inserida na cinética de reação no Aspen Plus® e a simulação do processo foi construída. Portanto, o processo consiste na reação de esterificação e transesterificação, juntamente com o processo de purificação do biodiesel. Com o mesmo software, também foi possível analisar possíveis economias de energia adicionando trocadores de calor de integração energética em comum quando a razão etanol/água na primeira coluna de destilação para reciclo de etanol variasse entre 7:3, 8:2 e 9:1. Por fim, foi feita a análise econômica do processo completo e a melhor razão etanol/água para a corrente de reciclo e make-up, bem como o melhor tempo de residência do reator de esterificação para otimização do processo foram escolhidos. Considerando a produção de biodiesel desejada, a avaliação econômica pôde ser realizada e o tempo de retorno do investimento foi calculado.

**Palavras-chave:** Biodiesel, óleo ácido, ácidos graxos, esterificação e transesterificação, simulação de processo



## ABSTRACT

The increasing demand for biodiesel is highly important and necessary, as petroleum fuels are not environmentally friendly, may have price fluctuations, and are not renewable. Even though Brazil's diesel price is 14% cheaper than the world's average price, it is still more expensive than United States, Bolivia, and Russia, for example, achieving only 57<sup>th</sup> place in the ranking of diesel price (Neder, 2019). It was also found that recently, gasoline sold in Brazil was the second most expensive in the world, where the first place belonged to the United Kingdom (Fontes, 2018). For these reasons, markets using renewable fuels are being continually studied and refined to enter the market competitively. Looking at Brazil's situation, most biodiesel-producing industries are in the midwest region, which holds 39% of the country's installed capacity, followed by the southern region, with 38%. Regarding several questions about sustainability, environment, and fuel economy, biodiesel's growing emphasis is notorious. This importance can be seen through the incentives for its use in diesel, as it was approved by the ANP to increase from 11 to 12% the biodiesel blend in diesel from March 2020 and with the intention to increase that value in the upcoming years. With a constant demand for alternative, environmentally friendly fuels, biodiesel shows up as the right choice for use instead of the petroleum-based ones. Even though biodiesel is obtained from vegetable oils or animal fat, another source is becoming very promising in the industry; the use of waste oil. As this new source usually includes a considerable amount of free fatty acids (FFAs), biodiesel production process must be adapted to achieve the necessary specifications. In this present work, different esterification reaction conditions, as oil type, temperature (50°C to 70°C), catalyst concentration (0.33 %wt to 0.66 %wt of total reaction mass), ethanol/water ratio (7:3 to 9:1), and ethanol/acid ratio (1:1 to 12:1) were varied to analyze the best condition set and, with the data, find the correct parameters for the reaction kinetics. The equation was then regressed and all the experimental points were used except for the ethanol/water ratio of 7:3 and four experiments with an ethanol/water ratio of 9:1, as it was further used for validation of the regressed parameters. Once the kinetics equation was defined, it was inserted on Aspen Plus<sup>®</sup> reaction kinetics, and the process simulation was built. Therefore, the process consists of the esterification and transesterification reaction, along with the biodiesel purification process. With the same Software, it was also possible to analyze potential energy savings by adding heat exchangers in common when the ethanol/water ratio on the first ethanol recycling distillation column corresponded to 7:3, 8:2, and 9:1. At last, the full process economic analysis was made, and the best ethanol/water ratio for both the recycle and make-up streams, as well as the best esterification reactor residence time for process optimization, were chosen. Considering the desired biodiesel production, the economic evaluation could be fulfilled, and the payout time was calculated.

**Keywords:** Biodiesel, acid oil, fatty acids, esterification and transesterification, simulation design

## LIST OF FIGURES

FIGURE 1 - EVOLUTION OF BIODIESEL PRODUCTION (B100) IN BRAZIL – 2008-2017 .....	20
FIGURE 2 - BIODIESEL DEMAND FOR DIFFERENT SCENARIOS .....	21
FIGURE 3 – WORLDWIDE FEEDSTOCK USED IN BIODIESEL PRODUCTION IN 2016 .....	22
FIGURE 4 - FEEDSTOCK USED IN BRAZIL FOR BIODIESEL PRODUCTION IN (a) 2017 AND (b) 2018.....	22
FIGURE 5 - SCHEMATIC REPRESENTATION OF THE (a) ESTERIFICATION AND (b) TRANSESTERIFICATION PROCESS WITH A GENERIC ALCOHOL.....	24
FIGURE 6 – MATERIALS USED FOR THE ESTERIFICATION REACTION .....	32
FIGURE 7 – SCHEMATIC REPRESENTATION OF THE PARAMETERS VARIED IN THE ESTERIFICATION REACTION.....	34
FIGURE 8 - PARAMETERS VARIED FOR THE FACTORIAL DESIGN AND ANOVA ANALYSIS .....	35
FIGURE 9 – GENERAL ESTERIFICATION REACTION EQUATION USING ETHANOL .	41
FIGURE 10 – REACTION BEHAVIOR TO THE USE OF DIFFERENT FATTY ACIDS WITH ETHANOL/WATER AND ETHANOL/ACID RATIO OF 9:1, 60°C, AND 0.33% CATALYST CONCENTRATION RELATED TO THE TOTAL REACTION MASS .....	43
FIGURE 11 - REACTION BEHAVIOR TO THE USE OF DIFFERENT CATALYST CONCENTRATION AT 50°C, ETHANOL/WATER AND ETHANOL/ACID RATIO OF 9:1, AND TWO POINTS WITH A TEMPERATURE VARIATION (70°C) .....	44
FIGURE 12 - REACTION BEHAVIOR TO THE USE OF DIFFERENT ETHANOL/WATER RATIOS WITH ETHANOL/ACID RATIO OF 9:1, 0.33% CATALYST CONCENTRATION RELATED TO THE TOTAL REACTION MASS, AND 60°C.....	45
FIGURE 13 - REACTION BEHAVIOR TO THE USE OF DIFFERENT ETHANOL/ACID RATIO ETHANOL/WATER RATIO OF 8:2, 0.33% CATALYST CONCENTRATION, AND 70°C.....	46
FIGURE 14 - REACTION BEHAVIOR UNDER DIFFERENT TEMPERATURES WITH ETHANOL/WATER RATIO OF 8:2, ETHANOL/ACID RATIO OF 9:1, AND 0.33% CATALYST CONCENTRATION .....	47
FIGURE 15 - REACTION BEHAVIOR TO THE USE OF ACID OIL (MURAD, 2017) .....	48

FIGURE 16 – SYSTEM BEHAVIOR OBTAINED CONSIDERING THE REGRESSED EQUATION .....	50
FIGURE 17 – RESULTS COMPARING REGRESSION FROM PARAMETERS OBTAINED BY (a) MURAD (2017) AND (b) FROM THIS WORK WITH ANHYDROUS ETHANOL, 50°C, 0.33%WT CATALYST, 12:1 ETHANOL/ACID RATIO (RED), 9:1 RATIO (GREEN), 6:1 RATIO (BLUE), AND 1:1 RATIO (YELLOW) .....	55
FIGURE 18 – REGRESSION RESULT FOR (a) 9:1 ETHANOL/WATER AND ETHANOL/ACID RATIO, UNDER 50°C AND 0.66%WT CATALYST (BLUE), 0.425%WT (RED), 0.33%WT (GREEN), AND 70°C AND 0.66%WT (BLACK). 7:3 ETHANOL/WATER RATIO (b) 9:1 ETHANOL/ACID RATIO EXPERIMENT UNDER 60°C AND 0.33%WT CATALYST; (c) 6:1 ETHANOL/ACID RATIO EXPERIMENT UNDER 70°C AND 0.33%WT CATALYST .....	56
FIGURE 19 – REGRESSION RESULT FOR ACID OIL 40% (a) WITH 0.33%WT CATALYST, 50°C AND 6:1 ETHANOL/ACID RATIO (RED), 50°C AND 12:1 ETHANOL/ACID RATIO (BLUE), 60°C AND 12:1 ETHANOL/ACID RATIO (GREEN), AND 70°C AND 12:1 ETHANOL/ACID RATIO (BLACK). (b) 9:1 RATIO WITH 0.33%WT CATALYST AND 40°C (GREEN), 50°C (RED), 60°C (BLACK), AND 70°C (BLUE).....	57
FIGURE 20 – (a) ANHYDROUS ETHANOL, 0.33%WT CATALYST, 50°C, AND ETHANOL/ACID RATIO OF 12:1 (BLUE), 9:1 (BLACK), 6:1 (RED), AND 1:1 (GREEN) (MURAD, 2017). 8:2 ETHANOL/WATER RATIO: (b) 9:1 ETHANOL/ACID RATIO, 0.33% CATALYST AND UNDER 70°C (RED) AND 60°C (BLACK); (c) 12:1 (BLACK), 9:1 (BLUE), AND 1:1 (RED) ETHANOL/ACID RATIO, 0.33% CATALYST, AND 70°C .....	58
FIGURE 21 – (a) NORMAL PROBABILITY PLOT CONSIDERING THE REGRESSED KINETICS AND THE EXPERIMENTAL DATA FROM THIS WORK (RED), AND MURAD'S (2017) (GREEN). (b) HISTOGRAM COMPARING THE RESIDUES FROM THIS WORK'S DATA AND (c) FROM MURAD'S (2017).....	59
FIGURE 22 – BIODIESEL PRODUCTION PROCESS DESIGN .....	61

## LIST OF TABLES

TABLE 1 – ADVANTAGES AND DISADVANTAGES OF CATALYST TYPES FOR TRANSESTERIFICATION REACTIONS .....	28
TABLE 2 – ETHANOL AND METHANOL PROPERTIES .....	29
TABLE 3 – FFA COMPOSITION (%WT/WT) FOR OILS USED IN BIODIESEL PRODUCTION PROCESSES .....	31
TABLE 4 - PLACKETT-BURMAN MATRIX.....	38
TABLE 5 - BASE TABLE FOR ANOVA CALCULATION (PÓ, 2014).....	40
TABLE 6 – EXPERIMENTAL RESULTS TO VERIFY ACID VALUE EQUATIONS .....	49
TABLE 7 – PARAMETER VALUES USED TO DESCRIBE ESTERIFICATION REACTION BEHAVIOR .....	49
TABLE 8 – ANOVA RESULTS FOR THE VARIABLES TESTED .....	51
TABLE 9 – PARAMETERS VALUES FROM THE REGRESSION .....	54
TABLE 10 – REGRESSED PARAMETERS BY MURAD (2017) .....	54
TABLE 11 – ETHANOL RECYCLING COLUMN RESULTS FOR DIFFERENT ETHANOL/WATER RATIOS.....	60
TABLE 12 – TRANSESTERIFICATION REACTION PARAMETERS FOR EACH STEP OF THE REACTION .....	63
TABLE 13 – SIMULATION AND STANDARD SPECIFICATIONS VALUES FOR BIODIESEL PROPERTIES.....	64
TABLE 14 – LIST OF PROPERTIES FROM EACH ENERGY-SAVING SCENARIO .....	69
TABLE 15 – PAYOUT PERIOD FOR DIFFERENT ETHANOL/WATER RATIOS IN THE RECYCLING STREAM AND MAKE-UP FOR SCENARIO 1* .....	72
TABLE 16 - PAYOUT PERIOD FOR DIFFERENT RECYCLING STREAM AND MAKE-UP ETHANOL/WATER RATIOS FOR SCENARIO 2 AND 3*.....	73
TABLE 17 – LIST OF PRICES OF THE COMPOUNDS AND UTILITIES USED IN THE PROCESS .....	74
TABLE 18 – SUMMARY OF SOME BIODIESEL PRODUCTION COSTS AND REVENUE .....	75

## LIST OF ABBREVIATIONS

AGL – Ácido graxo livre

ANOVA – Analysis of variance

ANP – Agência Nacional do Petróleo, Gás Natural e Biocombustíveis

APROBIO – Associação dos Produtores de Biocombustíveis do Brasil

CSTR – Continuous stirred tank reactor

DAG – Diglyceride

ELECNRTL – Electrolyte non-random two-liquid model

EO – Ethyl oleate (ester)

ET – Ethanol

FAEE – Fatty acid ethyl ester

FAME – Fatty acid methyl ester

FFA – Free fatty acid

FFE – Free fatty ester

GLY - Glycerol

MAG – Monoglyceride

NRTL – Non-random two-liquid model

PNPB – Programa Nacional de Produção e Uso do Biodiesel

TAG – Triglyceride

UCO – Used cooking oil

UNIFAC-Dortmund – Modified Universal quasi-chemical Functional-group Activity Coefficients (Dortmund)

## LIST OF SYMBOLS

- a – Equation constant
- A – Pre-exponential factor
- $C$  – Component concentration
- C – Catalyst concentration
- DF – Degrees of freedom
- E – Activation energy
- F – Ethanol to free fatty acid ratio
- $k$  – Kinetic constant
- k – Number of different condition values
- M – Molarity
- m – Mass quantity
- MM – Molar mass
- MQ – Mean square sum
- n – Population number
- N – Standardized molar concentration
- r – Reaction rate
- R – Ideal gas constant
- SQ – Square sum
- T – Temperature
- $v$  – Molar quantity
- V – Volume
- W – Ethanol to water ratio
- x – Molar fraction
- $\chi$  – Experimental conversion
- $y_i$  – Conversion in the  $i$ th point
- %wt – Weight percentage

## TABLE OF CONTENTS

<b>1</b>	<b>INTRODUCTION.....</b>	<b>16</b>
1.1	OBJECTIVES.....	17
1.1.1	Overall objective.....	17
1.1.2	Specific objectives.....	17
1.2	STATE OF ART.....	17
<b>2</b>	<b>LITERATURE REVIEW.....</b>	<b>19</b>
2.1	BIODIESEL.....	19
2.2	BIODIESEL PRODUCTION ROUTES.....	24
2.2.1	Esterification and Transesterification.....	24
2.2.2	Transesterification using Heterogeneous catalysts.....	25
2.2.3	Enzymatic transesterification.....	25
2.2.4	Homogeneous acid esterification followed by base transesterification.....	26
2.3	RAW MATERIALS.....	29
2.3.1	Alcohol.....	29
2.3.2	Oil.....	30
<b>3</b>	<b>MATERIALS AND METHODS.....</b>	<b>32</b>
3.1	MATERIALS.....	32
3.2	METHODOLOGY.....	34
3.2.1	Reaction.....	34
3.2.2	Simulation.....	36
3.3	BASE EQUATIONS AND CALCULATIONS.....	37
3.4	KINETICS MODELLING.....	41
<b>4</b>	<b>RESULTS AND DISCUSSION.....</b>	<b>43</b>
4.1	REACTION RESULTS.....	43
4.1.1	Fatty acid type influence.....	43
4.1.2	Catalyst concentration influence.....	44
4.1.3	Ethanol/water ratio influence.....	45
4.1.4	Ethanol/acid ratio influence.....	46
4.1.5	Temperature influence.....	47
4.1.6	Influence of acid oil use.....	48
4.1.7	Final Acid Value.....	48
4.1.8	Factorial design and ANOVA.....	49

4.2	SIMULATION RESULTS.....	52
4.2.1	Scilab™ analysis .....	52
4.2.2	Aspen Plus® analysis .....	59
4.2.2.1	Ethanol recycling.....	60
4.2.2.2	Thermodynamic models .....	60
4.2.2.3	Simulation design: Base case description .....	61
4.2.2.4	Main equipment conditions.....	65
4.2.2.5	Energy analysis.....	68
4.2.2.6	Economic analysis .....	71
<b>5</b>	<b>CONCLUSION .....</b>	<b>77</b>
	<b>SCIENTIFIC PRODUCTIONS.....</b>	<b>78</b>
	<b>REFERENCES.....</b>	<b>79</b>
	<b>APPENDIX I.....</b>	<b>87</b>



## 1 INTRODUCTION

Considering fuels as gasoline and diesel are derived from petroleum, there are uncertainties about market fluctuations and resource availability. Also, with today's constant and strict environmental control, it is necessary to use environmentally friendly fuel to maintain economic stabilization and have a less hazardous product.

The necessity of fuel production expansion is more than expected for the next years in Brazil, as a 35% growth in diesel B demand and 15% of biodiesel addition on diesel is foreseen until 2026 (ANP, 2018).

Biodiesel can be obtained from vegetable oil or animal fat, which helps this product's market stability (Krawczyk, 1996). Besides, in biodiesel production, it is used short-chain alcohols, such as ethanol, a widely produced alcohol in Brazil. Regarding the final product, the alcohol choice has a considerable influence on esters characteristics. For example, the fatty acid ethyl esters have higher stability toward oxidation, better lubricity, higher heat capacity and cetane number, and lower cloud and pour point than fatty acid methyl esters (Stamenković et al., 2011).

Even with biodiesel production from vegetable oil being widely used, the possible use of residual oils for manufacture could benefit its market even more, with no need for edible raw materials for biodiesel obtainment and promoting the use of something, in principle, disposable.

Several operations for the production of biodiesel have been and are being developed, but the process using esterification followed by transesterification has the advantage of obtaining satisfactory results even in milder conditions. In this process, due to the possibility of having soap production in the transesterification part, the acid from the residual oil reacts with alcohol to obtain long-chain esters through esterification. Then the oil reacts with the alcohol to produce biodiesel.

The esterification reaction study with the modeling from the experimental data obtained allows predicting the reaction's behavior. With the necessary data available, it is possible to simulate the process. This simulation will allow better visualization of the process, such as the operating conditions, optimization points, and economic evaluation, verifying the product's final price, and identifying possible ways to reduce and optimize costs in the unit.

## 1.1 OBJECTIVES

### 1.1.1 Overall objective

The main objective of this work is to propose a suitable biodiesel production process from acid waste oil by combining esterification and transesterification reactions, analyze possible optimization points and energy savings, and evaluate the viability of the process economically.

### 1.1.2 Specific objectives

- 1) Gather experimental data for the esterification reaction on different conditions;
- 2) Choose the best conditions for esterification reaction;
- 3) Acquire the esterification reaction kinetics;
- 4) Verify most economical ethanol/water ratios;
- 5) Analyze optimum esterification and transesterification reaction time;
- 6) Study the possibility to use a reactive distillation column after esterification reactor;
- 7) Identify energy-saving points and include energy-saving heat exchangers;
- 8) Make an economic evaluation of the full biodiesel production process.

## 1.2 STATE OF ART

Concerning the available data in the literature, it is unusual to find studies using homogenous esterification using ethanol with high water content (above 10%mol). Even though some studies (Murad, 2017) verified the influence of water presence in ethanol for the esterification reaction, the tests were made only with anhydrous ethanol. Other works (Aranda et al., 2009) also reported the influence of water presence on the heterogeneous esterification reaction with methanol (4%wt of water), the most commonly used alcohol for esterification reactions.

It is possible to mention other studies that were developed with higher water content (10%wt or 7.8:2.2 ethanol to water molar ratio), but using supercritical ethanol, which was verified that, opposing to homogenous catalyzed reaction, water presence actually promotes the conversion to esters and decreases the degree of decomposition (Silva et al., 2012).

Esterification reaction kinetics with homogeneous acid catalyst was also studied considering water content from 0 to 20%v/v (25%wt) and ethanol, but with acrylic acid. The ester formed is not used in the biodiesel industry; instead, ethyl acrylate can be used as a reactive building block to produce coatings and inks, adhesives, sealants, textiles, plastics, and elastomers (Jyoti et al., 2016).

Therefore, the study of the esterification reaction of FFA in the biodiesel industry considering higher contents of water is still lacking. Both the visualization of water content influence on the reaction and the kinetics regression considering the range studied are essential to evaluate the possibility of using ethanol with higher water content from a sub-product or a recycling stream.

Besides the esterification reaction kinetics study, the use of a simulation tool to build a biodiesel production process using acid oil and hydrous ethanol, and making energy and economic analysis was a gap to be fulfilled.

As methanol is the most common alcohol used for the biodiesel production process due to its attractive price, most available research in the literature considers using methanol, instead of ethanol, in their studies. One of these researches (Vinay et al., 2016) studied biodiesel production from sesame oil, also using the Aspen Plus® simulation tool, and an economic analysis was made from the process built. Another important work (MYINT, 2007) was developed considering energy integration and economic analysis, but the raw materials used were methanol and vegetable oil with low FFA content (0.05%).

Filtering by the use of ethanol in the simulation, the number of search results dramatically decrease. Some of these studies use different methodologies to produce biodiesel (Machado et al., 2013). Others focus on a specific part of the process (esterification) for a detailed simulation (Murad, 2017). There are also works with the biodiesel process project simulated (Margarida and Luz Jr., 2018). However, most of these studies lack energy integration and economic analysis, which are of great importance in a project.

Therefore, the production of a research enabling the connection of not only laboratory experiments and kinetics regression, but also the simulation process and optimization construction, along with economic evaluation, is of great importance in the biodiesel industry and future studies.

## 2 LITERATURE REVIEW

### 2.1 BIODIESEL

Biodiesel can be considered a renewable fuel obtained through a transesterification process, which converts oils and fats into long-chain esters and glycerol through the reaction with an alcohol, usually methanol or ethanol (ANP, 2019). The set of esters formed is marketed as biodiesel after purification processes.

Demand and research for biofuels worldwide were most evident after the 1973 oil crisis. Although there were already studies on biodiesel in Brazil at that time, its importance was better established after the creation of the National Biodiesel Production Program (PNPB) in 2004 (ACARRINI, 2014).

The importance of biodiesel can be seen in the incentives for its use in diesel, as determined by Law N<sup>o</sup>. 13.263/2016, which provides for the biodiesel to diesel addition percentage commercialized in national territory, in which the minimum addition of 10% by volume of biodiesel was authorized by 2019. Even though the law had provided a 10% increase by March 2019, in December 2017, it was decreed that this increase in blending percentage should be anticipated to early March 2018. With that, the managing director of the Brazilian Biodiesel Producers Association (APROBIO), Julio Cesar Minelli, presented a proposal to increase biodiesel blends in diesel to 11% in 2019. Minelli also proposed a unit percentage increase each year until the use of B15 after 5 years (APROBIO, 2018).

The international scenario also demonstrates the increasing importance of biodiesel use, as in the United States, where diesel blends with 20% biodiesel (B20) are used in trucks and buses. Even though diesel blends with high percentages of biodiesel become more sensitive to cold weather, other measures are taken, as the addition of anti-freeze substances (U.S. Energy Information Administration (EIA), 2019).

It is already known that the increase of biodiesel in diesel blends can have a considerable improvement in the environment. If there was the use of B20 in the urban bus fleet in the 40 Brazilian cities with more than 500,000 inhabitants, for example, it could reduce CO<sub>2</sub> emissions by up to 70%, meaning the reduction of 18 tons/year CO<sub>2</sub>, equivalent to planting 132 new trees per year (RENOVABIO, 2018).

With incentives for biodiesel production, the market response was evidenced by the considerable increase in its production over the years. This behavior can be observed in FIGURE 1.

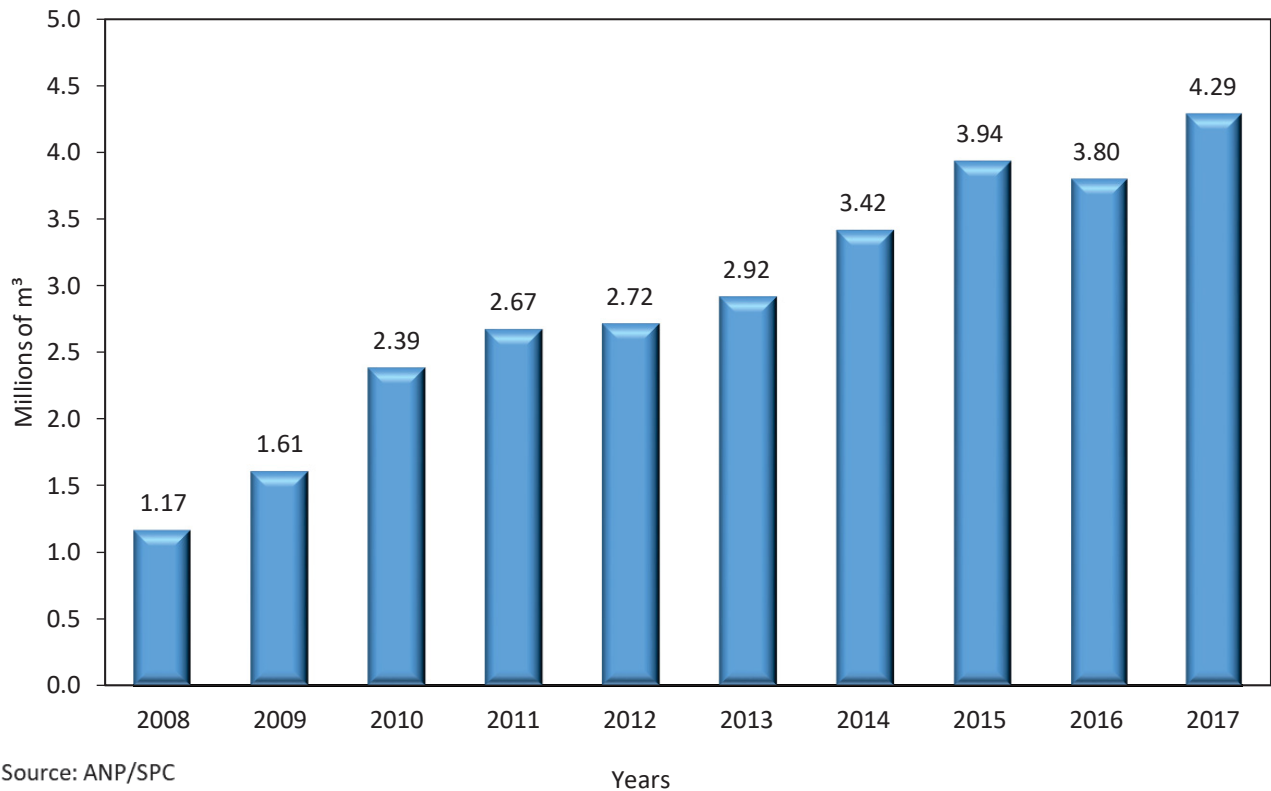
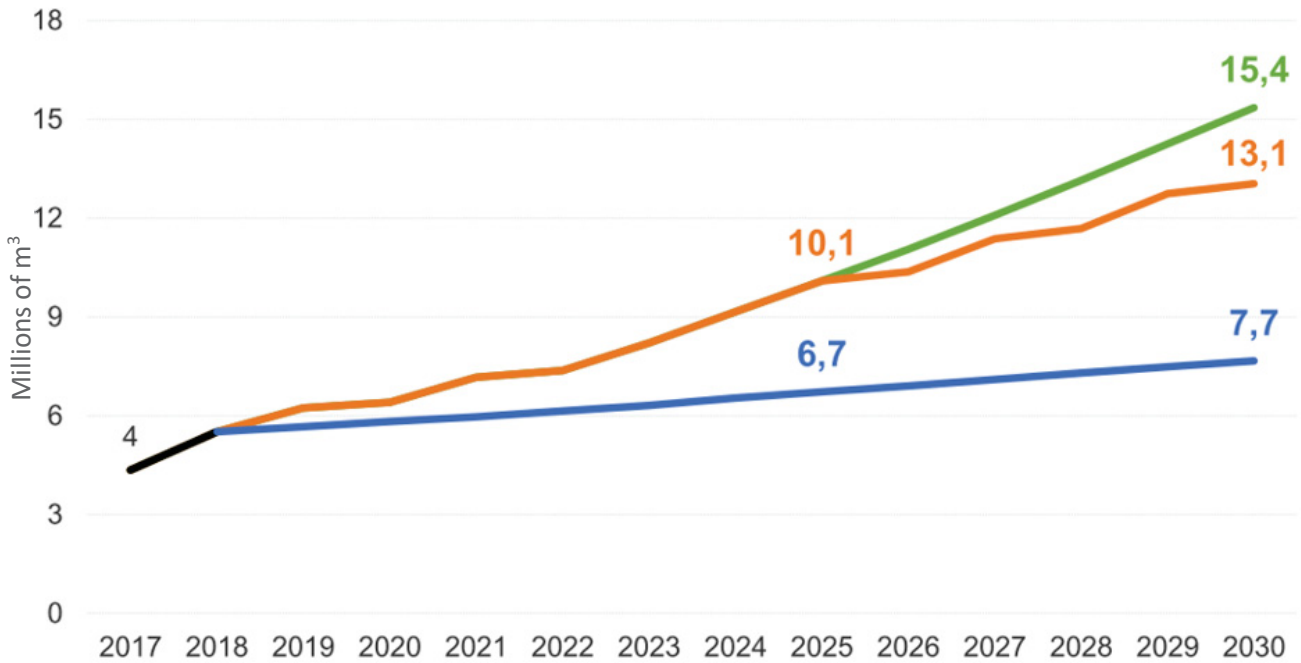


FIGURE 1 - EVOLUTION OF BIODIESEL PRODUCTION (B100) IN BRAZIL – 2008-2017

Besides the actual values shown in FIGURE 1, some projections considering possible biodiesel addition in diesel blend scenarios were studied, as shown in FIGURE 2. The first prediction (blue) is already outdated as it considers a 10% addition, and a 12% biodiesel addition was already approved in 2020. Either way, it is a useful comparison data to be considered on evaluation. The other two scenarios consider a 17% (orange) and 20% (green) addition, respectively, into diesel until 2030.

In FIGURE 2, it is possible to see the comparison between these three scenarios. The blue line represents the first scenario with a 10% addition, which would increase biodiesel demand by about 4.4% per year. The orange line represents the second scenario with a 17% addition, increasing biodiesel demand by around 8.8% each year. Finally, the green line represents the last scenario with 20% addition, corresponding to an increase in biodiesel demand of 10.2% per year.



Fonte: EPE

FIGURE 2 - BIODIESEL DEMAND FOR DIFFERENT SCENARIOS

This increase in biodiesel demand is significant and increasingly necessary as petroleum fuels are not environmentally friendly, may have price fluctuations, and are not renewable. In addition, it was found that currently, gasoline sold in Brazil is the second most expensive in the world, surpassed only by the United Kingdom (Fontes, 2018). For these reasons, markets using renewable fuels are continually being studied and refined to enter the market competitively.

Looking at Brazil's situation, most biodiesel-producing industries are in the midwest region, which holds 39% of the country's installed capacity, followed by the southern region, with 38% (DBio, 2017).

Although biodiesel is produced worldwide, each country uses different oil/fat sources, depending on its production and necessities. In 2016, worldwide biodiesel production was 34.08 million tonnes, with about 10% of Brazil's participation in this value. Considering the world's feedstock used in biodiesel production, as presented in FIGURE 3, it is possible to see that, mainly, vegetable oils are used as raw material, even though the participation of animal fats and used cooking oil (UCO) are also considered (UFOP, 2017).

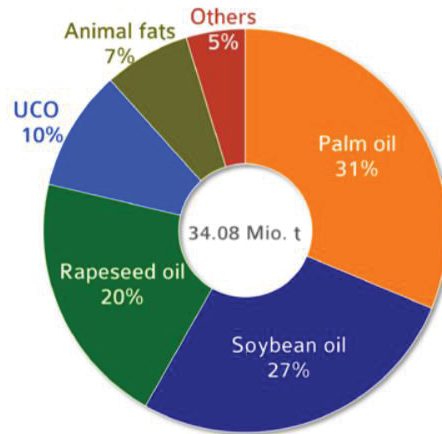
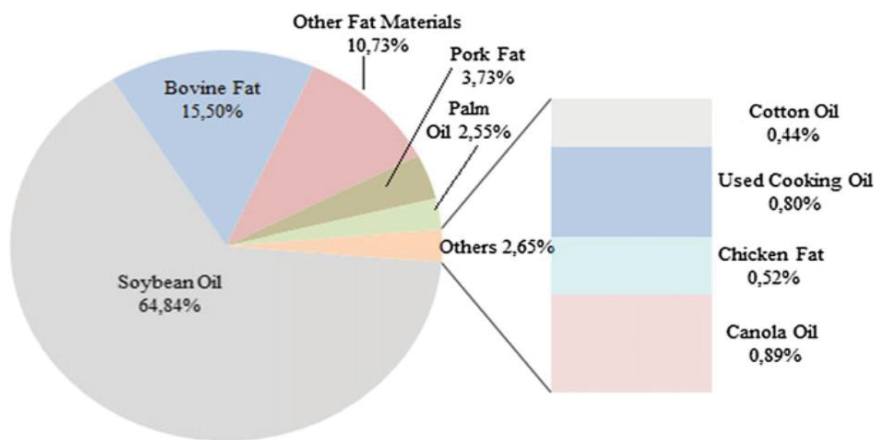
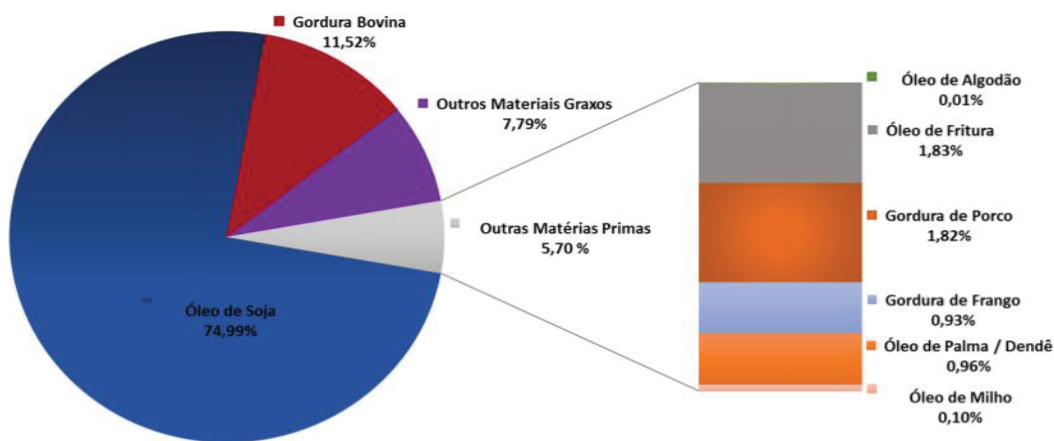


FIGURE 3 – WORLDWIDE FEEDSTOCK USED IN BIODIESEL PRODUCTION IN 2016

Comparing Brazil’s feedstock used in biodiesel production in 2017 and 2018 as presented in FIGURE 4 ((a)Martins, Fernández and Camara, 2018; (b) ANP, 2018), it is possible to analyze the difference in the raw materials used. Even though soybean oil is still ahead, the use of some animal fats and used cooking oil is rising. By looking at the used cooking oil values, it increased from 0.80% in 2017 to 1.83% in 2018.



(a)



(b)

FIGURE 4 - FEEDSTOCK USED IN BRAZIL FOR BIODIESEL PRODUCTION IN (a) 2017 AND (b) 2018

Another important point is that despite that soybean oil is the most used raw material for biodiesel production, it is not a rule in all Brazil's regions. In the southeast, only 29.8% of the production uses soy oil, while beef tallow represents 55.4%. Similar behavior is observed in the north and northeast regions, where the latest has almost equal participation of soy oil (56.4%) and beef tallow (43.5%). The first one has almost no soy oil participation in biodiesel production, being beef tallow (33%), and other fatty materials (67%), the main contributors for the statistics (ANP, 2016).

Therefore, it can be seen that for different regions, there is a demand for different sources of raw material, resulting in a variety of biodiesel compositions and different processes to achieve the product within specification.

Given this progressive increase in the use of biodiesel in diesel and several possible feedstock materials for its production, it can be considered that more extensive studies to obtain biodiesel at lower costs is of great interest to industries in the field.



## 2.2 BIODIESEL PRODUCTION ROUTES

### 2.2.1 Esterification and Transesterification

The esterification reaction consists of an ester production by reacting a carboxylic acid with an alcohol in the proportion of 1:1. In contrast, the transesterification reaction consists of esters and glycerol production by reacting a triglyceride with an alcohol in the proportion of 1:3 (West et al., 2008). The catalyst will act by previously reacting with the alcohol, forming alkoxides, which will later react with the glycerides. In this reaction, triglyceride is transformed into diglyceride, monoglyceride, and finally, glycerol. Both general reactions are represented in FIGURE 5.

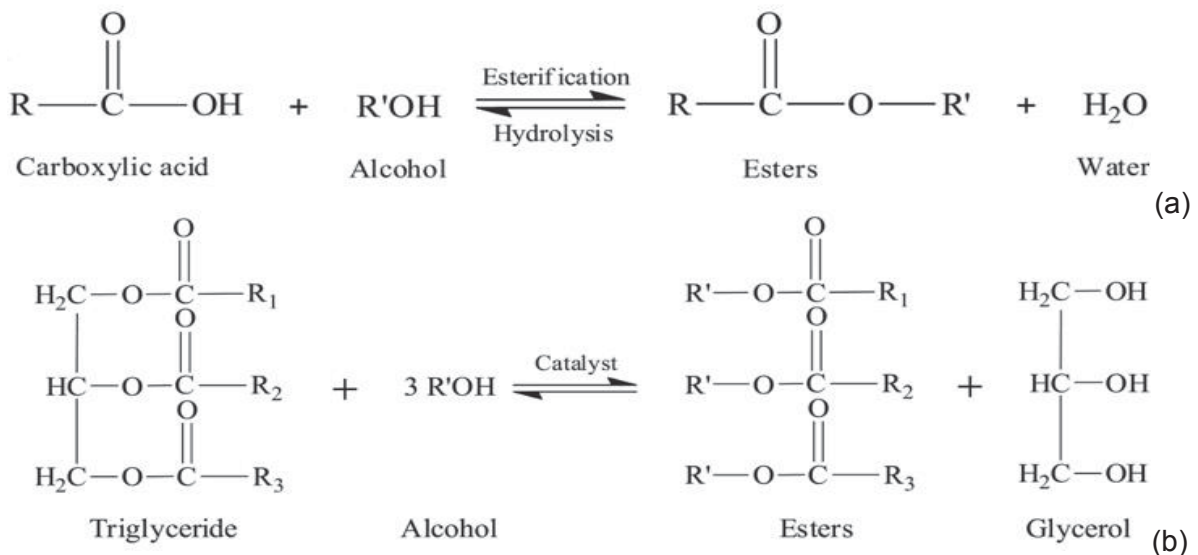


FIGURE 5 - SCHEMATIC REPRESENTATION OF THE (a) ESTERIFICATION AND (b) TRANSESTERIFICATION PROCESS WITH A GENERIC ALCOHOL

The chosen alcohol is of great importance in the transesterification reaction since it will influence the biodiesel properties obtained. Although both long and short carbonic chains could be used to synthesize biodiesel, it has been proven that with the use of long-chain carbon alcohols, less conversion is achieved for the same reaction time (Filho, 2010). In general, methanol is widely used because it is cheaper, reactive, and has considerably less water than ethanol. However, since methanol is generally obtained from petrochemical materials, such as methane, derived from natural gas, there is a discussion about the limitations involving environmental conditions and renewable materials for alcohol production (Khirsariya and Mewada, 2013).

Analyzing Brazil's situation, where there is a high ethanol production, this one's price becomes competitive relative to methanol. Considering the environmental factor, ethanol is considerably less toxic than methanol and can be obtained by processing renewable materials (Geris et al., 2007). Therefore, for a country with high ethanol production, the use of this alcohol is economically favorable and environmentally friendly.

### 2.2.2 Transesterification using Heterogeneous catalysts

In general, catalysts can be divided into two groups (Helwani et al., 2009); acid catalysts, which can be used in both esterification and transesterification reactions (Di Serio et al., 2008), and basic catalysts, which are not suitable for catalyzing esterification reactions, but require less of them for transesterification reactions (Ramos et al., 2017).

The process using heterogeneous catalysts has some advantages over homogeneous transesterification. It can reduce biodiesel purification steps, facilitate catalyst reuse, and do not form soap (Vicente et al., 1998), and can be easily separated, which reduces process costs (Choudary et al., 2000). Such catalysts may also be modified to be more resistant to acid present in the feedstock or to water formed during the reaction (Ramos et al., 2017).

Although apparently the process using heterogeneous catalysts is better, one should keep in mind that the transesterification reaction along this route is considerably slower (Ramos et al., 2017), requires more severe reaction conditions, and there may be a rapid loss of activity regarding the transesterification catalyst (Schuchardt et al., 1996), leading to high costs. Another vital factor to consider for heterogeneous catalysts is the mass transfer, an essential factor for conversion (Musa, 2016).

### 2.2.3 Enzymatic transesterification

The use of enzymatic catalysts for biodiesel synthesis is growing, especially lipases, which can catalyze, with high selectivity, esterification, interesterification, acidolysis, aminolysis, and alkolysis reactions under organic conditions (Sharma and Kanwar, 2014). Its advantage is that it requires the reaction to take place at warmer temperatures (30 - 40°C), glycerol can be easily recovered (Macedo and Macedo, 2004), and it is possible to have a full conversion of the fatty acid present in oils to ethyl esters (Meher et al., 2006). Such catalysts also have high specificity and fewer reaction steps (Pandey et al., 1999).

With such technology, there is no need for the oil to be free of moisture or free fatty acids (Ramos et al., 2017), reducing raw material costs.

Although the use of lipases or other types of enzymes for the biodiesel synthesis process has significant advantages, there are still many limitations regarding their cost and availability, making their use in large-scale processes difficult (Melo et al., 2016). Another important detail is the conversion time, which is much higher than other processes (from 48 to 72 hours) (Schuchardt et al., 1998).

#### 2.2.4 Homogeneous acid esterification followed by base transesterification

For proper operation, the catalyst materials need to be suitable, and the raw material needs to be adequately analyzed in order to choose the most suitable process, or to adapt the same process. As mentioned earlier, oils with high acidity tend to form soap during the transesterification reaction using basic catalysts, compromising conversion and purity, among other vital aspects. A good alternative for obtaining biodiesel from acid oils is using an earlier step to remove some of this acidity. The method used for this is acid esterification.

Acid esterification transforms fatty acids into esters, reducing the oil's acidity and enabling the basic transesterification step without high soap yields. A procedure using transesterification in a basic medium was performed by Machado, 2013.

In the experiment, 1.5% KOH base catalyst concentration was used, with a 6:1 ethanol:oil molar ratio, 50°C temperature, and 30 minutes reaction time, under stirring. The formed product was separated by decantation using a funnel, resulting in a phase rich in glycerol and one rich in esters.

Transesterification can be performed in both basic and acid medium. However, the second option is not so recommended because it requires more energetic conditions, where it is common to use temperatures near the boiling point of acid, besides having high reaction time, and alcohol:oil ratios greater than 30:1 (Ramos et al., 2017).

As mentioned above, the most common biodiesel synthesis process is through homogeneous catalysis using a base, which has the advantage of being able to operate under milder conditions. At ambient pressure, it is possible to conduct such a reaction at temperatures close to 40°C (Ramos et al., 2017), and it should be borne in mind that at elevated temperatures, undesirable reactions may be increased or formed.

One of the problems caused by using a basic catalyst in the transesterification process is soap formation, especially in oils with a higher acidity than recommended. To do

so, an alternative would be to add excess NaOH. However, for products with higher acidity (>3%wt) and high content of water (with the second one being more critical to the process than FFA content), an alternative would be to perform the esterification reaction in an acid medium followed by transesterification in an alkaline medium (Ribeiro et al., 2011; Wang, 2008).

It is also common to use an excess of alcohol to facilitate the reaction, but usually at maximum alcohol:oil ratios of 12:1, as for higher ratios, the separation of the formed glycerol is difficult (Musa, 2016).

Besides, other studies (Tavares, 2017) using high temperatures (>300°C) and high pressures (15MPa) also obtained satisfactory results with conversions higher than 96% on the esterification reaction.

Therefore, for very acid oils, when using acid esterification followed by basic transesterification, the reaction speed is exceptionally beneficial, and the process conditions are mild.

As it was possible to see, there are various esterification/transesterification routes to produce biodiesel. Furthermore, the use of different catalysts can influence both the reaction conversion and conditions to achieve the desired results. TABLE 1 summarizes some of the main catalyst types used in the biodiesel production processes, also considering each one's advantages and disadvantages.

TABLE 1 – ADVANTAGES AND DISADVANTAGES OF CATALYST TYPES FOR TRANSESTERIFICATION REACTIONS

	<b>Advantages</b>	<b>Disadvantages</b>
<b>Homogeneous base catalyst</b>	<ul style="list-style-type: none"> <li>• can catalyze reaction at lower temperatures and atmospheric pressure</li> <li>• high conversion can be achieved in a minimal time<sup>1</sup></li> <li>• widely available and economical<sup>2</sup></li> </ul>	<ul style="list-style-type: none"> <li>• limited only for refined vegetable oil with less<sup>3</sup> than 0.5%wt FFA or acid value less<sup>4</sup> than 1 mg KOH/g</li> </ul>
<b>Homogeneous acid catalyst</b>	<ul style="list-style-type: none"> <li>• insensitive to the presence of FFA<sup>5</sup></li> <li>• can simultaneously catalyze esterification and transesterification reactions<sup>6</sup></li> <li>• more efficient when the amount of FFA in the oil exceeds 1%wt<sup>1</sup></li> </ul>	<ul style="list-style-type: none"> <li>• slower reaction rate</li> <li>• needs high reaction temperature</li> <li>• requires high alcohol to oil molar ratio</li> <li>• serious corrosion-related and environmental problem<sup>5</sup></li> </ul>
<b>Heterogeneous base catalyst</b>	<ul style="list-style-type: none"> <li>• high reaction rate</li> <li>• easy separation, regeneration, and recycling of the catalyst from the reaction medium</li> <li>• lower product contamination level<sup>8</sup></li> </ul>	<ul style="list-style-type: none"> <li>• sensitive to FFA in oil/fat<sup>7</sup></li> <li>• water affects the biodiesel yield</li> <li>• susceptible to poisoning</li> <li>• mass transfer limitations</li> </ul>
<b>Heterogeneous acid catalyst</b>	<ul style="list-style-type: none"> <li>• the same as for heterogeneous base catalyst</li> <li>• they are insensitive to FFA content</li> <li>• esterification and transesterification occurs simultaneously<sup>5</sup></li> <li>• reduce corrosion problem, even with the presence of acid species<sup>9</sup></li> </ul>	<ul style="list-style-type: none"> <li>• slow reaction rate</li> <li>• possible undesirable side reactions<sup>10</sup></li> <li>• susceptible to poisoning</li> <li>• mas transfer limitations</li> </ul>
<b>Homogeneous acid-catalyzed esterification followed by base-catalyzed transesterification</b>	<ul style="list-style-type: none"> <li>• combines the advantages of homogeneous base-catalyzed transesterification with the possibility to use oils with higher FFA content</li> </ul>	<ul style="list-style-type: none"> <li>• requires extra separation steps</li> <li>• use of extra catalyst for neutralization<sup>10</sup></li> </ul>
<b>Enzymatic catalyst</b>	<ul style="list-style-type: none"> <li>• do not generate by-products</li> <li>• easy recovery of product</li> <li>• mild reaction conditions</li> <li>• insensitive to high FFA presence</li> <li>• can be reused<sup>5</sup></li> </ul>	<ul style="list-style-type: none"> <li>• high enzyme cost</li> <li>• slow reaction rate</li> <li>• enzyme deactivation<sup>11</sup></li> </ul>
<sup>1</sup> (Loterio et al., 2005)	<sup>5</sup> (Kulkarni and Dalai, 2006)	<sup>9</sup> (Suarez et al., 2007)
<sup>2</sup> (Zhang et al., 2003)	<sup>6</sup> (Jacobson et al., 2008)	<sup>10</sup> (Lam et al., 2010)
<sup>3</sup> (Wang et al., 2006)	<sup>7</sup> (Abdurakhman et al., 2017)	<sup>11</sup> (Bajaj et al., 2010)
<sup>4</sup> (Felizardo et al., 2006)	<sup>8</sup> (Wilson and Clark, 2000)	

## 2.3 RAW MATERIALS

### 2.3.1 Alcohol

One of the crucial choices considering biodiesel production is the alcohol used for both esterification (if necessary) and transesterification reactions. Even though methanol is commonly used in the biodiesel industry, Brazil's ethanol production makes it competitive comparing to methanol.

In fact, long-chain alcohols could also be used, but as it was proved that short-chain alcohols increase the reaction conversion, methanol and ethanol are usually preferred.

Some properties concerning these two alcohols can be seen in TABLE 2.

TABLE 2 – ETHANOL AND METHANOL PROPERTIES

Property	Ethanol	Methanol
<b>Molecular mass (g/mol)</b>	46.07	32.04
<b>Density at 20°C (kg/m<sup>3</sup>)</b>	789	792
<b>Vapor pressure (kPa, 20°C)</b>	5.95	13.02
<b>Melting Point (°C)</b>	-115	-97.6
<b>Boiling Point (°C)</b>	78.4	64.7

Source: Yusoff et al. (2014)

As it can be seen, methanol's boiling point is much lower than ethanol's, indicating more considerable attention when working with the first one, as higher temperatures improve the reaction speed, but may increase the raw material loss due to vaporization.

These two alcohols properties differ, but their impact on the reaction and environment is considerable. Concerning methanol, for example, its price is lower than ethanol's, although ethanol's price in Brazil is more competitive. Methanol is also more reactive, the process using this alcohol demands less energy (especially steam), and its equipment volume is usually 25% lower than the ones used in the ethanol route. All these methanol advantages come with the price of being much more toxic and with higher fire risks, as it is more volatile, and its flame is invisible (Coelho, 2011). Even though methanol can be obtained from the hydrogenation of hydrocarbons, natural gas, or biomass, still nowadays, it is mainly produced from petroleum sources (Yusoff et al., 2014).

On the other side, ethanol has less fire risk and is produced from biomass. With this alcohol, it is possible to obtain 100% renewable biodiesel with a higher cetane number and lubricity than the biodiesel produced from methanol. The disadvantages concerning ethanol

use are the difficulty of posterior glycerin separation, increase in equipment and operational process costs, and it forms an azeotrope with water, an important component in the reactions, as higher moisture content prejudices both esterification and transesterification reactions. (Yusoff et al., 2014).

Comparing the FAME (fatty acid methyl esters) with FAEE (fatty acid ethyl esters), the latter has higher stability toward oxidation, better lubricity, higher heat capacity and cetane number, and lower cloud, pour, and cold filter plugging point (Stamenković et al., 2011; Yusoff et al., 2014).

### 2.3.2 Oil

Oil and animal fat are composed of a mixture of triglycerides with fatty acids containing 8 to 20 carbon chains (CETEC, 1983). They are both made of carbon, hydrogen, and oxygen, and their main difference is the composition of saturated fatty acids. In fats, there is a high presence of saturated compounds, and so they stay in the solid form at room temperature, while oils, with high contents of unsaturated fatty acids, stay in the liquid form.

It is possible to produce biodiesel from both sources. However, it is essential to keep in mind that the process itself will vary depending on the raw material, as oils coming from different types of plants will also have different components. The same may be said to animal fat or even to used fried oil.

It is common to find a considerable quantity of FFAs in oil and fat generated by the hydrolysis of these sources. The level of FFA varies with the oil/fat type and its exposure to different temperature and moisture content, and various environments such as storage, processing, heating, or frying. It is also important to consider that the commercial value of oils and fats is strongly linked to FFA presence (Mahesar et al., 2014).

For biodiesel production, the oil chosen is of great importance, as its composition may alter the types of operation and equipment of the process. Considering the FFA present in oils and fats, they can be separated into three groups, saturated, monounsaturated, and polyunsaturated.

Saturated fatty acids contain only simple (sigma) bonds, are solid at ambient temperature, and their FAME and FAEE present a cetane number above 60. They also have lower ionic and saponification values due to the absence of unsaturation (CETEC, 1983).

Monounsaturated and polyunsaturated fatty acids contain one or more double (pi) bonds. Because of that, its FAME and FAEE present higher ionic and saponification values,

and cetane number usually above 40. The presence of polyunsaturated fatty acids may also provide some problems to the engine and its lubricant concerning gum generation and lubricant degradation (Bueno, 2009).

FFA composition for some oil and fat types are shown in TABLE 3.

TABLE 3 – FFA COMPOSITION (%WT/WT) FOR OILS USED IN BIODIESEL PRODUCTION PROCESSES

FFA	Sunflower oil	Rapeseed oil	Beef tallow	Soybean oil	Used frying oil
<b>Saturated fatty acids</b>					
Lauric	-	-	-	-	1.98
Palmitic	6.20	4.90	26.00	10.30	15.65
Myristic	-	-	1.25	0.10	-
Stearic	3.70	1.60	22.00	3.80	3.10
Behenic	0.70	-	-	-	0.24
Lignoceric	0.20	-	-	-	0.30
<b>Monounsaturated fatty acids</b>					
Palmitoleic	0.10	-	2.50	5.20	0.31
Oleic	25.20	33.00	41.50	22.80	29.57
Erucic	0.10	23.00	-	-	0.02
<b>Polyunsaturated fatty acids</b>					
Linolenic	0.30	7.90	<1	6.80	1.04
Linoleic	63.10	20.40	<1	51.00	41.53
Eicosenoic	0.20	9.30	0.01	-	0.11

Source: ANASTOPOULOS et al. (2009); OLADIJI et al. (2009); ROHMAN et al. (2012)

From this table, it is possible to observe the proportion between saturated and unsaturated free fatty acids from different oils and fat. As expected, beef tallow, an animal fat, is mostly composed of saturated FFA, while vegetable oil has a considerable proportion of unsaturated compounds.

Considering the use of oil/fat for biodiesel production, the major feedstocks used are vegetable oils both in Brazil and worldwide.



### 3 MATERIALS AND METHODS

#### 3.1 MATERIALS

All reagents in the experiments were used as received. For laboratory experiments, different carboxylic acids, such as lauric acid 98% (CAS N°143-07-7), stearic acid 98% (CAS N°57-11-4), and oleic acid 90% (CAS N°112-80-1), all from Sigma-Aldrich, and ethanol 99.5% (CAS N°64-17-5) from Neon were used for the esterification reaction. The catalyst used was sulfuric acid 98% (CAS N°7664-93-9), and the base for neutralization was sodium hydroxide (CAS N°1310-72-3), both from Vetec. For acid value analysis, potassium hydroxide 85% (CAS N°1310-58-3) from Anidrol and soy oil from the Soya brand, produced in São Paulo (Brazil), were used.

The reaction temperature was controlled using a thermic bath, a magnetic stirrer with heating, and a thermometer. An analytical balance and a Digital Burette (Hirschmann), along with Phenolphthalein 1% (ethanolic solution) (CAS N°77-09-8) and a magnetic stirrer without heating, were used on the neutralization reaction to obtain the experimental results.

Some of the materials used during the esterification reaction experiments are presented in FIGURE 6. The reaction was developed in a closed Becker (left side), and on the right side is the neutralization equipment.



FIGURE 6 – MATERIALS USED FOR THE ESTERIFICATION REACTION

The Scilab™ and Aspen Plus® Softwares were used to gather the esterification reaction parameters and simulate, optimize, and make the economic analysis of the biodiesel process.

Scilab™ is a scientific software for numerical computing. It was used in this work to obtain the esterification parameters through solving differential equations. Graphics were also built using this tool, so it was possible to compare the experimental to predicted reaction behavior. To obtain the esterification conversion at different reaction times, it was necessary to calculate the components' concentration using each one's density and molar mass and experimental data. The results could be obtained after solving ordinary differential equations by the “*ode*” function and estimating different values for the reaction rate parameters, comparing the absolute error associated with each estimation. For the optimization, “*fminsearch*” was used to find the minimum of a multivariable function through the simplex search method (Lagarias et al., 1998).

Aspen Plus® is a software package designed to allow the user to build and simulate a process model. It is used in this work to evaluate the possible optimizations in the biodiesel production process and the economic evaluation of the unit. For software calculations, the Aspen Plus® databank was used, while concerning the thermodynamic models, NRTL, ELECNRTL, and UNIFAC-Dortmund were adopted in the simulation. With this tool, the best reaction and separation units could be proposed.

## 3.2 METHODOLOGY

### 3.2.1 Reaction

The esterification reaction condition tests were divided into 5 different parameters; ethanol/water ratio, type of fatty acids, ethanol/acid ratio, catalyst concentration, and temperature. The evaluation of the ethanol/water ratio was chosen to verify the influence of a higher concentration of water in the reaction. Most of the other parameters evaluated are present in the literature, however, they were also evaluated in this research to verify if higher water concentrations would influence their results. More information about these parameters tests may be seen in FIGURE 7.

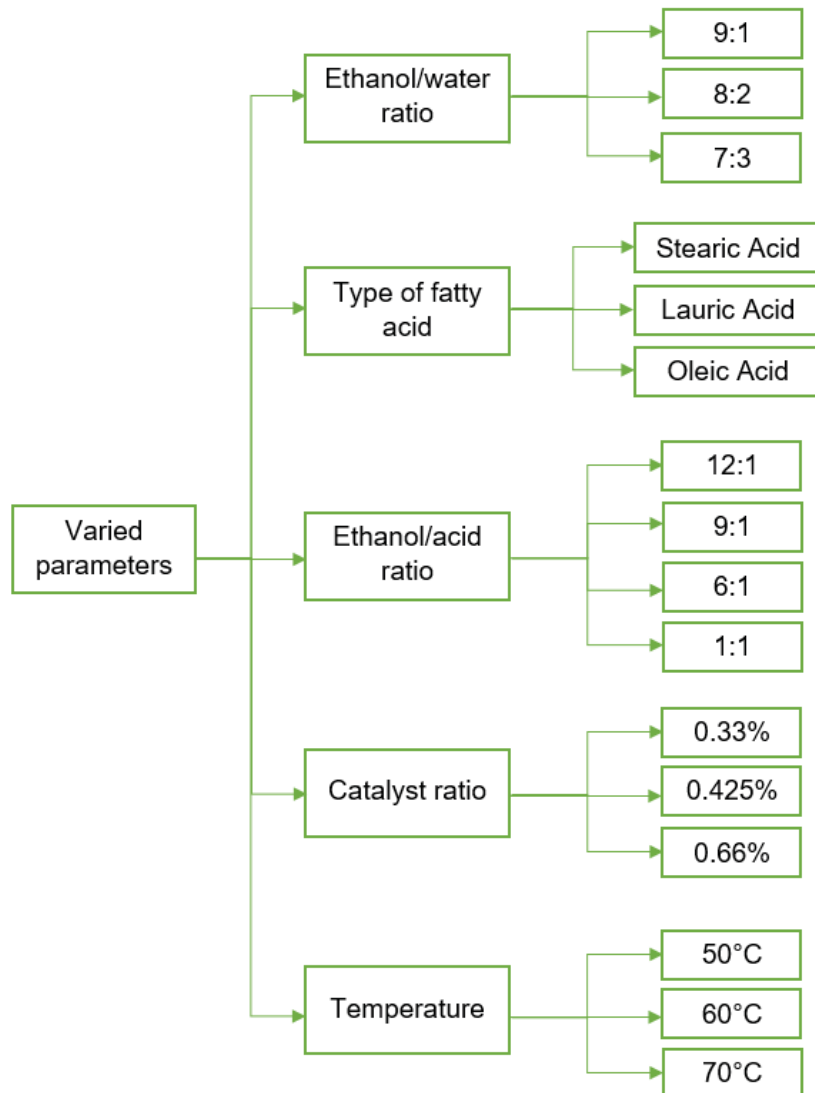


FIGURE 7 – SCHEMATIC REPRESENTATION OF THE PARAMETERS VARIED IN THE ESTERIFICATION REACTION

In the reaction, water, ethanol, and the fatty acid were mixed in a Becker under agitation. The sulfuric acid catalyst was added posteriorly when the temperature reached a stable point, so that the reaction would begin. As attested in previous work (Murad, 2017), no reaction would occur without the catalyst presence under the tested conditions, so there should be no concern about the time taken for the system to achieve temperature stability.

Samples (around 250  $\mu\text{L}$ ) were collected along a 6-8 hour reaction time and submitted to titration using sodium hydroxide 0.1M and phenolphthalein (1% ethanolic solution) as an indicator, stopping the reaction after neutralization. The calculation method used to determine the remaining fatty acid quantity in the sample is explained in the “Base Equations and Calculations” topic.

After gathering some data, it was also proposed to evaluate each parameter's influence through factorial design and ANOVA. Thus, another set of condition variation was tested. By having the results from previous experiments, some tests could be reused for this analysis. Therefore, the properties evaluated are presented in FIGURE 8.

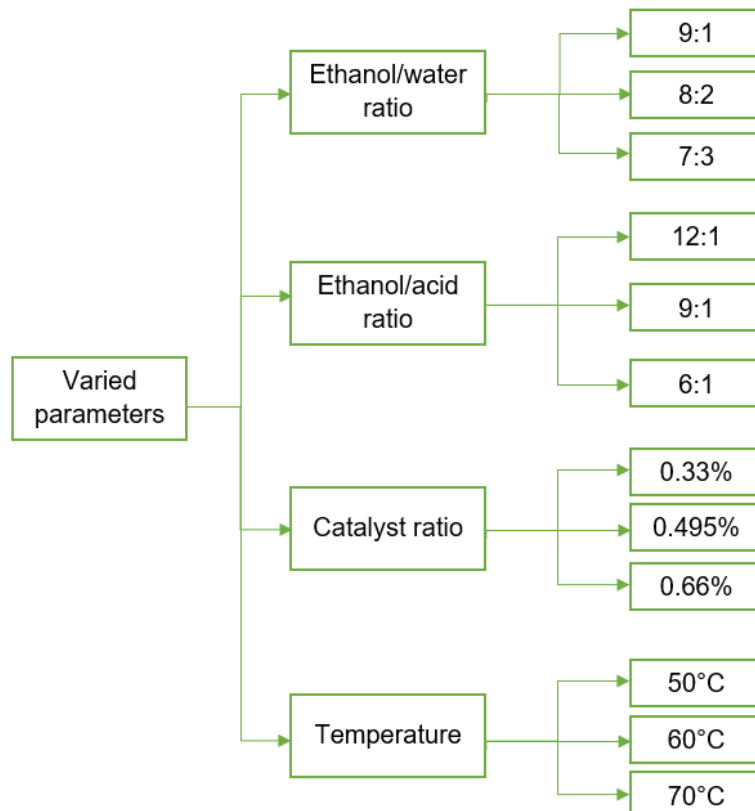


FIGURE 8 - PARAMETERS VARIED FOR THE FACTORIAL DESIGN AND ANOVA ANALYSIS

### 3.2.2 Simulation

Before performing the experiments, a previous test using Aspen Plus<sup>®</sup> was made. A distillation column was simulated to verify the influence that the ethanol purity in the recycle stream would have on the equipment. Then, after analyzing possible scenarios, the experiments were fulfilled.

Once all the experimental data was obtained, the reactor simulator's reaction parameters were calculated. With regressed values, it was possible to obtain the final equation for the esterification reaction rate.

Knowing the reaction behavior, the biodiesel production process, along with energy and economic analysis, was performed using the Aspen Plus V10<sup>®</sup> and Aspen Energy Analyzer V10<sup>®</sup>. It is essential to say that literature data was used for the process's transesterification and purification stages.

### 3.3 BASE EQUATIONS AND CALCULATIONS

Before performing the reaction itself, it was first necessary to standardize the sodium hydroxide with potassium biphthalate (CAS N°877-24-7) following AOCS Specification H 12-52, as presented in Equation (1).

$$N = \frac{m_{\text{KHC}_8\text{H}_4\text{O}_4}}{V_{\text{NaOH}} \cdot 0.2044} \quad (1)$$

Being  $N$  the sodium hydroxide molar concentration,  $m_{\text{KHC}_8\text{H}_4\text{O}_4}$  the potassium biphthalate mass, and  $V_{\text{NaOH}}$  the sodium hydroxide solution volume.

For the conversion calculation, the percentage of free fatty acid in the sample was first determined following the standardization of the "AOCS Official Method" Ca 5a-40, as shown in Equation (2).

$$\text{FFA}(\%) = \frac{V_{\text{NaOH}} \cdot N \cdot \text{MM}_{\text{fatty acid}}}{m_{\text{sample}}} \quad (2)$$

Where  $\text{MM}_{\text{fatty acid}}$  is the molar mass of the fatty acid and  $m_{\text{sample}}$  is the taken sample mass.

Once the percentage of free fatty acid was obtained, the conversion was determined with Equation (3).

$$\chi(\%) = \frac{v_{\text{initial}} - v_{\text{final}}}{v_{\text{initial}}} \cdot 100 \quad (3)$$

Where  $v$  is the molar quantity of the reagent.

The acid value calculation for the final biodiesel production simulated followed Equation (5) for lauric acid (Nielsen, 2014). However, the traditional acid value verification test was fulfilled beforehand to have a comparison method to use this first equation. Equation (4) (Danieletto et al., 2010) was used to calculate the experimental acid value for a system proposed.

$$\text{Acid value} = \frac{56.1 V_{KOH} N}{m_{oil}} \quad (4)$$

$$\text{Acid value} = \text{FFA (\%)} \cdot 2.81 \quad (5)$$

Being  $V_{KOH}$  the potassium hydroxide volume used in mL,  $N$  the base molarity, and  $m_{oil}$  the oil mass in grams. The value 2.81 represents that the FFA measured corresponds to lauric acid, and the value 56.1 corresponds to the potassium hydroxide molar mass.

For factorial design, the Plackett-Burman matrix was built, as indicated in TABLE 4. This method was chosen as it considerably reduces the amount of data needed to be collected and can help determine which factors demand a greater focus. In TABLE 4, M corresponds to the positive coefficients column, T represents the temperature, W the ethanol to water ratio, F the ethanol to FFA ratio, and C the catalyst concentration. The column with more than one letter corresponds to the two or more components interaction.

TABLE 4 - PLACKETT-BURMAN MATRIX

M	T	W	F	C	T.W	T.F	T.C	W.F	W.C	F.C	T.W.F	T.W.C	T.F.C	W.F.C	T.W.F.C
+1	-1	-1	-1	-1	+1	+1	+1	+1	+1	+1	-1	-1	-1	-1	+1
+1	-1	-1	-1	+1	+1	+1	-1	+1	-1	-1	-1	+1	+1	+1	-1
+1	-1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	+1	-1
+1	-1	-1	+1	+1	+1	-1	-1	-1	-1	+1	+1	+1	-1	-1	+1
+1	-1	+1	-1	-1	-1	+1	+1	-1	-1	+1	+1	+1	-1	+1	-1
+1	-1	+1	-1	+1	-1	+1	-1	-1	+1	-1	+1	-1	+1	-1	+1
+1	-1	+1	+1	-1	-1	-1	+1	1	-1	-1	-1	+1	+1	-1	+1
+1	-1	+1	+1	+1	-1	-1	-1	+1	+1	+1	-1	-1	-1	+1	-1
+1	+1	-1	-1	-1	-1	-1	-1	+1	+1	+1	+1	+1	+1	-1	-1
+1	+1	-1	-1	+1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1
+1	+1	-1	+1	-1	-1	+1	-1	-1	+1	-1	-1	+1	-1	+1	+1
+1	+1	+1	-1	-1	+1	-1	-1	-1	-1	+1	-1	-1	+1	+1	-1
+1	+1	+1	-1	+1	+1	-1	+1	-1	+1	-1	-1	+1	-1	-1	-1
+1	+1	+1	+1	-1	+1	+1	-1	+1	-1	-1	+1	-1	-1	-1	-1
+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1

The positive signs represent the upper conditions tested for that parameter, as the negative represents the lower conditions. For deviation calculation, 4 tests considering central point conditions were undertaken.

To find the most suitable equation using the parameters with considerable influence in the final conversion, Equation (6) should be calculated.

$$F = \sum_{i=1}^N (y_i^{exp} - y_i^{reg})^2 \quad (6)$$

Being  $N$  the total number of experiments,  $y_i^{exp}$  the experimental conversion in the  $i$ th point, and  $y_i^{reg}$  the calculated conversion in the  $i$ th point.

The  $y_i^{reg}$  is calculated using Equation (7), and by substituting this term in (6), Equation (8) is obtained.

$$y_i^{reg} = a_0 + a_1 T + a_2 W + a_3 F + a_4 C + a_{12} T W + a_{13} T F + a_{14} T C + a_{23} W F + a_{24} W C + a_{34} F C + a_{123} T W F + a_{124} T W C + a_{134} T F C + a_{234} W F C + a_{1234} T W F C \quad (7)$$

$$F = \sum_{i=1}^N (y_i^{exp} - (a_0 + a_1 T + a_2 W + a_3 F + a_4 C + a_{12} T W + a_{13} T F + a_{14} T C + a_{23} W F + a_{24} W C + a_{34} F C + a_{123} T W F + a_{124} T W C + a_{134} T F C + a_{234} W F C + a_{1234} T W F C))^2 \quad (8)$$

To find the function minimum, and considering orthogonality, the partial derivate of this function on each independent variable should equal zero, as presented in Equation (9).

$$\frac{\partial F}{\partial a_x} = 0 \quad (9)$$

Using this equation on each independent variable and organizing it into a matrix, it is possible to obtain a 16x16 diagonal matrix  $Q$  and two column-matrix:  $A$  (with the independent variables) and  $B$  (experimental values).

Regarding matrix  $Q$ , the first component ( $q_{11}$ ) corresponds to the total number of experiments. In contrast, for the other diagonal components, the value will correspond to the total number of experiments except from the central point ones.

The summarized equation structure from the matrix calculations and the rearranged one for parameter determination can be seen in (10) and (11).

$$Q A = B \quad (10)$$

$$A = Q^{-1} B \quad (11)$$



Once the correct parameters are obtained, the conversion is calculated, and the sum of all deviations square value is acquired. The last necessary calculation is related to the associated deviation to each parameter.

First, it is necessary to obtain a diagonal matrix by multiplying the sum of square deviations by the  $Q^{-1}$  matrix to find the deviation values. Then, this matrix's square root is multiplied by the Student's t-distribution for a two-tailed test with a 5% level of significance. For a 20-set of experiments with 4 degrees of freedom, this value corresponds to 2.7764.

For the ANOVA calculations, it is possible to summarize the used equations into TABLE 5.

TABLE 5 - BASE TABLE FOR ANOVA CALCULATION (PÓ, 2014)

Variation	Square sum	Degrees of freedom	Mean square sum	Calculated F
Between groups	$SQ_b$	$DF_b = k-1$	$MQ_b = \frac{SQ_b}{DF_b}$	$\frac{MQ_b}{MQ_i}$
In the groups	$SQ_i$	$DF_i = n-k$	$MQ_i = \frac{SQ_i}{DF_i}$	
Total	$SQ_t$	$DF_t = n-1$		

Being  $k$  the number of different condition values for the same property evaluated, and  $n$  the population number. The terms available in the table can be calculated through Equation (12), (13), and (14).

$$SQ_b = \sum_{i=1}^k (\bar{y} - \bar{y}_i)^2 \quad (12)$$

Where  $\bar{y}$  corresponds to the average conversion among all experimental data, and  $\bar{y}_i$  the average conversion among each condition value of the same property (e.g., for the temperature,  $\bar{y}_i$  would correspond to the average of the experiments with 50°C ( $i=1$ ), 60°C ( $i=2$ ), and 70°C ( $i=3$ )).

$$SQ_i = \sum_{i=1}^n (\bar{y}_i - y_i)^2 \quad (13)$$

$$SQ_t = SQ_b + SQ_i \quad (14)$$

### 3.4 KINETICS MODELLING

A general equation for the esterification reaction's experimental data using ethanol is shown in FIGURE 9, where FFA is the free fatty acid, and FFE is the free fatty ester formed during the reaction. In the experiments, the catalyst employed was sulfuric acid.

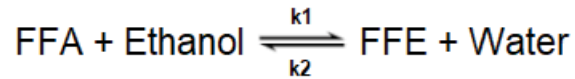


FIGURE 9 – GENERAL ESTERIFICATION REACTION EQUATION USING ETHANOL

The kinetic model used to describe the esterification reaction with ethanol is defined by the differential Equations (15) to (18).

$$\frac{dN_{FFA}}{dt} = r_{FFA} V \quad (15)$$

$$\frac{dN_{FFE}}{dt} = -r_{FFA} V \quad (16)$$

$$\frac{dN_{Ethanol}}{dt} = r_{FFA} V \quad (17)$$

$$\frac{dN_{Water}}{dt} = -r_{FFA} V \quad (18)$$

Being  $N_{FFA}$ ,  $N_{FFE}$ ,  $N_{Ethanol}$ , and  $N_{Water}$  the number of moles of free fatty acid, ester, ethanol, and water, respectively.  $V$  is the reaction volume, while  $r_{FFA}$  is the reaction rate of free fatty acid, considering the esterification an elementary and reversible reaction. Equations (19) and (20) were used to calculate both reaction volume and rate.

$$V = \sum_{i=1}^{NC} N_i V_{mi} \quad (19)$$

$$r_{FFA} = -k_1 C_{FFA} C_{Ethanol} + k_2 C_{FFE} C_{Water} \quad (20)$$

Where subscript  $i$  corresponds to reagent/product's component,  $NC$  is the number of reaction components,  $N_i$  is the number of moles of component  $i$ , and  $V_{mi}$  is the molar

volume of component  $i$ .  $k_1$  and  $k_2$  are kinetic constants and can be calculated through the Arrhenius equation, as shown in (21) and (22):

$$k_1 = A_1 e^{\left(-\frac{E_1}{RT}\right)} \quad (21)$$

$$k_2 = A_2 e^{\left(-\frac{E_2}{RT}\right)} \quad (22)$$

Being  $E_1$  and  $E_2$  the activation energy,  $R$  the ideal gas constant,  $T$  the absolute temperature, and  $A_1$  and  $A_2$  the pre-exponential factors, defined by Equations (23) and (24):

$$A_1 = a_1 (C_{SULF}/(c_3 C_{ET}^{c4} + c_2 C_{H2O}^{c1})) \text{ term} \quad (23)$$

$$A_2 = a_2 (C_{SULF}/(c_3 C_{ET}^{c4} + c_2 C_{H2O}^{c1})) \text{ term} \quad (24)$$

Both  $a_1$  and  $a_2$  are constants on the equation. The reaction also has a strong influence concerning the pH, which is included on *term*, represented by Equation (25):

$$\text{term} = (c_5 \exp(\text{pH } c_6)) \quad (25)$$

The idea of working with pH was to verify if there is a considerable influence of the acid catalyst and water (electrolytes) in the kinetics equation, as it is already known that the protonation of carbonyl oxygen by acid makes the carbonyl carbon a much better electrophile in the esterification reaction (Ashenurst, 2020).

The pH should be rewritten using the reaction components' molar fraction to further use the equation on the Aspen Plus® simulation. The general equation for pH calculation is represented in Equation (26), where “a, b and c” are the regressed constants. The parameters chosen to be evaluated were tested with different reaction component groups using Excel's regression tool, where the best results were obtained with ethanol-water-FFA molar fraction data. The final equation using molar fractions representing the pH values is discussed and presented on *Scilab™ analysis*.

$$\text{pH} = a X_{\text{Ethanol}} + b X_{\text{Water}} + c X_{\text{FFA}} \quad (26)$$

## 4 RESULTS AND DISCUSSION

### 4.1 REACTION RESULTS

Before any simulation procedure, the esterification reaction experiments were performed to have both data for regression and a critical analysis for the reaction conditions to be used in further simulation.

#### 4.1.1 Fatty acid type influence

As waste oils contain more than one type of fatty acid, it is vital to verify the behavior for at least the commonly present ones and with different structures, as unsaturation presence. Therefore, three different types of fatty acids were tested; stearic ( $C_{18}H_{36}O_2$ ), oleic ( $C_{18}H_{34}O_2$ ), and lauric acid ( $C_{12}H_{24}O_2$ ). The result of each type is presented in FIGURE 10.

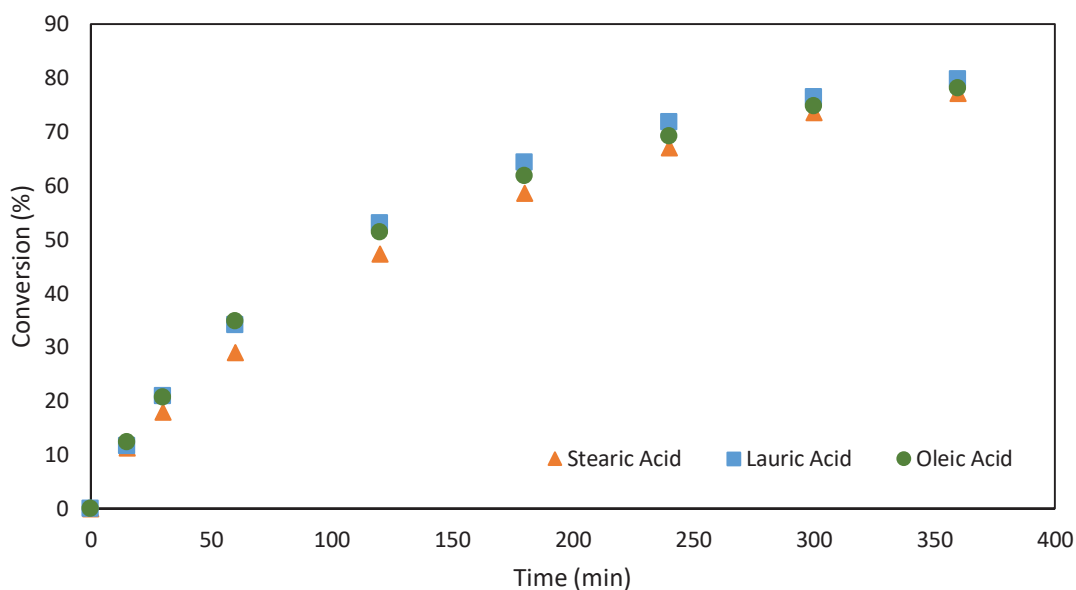


FIGURE 10 – REACTION BEHAVIOR TO THE USE OF DIFFERENT FATTY ACIDS WITH ETHANOL/WATER AND ETHANOL/ACID RATIO OF 9:1, 60°C, AND 0.33% CATALYST CONCENTRATION RELATED TO THE TOTAL REACTION MASS

As it is possible to see, all the acids have similar behavior, implying that the type of acid chosen will have a low impact on the reaction. Other authors have reported similarities in the final conversion using various fatty acids under different conditions as well (Bouguerra Neji et al., 2009; Kastratović and Bigović, 2018; Reis et al., 2015). In addition, the use of

acid oil was investigated by Murad (2017), and it showed a very similar behavior compared with the results obtained with the same three fatty acids investigated in this study.

Considering the molecule structure, the main difference between lauric acid and stearic acid is the number of carbons present, while for the oleic, the difference is on the unsaturation. Through these tests, molecule particularities as the size or unsaturation presence, which could cause deviations, were embraced, indicating a high possibility that most of the fatty acids present in the oil would have similar behavior as lauric acid.

Considering the higher difficulty when handling stearic acid due to its low solubility and lower purity of oleic acid, lauric acid was chosen to be used in further experiments.

#### 4.1.2 Catalyst concentration influence

In all experiments, only sulfuric acid was tested, as it was already proved that for acid oils, (FFAs content over 0.5% (Freedman et al., 1981) or over 1% (Canakci and Gerpen, 1999)) especially with high presence of water, homogeneous base catalysts improves soap formation, being difficult to remove, and also to purify biodiesel at further process stages.

FIGURE 11 shows the reaction behavior for different catalyst concentrations and two points with a temperature variation. Lauric acid was used as the fatty acid in this analysis.

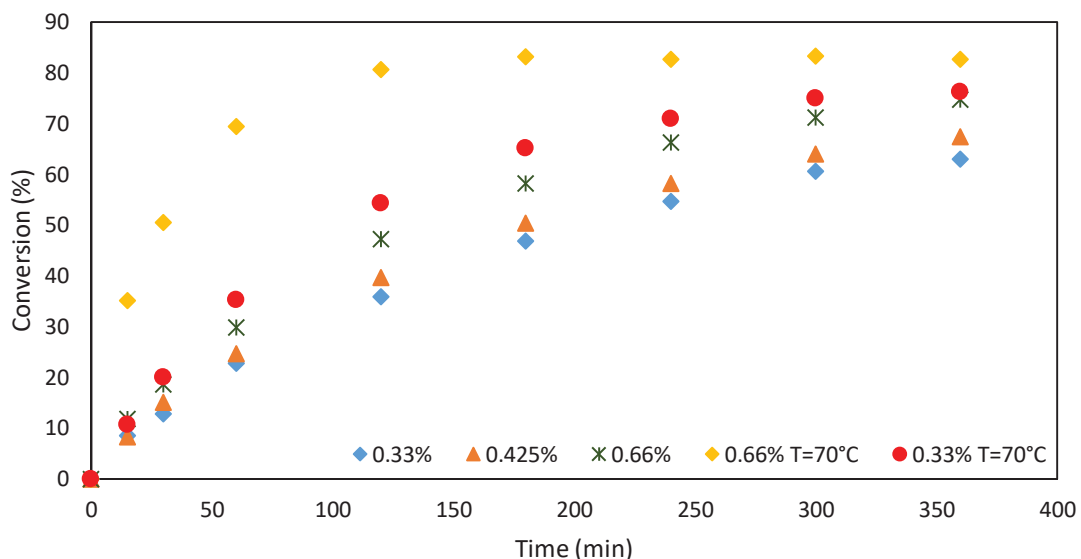


FIGURE 11 - REACTION BEHAVIOR TO THE USE OF DIFFERENT CATALYST CONCENTRATION AT 50°C, ETHANOL/WATER AND ETHANOL/ACID RATIO OF 9:1, AND TWO POINTS WITH A TEMPERATURE VARIATION (70°C)

Through this figure, it is possible to verify that higher catalyst concentration improves the reaction speed, although this difference is considerably smaller than a temperature variation, for example. The graphic also shows that the conversion at the end of the batch at higher temperatures is closer at both lower and higher catalyst concentrations.

It is crucial to consider that the higher catalyst concentration, the higher neutralization and purification process cost will be. It is worth saying that without the catalyst, experiments show that the reaction under the tested conditions does not occur at all (Murad, 2017). Thus, a 0.33 %wt of catalyst was used on other experiments in this work.

#### 4.1.3 Ethanol/water ratio influence

For this analysis, experiments with three different ethanol/water ratios were tested. It is relevant to say that this proportion has a strong influence on the reaction conversion. However, it also interferes with the ethanol recycling distillation column, as this mixture has an azeotrope point around a 9:1 molar ratio. Therefore, it is logical to say that a higher ratio improves the reaction conversion, at the price of higher equipment and process costs.

FIGURE 12 shows the influence in the reaction conversion for the different ratios tested. Lauric acid was used as the fatty acid in this analysis.

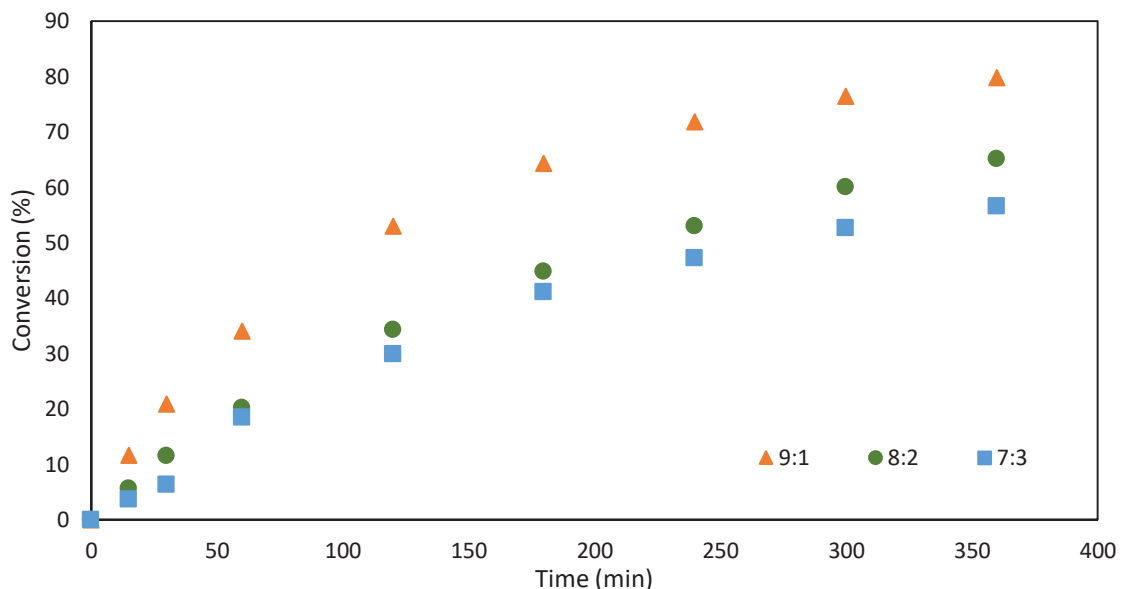


FIGURE 12 - REACTION BEHAVIOR TO THE USE OF DIFFERENT ETHANOL/WATER RATIOS WITH ETHANOL/ACID RATIO OF 9:1, 0.33% CATALYST CONCENTRATION RELATED TO THE TOTAL REACTION MASS, AND 60°C

As expected, the reaction conversion improves at higher ratios, varying from 80% at 9:1 to 57% at 7:3. Although it may seem logical that a higher conversion also implies having a higher income, the correct choice of which ratio gives the best economic return was only possible through an economic evaluation with the Aspen Plus<sup>®</sup> tool, as discussed in the “Economic Analysis” topic.

A study with anhydrous ethanol under the same conditions provided a final conversion of 90%, reinforcing the strong influence of water on the reaction (Murad et al., 2017). Although in most studies, anhydrous methanol or ethanol, or these alcohols with lower water content (up to 4%), (Rosset et al., 2013) was used for the esterification reaction, all of them demonstrated the negative influence of the presence of water (Aranda et al., 2009).

As will be further explained, the cost of the recycling process is lower for ratios under 9:1. For that reason, the other experiments were conducted with 8:2 and 7:3 ratios.

#### 4.1.4 Ethanol/acid ratio influence

Another important condition for the esterification is the ethanol/acid molar ratio, as it is crucial for the reaction speed itself and for further purification stages.

As is seen in FIGURE 13, four ethanol/acid ratios were tested. Lauric acid was used as the fatty acid in this analysis.

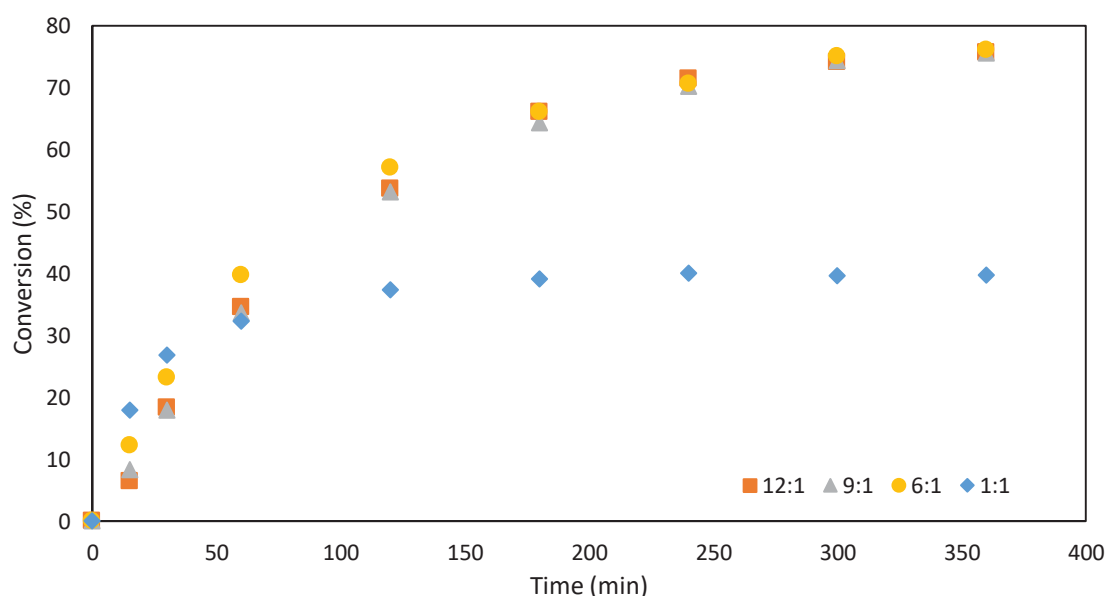


FIGURE 13 - REACTION BEHAVIOR TO THE USE OF DIFFERENT ETHANOL/ACID RATIO ETHANOL/WATER RATIO OF 8:2, 0.33% CATALYST CONCENTRATION, AND 70°C

The most problematic ratio corresponds to 1:1, while the other ones have a very similar behavior from the beginning until reaching the equilibrium state, which is in accordance with literature data (Suppalakpanya et al., 2011). Knowing this, choosing a 6:1 or 9:1 ratio will already be more than a good option to work with when making an esterification reaction, without the need to have considerably high reagent costs.

Some authors reported similar results for the 6:1 and 9:1 ratios using anhydrous ethanol, which is why a 6:1 ratio is usually adopted in other studies (Marchetti et al., 2010; Suppalakpanya et al., 2011). However, as reported by Murad (2017), in more unfavorable conditions, the 6:1 ethanol/acid ratio has a lower final conversion in relation to the other two higher proportions, which had similar behavior between themselves. Therefore, to guarantee a better result, the other experiments were mainly conducted using the 9:1 ethanol/acid ratio.

#### 4.1.5 Temperature influence

The reaction temperature has a significant influence on the esterification speed. For instance, for the 9:1 ethanol/water ratio, a temperature of 50°C was not enough to achieve the equilibrium state after 6 hours. Therefore, the 8:2 ethanol/water experiments were tested at 60°C and 70°C using lauric acid as the fatty acid in this analysis.

The reaction behavior for each temperature can be seen in FIGURE 14.

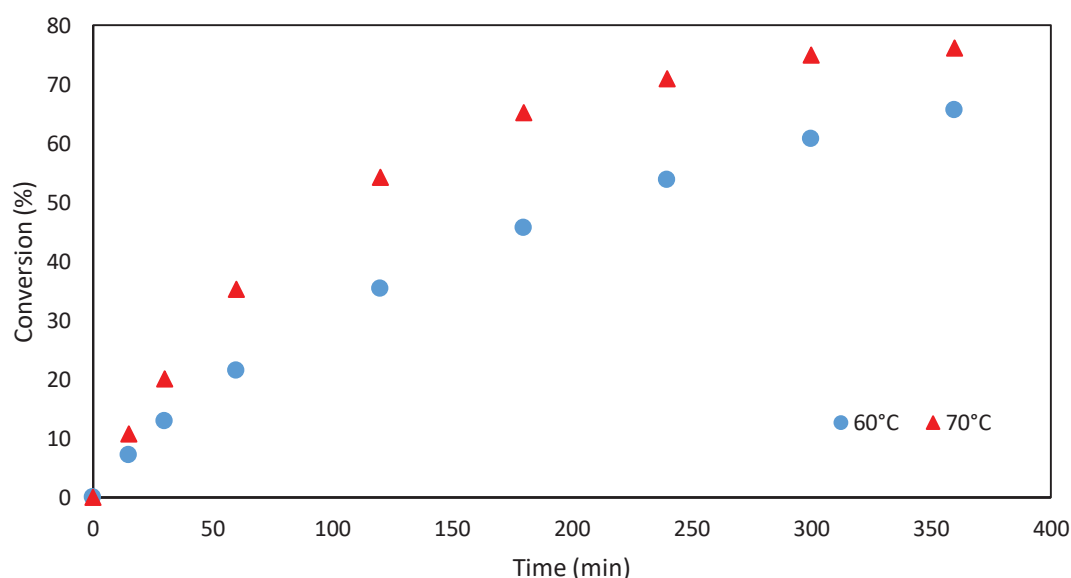


FIGURE 14 - REACTION BEHAVIOR UNDER DIFFERENT TEMPERATURES WITH ETHANOL/WATER RATIO OF 8:2, ETHANOL/ACID RATIO OF 9:1, AND 0.33% CATALYST CONCENTRATION



Another important detail is that higher temperatures were not tested as it was close to the alcohol boiling point, which could give an incorrect behavior for the reaction.

It is possible to verify in the graphic that the temperature has a strong influence on the reaction speed, even for a change of only 10°C.

#### 4.1.6 Influence of acid oil use

The work developed by Murad (2017) showed the influence of FFA presence in acid oil, as shown in FIGURE 15. Tests with 10 and 40% of lauric acid in oil, 50°C, 0.33% catalyst concentration, anhydrous ethanol, and under 12:1 and 6:1 ethanol/acid ratios were developed to verify the importance of the reagents' concentration in the reaction.

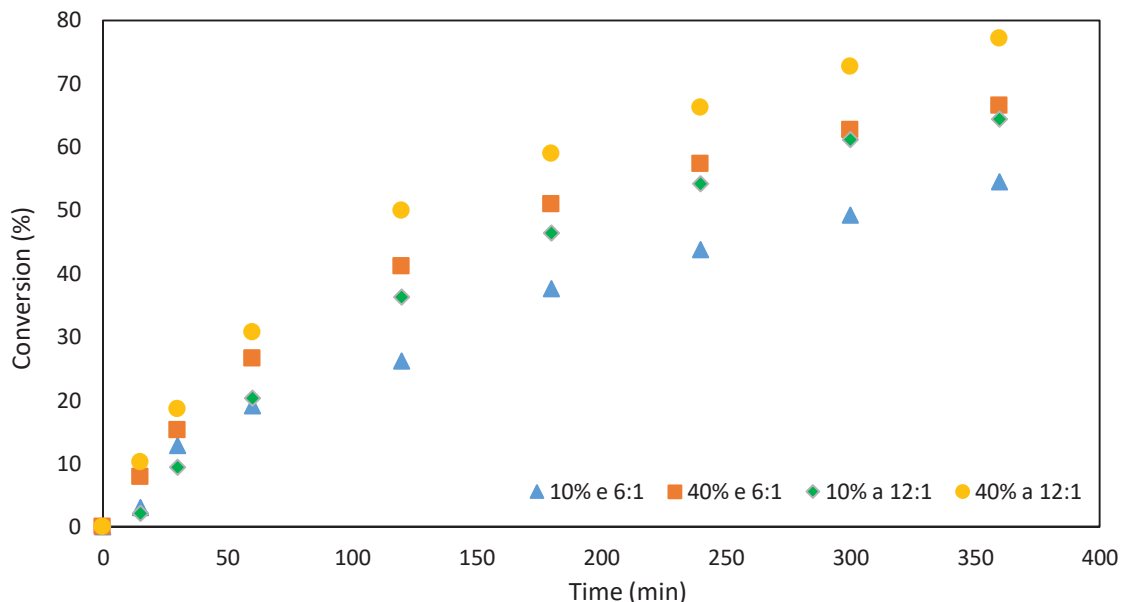


FIGURE 15 - REACTION BEHAVIOR TO THE USE OF ACID OIL (MURAD, 2017)

As can be seen, there is a considerable difference concerning the FFA concentration in the oil in the esterification reaction. For higher lauric acid concentration, a higher conversion is achieved. A higher ethanol/acid ratio also contributes to the reaction, as was expected through previous tests varying this ratio.

#### 4.1.7 Final Acid Value

To verify the possible use of Equation (5), the acid value test was made.

First, the total volume of potassium hydroxide necessary to neutralize a pure oil, quantity that will be abated when calculating the value for the further tested mixture, and a mixture of the same oil with a known quantity of lauric acid was verified.

Equation (4) is used in the first two lines, while the third line represents the results from Equation (5). The values obtained may be consulted in TABLE 6.

TABLE 6 – EXPERIMENTAL RESULTS TO VERIFY ACID VALUE EQUATIONS

Oil (g)	Lauric acid (g)	FFA (%)	Volume of KOH (mL)	Acid Value (mg KOH/ g oil)
64.33	-	-	1.15	0.106
64.63	1.64	2.47	75.59	6.84
-	-	2.47	-	6.94

It is possible to verify from these results that both equations presented before may predict well the acid value for the oil, with only a 3% difference. Therefore, it is possible to know the acid value only by knowing the FFA content in the oil.

#### 4.1.8 Factorial design and ANOVA

The parameter values for the equation, along with the deviation values, are presented in TABLE 7.

TABLE 7 – PARAMETER VALUES USED TO DESCRIBE ESTERIFICATION REACTION BEHAVIOR

Parameter	Value	Deviation
$a_0$	63.461	$\pm 2.83$
$a_1$	11.691	$\pm 3.17$
$a_2$	10.815	$\pm 3.17$
$a_3$	-0.2611	$\pm 3.17$
$a_4$	2.9475	$\pm 3.17$
$a_{12}$	-2.6209	$\pm 3.17$
$a_{13}$	-0.2116	$\pm 3.17$
$a_{14}$	-1.5317	$\pm 3.17$
$a_{23}$	1.3314	$\pm 3.17$
$a_{24}$	-1.2569	$\pm 3.17$
$a_{34}$	-0.9346	$\pm 3.17$
$a_{123}$	-0.8184	$\pm 3.17$
$a_{124}$	-0.5072	$\pm 3.17$
$a_{134}$	0.5600	$\pm 3.17$
$a_{234}$	-0.4648	$\pm 3.17$
$a_{1234}$	-0.5105	$\pm 3.17$

Considering the parameters with a value lower than its deviation disposable, as they can also have zero value, the parameters with considerable influence in the reaction are the temperature and ethanol to water ratio. Considering that, the final equation for the esterification representation is presented in (27).

$$y^{reg} = 63.461 + 11.691.T + 10.815.W \quad (27)$$

Being T and W values in a connotation from -1 to +1 from the lower to upper value for that corresponding variable. For temperature, these bonds range from 50°C to 70°C, and for the ethanol to water ratio, it ranges from 7:3 to 9:1.

These results are following the study developed by Paiva (2015). In his analysis, a heterogeneous catalyst (zinc laurate) was used, and the evaluated properties were the ethanol/acid molar ratio, temperature, and the amount of catalyst. The analysis was carried out with anhydrous (99.7%) and hydrous ethanol (93.7%), and in both tests, the temperature had the most significant influence on the system.

Using Equation (27), it is possible to plot a 3-dimensional graphic to visualize the influence of these variables in the reaction conversion, as shown in FIGURE 16, being X the conversion in percentage.

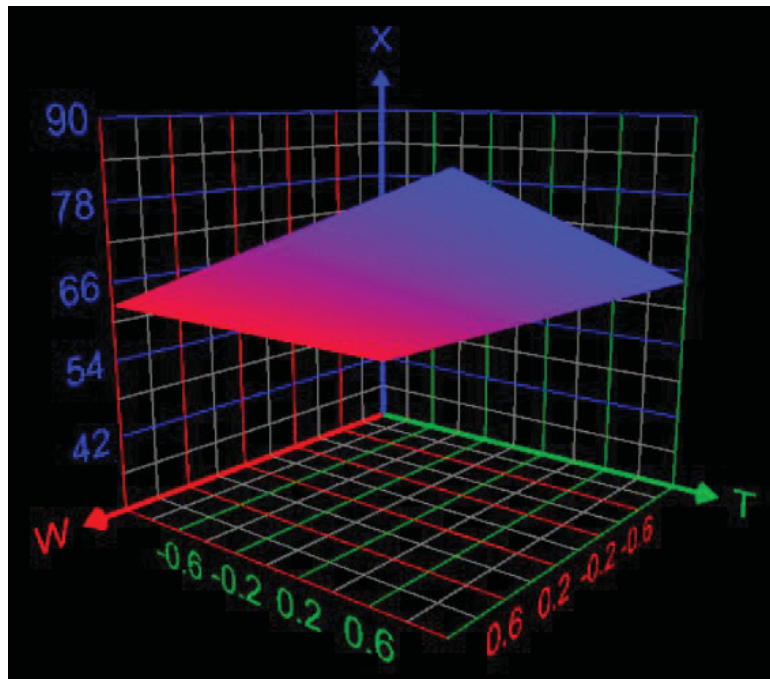


FIGURE 16 – SYSTEM BEHAVIOR OBTAINED CONSIDERING THE REGRESSED EQUATION

The variable interaction calculations were also performed through ANOVA, resulting in TABLE 8.

TABLE 8 – ANOVA RESULTS FOR THE VARIABLES TESTED

<b>Variable</b>	<b>F statistic</b>	<b>F calculated</b>	<b>Null hypothesis</b>
T	3.59	21.90	Refused
W	3.59	16.61	Refused
F	3.59	0.683	Accepted
C	3.59	1.386	Accepted
TxW	7.709	1.232	Accepted
TxF	7.709	0.008	Accepted
TxC	7.709	0.421	Accepted
WxF	7.709	0.318	Accepted
WxC	7.709	0.283	Accepted
FxC	7.709	0.157	Accepted

The single and binary interaction variables follow the response obtained through factorial design, so there should be no need for further speculation on the other variable interactions. The ANOVA calculations have confirmed the parameters' values obtained for the esterification equation and the conclusion regarding which variables effectively influence the reaction.

Through the analysis of temperature, ethanol/water ratio, ethanol/FFA ratio, and catalyst concentration, it was observed that only the two first had considerate influence in the reaction, considering a temperature range from 50°C to 70°C, and ethanol/water range from 7:3 to 9:1. As both parameters' values are positive, they improve the reaction conversion when approaching their upper bounds. Therefore, the higher the temperature and ethanol/water ratio, the higher the esterification conversion. It was also observed that the catalyst positively influenced the reaction at very unfavorable conditions, but had little or no difference when at favorable conditions. Thus, it should be one reason the final parameter's evaluation had the catalyst concentration out of the main equation.

## 4.2 SIMULATION RESULTS

### 4.2.1 Scilab™ analysis

Once obtained all the data from these experiments and the ones developed by Murad (2017), it was possible to propose a new expression for the esterification reaction considering a more comprehensive range of water presence in ethanol.

All expression parameters were estimated by fitting the model to the experimental data. The error has been reduced by minimizing the sum of the squared errors between calculated and experimental conversion values. The ode function was used to solve the initial value problem defined by the set of ordinary differential equations associated with their initial conditions. Furthermore, the function `fminsearch` was used to minimize the objective function associated with the squared errors using the Nelder-Mead algorithm. Therefore, the group of parameters that would lead to a lower global error was chosen.

This new kinetics improves Murad's range, as that one works well with low water concentration. A set of 38 experimental data (22 from Murad and 16 from this work) comprising 305 information points for parameter regression and validation were used.

To obtain the kinetics equation that best represented the data evaluated, different steps were followed. The base equation tested was the same one obtained by Murad et al. (2017), as presented in Equation (28):

$$r = (-k_1 C_{\text{FFA}} C_{\text{ET}} + k_2 C_{\text{ESTER}} C_{\text{H}_2\text{O}})(C_{\text{H}_2\text{SO}_4}/C_{\text{ET}}) \quad (28)$$

Where the C's correspond to the components' concentration and k's to the kinetic factors, which are calculated by Equation (29):

$$k_{\#} = a_{\#} \exp(-E_{\#}/T) \quad (29)$$

Being T the temperature (K), *a* the pre-exponential factor, and E the activation energy divided by the ideal gas constant (K). The # represents the equation number subscription, where 1 is the direct reaction, and 2 is the inverse.

As the use of this equation did not well represent the data, the influence of water was added to the last term, and different weights were evaluated for the ethanol and water terms, as shown in Equation (30):

$$r = (-k_1 C_{FFA} C_{ET} + k_2 C_{ESTER} C_{H_2O}) (C_{H_2SO_4} / (C_3 C_{ET}^{c_4} + C_2 C_{H_2O}^{c_1})) \quad (30)$$

Where the  $c$ 's are the constants calculated to minimize error.

Even though the results had been better in this case, they were not entirely satisfactory for all tested data. As we are dealing with a higher concentration of water, the possibility of acidity influence was considered. To make the regressed values better suit the experimental ones, it was proposed to verify the influence of pH in the reaction kinetics.

The pH values for each esterification reaction process was obtained using Aspen Plus<sup>®</sup>. As the molar fraction is used in both the Scilab<sup>™</sup> and Aspen Plus<sup>®</sup> calculations, an equation using those parameters was proposed. Different scenarios were tested considering the influence of ethanol, water, FFA, FFE, and sulfuric acid concentrations and fractions. They were grouped into couples, triples, four, and all parameters. The value for each multiplying constant was calculated to obtain a set that would minimize the experimental to calculated pH value. By using the excel regression tool for the calculations, an optimal equation considering ethanol, water, and FFA molar fractions was found to be the one that represented the correct pH values best, as presented in Equation (31).

$$pH = -3.7988 x_{ET} + 1.1425 x_{H_2O} - 2.6294 x_{FFA} \quad (31)$$

After including the term relating to the pH, the parameters' set that had lower residue value for the data points tested was obtained, and it was chosen to represent the esterification reaction behavior. The base equation obtained for the esterification rate is represented in Equation (32).

$$r = (-k_1 C_{FFA} C_{ET} + k_2 C_{ESTER} C_{H_2O}) (C_{H_2SO_4} / (C_3 C_{ET}^{c_4} + C_2 C_{H_2O}^{c_1})) \text{ term} \quad (32)$$

Where *term* is calculated using Equation (25). Therefore, the final kinetics equation obtained could be written as in Equation (33).

$$r = (-k_1 C_{FFA} C_{ET} + k_2 C_{ESTER} C_{H_2O}) K' \quad (33)$$

Where the term  $K'$  is calculated through Equation (34).

$$K' = (C_{H_2SO_4} / (c_3 C_{ET}^{c_4} + c_2 C_{H_2O}^{c_1})) c_5 \exp(pH c_6) \quad (34)$$

To verify the quality of the equation's prediction for a different set, all 7:3 and a group of four experiments of the 9:1 ethanol/water ratio experiments data set were not included in the regression calculation. The results obtained from these experiments were only analyzed considering the constants and parameters obtained from the included data experiments.

At the end of the regression, the parameters set values that reduced the overall error are presented in TABLE 9.

TABLE 9 – PARAMETERS VALUES FROM THE REGRESSION

Parameter	Value	Units
<b>a<sub>1</sub></b>	1.205×10 <sup>1</sup>	L.mol <sup>-1</sup> .s <sup>-1</sup>
<b>a<sub>2</sub></b>	1.235×10 <sup>0</sup>	L.mol <sup>-1</sup> .s <sup>-1</sup>
<b>E<sub>1</sub>/R</b>	7.256×10 <sup>3</sup>	K
<b>E<sub>2</sub>/R</b>	6.497×10 <sup>3</sup>	K
<b>c<sub>1</sub></b>	1.272×10 <sup>0</sup>	-
<b>c<sub>2</sub></b>	4.320×10 <sup>-6</sup>	-
<b>c<sub>3</sub></b>	2.021×10 <sup>-6</sup>	-
<b>c<sub>4</sub></b>	-5.768×10 <sup>-1</sup>	-
<b>c<sub>5</sub></b>	1.385×10 <sup>1</sup>	-
<b>c<sub>6</sub></b>	-9.649×10 <sup>-1</sup>	-

Comparing these parameters with the ones found in another work (Murad, 2017), as presented in TABLE 10, it can be seen that the new parameters consider a more extensive range of results, as it also considers more parameters and components' influence.

TABLE 10 – REGRESSED PARAMETERS BY MURAD (2017)

<b>A<sub>1</sub> (L.mol<sup>-1</sup>.s<sup>-1</sup>)</b>	<b>A<sub>2</sub> (L.mol<sup>-1</sup>.s<sup>-1</sup>)</b>	<b>E<sub>1</sub>/R (K)</b>	<b>E<sub>2</sub>/R (K)</b>
9.1×10 <sup>7</sup>	3.9×10 <sup>4</sup>	6.56×10 <sup>3</sup>	3.87×10 <sup>3</sup>

With a more complex model, the difference in the data results from another work compared with the new regression was first observed. Using the experimental data from Murad's study and comparing each model's adjustment, FIGURE 17 is obtained. Even though both groups of parameters enable a good system representation, the regression considering water and pH influence better describes the reaction's behavior. This improvement can be attributed to the fact that although anhydrous ethanol had been used in Murad's experiments, this component would be further formed in the esterification reaction,

and therefore it would influence the reaction behavior. Thus, using an equation that considers the stronger influence of water enabled a better model adjustment.

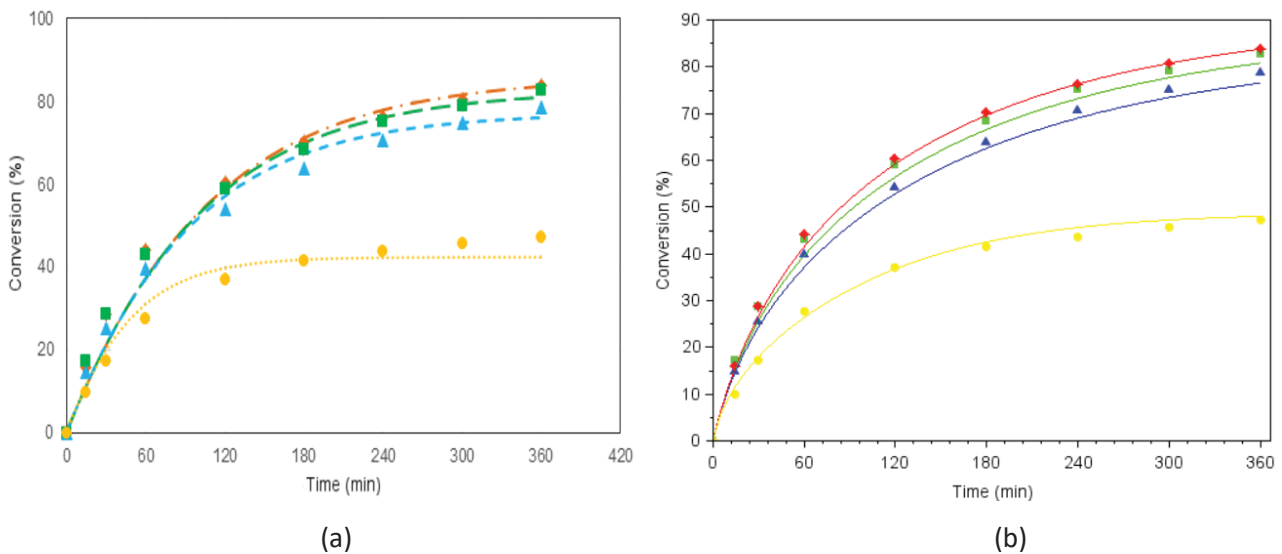
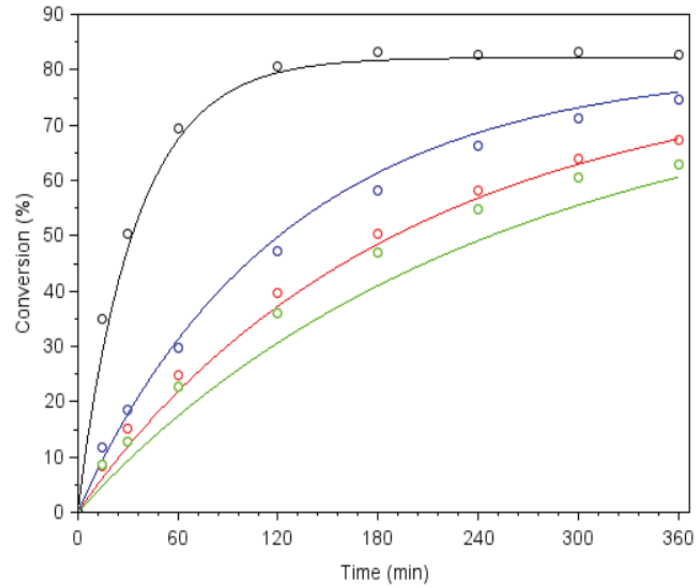


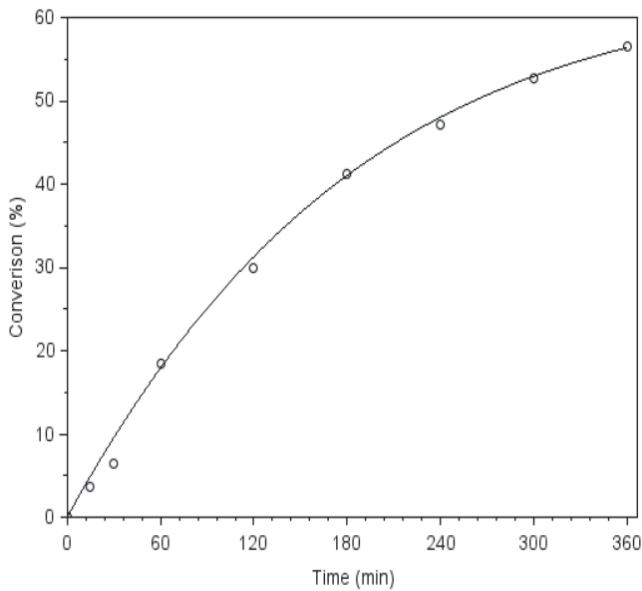
FIGURE 17 – RESULTS COMPARING REGRESSION FROM PARAMETERS OBTAINED BY (a) MURAD (2017) AND (b) FROM THIS WORK WITH ANHYDROUS ETHANOL, 50°C, 0.33%WT CATALYST, 12:1 ETHANOL/ACID RATIO (RED), 9:1 RATIO (GREEN), 6:1 RATIO (BLUE), AND 1:1 RATIO (YELLOW)

After the parameters are regressed, the 7:3 and 9:1 ratio data (not used for parameter estimation) response is verified to prove if the values found are compatible with other conditions. The results can be seen in FIGURE 18. The dots represent experimental points, while the lines were obtained through regression.

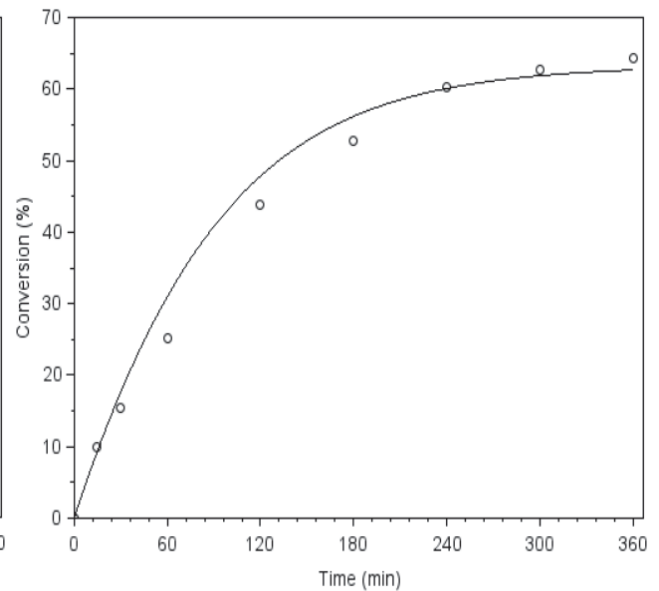




(a)



(a)



(b)

FIGURE 18 – REGRESSION RESULT FOR (a) 9:1 ETHANOL/WATER AND ETHANOL/ACID RATIO, UNDER 50°C AND 0.66%WT CATALYST (BLUE), 0.425%WT (RED), 0.33%WT (GREEN), AND 70°C AND 0.66%WT (BLACK). 7:3 ETHANOL/WATER RATIO (b) 9:1 ETHANOL/ACID RATIO EXPERIMENT UNDER 60°C AND 0.33%WT CATALYST; (c) 6:1 ETHANOL/ACID RATIO EXPERIMENT UNDER 70°C AND 0.33%WT CATALYST

From the results obtained, it is possible to affirm that the model is suitable to be used with higher water concentrations, as it well predicted the 7:3 ethanol/water group data, which was not included in the regression.

It could also be observed that prior experiments (Murad, 2017) with 9:1 ethanol/acid ratio and with acid oil were well adjusted considering the parameters obtained, as can be seen in FIGURE 19.

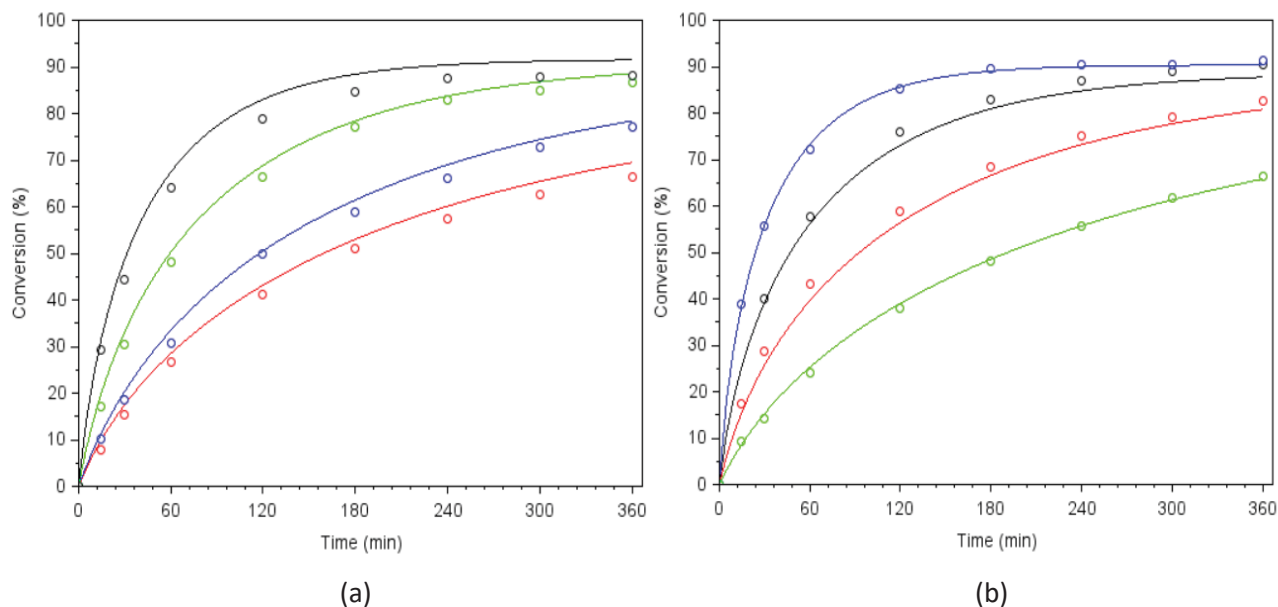


FIGURE 19 – REGRESSION RESULT FOR ACID OIL 40% (a) WITH 0.33%WT CATALYST, 50°C AND 6:1 ETHANOL/ACID RATIO (RED), 50°C AND 12:1 ETHANOL/ACID RATIO (BLUE), 60°C AND 12:1 ETHANOL/ACID RATIO (GREEN), AND 70°C AND 12:1 ETHANOL/ACID RATIO (BLACK). (b) 9:1 RATIO WITH 0.33%WT CATALYST AND 40°C (GREEN), 50°C (RED), 60°C (BLACK), AND 70°C (BLUE)

For the 8:2 ethanol/water ratio, the regression could predict well the reaction behavior except for the 1:1 ethanol/acid ratio, which had a response for the reaction conversion with a 10% difference from the experimental data, even though for the anhydrous ethanol data, the same point had a good prediction. The difference regarding this set could be due to ethanol evaporation, as for a lower ethanol/acid ratio, its lack would have more influence on the reaction. This alternative was considered consistent once compared with the same experiments performed with anhydrous ethanol. For this one, the experiment's temperature was milder (50°C), and the predictions were much more in accordance with the obtained data. The regression of these data is present in FIGURE 20.

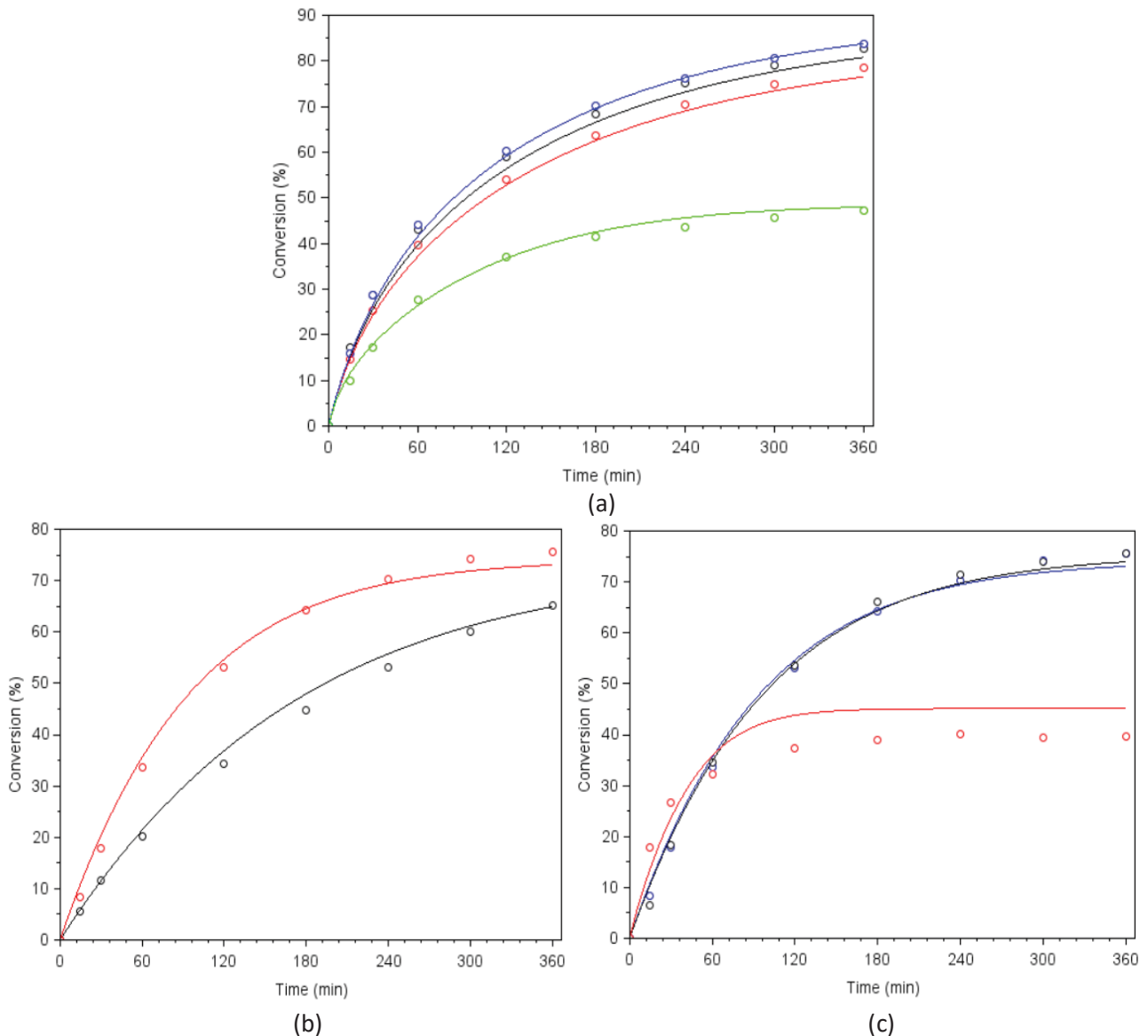


FIGURE 20 – (a) ANHYDROUS ETHANOL, 0.33%WT CATALYST, 50°C, AND ETHANOL/ACID RATIO OF 12:1 (BLUE), 9:1 (BLACK), 6:1 (RED), AND 1:1 (GREEN) (MURAD, 2017). 8:2 ETHANOL/WATER RATIO: (b) 9:1 ETHANOL/ACID RATIO, 0.33% CATALYST AND UNDER 70°C (RED) AND 60°C (BLACK); (c) 12:1 (BLACK), 9:1 (BLUE), AND 1:1 (RED) ETHANOL/ACID RATIO, 0.33% CATALYST, AND 70°C

As observed from all these data, the regression could predict the behavior of the systems not used on the parameters' estimation, as of prior experiments developed by previous work, and had a good response for the reaction behavior for the experiments developed in this work. To have an overall evaluation of the associated deviations concerning the use of the regressed kinetics, the normal probability plot was constructed, along with two histograms (one for the experimental data obtained in this work and another for experimental data from Murad (2017)). The results can be observed in FIGURE 21.

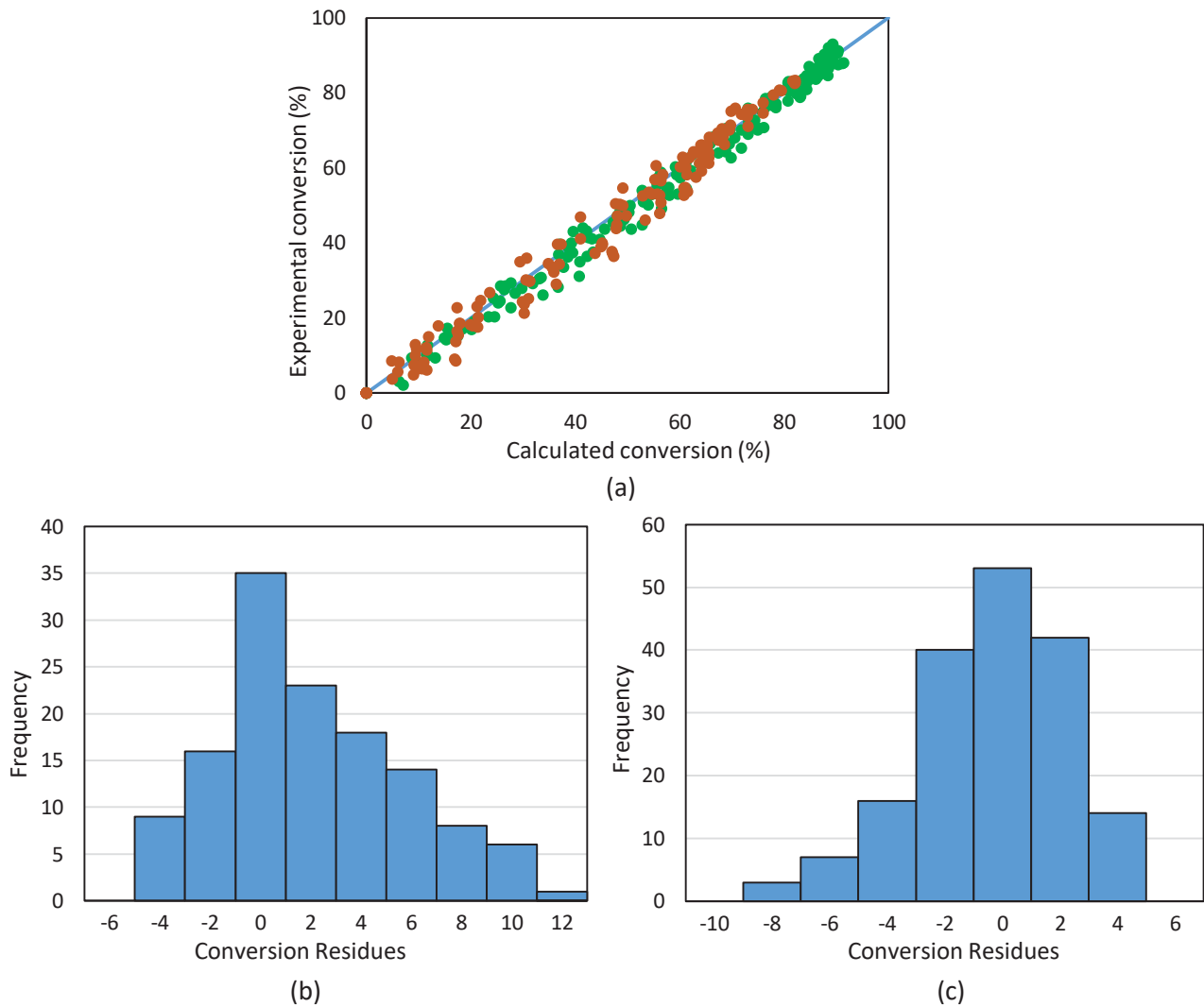


FIGURE 21 – (a) NORMAL PROBABILITY PLOT CONSIDERING THE REGRESSED KINETICS AND THE EXPERIMENTAL DATA FROM THIS WORK (RED), AND MURAD'S (2017) (GREEN). (b) HISTOGRAM COMPARING THE RESIDUES FROM THIS WORK'S DATA AND (c) FROM MURAD'S (2017)

So, with the kinetics' parameters found, a good range of reaction conditions, especially involving higher quantities of water, can be predicted. With these data, it is possible to move forward to the biodiesel production simulation in Aspen Plus®.

#### 4.2.2 Aspen Plus® analysis

The parameters obtained from the calculations are now inserted in Aspen Plus® reaction kinetics for the esterification. Literature values regarding the transesterification reaction (Reyero et al., 2015) and solubilization (System, 2019; Wells, 1923) were used to simulate these processes.

#### 4.2.2.1 Ethanol recycling

Before the full simulation construction and experiments' conduction, to help inspect the most economically feasible set of ethanol/water ratios, this property's influence in the recycling stream after distillation was verified.

As inferred in *Ethanol/water ratio influence*, the fatty acid to ester conversion is better for higher ethanol/water ratios. However, the best economical option can only be determined through a separation process simulation. For this analysis, the Software Aspen Plus® was used to design the distillation column for ethanol recycle. A primary evaluation was made using only ethanol and water in the column, as there was no experimental data at that point for oil, acid, or ester estimation. The results obtained through the simulation tests are presented in TABLE 11.

TABLE 11 – ETHANOL RECYCLING COLUMN RESULTS FOR DIFFERENT ETHANOL/WATER RATIOS

<b>Ethanol/Water ratio</b>	<b>9:1</b>	<b>8:2</b>	<b>7:3</b>
Reflux Ratio	7.6	0.80	0.72
Number of Stages	65	13	6
Ethanol molar recovery (recycled)	0.95	0.999	0.999
Heat duty (reboiler) (kW)	767.77	195.10	203.31
Heat duty (condenser) (kW)	-771.29	-188.63	-199.60

Comparing these three scenarios, they show that a higher ethanol/water ratio on this recycling involves equipment with a higher cost and the need for a higher reflux ratio, which includes economic issues.

With this data, it was concluded that the most probable range to reduce costs for the distillation column operation would be between 8:2 and 7:3 ratios.

The best ethanol/water ratio is further discussed in the *Economic Analysis* topic. In this section, the optimal value is verified through the economic evaluation concerning all the project costs, including raw material, utilities, equipment, and products income, as these variables are strongly connected to any variation in this distillation column properties.

#### 4.2.2.2 Thermodynamic models

The base thermodynamic model used for the process was NRTL. A relatively simple model, good with simulations involving liquid/liquid equilibrium and also adequate to handle polar components, as it considers the strong interactions present in systems such as

hydrogen bonding, which results in deviations from ideal mixture behavior (Matos et al., 2018). This model works well when operating with pressures up to 10 bar, a value that is not surpassed at any stage in the simulation. When dealing specifically with electrolytes, as occurs on the neutralization reactor, the model was changed to ELECNRTL. Otherwise, the heat of the reaction was wrongly calculated. The other equipment with thermodynamic model change was the extractor, as the NRTL model would lead to an internal error in Aspen Plus®, making the simulation progress unfeasible. The possible error was pointed out to be relative to liquid-liquid equilibrium involving FAEE + glycerol + ethanol system.

As reported in the literature (Do Carmo et al., 2014), modifications on the UNIFAC model favored UNIFAC-Dortmund to describe better biodiesel + glycerol + alcohol (methanol and ethanol) systems. Therefore, this model was chosen to be used in the extractor.

#### 4.2.2.3 Simulation design: Base case description

Once the best esterification and transesterification reaction conditions were settled, the simulation design could be done. FIGURE 22 shows the biodiesel production simulation built to evaluate the process's feasibility and the costs involved. The detailed flowsheet with stream data is available in APPENDIX I.

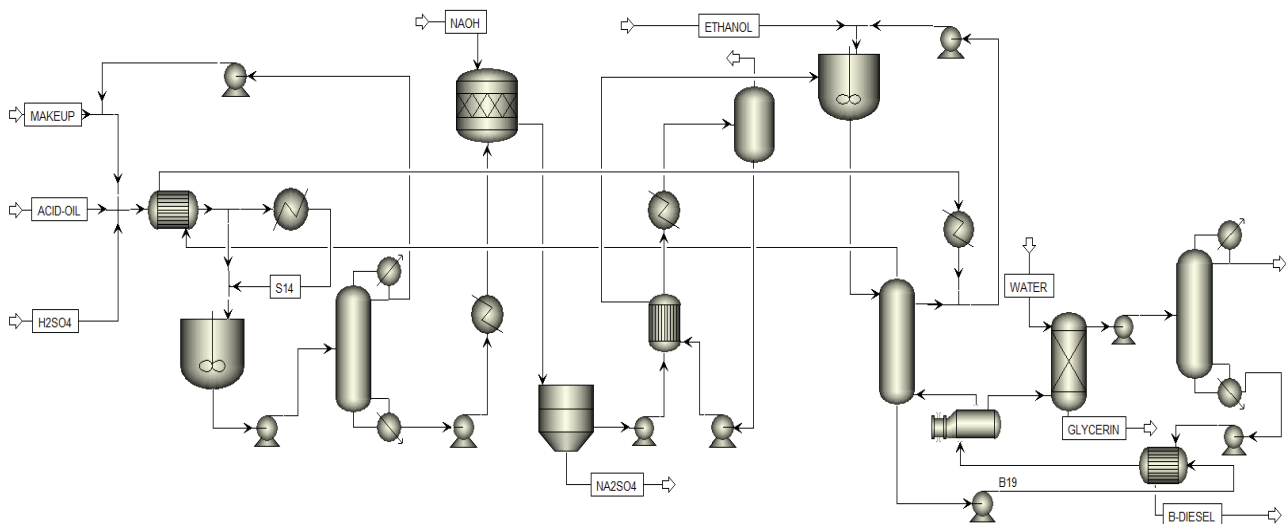


FIGURE 22 – BIODIESEL PRODUCTION PROCESS DESIGN

The process starts with the addition of acid oil composed of 90% weight of triolein and 10% of fatty acid (represented by lauric acid), hydrous ethanol, and catalyst to the continuous stirred-tank reactor (CSTR). Initially, it was tested with a batch reactor to verify and compare the results from the regression with the simulation results, and later it was

replaced with the CSTR. The fatty acid proportion was chosen considering the average percentages among crude vegetable oils and waste cooking oil, which is usually less than 7% (Kan and Strezov, 2014). For this reason, a higher percentage was employed to have a more reliable range. The conditions chosen were 9:1 ethanol/acid ratio, catalyst concentration of 0.33%wt, and 70°C. The ethanol/water ratio used was 8:2, and the reason for this choice is further discussed at *Economic Analysis*. It is important to observe that the possibility of using higher water content in alcohol in the process may benefit it, as most recycling streams present contain a considerable amount of water content.

A 73% conversion is achieved on the esterification reactor, and then the products flow to the ethanol recycling distillation column. Two base situations were tested on this equipment, using a reactive distillation column and a normal one. Considering that the esterification demands a high quantity of ethanol to allow the reaction to occur properly, if the column were to be a reactive one, less ethanol would be recycled. Therefore, it would result in the process being more expensive, as the produced FAEE quantity is not sufficient to surpass the raw material costs of the make-up stream, containing ethanol 80% molar.

Tests executed under a higher ethanol recovery and a reactive distillation column were unsuccessful as the inverse reaction prevailed. These tests were first performed by acquiring the simulation results regarding the respective components concentration and mole fraction of each stage of a non-reactive column. With them, it was possible to calculate the esterification parameters for the reaction on each column stage. After the first substitution on the simulation and changing the column to a reactive one, new concentration and mole fraction values were obtained. The reaction parameters were updated by using these new values, and these steps were repeated until convergence. In the end, due to the low ethanol recovery at the top of the column, increasing raw material costs, and insufficient alcohol present in the equipment for a satisfactory reaction, it was concluded that a non-reactive distillation column would be economically favorable for the process.

The column's top product returns to the process. In contrast, the bottom product is then carried to a neutralizer and filter, removing the sodium sulfate formed and the neutralized FFA that did not react on the esterification reactor. A 94% conversion of the FFA was considered, as it is expected high conversion when lauric acid reacts with sodium hydroxide. It was used to determine the FFA conversion on the esterification reaction experiments. Both sodium sulfate and the sodium laurate that was not diluted in water were removed using a filter. The solubility considered for sodium laurate was 5 times its solubility at 25°C (System, 2019), corresponding to 16.22 g/L of water.

The liquid flows to the flash to remove the water for the transesterification reaction, which can have a maximum water content of 0.06% (Silva and Oliveira, 2014).

After the flash equipment, the stream flows to the transesterification reactor, which operates under 70°C, 1.6 bar, 7:1 ethanol/oil ratio, and catalyst/oil concentration of 0.18%wt. Due to the high saponification process, it is recommended that a maximum amount of 3%wt of FFA is present in the transesterification reaction (Ribeiro et al., 2011; Thaiyasuit et al., 2012). A FFA content up to 0.5% (West, 2006) can also be considered when the process has the esterification reaction as a pre-step, even though water content is more critical to the process than FFA content (Wang, 2008). Both water and FFA mass fractions are in accordance with these values, corresponding to 0.058% of water and 0.12% of fatty acid content.

In the transesterification reaction kinetics, the pre-exponential factor and activation energy values considering a reference temperature of 50°C for each step of the reaction are presented in TABLE 12 (Reyero et al., 2015). In the reaction, there is the presence of ethanol (ET), triglyceride (TAG), diglyceride (DAG), monoglyceride (MAG), glycerol (GLY), and the ester (EO).

TABLE 12 – TRANSESTERIFICATION REACTION PARAMETERS FOR EACH STEP OF THE REACTION

Reaction	Pre-exponential factor (L <sup>2</sup> /mol <sup>2</sup> .s)	Activation Energy (kJ/mol)
ET + TAG → DAG + EO	0.110	48.7
ET + DAG → MAG + EO	0.171	49.3
ET + MAG → GLY + EO	0.076	53.9
EO + DAG → TAG + ET	0.034	48.7
EO + MAG → DAG + ET	0.054	49.3
EO + GLY → MAG + ET	0.001	53.9

The reaction conversion considering a residence time of 30 minutes is 99.8%. The transesterification product is directed to a new distillation column to recover part of the ethanol remaining from the prior reaction. This equipment operates under a 0.01 reflux ratio and 0.35 distillate to feed ratio. It is essential to have in mind that a higher ethanol/oil ratio for the transesterification reaction improves the reaction time and conversion. However, for ratios over 12:1, the separation of the glycerol formed is difficult (Encinar et al., 2002).

The bottom stream then enters an extractor to remove the glycerol, which leaves the equipment with 87%wt, within specifications for crude glycerol. Even though the glycerol formed in this project simulation is directly sold, some authors already showed the possibility



of glycerin use in biofuel production. One example is converting water/glycerin mixture into syngas for power production (Pickett et al., 2018).

Finally, the product enters the third distillation column to remove the remaining ethanol and water, and reach biodiesel specifications. It operates with a 0.1 reflux ratio and 0.24 distillate to feed ratio. In the end, it is produced around 330,000 m<sup>3</sup>/year of biodiesel.

All distillation columns used in this simulation were first tested using the shortcut design (DSTWU) model present in the software, and posteriorly they were changed to the rigorous model RadFrac. Design Specifications were added to achieve the desired product recovery and purity by adjusting the reflux ratio values and distillation to feed ratio.

Concerning the process involved, three scenarios were studied. The first and main one studied (described above) considers that the fatty acid on the transesterification reactor only reaches specification after at least 77% of the remaining FFA from the esterification reactor is neutralized in the catalyst neutralization reactor. The second one considers that the FFA content already reaches specification for the transesterification reaction when reacted in the esterification reactor. The last scenario tested considers the same things as the second one, but with less FFA content in the feed (7%).

The first and second scenarios were tested to compare the gain from the remaining FFA's esterification instead of only disposing of it. The third scenario was performed to evaluate the economic influence on feed purity.

Therefore, after finishing the simulation concerning the main case, the other two scenarios were tested under the same project design. Considering that all scenarios developed produced biodiesel within specifications, some of these parameters limit values from ANP (Petroleum National Agency), and European standard EN 14214 were compared with the ones obtained through the simulations, as presented in TABLE 13.

TABLE 13 – SIMULATION AND STANDARD SPECIFICATIONS VALUES FOR BIODIESEL PROPERTIES

Property	ANP limits	EN 14214 limits	Scenario 1	Scenario 2	Scenario 3
Density (kg/m <sup>3</sup> , 15°C for EN14214 and 20°C for ANP)	850-900	860-900	~870 (for 15 and 20°C)	~870 (for 15 and 20°C)	~870 (for 15 and 20°C)
Kinematic viscosity (cSt, 40°C)	3.0-6.0	3.5-5.0	4.30	3.94	4.12
Water content (mg/kg)	200 max	500 max	170	170	170
Monoglyceride content (%wt/wt)	0.7 max	0.80 max	0.38	0.37	0.38
Diglyceride content (%wt/wt)	0.20 max	0.20 max	0.18	0.18	0.18
Triglyceride content (%wt/wt)	0.20 max	0.20 max	0.12	0.11	0.11
Total glycerol (%wt/wt)	0.25 max	0.25 max	0.15	0.13	0.13
Ester content (%wt/wt)	96.5 min	96.5 min	98.8	98.7	98.7

From this table, it is possible to observe that all requirements are achieved, being adequate considering both ANP and European Standard.

As our main case study corresponds to the first scenario, specific details about this unit's equipment and operation are presented. In contrast, for the other scenarios, only the economic analysis and optimization details are discussed.

#### 4.2.2.4 Main equipment conditions

All conditions and equipment properties were evaluated for biodiesel production of 330,000 m<sup>3</sup>/year in the first scenario.

##### **Esterification reactor:**

- Inlet and outlet temperature: 70°C
- Liquid phase
- Reaction class: Custom (with the values and kinetics structure as presented in *Scilab<sup>TM</sup> analysis* topic)
- Pressure: 1.5 bar
- Volume: 112 m<sup>3</sup>
- Residence time: 1.75 h
- Heat Duty: 79.26 kW
- Utility: Low-pressure steam (Aspen's default)

##### **First ethanol recycling distillation column (post-esterification):**

- Inlet temperature: 70°C
- Outlet top temperature: 79°C
- Outlet bottom temperature: 118°C
- Pressure drop per stage: 0.035 bar
- Number of stages: 10
- Feed stage: 3
- Reflux molar ratio: 1.2
- Distillate to feed molar ratio: 0.72

- Total condenser
- Condenser utility: Cooling water (30° to 45°C)
- Condenser heat duty: -3904 kW
- Type of reboiler: Kettle
- Reboiler utility: Medium-pressure steam (Aspen's default)
- Reboiler heat duty: 4908 kW

**Filter:**

- Operating temperature: 77°C
- Operating pressure: 1.6 bar
- Residual moisture (wet basis): 0.3

**Flash:**

- Inlet pressure: 8.3 bar
- Outlet pressure: 1
- Operation temperature: 191°C
- Vapor mole fraction: 0.32

**Transesterification Reactor:**

- Inlet and outlet temperature: 70°C
- Liquid phase
- Reaction class: Powerlaw (with the values and kinetics structure as presented in TABLE 12)
- Pressure: 1.6 bar
- Volume: 24.4 m<sup>3</sup>
- Residence time: 0.5 h
- Heat Duty: 172 kW
- Utility: Low-pressure steam (Aspen's default)

**Second ethanol recycling distillation column (post-transesterification):**

- Inlet temperature: 70°C
- Outlet top temperature: 78°C
- Outlet bottom temperature: 107°C
- Pressure drop per stage: 0.035 bar
- Number of stages: 4
- Feed stage: 2
- Phases: Vapor-Liquid-Liquid
- Reflux molar ratio: 0.01
- Distillate to feed molar ratio: 0.35
- Total condenser
- Condenser utility: Cooling water (30° to 45°C)
- Condenser heat duty: -322 kW
- Type of reboiler: Kettle
- Reboiler utility: Low-pressure steam (Aspen's default)
- Reboiler heat duty: 860 kW

**Extractor:**

- Number of stages: 6
- Pressure: 1 bar
- Adiabatic
- Water inlet mass flow: 230 kg/h
- Inlet top stream (water) temperature: 25°C
- Inlet bottom stream temperature: 107°C
- Outlet top stream temperature: 101°C
- Outlet bottom stream temperature: 104°C

**Biodiesel purification distillation column:**

- Inlet temperature: 105°C
- Outlet top temperature: 51°C

- Outlet bottom temperature: 142°C
- Pressure: 0.29 bar
- Number of stages: 4
- Feed stage: 3
- Reflux molar ratio: 0.10
- Distillate to feed molar ratio: 0.24
- Total condenser
- Condenser utility: Cooling water (30° to 45°C)
- Condenser heat duty: -458 kW
- Type of reboiler: Kettle
- Reboiler utility: Medium-pressure steam (Aspen's default)
- Reboiler heat duty: 1205 kW

#### 4.2.2.5 Energy analysis

The base case for the biodiesel production process is adequate regarding its production. However, by turning the Energy Savings on, it can save almost 60% of the energy spent, considering this first scenario does not have any energy integration.

For this reason, different configurations of newly included heat exchangers were tested using Aspen Plus<sup>®</sup> Energy Analysis. The strategy used to determine the best configuration was to verify which heat exchangers were needed in the three situations; for the ethanol/water ratio on the recycle stream of the first distillation column to be 9:1, 8:2, and 7:3. A base case of the overall energy analysis generated for an 8:2 ratio can be seen in APPENDIX I.

The two best results obtained were considering three and four heat exchangers. It was observed that for higher ethanol/water ratios, the difference between savings was less than 1%, being more considerable for the 7:3 ratio. As explained in Economic Analysis, the optimal ratio is much closer to 8:2, which is also the one that the use of three heat exchangers had better energy saving. Therefore, the three heat exchangers configuration was chosen to be included in the project. The information summary regarding the configurations' tests can be observed in TABLE 14.

TABLE 14 – LIST OF PROPERTIES FROM EACH ENERGY-SAVING SCENARIO

<b>9:1</b>		
Property	3 heat exchangers	4 heat exchangers
<b>Total capital cost (US\$)</b>	52,743	75,905
<b>Payback period (year)</b>	0.31	0.44
<b>Energy cost Saving (%)</b>	43.1	43.6
<b>8:2</b>		
Property	3 heat exchangers	4 heat exchangers
<b>Total capital cost (US\$)</b>	51,403	68,792
<b>Payback period (year)</b>	0.30	0.42
<b>Energy cost Saving (%)</b>	43.7	42.3
<b>7:3</b>		
Property	3 heat exchangers	4 heat exchangers
<b>Total capital cost (US\$)</b>	46,165	71,818
<b>Payback period (year)</b>	0.27	0.41
<b>Energy cost Saving (%)</b>	40.7	44.1

Considering the three exchangers configuration, the first heat exchanger uses the heat from the flash bottom stream (hot stream) to pre-heat the one that will enter the flash (cold stream) until the first one reaches 90°C, before entering the transesterification reaction. Even though 90°C is higher than the reaction's specified temperature, once it is mixed with the ethanol stream, the temperature lowers significantly, being close to the desired 70°C.

A summary of the conditions and equipment properties for this first energy-saving heat exchanger can be consulted below:

#### **First energy-saving heat exchanger:**

- Inlet hot stream temperature: 191°C
- Inlet cold stream temperature: 78°C
- Outlet hot stream temperature: 90°C
- Outlet cold stream temperature: 177°C
- Hot stream pressure: 1.6 bar
- Cold stream pressure: 8.6 bar
- Flow Direction: Countercurrent
- Heat Duty: 2023 kW
- Exchanger area: 183 m<sup>2</sup> (1975 ft<sup>2</sup>)
- Overall heat transfer coefficient (U-value): 850 W/m<sup>2</sup>.K (Aspen's default)

The second exchanger uses heat from the second distillation column's top stream (hot stream) to heat the stream entering the esterification reactor (cold stream) until the latter reaches 70°C. A second heat exchanger is used for the hot stream to condense, where it is redirected to the column as reflux and to the transesterification reactor. In this system, a third heat exchanger is also necessary before the esterification reactor to heat the stream in the start-up of the process, as no hot fluid flows in the energy-saving heat exchanger on the first run. Therefore, once there is hot fluid in the energy-saving exchanger, the flow to this third exchanger may be blocked. A summary of the overall conditions and equipment properties for this exchanger can be consulted below:

### **Second energy-saving heat exchanger:**

- Inlet hot stream temperature: 79°C
- Inlet cold stream temperature: 40°C
- Outlet hot stream temperature: 78°C
- Outlet cold stream temperature: 70°C
- Hot stream pressure: 1 bar
- Cold stream pressure: 1.5 bar
- Flow Direction: Countercurrent
- Heat Duty: 777 kW
- Exchanger area: 45 m<sup>2</sup> (484 ft<sup>2</sup>)
- Overall heat transfer coefficient (U-value): 850 W/m<sup>2</sup>.K (Aspen's default)

The last exchanger uses the heat from the third distillation column's bottom stream (hot stream) to pre-heat the second distillation column's bottom stream (cold stream). It will raise its temperature until the outlet hot stream temperature reaches 90°C. There will be the need for a reboiler after pre-heating the cold stream before giving the steam back to the column. Some conditions and properties for this exchanger may be consulted below:

### **Third energy-saving heat exchanger:**

- Inlet hot stream temperature: 142°C
- Inlet cold stream temperature: 85°C

- Outlet hot stream temperature: 90°C
- Outlet cold stream temperature: 94°C
- Hot stream pressure: 1 bar
- Cold stream pressure: 1.035 bar
- Flow Direction: Countercurrent
- Heat Duty: 1176 kW
- Exchanger area: 92 m<sup>2</sup> (990 ft<sup>2</sup>)
- Overall heat transfer coefficient (U-value): 850 W/m<sup>2</sup>.K (Aspen's default)

With these three exchangers, it was possible to decrease the possibility of energy saving percentage from almost 60% to less than 12%. It is important to remember that this remaining 12% is due to the working situation's choice, as these three exchangers work properly for a range of ethanol recycling on the first distillation column from 7:3 to 9:1 ratio. The configuration obtained through this analysis was applied to all tested scenarios.

#### 4.2.2.6 Economic analysis

After including the energy-saving exchangers, another important measure to take is optimizing the esterification reaction and ethanol recycling, the most sensitive part of the simulation, as the ethanol/water ratio entering the reactor influences the FFA conversion, reaction time, and posterior separation process. For this evaluation, two different cases were tested, and the criteria used to judge the best configuration was the payout time, as a lower value is desired. In the first case, the ethanol/water ratio is varied in the recycling stream while the make-up enters in a 9:1 ratio. In the second case, there is also a variation of the ethanol/water ratio in the recycling stream, but with an 8:2 ratio make-up.

The tests made by varying the ethanol/water ratio in the recycling stream for each case resulted in TABLE 15. The first point corresponds to the 7.6:2.4 ratio, and the fifth will be the 8.4:1.6 ratio.



TABLE 15 – PAYOUT PERIOD FOR DIFFERENT ETHANOL/WATER RATIOS IN THE RECYCLING STREAM AND MAKE-UP FOR SCENARIO 1\*

Recycling Stream	Make-up 9:1	Make-up 8:2
7.6:2.4	2.85	2.86
7.8:2.2	2.83	2.84
8.0:2.0	2.81	2.77
8.2:1.8	2.79	2.80
8.4:1.6	2.83	4.91

\*Already considers the energy integration heat exchangers

It is important to say that the points 7.6:2.4 and 7.8:2.2 were discarded, as the corresponding ratios could not result in a biodiesel within the specifications. Therefore, the best economic point would be the third one, corresponding to an 8:2 ratio on the recycle stream and make-up through these obtained payout values.

After the modification, different esterification reaction times were tested, and both conversion and payout periods were verified. In a time interval from 0.25 to 6 hours, the conversion varied from 35 to 89%. It was observed that until at least 1.75 hours of reaction, the final biodiesel would not reach the specifications. Therefore, the economic analysis was made from one point before (non-operable 1.5 hours) until 2.5 hours. The conversion varied from 71.03% for 1.5 hours to 77.92% for 2.5 hours.

Even though the difference between payout periods was small, higher residence times result in less lauric acid further on the process, at the cost of raising the investment time return. As the minimum conversion necessary to achieve FFA specification is 74%, the most economical residence time chosen was 1.75 hours (74.13% conversion).

Adopting the same criteria for the other scenarios, the payout period using different ethanol/water ratios in the recycling stream and make-up, and the residence time in the esterification reactor was observed in scenarios 2 and 3. In these cases, it was not possible to use high quantities of water, as the final product would not achieve specifications. Thus, the ethanol concentration used in the make-up was slightly modified. Instead of using 8:2 and 9:1 ethanol/water molar ratios, as used in the first scenario, a comparison considering the use of hydrous (9:1) and anhydrous ethanol in the make-up stream was made. The results obtained when varying the ratios in the recycling and make-up streams in both scenarios can be seen in TABLE 16.

TABLE 16 - PAYOUT PERIOD FOR DIFFERENT RECYCLING STREAM AND MAKE-UP ETHANOL/WATER RATIOS FOR SCENARIO 2 AND 3\*

Scenario 2			Scenario 3		
Recycling Stream	Make-up hydrous	Make-up anhydrous	Recycling Stream	Make-up hydrous	Make-up anhydrous
8.1:1.9	2.81	2.82	8.5:1.5	2.70	2.70
8.3:1.7	2.81	2.82	8.6:1.4	2.72	2.74
8.5:1.5	2.85	2.83	8.7:1.3	3.02	2.77
8.7:1.3	4.09	3.17	8.8:1.2	4.11	2.85

\*Already considers the energy integration heat exchangers

In both cases, the first two points were discarded as product specifications could not be met. Therefore the optimal conditions for scenario 2 would be the use of anhydrous ethanol in the make-up and an 8.5:1.5 ethanol/water ratio in the recycling stream. For scenario 3, the best economic point corresponds to anhydrous ethanol in make-up and an 8.7:1.3 ethanol/water ratio in the recycling stream. It is possible to observe that higher ethanol/water ratios are necessary to achieve specifications by lowering acid content in the oil.

Usually, it is expected that the use of anhydrous ethanol would bring higher costs for the process. However, considering the same ethanol/water ratio on the recycle stream, there would be higher ethanol recovery for the anhydrous ethanol, reducing by almost 30% the make-up stream cost in the chosen operational ratio. Therefore, the use of anhydrous ethanol would be economically better than hydrous ethanol in these cases.

Considering the esterification residence time for scenario 2, the range evaluated varied from 3.5 (94.79% conversion) to 4.5 hours (95.85%). Similarly as happened in the first scenario, there would be almost no difference regarding the payout period. As the minimum conversion necessary to achieve FFA specification was 95%, the most economical residence time chosen was 3.75 hours.

The same evaluation was performed in scenario 3, where the range evaluated varied from 2 (92.27% conversion) to 3 hours (94.66%). As the minimum conversion necessary to achieve FFA specification in this scenario was 92.8%, the most economical residence time chosen was 2.25 hours.

Proceeding with the economic analysis, the product and raw material price values were searched while, for most utilities, Aspen's default cost was used. The considered acid oil price was half of the soy oil. The values used in the simulation are present in TABLE 17.

TABLE 17 – LIST OF PRICES OF THE COMPOUNDS AND UTILITIES USED IN THE PROCESS

<b>Compound / Utility</b>	<b>Price</b>
<b>Hydrous Ethanol<sup>a</sup></b>	US\$ 0.42/L
<b>Anhydrous Ethanol<sup>a</sup></b>	US\$ 0.46/L
<b>Soy Oil<sup>b</sup></b>	US\$ 0.62/kg
<b>Acid Oil (consideration)</b>	US\$ 0.31/kg
<b>Sulfuric Acid<sup>c</sup></b>	US\$ 0.032/kg
<b>Sodium Hydroxide<sup>c</sup></b>	US\$ 0.55/kg
<b>Sodium Sulfate<sup>c</sup></b>	US\$ 0.117/kg
<b>Biodiesel<sup>d</sup></b>	US\$ 0.65/L
<b>Crude Glycerin<sup>e</sup></b>	US\$ 0.21/kg
<b>Water<sup>f</sup></b>	US\$ 0.0016/kg
<b>Low Pressure Steam<sup>g</sup></b>	US\$ 0.0042/kg
<b>Medium Pressure Steam<sup>g</sup></b>	US\$ 0.0043/kg
<b>High Pressure Steam<sup>g</sup></b>	US\$ 0.0043/kg
<b>Electrical Energy<sup>g</sup></b>	US\$ 77.5/MWh

<sup>a</sup> Tecnologia, 2019  
<sup>b</sup> Markets Insider, 2019  
<sup>c</sup> Echemi, 2019  
<sup>d</sup> De Homologação, 2019  
<sup>e</sup> Landress, 2019  
<sup>f</sup> AGEPAR, 2019  
<sup>g</sup> Aspen's default

With these costs, it is possible to use the economic analysis in Aspen Plus<sup>®</sup>. The software then gives equipment, utility, and raw material costs. Furthermore, considering the products' price, it also provides product sales and payout time.

As observed, for the initial estimated production (8 million liters per year), there would be no investment return in 10 years. For this reason, more in-depth research was made to see the average biodiesel industry production in Brazil.

It was found that in 2017, Brazil's average biodiesel production per unit was 160 million liters, and for the south region, it was 230 million (DBio, 2017). An estimation of biodiesel production in the upcoming years may also provide a better scenario estimative. Regarding the rise from 11 to 12% of biodiesel in diesel in 2020, it is possible to see an optimistic scenario for this biofuel, especially in Brazil.

Considering the rise in biodiesel addition in diesel to improve 1% every 2 years, there is a prediction that in 2025, biodiesel demand will reach 10 billion liters, while in 2030, it will be around 13 billion liters (Coelho, 2017). Considering all that, an average of 330 million liters per year of biodiesel production was established for the first scenario, so it would still operate well with higher demand. For the other scenarios, it was used the same oil volume inlet flow as the first. Therefore, scenarios two and three would have an average biodiesel production of 345 and 370 million liters per year, respectively.

As presented in TABLE 17, the cost of acid oil was considered half of the soy oil price. However, it is also possible to investigate a price range for this material by verifying its influence on the payout period. Three situations were tested for all three scenarios for the economic analysis, considering the initially adopted acid oil price, 20% cheaper, and 20% more expensive. The final investment results can be observed in TABLE 18.

TABLE 18 – SUMMARY OF SOME BIODIESEL PRODUCTION COSTS AND REVENUE

<b>Scenario 1*</b>			
Acid oil price (US\$)	0.372	0.31	0.248
Total Capital Cost (million US\$)	12.885	12.885	12.885
Total Operating Cost (million US\$/Year)	170.93	151.85	132.77
Total Raw Materials Cost (million US\$/Year)	148.45	130.78	113.12
Total Utilities Cost (million US\$/Year)	7.7668	7.7668	7.7668
Equipment Cost (million US\$)	2.0750	2.0750	2.0750
Total Installed Cost (million US\$)	5.2682	5.2682	5.2682
Total Product Sales (million US\$/Year)	220.64	220.64	220.64
Payout Period (Year)	3.78	2.77	2.20
<b>Scenario 2*</b>			
Acid oil price (US\$)	0.372	0.31	0.248
Total Capital Cost (million US\$)	14.165	14.165	14.165
Total Operating Cost (million US\$/Year)	167.22	148.15	129.07
Total Raw Materials Cost (million US\$/Year)	145.44	127.78	110.12
Total Utilities Cost (million US\$/Year)	7.2243	7.2243	7.2243
Equipment Cost (million US\$)	2.8518	2.8518	2.8518
Total Installed Cost (million US\$)	6.1390	6.1390	6.1390
Total Product Sales (million US\$/Year)	217.15	217.15	217.15
Payout Period (Year)	3.81	2.81	2.23
<b>Scenario 3*</b>			
Acid oil price (US\$)	0.372	0.31	0.248
Total Capital Cost (million US\$)	12.832	12.832	12.832
Total Operating Cost (million US\$/Year)	181.84	161.27	140.69
Total Raw Materials Cost (million US\$/Year)	161.10	142.05	123.00
Total Utilities Cost (million US\$/Year)	5.1987	5.1987	5.1987
Equipment Cost (million US\$)	2.2086	2.2086	2.2086
Total Installed Cost (million US\$)	5.2939	5.2939	5.2939
Total Product Sales (million US\$/Year)	234.15	234.15	234.15
Payout Period (Year)	3.78	2.75	2.17

\* Already considers the energy integration heat exchangers

The total capital cost includes the purchased equipment and its instrumentation, painting, piping, and other expenses. The operating costs include raw material cost, utilities, maintenances, and operating labor, for example. Considering all these categories and the specified biodiesel price (half of soy oil price), there would be a minimum payout period of 2.8 years.

Still analyzing acid oil price variation, by considering a production of 330 million liters per year in the first scenario, for the investment to have a payout period of 5 years, varying only the acid oil price, it would have to be US\$0.414, 67% of the soy oil price. Moreover, to

have a payout period of 10 years, it would cost US\$0.483, 78% of the soy oil price. These results are in accordance with all scenarios tested.

The time for investment return estimated on this project is even better than a typical payout period of 5 to 10 years for conventional biofuels plants (Mestre, 2017), or the recommended 3-5 years (SUNHO BIODIESEL CORPORATION, 2019), indicating an important alternative for biodiesel production.

## 5 CONCLUSION

The overall experimental results verified that using different free fatty acids would not influence the reaction, as the three types tested provided similar behavior. Concerning the reaction conditions, a higher temperature, catalyst concentration, ethanol to water, and ethanol to acid ratios, have very positive effects on the final esterification conversion, especially the temperature and ethanol/water ratio. However, having better conditions for the reaction does not necessarily mean having better financial results.

Analyzing the simulation, the reaction kinetics could be regressed considering higher water concentration in the esterification. A biodiesel production process could also be created to evaluate and improve the project's points of optimization. Three scenarios for biodiesel production were tested, and, in all scenarios, biodiesel is produced within specification from both ANP and EN resolutions, and presented a similar payout period. In the first scenario, the use of an ethanol/water ratio of 8:2 in the process reduced raw material, utilities, and equipment costs, achieving biodiesel specifications and showing satisfactory economic results. Although anhydrous ethanol was used in the other scenarios' make-up, because of the first column recycling stream concentration, an ethanol/water ratio of 8.6:1.4 and 8.9:1.1 were used in the esterification reaction in scenarios two and three, respectively. Therefore, the tested scenarios demonstrated promising results in the esterification reaction even with higher water concentration, indicating the possibility of its use in real processes. Optimizations considering energy analysis showed that the base case could be adapted to seize the heat from the streams in the process. By inserting three energy-saving heat exchangers, the total utilities cost could be reduced by 40%, an investment in equipment that would finance itself in less than a trimester.

Concerning economic aspects, it was observed that raw material costs are the major economic influencers in the project, being responsible for over 85% of the total operating costs. To reduce operating costs, a distillation column for ethanol recycling was added to the project, reducing raw material costs by 40%. By varying the acid oil price, its strong influence in the final payout period could be verified. A 20% increase in its cost would raise the payout period by 38%, depending on the scenario. A maximum acid oil price of 78% of the soy oil was found to have a maximum payout period for the unit of 10 years, or 67% of the soy oil price for a payback time of 5 years. Including all scenarios, the final simulated biodiesel production process would have a payout period of less than 3 years, a very positive result considering the usual payback time in the biofuels industry.

## SCIENTIFIC PRODUCTIONS

- Tentative title for congress submission: Reaction analysis and simulation of fatty esters production from acid oil using a hybrid process. 2021.
- An overall analysis of biodiesel production process from acid oil using methanol and ethanol. Accepted for presentation at 23° Congresso Brasileiro de Engenharia Química – COBEQ, 2021.
- Simulation, optimization and economic analysis of process to obtain esters from fatty acids. Accepted for publication in Biofuels, Bioproducts and Biorefining journal, Wiley, 2020.
- Process Analysis of Biodiesel Production – Kinetic Modeling, Simulation, and Process Design. Book Chapter of “Process Systems Engineering for Biofuels Development”, Wiley, 2020.
- Simulation and optimization of biodiesel production process using acid oil and a reactive distillation column. Banner presentation at VII Congresso da Rede Brasileira de Tecnologia e Inovação de Biodiesel, 2019.
- Tentative title for article submission: “Optimization of esterification reaction conditions through the analysis of the main significant variables”, in production.
- Comprehensive analysis of different iron nanoparticles synthesis techniques used for remediation of contaminated areas. Banner presentation at Groundwater Remediation using Nano/biotechnology with focus on the Contaminated Resources in Brazil (GRUN), 2019.

Recommendations for future works:

- ✓ Run Dynamic Simulation considering esterification reactor and first distillation column
- ✓ Propose control systems in the unit
- ✓ Test the biodiesel production process with different types of oils and FFAs
- ✓ Search possible industry location

## REFERENCES

- ABDURAKHMAN YB, PUTRA ZA, BILAD MR. Process simulation and economic analysis of biodiesel production from waste cooking oil with membrane bioreactor. **AIP Conf Proc** 2017;1891. doi:10.1063/1.5005344.
- ACARRINI JH. Biodiesel no Brasil: conquistas, desafios e perspectivas. **Biodieselbr Conferência Int** 2014.
- ANASTOPOULOS G, ZANNIKOU Y, STOURNAS S, KALLIGEROS S. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. **Energies** 2009;2:362–76. doi:10.3390/en20200362.
- ANP. Seminário de Avaliação do Mercado de Combustíveis. v. 2018, p. 1–102, 2018.
- APROBIO. APROBIO defende começo da mistura B11 em março de 2019 | **APROBIO** 2018. Available at: <<https://aprobio.com.br/2018/03/28/aprobio-defende-comeco-da-mistura-b11-em-marco-de-2019/>> (accessed September 25, 2019).
- ARANDA DAG, DE GONCALVES JA, PERES JS, et al. The use of acids, niobium oxide, and zeolite catalysts for esterification reactions. **J Phys Org Chem** 2009;22:709–16. doi:10.1002/poc.1520.
- ASHENHURST, J. Acid Catalysis of Organic Reactions: Why It Works. Disponível em: <<https://www.masterorganicchemistry.com/2010/04/21/the-power-of-acid-catalysis/>>. Acesso em: 15/4/2020.
- BAJAJ A, LOHAN P, JHA PN, MEHROTRA R. Biodiesel production through lipase catalyzed transesterification: An overview. **J Mol Catal B Enzym** 2010;62:9–14. doi:10.1016/j.molcatb.2009.09.018.
- BOUGUERRA NEJI, S., TRABELSI, M. & FRIKHA, M. H. Esterification of fatty acids with short-chain alcohols over commercial acid clays in a semi-continuous reactor. **Energies** 2009, v. 2, 1107–1117.
- BUENO L DE SR. Estudo da Influência da Composição do Óleo Vegetal sobre Algumas Propriedades do Biodiesel. **Dissertation** (Masters in Chemical Engineering). Pontifical Catholic University of Parana, 2009.
- CANAKCI M, GERPEN J VAN. Biodiesel Production Via Acid Catalysis. **Am Soc Agric Eng** 1999;42:1203–10.
- CETEC. Produção de combustíveis líquidos a partir de óleos vegetais. 1983.
- CHOUDARY, B.; LAKSHMI KANTAM, M.; VENKAT REDDY, C.; et al. Mg–Al–O–t-Bu hydrotalcite: a new and efficient heterogeneous catalyst for transesterification. **ICT Communication No.:** 4439. **Journal of Molecular Catalysis A: Chemical**, v. 159, n. 2, p. 411–416, 2000.



COELHO JM. Quanto de Biodiesel o Brasil Vai Precisar Até 2030? Empresa de Pesquisa energética (EPE). Ministério de Minas e Energia, 2017.

COELHO RA. Equilíbrio Líquido-Vapor de Sistemas Binários Envolvendo Ésteres Etílicos do Biodiesel (Glicerol ou Água) + Etanol: Dados Experimentais e Modelagem Termodinâmica. **Dissertation** (Masters in Chemical Engineering). Federal University of Parana, 2011.

DANIELETTO R, FM T, CARLA J, IC R, GOMES M, IC L. Avaliação do Índice de acidez de óleo submetido a processo de fritura intermitente. **Soc Bras Química** 2010.

DBIO. Boletim Dos Biocombustíveis. Ministério de Minas e Energia Secretaria de Petróleo, Gás Natural e Biocombustíveis Departamento de Biocombustíveis. 110° Edition, 2017.

DE HOMOLOGAÇÃO. Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, 2019.

DI SERIO, M., TESSER, R., PENGMEI, L., & SANTACESARIA, E. Heterogeneous Catalysis for Biodiesel Production. **Energy & Fuels**, n. 22, p. 207–217, 2008.

Do CARMO FR, EVANGELISTA NS, De SANTIAGO-AGUIAR RS, FERNANDES FAN, De SANT'ANA HB. Evaluation of optimal activity coefficient models for modeling and simulation of liquid-liquid equilibrium of biodiesel + glycerol + alcohol systems. **Fuel** 2014;125:57–65. doi:10.1016/j.fuel.2014.01.108.

Echemi. Price Market Analysis – Echemi. Available at: <<https://www.echemi.com/products/Information/pd20150901041-caustic-soda-pearls.html>> (accessed August 13, 2019).

ENCINAR JM, GONZÁLEZ JF, RODRÍGUEZ JJ, TEJEDOR A. Biodiesel fuels from vegetable oils: Transesterification of *Cynara cardunculus* L. Oils with ethanol. **Energy and Fuels** 2002;16:443–50. doi:10.1021/ef010174h.

FELIZARDO P, NEIVA CORREIA MJ, RAPOSO I, MENDES JF, BERKEMEIER R, BORDADO JM. Production of biodiesel from waste frying oils. **Waste Manag** 2006;26:487–94. doi:10.1016/j.wasman.2005.02.025.

FONTES, G. Gasolina vendida no Brasil é a 2ª mais cara do mundo. Entenda por quê. Available at: <<https://www.gazetadopovo.com.br/politica/republica/gasolina-vendida-no-brasil-e-a-segunda-mais-cara-do-mundo-entenda-o-porque-bkz9lzzq79liz39447wjdy4cp/>>. (accessed August 8, 2019).

FREEDMAN B, MOUNTS TL, PRYDE EH. Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils 1. **Am Oil Chem Soc** 1981;2:385–90. doi:10.1007/BF02541649.

FONTES G. Gasolina vendida no Brasil é a 2ª mais cara do mundo. Entenda por quê. **Gazeta do Povo** 2018. Available at: <<https://www.gazetadopovo.com.br/politica/republica/gasolina-vendida-no-brasil-e-a-segunda-mais-cara-do-mundo-entenda-o-porque-bkz9lzzq79liz39447wjdy4cp/>> (accessed August 19, 2019).

GERIS, R.; ALESSANDRA, N.; AMARAL, B. A.; et al. Biodiesel de soja: reação de transesterificação para aulas práticas de química orgânica. **Quim. Nova**, v. 30, n. 5, p. 1369–1373, 2007.

HELWANI, Z.; OTHMAN, M. R.; AZIZ, N.; KIM, J.; FERNANDO, W. J. N. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. **Applied Catalysis A: General**, v. 363, n. 1–2, p. 1–10, 2009.

JACOBSON K, GOPINATH R, MEHER LC, DALAI AK. Solid acid catalyzed biodiesel production from waste cooking oil. **Appl Catal B Environ** 2008;85:86–91. doi:10.1016/j.apcatb.2008.07.005.

JYOTI G, KESHAV A, ANANDKUMAR J. Experimental and Kinetic Study of Esterification of Acrylic Acid with Ethanol Using Homogeneous Catalyst. **Int J Chem React Eng** 2016;14:571–8. doi:10.1515/ijcre-2015-0131.

KASTRATOVIĆ, V. & BIGOVIĆ, M. Esterification of stearic acid with lower monohydroxylic alcohols. **Chem. Ind. Chem. Eng. Q.** 2018, 24, 283–291.

KHIRSARIYA, P. & MEWADA, R. K. Single step oxidation of methane to methanol - Towards better understanding. **Procedia Eng.** 2013, 51, 409–415.

KRAWCZYK, T. Biodiesel - Alternative Fuel Makes Inroads but Hurdles Remain. **Inform** 1996, 7 (8), 801–829.

KULKARNI MG, DALAI AK. Waste cooking oil - An economical source for biodiesel: A review. **Ind Eng Chem Res** 2006;45:2901–13. doi:10.1021/ie0510526.

LAGARIAS JC, REEDS JA, WRIGHT MH, WRIGHT PE. Convergence properties of the nelder–mead simplex method in low dimensions. **SIAM J Optim.** 1998, 9 (1),112–47.

LAM MK, LEE KT, MOHAMED AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. **Biotechnol Adv** 2010;28:500–18. doi:10.1016/j.biotechadv.2010.03.002.

LANDRESS L. US crude glycerine prices could dip as spring nears - ICIS Explore. Available at:<<https://www.icis.com/explore/resources/news/2018/02/14/10193613/us-crude-glycerine-prices-could-dip-as-spring-nears/>> (accessed August 15, 2019).

LOTERO E, LIU Y, LOPEZ DE, SUWANNAKARN K, BRUCE DA, GOODWIN JG. Synthesis of biodiesel via acid catalysis. **Ind Eng Chem Res** 2005; 44:5353–63. doi:10.1021/ie049157g.

MACEDO, G. A.; MACEDO, J. A. Produção de biodiesel por transesterificação de óleos vegetais. **Biotecnologia Ciência & Desenvolvimento**, v. 32, p. 38–46, 2004.

MACHADO GD, PESSOA FLP, CASTIER M, ARANDA DAG, CABRAL VF, CARDOZO-FILHO L. Biodiesel production by esterification of hydrolyzed soybean oil with ethanol in reactive distillation columns: Simulation studies. **Ind Eng Chem Res** 2013;52:9461–9. doi:10.1021/ie400806q.

MACHADO S.A. Estudo da produção de biodiesel a partir do óleo de macaúba (*Acrocomia aculeata*) pela rota etílica. **Thesis**, p. 130, 2013.

MAHESAR SA, SHERAZI STH, KHASKHELI AR, KANDHRO AA, UDDIN S. Analytical approaches for the assessment of free fatty acids in oils and fats. **Anal Methods** 2014;6:4956–63. doi:10.1039/c4ay00344f.

MARCHETTI, J. M. & ERRAZU, A. F. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. **Biomass and Bioenergy** 2008, 32, 892–895.

MARGARIDA BR, LUZ JR. LF L. Simulação de processo para tratamento de óleos ácidos e produção de biodiesel. **Conf Pap** 2018:214–21. doi:10.5380/19847521.3simproc 2018.a29p214-221.

MARKETS INSIDER. Soybean Oil PRICE Today | Soybean Oil Spot Price Chart | Live Price of Soybean Oil per Ounce | Markets Insider 2019. Available at: <<https://markets.businessinsider.com/commodities/soybean-oil-price>> (accessed August 13, 2019).

MARTINS CA, FERNÁNDEZ PS, CAMARA GA. Increased Biodiesel Efficiency: Alternatives for Production, Stabilization, Characterization and Use of Coproduct. **Springer, Cham** 2018. doi:10.1007/978-3-319-73552-8.

MATOS IQ, VARANDAS JS, SANTOS JPL. Thermodynamic modeling of azeotropic mixtures with [EMIM][TFO] with cubic-plus-association and cubic EOSS. **Brazilian J Chem Eng** 2018;35:363–72. doi:10.1590/0104-6632.20180352s20160025.

MEHER, L. C.; VIDYA SAGAR, D.; NAIK, S. N. Technical aspects of biodiesel production by transesterification - A review. **Renewable and Sustainable Energy Reviews**, v. 10, n. 3, p. 248–268, 2006.

MELO, R. R.; et al. An Overview on Vegetable Oils and Biocatalysis. **Nova Science Publishers**, p.1-24, 2016.

MESTRE C. Crop-based biofuels-facts and figures about investments and jobs. **Transp Environment** 2017.

MURAD, P.C., HAMERSKI, F., CORAZZA, M.L. et al. Estudo de Viabilidade da Produção de Biodiesel via Esterificação de Óleo Ácido. **Dissertation** (Masters in Chemical Engineering). Federal University of Parana, 2017.

MURAD, P. C.; HAMERSKI, F.; CORAZZA, M. L.; LUZ, L. F. L.; VOLL, F. A. P. Acid-catalyzed esterification of free fatty acids with ethanol: an assessment of acid oil pretreatment, kinetic modeling and simulation. **Reaction Kinetics, Mechanisms and Catalysis**, v. 123, n. 2, p. 505–515, 2017. Springer Netherlands. Disponível em: <<https://doi.org/10.1007/s11144-017-1335-3>>. .

MUSA, I. A. The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process. **Egyptian Journal of Petroleum**, v. 25, n. 1, p. 21–31, 2016. Egyptian Petroleum Research Institute.

MYINT LL. Process Analysis and Optimization of Biodiesel Production from Vegetable Oils. **Dissertation** 2007:100.

NEDER V. Preço médio do diesel no Brasil está 14% abaixo da média mundial. **Estadão** 2019.

NIELSEN S. Food Analysis. 4th ed. Media, **Springer Science & Business**, v. 4, p. 602, 2014.

OLADIJI AT, SHOREMEKUN KL, YAKUBU MT. Physicochemical properties of the oil from the fruit of blighia sapida and toxicological evaluation of the oil-based diet in wistar rats. **J Med Food** 2009;12:1127–35. doi:10.1089/jmf.2008.0219.

PAIVA, E. J. M. Esterificação De Ácidos Graxos De Cadeia Longa Com Etanol, 1-Butanol E 1-Hexanol Na Presença De Carboxilatos De Zinco – Modelagem Cinética E Avaliação De Processo. **Tese** (PhD in Engineering and Materials Science), Federal University of Parana, 2015.

PANAWALA L. Difference Between Fats and Oils. **Pediaa** 2017.

PANDEY, A.; CR, S.; P, S.; et al. Recent Developments in Microbial Inulinases: Its Production, Properties, and Industrial Applications. **Journal of the Food Hygienic Society of Japan**, v. 81, n. 1, p. 35–52, 1999.

PICKETT, D.; DEPCIK, C.; STAGG-WILLIAMS, S. Use of the Glycerin By-Product from Biodiesel Production for Power Generation. **J. Eng. Gas Turbines Power** 2018, 140 (10), 1–8. <https://doi.org/10.1115/1.4039819>.

PÓ, M. V. Testes de Variância e Análise de Variância (ANOVA). 2014, 32.

RAMOS, L. P.; KOTHE, V.; CÉSAR-OLIVEIRA, M. A. F.; et al. Biodiesel: Raw materials, production technologies and fuel properties. **Revista Virtual de Química**, v. 9, n. 1, p. 317–369, 2017.

REIS, M. C. et al. Produção de biodiesel a partir de ácidos graxos provenientes do refino de óleos vegetais via catálise ácida heterogênea e micro-ondas. **Quim. Nova** 2015, 38, 1307–1312.

RENOVABIO. Biocombustíveis: aliados do Brasil na busca da transição para a energia limpa | BiodieselBR.com 2018. Available at: <<https://www.biodieselbr.com/noticias/regulacao/rbio/biocombustiveis-aliados-do-brasil-na-busca-da-transicao-para-a-energia-limpa-300818>>. (accessed September 25, 2019).

REYERO I, ARZAMENDI G, ZABALA S, GANDÍA LM. Kinetics of the NaOH-catalyzed transesterification of sunflower oil with ethanol to produce biodiesel. **Fuel Process Technol** 2015;129:147–55. doi:10.1016/j.fuproc.2014.09.008.

RIBEIRO A., CASTRO F, CARVALHO J. Influence of Free Fatty Acid Content in Biodiesel Production on Non-Edible Oils. **Int Conf Waste Solut Treat Oppor**, 2011.

ROHMAN A, TRIYANA K, SISINDARI, ERWANTO Y. Differentiation of lard and other animal fats based on triacylglycerols composition and principal component analysis. **Int Food Res J** 2012;19:475–9.

ROSSET, I. G., CAVALHEIRO, M. C. H. T., ASSAF, E. M. & PORTO, A. L. M. Enzymatic Esterification of Oleic Acid with Aliphatic Alcohols for the Biodiesel Production by *Candida antarctica* Lipase. **Catal. Letters** 2013, 143, 863–872.

SCHUCHARDT, U.; SERCHELI, R.; MATHEUS, R. Transesterification of vegetable oils: a review general aspects of transesterification. **J. Braz. Chem. Soc.**, v.9, n.1, p.199-210, 1998.

SCHUCHARDT, U.; VARGAS, R. M.; GELBARD, G. Transesterification of soybean oil catalyzed by alkylguanidines heterogenized on different substituted polystyrenes. **Journal of Molecular Catalysis A: Chemical**, v. 109, n. 1, p. 37–44, 1996.

SHARMA, S.; KANWAR, S. S. Organic solvent tolerant lipases and applications. **The Scientific World Journal**, v. 2014, p. 15, 2014.

SILVA C, VIEITEZ I, JACHMANIÁN I, CASTILHOS F, FILHO LC, OLIVEIRA JV. Non-Catalytic Production of Ethyl Esters Using Supercritical Ethanol in Continuous Mode. **IntechOpen** 2012:31. doi:http://dx.doi.org/10.5772/57353.

SILVA C DA, OLIVEIRA JV. Biodiesel production through non-catalytic supercritical transesterification: current state and perspectives. **Brazilian J Chem Eng** 2014; 31:271–85. doi:10.1590/0104-6632.20140312s00002616.

SILVA FILHO, J. B. Produção de biodiesel etílico de óleos e gorduras residuais (ogr) em reator química do baixo custo, **Dissertation** (Masters in Material and Mechanical Engineering), Federal University of Paraná 2010.

STAMENKOVIĆ OS, VELIČKOVIĆ A V., VELJKOVIĆ VB. The production of biodiesel from vegetable oils by ethanolysis: Current state and perspectives. **Fuel** 2011; 90:3141–55. doi:10.1016/j.fuel.2011.06.049.

STREZOV V, EVANS TJ. Biomass processing technologies. 1st Edition. **CRC Press**, 2014.

SUAREZ PAZ, MENEGHETTI SMP, MENEGHETTI MR, WOLF CR. SUAREZ, P. A. Z., MENEGHETTI, S. M. P., MENEGHETTI, M. R., & WOLF, C. R. (2007). Transformação de triglicerídeos em combustíveis, materiais poliméricos e insumos químicos: algumas aplicações da catálise na oleoquímica. **Quim Nov** 2007;30:667–76. doi:10.1016/j.fertnstert.2018.07.483.

SUNHO BIODIESEL CORPORATION. Wider applications | Sunho Biodiesel Corporation - New Enzymatic Biodiesel Technology. Available at: <<http://sunhobiodiesel.com/et-process-for-biodiesel/wider-applications/>> (accessed August 17, 2019).

SUPPALAKPANYA, K., RATANAWILAI, S., NIKHOM, R. & TONGURAI, C. Production of ethyl ester from crude palm oil by two-step reaction using continuous microwave system. **Songklanakarin J. Sci. Technol** 2011, 33, 79–86.

SYSTEM TI. Sodium laurate. Available at: <<http://www.thegoodscentcompany.com/data/rw1303231.html>> (accessed September 29, 2019).

TAVARES J.H. de O. Esterificação em meio contínuo pressurizado em reator de leito fixo com presença de inertes. **Thesis**, p. 44, 2017.

TECNOLOGIA I. Etanol - Centro de Estudos Avançados em Economia Aplicada - CEPEA-Esalq/USP, 2019.

THAIYASUIT P, PIANTHONG K, WORAPUN I. Acid Esterification-Alkaline transesterification process for methyl ester production from crude rubber Seed Oil. **J Oleo Sci** 2012;61:81–8. doi:10.5650/jos.61.81.

UFOP. Union Zur Förderung Von Oel- Und Proteinpflanzen E.V. (UFOP). Report on Global Market Supply 2017/2018. **Union Zur Förderung Von Oel- Und Proteinpflanzen EV** 2017:51.

U.S. Energy Information Administration (EIA). Biofuels explained Use of biodiesel 2019. Available at: <<https://www.eia.gov/energyexplained/biofuels/use-of-biodiesel.php>>. (accessed September 25, 2019).

VICENTE, G.; COTERON, A.; MARTINEZ, M.; ARACIL, J. Application of the factorial design of experiments and response surface methodology to optimize biodiesel production. **Industrial Crops and Products**, v. 8, n. 1, p. 29–35, 1998.

VINAY S, AMARA B, BATTERIES R, EFFICIENCY IF, BATTERY LA, PEROXIDE H, et al. Aspen simulation of Biodiesel production plant Production of Bio-Diesel from Sesame Oil Using Aspen Simulation. **Undergraduate thesis** 2016. doi:10.13140/RG.2.1.2154.9204.

WANG L. Energy efficiency and management in food processing facilities. **CRC Press**, 2009.

WANG Y, OU S, LIU P, XUE F, TANG S. Comparison of two different processes to synthesize biodiesel by waste cooking oil. **J Mol Catal A Chem** 2006; 252:107–12. doi:10.1016/j.molcata.2006.02.047.

WELLS RC. Sodium sulphate: Its sources and uses. **USGS Bull 717** 1923;717:47.

WEST A. H. Process Simulation and Catalyst Development for Biodiesel Production. **Thesis**, p.74, 2006.

WEST, A. H.; POSARAC, D.; ELLIS, N. Assessment of four biodiesel production processes using HYSYS.Plant. **Bioresource Technology**, v. 99, n. 14, p. 6587–6601, 2008.

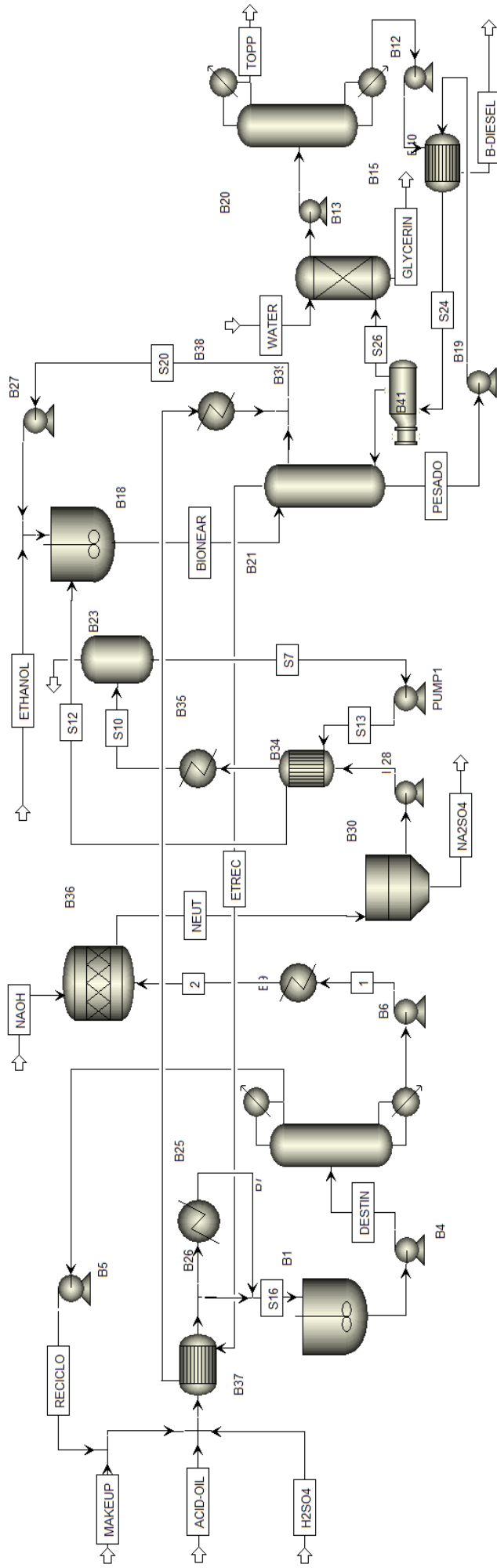
WILSON K, CLARK JH. Solid acids and their use as environmentally friendly catalysts in organic synthesis. **Pure Appl Chem** 2000;72:1313–9. doi:10.1351/pac200072071313.



YUSOFF MFM, XU X, GUO Z. Comparison of fatty acid methyl and ethyl esters as biodiesel base stock: A review on processing and production requirements. **JAOCS, J Am Oil Chem Soc** 2014;91:525–31. doi:10.1007/s11746-014-2443-0.

ZHANG Y, DUBÉ MA, MCLEAN DD, KATES M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. **Bioresour Technol** 2003;89:1–16. doi:10.1016/S0960-8524(03)00040-3.

APPENDIX I



Stream Name	Units	Material																									
		1	2	ACID-OIL	BDIESEL	BIONEAR	DESTIN	ETHANOL	ETREC	GLYCERIN	H2SO4	MAKEUP	NAOH	NA2SO4	NEUT	PESADO	RECICLO	S7	S10	S12	S16	S20	S24	S26	TOPP	WATER	
Temperature	C	117,6	40	25	90,0	70	25	79,6	102	25	25	25	25	78,2	85,4	79,2	191	191	90	70	78	93,6	106,8	51	25		
Pressure	bar	2,2	1,9	1,5	1,6	1,6	1,6	1,6	1	1,5	1,5	1,9	1,9	1,6	1	1,5	1,5	8,3	1,6	1,5	1,5	1	1	0,29	1		
Mole Flows	kmol/hr	63,754	63,754	47,852	114,008	279,463	226,648	130,762	98,608	41,759	1	14,453	13,648	1,475	72,842	318,021	162,895	45,917	67,304	45,917	226,648	100,648	318,021	178,814	35,814	12,767	
ETHANOL	kmol/hr	0,009	0,009	0	0,838	132,527	130,307	128,536	98,096	8,629	0	11,553	0	0	0,009	170,667	130,298	0	0,009	0,674	0	141,851	100,112	170,667	32,415	22,948	0
H2O	kmol/hr	14,590	14,590	0	0,316	1,366	47,186	0,164	0,509	0,418	0,145	2,900	0	0,051	21,702	1,718	32,257	0,674	21,649	0,674	35,642	0,533	1,718	0,833	12,865	12,767	0
ETLAURAT	kmol/hr	11,545	11,545	0	11,475	11,483	11,544	0	0,003	0,005	0	0	0	0,028	11,908	11,506	0	11,480	11,879	11,480	0	0,003	11,506	11,480	0	0	0
ACLAURIC	kmol/hr	4,216	4,216	15,761	0,253	0,255	4,216	0	0	0,002	0	0	0	0,001	0,259	0,255	0	0,255	0,259	0,255	15,761	0	0,255	0,255	0	0	0
TRIOLEIN	kmol/hr	32,091	32,091	32,091	0,044	0,044	32,091	0	0	0,001	0	0	0	0,079	33,042	0,044	0	32,961	32,961	32,961	32,091	0	0,044	0,044	0	0	0
GLYCERIN	kmol/hr	0	0	0	0	32,464	0	0	0,001	32,082	0	0	0	0	32,504	0	0	0	0	0	0	0,001	32,504	32,463	0	0	0
NAOH	kmol/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2SO4	kmol/hr	1,304	1,304	0	0	0	1,304	0	0	0	1,304	0	0	0	0	0	0	0	0	0	1,304	0	0	0	0	0	0
NA+	kmol/hr	0	0	0	1,012	1,320	0	1,031	0	0,308	0	0	6,824	0,001	0,259	1,320	0	0,259	0,259	0,259	0	0	1,320	1,320	0	0	0
OH-	kmol/hr	0	0	0	1,012	1,320	0	1,031	0	0,308	0	0	6,824	0,001	0,259	1,320	0	0,259	0,259	0,259	0	0	1,320	1,320	0	0	0
SO4--	kmol/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3O+	kmol/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SODIU+01	kmol/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ETILOLEA	kmol/hr	0	0	0	98,197	98,201	0	0	0	0,004	0	0	1,304	1,342	0	0	0	0	0	0	0	0	0	98,204	98,201	0	0
DIOLE-01	kmol/hr	0	0	0	0,097	0,097	0	0	0	0	0	0	0	0	0,097	0	0	0	0	0	0	0	0,097	0,097	0	0	0
MONOO-01	kmol/hr	0	0	0	0,356	0,358	0	0	0	0,002	0	0	0	0	0,358	0	0	0	0	0	0	0	0,358	0,358	0	0	0
SODIU-02	kmol/hr	0	0	0	0,029	0,030	0	0	0	0,030	0	0	4,021	4,061	0,030	0	0,030	0,030	0,030	0,030	0	0	0,030	0,030	0	0	0

FIGURE A.1 – PROCESS FLOWCHART AND MASS BALANCE



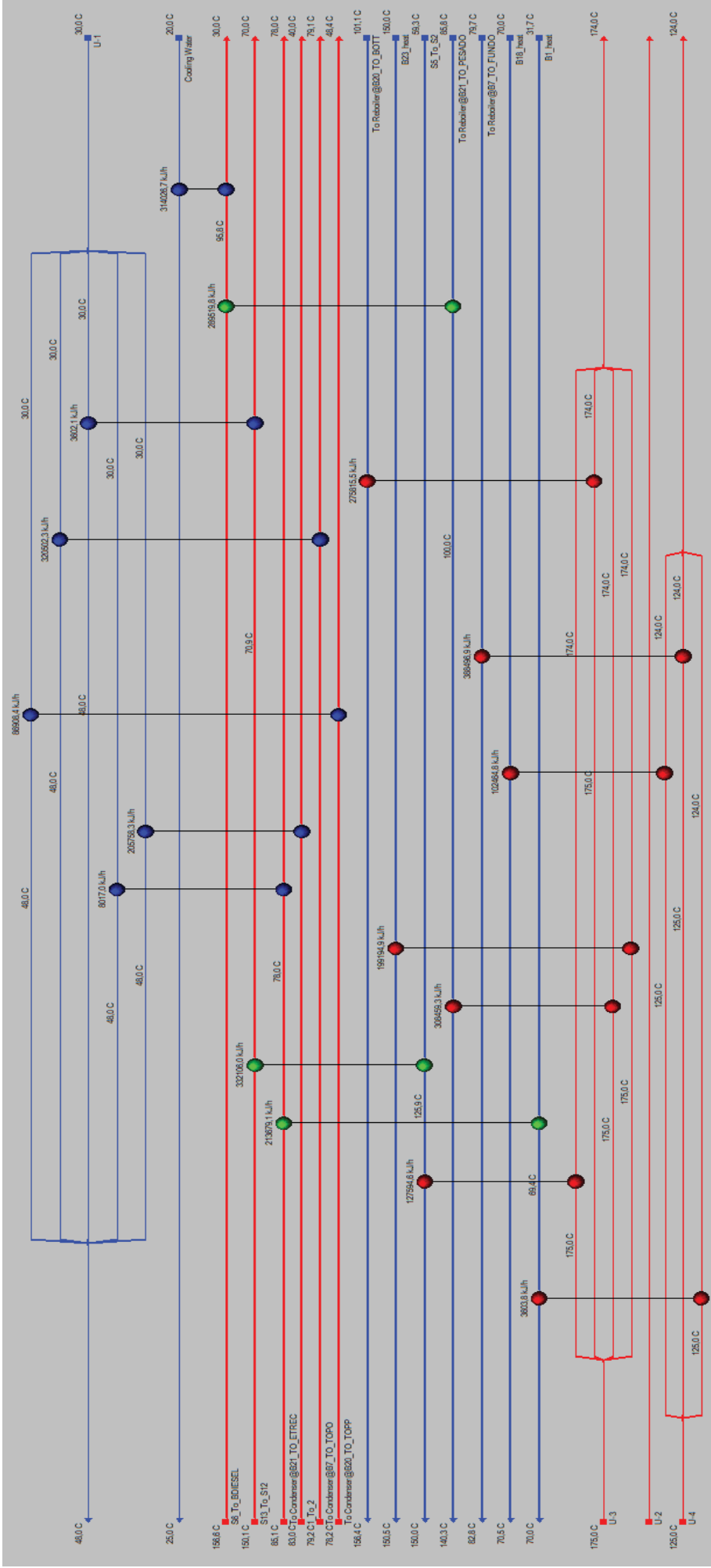


FIGURE A.2 – HEAT INTEGRATION SCHEME FOR THE ADDITION OF ENERGY-SAVING HEAT EXCHANGERS

## ATA DE SESSÃO PÚBLICA DE DEFESA DE MESTRADO PARA A OBTENÇÃO DO GRAU DE MESTRE EM ENGENHARIA QUÍMICA

No dia vinte e oito de janeiro de dois mil e vinte e um às 09:00 horas, na sala Plataforma Microsoft Teams, Plataforma online, em função da portaria 754/2020 da Reitoria - UFPR, foram instaladas as atividades pertinentes ao rito de defesa de dissertação da mestranda **BRUNA RICETTI MARGARIDA**, intitulada: **Esterification of fatty acids analysis using different contents of water: Simulation and economic evaluation of biodiesel production from waste oil**, sob orientação do Prof. Dr. LUIZ FERNANDO DE LIMA LUZ JUNIOR. A Banca Examinadora, designada pelo Colegiado do Programa de Pós-Graduação em ENGENHARIA QUÍMICA da Universidade Federal do Paraná, foi constituída pelos seguintes Membros: LUIZ FERNANDO DE LIMA LUZ JUNIOR (UNIVERSIDADE FEDERAL DO PARANÁ), ALEXANDRE FERREIRA SANTOS (UNIVERSIDADE FEDERAL DO PARANÁ), MARIA JOSE JERONIMO DE SANTANA PONTE (UNIVERSIDADE FEDERAL DO PARANÁ ). A presidência iniciou os ritos definidos pelo Colegiado do Programa e, após exarados os pareceres dos membros do comitê examinador e da respectiva contra argumentação, ocorreu a leitura do parecer final da banca examinadora, que decidiu pela APROVAÇÃO. Este resultado deverá ser homologado pelo Colegiado do programa, mediante o atendimento de todas as indicações e correções solicitadas pela banca dentro dos prazos regimentais definidos pelo programa. A outorga de título de mestre está condicionada ao atendimento de todos os requisitos e prazos determinados no regimento do Programa de Pós-Graduação. Nada mais havendo a tratar a presidência deu por encerrada a sessão, da qual eu, LUIZ FERNANDO DE LIMA LUZ JUNIOR, lavrei a presente ata, que vai assinada por mim e pelos demais membros da Comissão Examinadora.

CURITIBA, 28 de Janeiro de 2021.

Assinatura Eletrônica

28/01/2021 11:15:02.0

LUIZ FERNANDO DE LIMA LUZ JUNIOR

Presidente da Banca Examinadora (UNIVERSIDADE FEDERAL DO PARANÁ)

Assinatura Eletrônica

28/01/2021 11:15:17.0

ALEXANDRE FERREIRA SANTOS

Avaliador Interno (UNIVERSIDADE FEDERAL DO PARANÁ)

Assinatura Eletrônica

28/01/2021 12:16:40.0

MARIA JOSE JERONIMO DE SANTANA PONTE

Avaliador Externo (UNIVERSIDADE FEDERAL DO PARANÁ )