Biodiesel Production using Waste Cooking Oil: Energy Optimization Study Using Pinch and Heat Exchanger Network (HEN) Analysis

By

Jeredraj Yaacob

Thesis submitted in partial fulfilment of the requirement for

Degree of Bachelor of Chemical Engineering

2022

ACKNOWLEDGEMENTS

Its great honour to thank everyone who has assisted me during my FYP and until the completion of this report. As a result, I'd want to convey my sincere gratitude to a few individuals for their contributions and support throughout this report.

Thank you to my supervisor, Professor Ir. Dr. Zainal Ahmad, for your patience, guidance, and support. I have benefited greatly from your wealth of knowledge and meticulous editing. I am extremely grateful that you took me on as a student and continued to guide me throughout this project.

Also, I extend my thanks to all my colleagues at Universiti Sains Malaysia for their continuous encouragement and support, as well as to all of my friends and colleagues from USM and outside for their time, advice and moral support.

Last, but not least, my warm and heartfelt thanks go to my friends and family for their tremendous support and hope they had given to me. Without that hope, this thesis would not have been possible. Thank you all for the strength you gave me. I love you all!

Table of Contents

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AEA	Aspen energy analyser
CO2	Carbon dioxide
CPO	Crude palm oil
CSTR	Continuous stirred tank reactor
EOS	Equation of state
FAME	Fatty acid methyl ester
FFA	Free fatty acid
HEN	Heat exchanger network
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
PAT	Pinch Analysis Technique
Qc_{min}	Minimum cooling energy requirement
Qh_{min}	Minimum heating energy requirement
SDG	Sustainable development goals
VOC	Volatile organic compound
WCO	Waste cooking oil

ABSTRAK

Dalam kerja ini, proses bersepadu untuk penghasilan biodiesel menggunakan sisa minyak masak (WCO) telah dilakukan dengan membina rangkaian penukar haba yang ideal (HEN) dan menjalankan kajian pengoptimuman tenaga menggunakan analisis pinch. Tenaga pemanasan dan penyejukan yang diperlukan untuk semua aliran proses telah disepadukan menggunakan teknologi pinch. Dalam penyelidikan ini, diandaikan bahawa Tmin = 10°C. Lengkung komposit haba digunakan untuk mengenal pasti suhu pinch. Suhu pinch, keperluan tenaga pemanasan dan penyejukan minimum, dan lengkung komposit semuanya diperoleh menggunakan perisian Aspen Energy Analyzer.

Suhu di mana pinch berlaku ialah 177°C, 165°C, 125°C, 115°C, 50°C dan 40°C. Untuk proses ini, utiliti panas minimum (Qh_{min}) ialah 10,411,031 kJ/jam, manakala utiliti sejuk minimum (Qc_{min}) ialah 7,967,105.73 kJ/jam. HEN baharu telah direka bentuk menggunakan reka bentuk yang disyorkan AEA, dan perbandingan antara semua kes reka bentuk dan kes asas telah dibuat untuk mengurangkan penggunaan tenaga proses dan meningkatkan integrasi tenaga antara aliran proses. Kerana ia lebih tenaga dan cekap dari segi ekonomi berbanding dua kes lain, kes reka bentuk 2 telah dipilih sebagai HEN terbaik. Perbandingan kes reka bentuk 2 dengan kes asas menunjukkan potensi penjimatan tenaga dan kos yang besar di mana 3,203,188.31Watt tenaga utiliti panas dan 3,306,114.41Watt tenaga utiliti sejuk boleh dijimatkan. Anggaran penjimatan kos tenaga adalah sekitar USD 295,146 setahun untuk utiliti panas dan USD 23,808 setahun untuk utiliti sejuk.

ABSTRACT

In this work, an integrated process for production of biodiesel using WCO was done by constructing the ideal heat exchanger network (HEN) and conducting an energy optimization study utilising pinch analysis. The heating and cooling energy necessary for all process streams was integrated using pinch technology. In this research, it is assumed that Tmin = 10°C. Heat composite curve was used to identify the pinch temperatures. The pinch temperature, minimum heating and cooling energy requirements, and drawing of the composite curve were all obtained using the Aspen Energy Analyzer software.

The temperatures at which the pinch occurs are 177°C, 165°C, 125°C, 115°C, 50°C, and 40°C. For this process, the minimum hot utility (Qh_{min}) is 10,411,031 kJ/hr, while the minimum cold utility (Qc_{min}) is 7,967,105.73 kJ/hr. New HENs were designed using the AEA-recommended design, and comparisons between all the design cases and the base case were made in order to decrease process energy consumption and improve energy integration between process streams. Because it is more energy and economically efficient than the other two cases, design case 2 has been chosen as the best HEN. Comparison of design case 2 with base case indicates massive energy and cost saving potential where 3,203,188.31Watt of hot utility energy and 3,306,114.41 Watt of cold utility energy can be saved. The estimation of energy cost saving will be around USD 295,146 per year for hot utility and USD 23,808 per year for cold utility.

CHAPTER 1 : INTRODUCTION

1.1 Introduction

This paper will be focusing on the development of heat exchanger network (HEN) for the production of biodiesel using WCO in order to minimize the heating and cooling energy requirement. Plant modeling and simulation file done by Patle, Ahmad et al (2014) will be used in this case study to develop the HEN. First, the simulation file will be run in Aspen Plus so that no warnings are present to ease out the HEN design. Validation needed to be done on the results obtained from the simulation to make sure that the results are valid and can be used to develop the HEN. After the simulation is validated, Aspen Energy Analyzer will be used on the simulation to find the pinch point for the hot and cold streams and design an optimum HEN. Through this, maximum heat recovery can be done for the plant which will lower the energy requirement and reduce in capital cost of the plant.

1.2 Background

The two greatest issues that humanity faces in this century are energy access and climate change. The rapidly growing population and rising income have resulted in a tremendous increase in energy demand. Human civilization is mostly based on the use of energy, which plays a significant role in socio-economic growth through raising living standards. For a long time, fossil fuel-based fuels such as petroleum, coal, and natural gas have been the primary sources of energy all over the world. Fossil fuel consumption has a number of public health and environmental dangers, as well as having widespread and potentially irreversible effects on global warming.

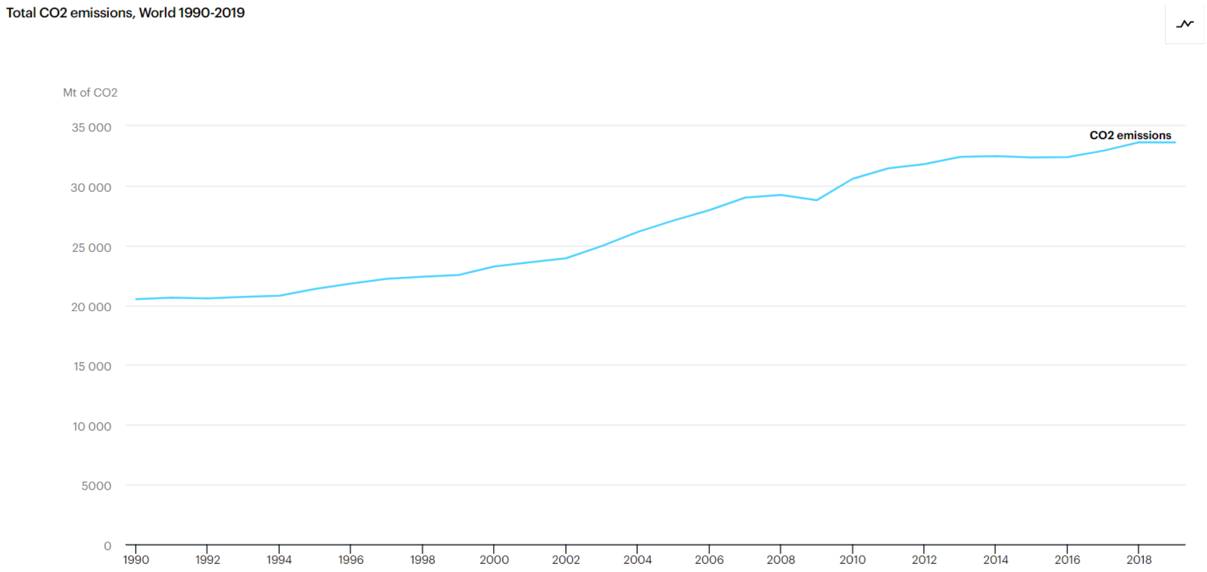


Figure 1.1: CO2 emission around the world (Bank, 2020)

It also causes a number of environmental challenges that may jeopardize our ecosystem's long-term viability. The production of greenhouse gases and other types of air pollutants such as sulphur dioxide and volatile organic compounds (VOCs) is one of the most pressing concerns. As shown in the Figure 1.1, the emission of CO_2 around the world keeps increasing every year which is very concerning because it will lead to acid rain and climate change in the end.

As a result, environmental concerns have grown, prompting researchers to look into alternative energy sources. Wind power, hydropower, biomass, and biofuels are all examples of renewable energy. Because of economic and environmental considerations, all of these resources must contribute, and biodiesel could be one of the solutions (Li et al., 2014). Biodiesel has long been regarded as the most promising petroleum diesel fuel replacement. It's a biofuel made from vegetable oils, animal fats, and, more recently, waste cooking oil. Biodiesel has a variety of advantages, including 1) biodegradability, 2) low particulate, carbon monoxide, and hydrocarbon emissions, 3) no Sulphur emissions, and 4) a high cetane number.

Biodiesel has been marketed as a significant alternative fuel for petroleum diesel due to its similar qualities to petroleum diesel, as well as the fact that it is a sustainable green fuel. The most widely utilized method for biodiesel production is the transesterification reaction. Various approaches, including alkaline, acidic, and biological catalysts, are typically used to catalyze the process (Semwal et al., 2011). Biodiesel is described as mono alkyl esters of long-chain fatty acids produced by the alcoholysis of triglycerides generated from various feedstocks (Abidin et al., 2012). Glycerol and fatty acid methyl esters are produced via transesterification of triglycerides with methanol in the presence of an alkaline catalyst (FAME). The FAME product can be refined and purified into biodiesel fuel, and the secondary product glycerol is often utilized in soap manufacturing. Fatty acid methyl ester (FAME) and water are produced when fatty acids are esterified with methanol (by-product).

At the moment, edible oils are the primary source of biodiesel feedstock. However, increased rivalry in the food sector has encouraged research into non-edible and waste oils (second generation feedstock). The second-generation feedstock is significantly less expensive than edible oil, cutting the overall cost of the biodiesel generated. Waste cooking oil (WCO) has been identified as a viable biodiesel feedstock since it is less expensive than fresh edible oils and aids to waste reduction (Sodhi et al., 2017). WCO's biodiesel manufacturing is environmentally beneficial because it recycles used cooking oil and produces renewable energy with less pollution. It reduces the cost of waste management while also substituting for some petrochemical oil imports (Avinash & Murugesan, 2017).

However, the lengthy process and high energy requirements drive up the cost of producing biodiesel. To overcome this problem, pinch and HEN analysis for transesterification of triglycerides and methanol for biodiesel production can be used. Pinch analysis has been used widely in heat recovery and in mass and energy integration applications which involves complex calculations for designing a heat exchanger network.

1.3 Problem Statement

The cost of refining, production capacity, and feedstock flexibility are all important problems for the biodiesel sector. Because of these production variables, biodiesel cannot compete with petroleum fuels, which are less expensive. As a result, improving biodiesel process modelling and optimization is the key to lowering biodiesel production costs without using a lot of oil. For the production of biodiesel from WCO, two-step transesterification is regarded as an acceptable method. After a pre-treatment esterification of free fatty acid (FFA) step with acidic catalysts, a transesterification step with alkaline homogeneous catalysts is performed. Nonetheless, the lengthy procedure and the requirement of tremendous energy raises the cost of biodiesel (Aghbashlo et al., 2018). Energy is a critical component of economic development because it delivers critical services that keep economic activity and human existence at a high level. According to the study done by Mohammadshirazi et al (2014), The total energy input and output are calculated to be 30.05 and 44.91 MJ L-1, respectively to produce one liter of biodiesel from waste cooking oil. Since the energy demand is very high, the production cost for biodiesel will spike and lead to higher prices and energy-intensive. In order to reduce the energy required for this process, energy integration can be done to maximize heat recovery in the industrial chemical process and reduce external heating and cooling utilities. In this paper, pinch and HEN analysis has been proposed for transesterification of triglycerides and methanol for biodiesel production. Pinch analysis has been used widely in heat recovery and in mass and energy integration applications which involves complex calculations for designing a heat exchanger network. This method entails determining the optimal approach temperature for a HEN design that results in the lowest total annual cost. In this case, Aspen Plus, an excellent simulation software needs to be used to identify the pinch temperature, minimum heating and cooling energy requirement and plotting composite curve for the process stream to design a heat exchanger network that can reduce the capital cost of the plant.

1.4 Research Objectives

The main objective of this study is to reduce the energy requirement and capital cost for biodiesel production from the WCO plant. The detailed objectives of this study are as follows:

1. To simulate an integrated process for biodiesel production using WCO.
2. To apply heat integration to improve the process performance in terms of energy usage.
3. To design an optimum HEN using a pinch analysis method.

1.5 Scope of Thesis

The scope of the study for this project is to solve the problem stated above in the problem statement through exergy analysis and development of the heat exchanger network (HEN). The case study of the project is to design a HEN using the existing simulation file for biodiesel production using WCO.

The project will be focusing on the feasibility of designing a heat exchanger network using the pinch analysis method. Pinch analysis has been used widely in heat recovery and in mass and energy integration applications because this method entails determining the optimal approach temperature for a HEN design that results in the lowest total annual cost.

Both the pinch analysis and HEN will be developed by using Aspen Plus software which was granted access from the license provided by Universiti Sains Malaysia, USM. The software provides a user-friendly interface with a set of divisions available depending on the need of the analysis. In this case, we will be using Aspen Energy Analyser (AEA) software. AEA is a powerful instrument that employs the pinch analysis method to create the best HEN for the least cost. By importing stream data from an excel sheet or the modelling software, AEA can work independently from Aspen Plus and Aspen HYSYS.

1.6 Sustainability

Figure 1.2: Sustainability development goals

As for sustainably, 3 of the sustainable development goals (SDG) are applicable for this project which are clean energy, industry and infrastructure, and responsible consumption. Clean energy is applied where the usage of the process streams itself for heating and cooling requirement will reduce the usage of the heating and cooling utilities thus reducing the power required to produce these utilities. Through the heat integration between the process streams, energy is preserved and less energy is required. This application makes the energy more affordable with the reduction of its application.

The second one will be industry and infrastructure. This involves building resilient infrastructure and fostering innovation. For instance, this project involves the heat integration of the process streams to reduce the heating and cooling utility and to make that happen, a heat exchanger network needs to be created. The heat exchanger network is considered as a resilient infrastructure as an example, the integration of the heat through heat exchangers is done and this innovation in the chemical industry reduces the capital cost and utility cost.

As for the third SDG, responsible consumption is taken into mind for this project. This goal strives to promote environmentally friendly manufacturing, reduce waste, and increase recycling where in this case, the usage of the hot and cold utility is being reduced with the implementation of the pinch analysis and heat exchanger network. The energy released by the streams are recycled and used to heat the streams that require energy. This for sure will reduce energy waste, and increase recycling and the implementation of the HEN is definitely an environmentally friendly move for the industry.

Sustainability is one of the most important aspects that needs more recognition in the industry. In order to protect the planet and our environment, these sustainable development goals must be implemented so that not only the industry will receive the reward for it but the people and the environment will also benefit from it.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

In chapter 1, the problems faced by the conventional biodiesel production are studied and one of the main problems faced by biodiesel production from WCO is energy, which is required for heating and cooling of the process streams. Therefore, to reduce the energy consumption of the plant, energy integration has been proposed to tackle this situation which will utilize the application of pinch analysis technique (PAT) to develop a heat exchanger network (HEN). In light of the foregoing observations, chapter 2 discusses past discoveries and reviews that can be found in reputable scientific archives and references that are relevant to the topic of this final year study. This chapter provides a description of biodiesel production using WCO using several ways, as well as energy analysis and requirements in the plant and the use of pinch analysis in the Aspen Energy Analyzer to build the optimum HEN.

2.2 Biodiesel Production Using Waste Cooking Oil (WCO)

The usage of fossil fuels is expected to be limited in the future due to finite supplies and environmental concerns. In the search for alternative sources of fuel, biodiesel is considered the most promising alternative to petroleum-based diesel fuel. It's a biofuel made from vegetable oils, animal fats, and, more recently, microalgae. Biodiesel is described as mono alkyl esters of long chain fatty acids produced by the alcoholysis of triglycerides generated from various feedstocks. The biodiesel that is produced from these feedstocks can be classified into 3 types, first-generation, second-generation and third-generation. The first-generation biodiesel is produced from edible vegetable oil, the second-generation is produced from non-edible oils such as waste cooking oil and the third- generation is produced from micro and macro-species including algae (Edeh, 2020).

In this paper, we will be using second-generation biofuel feedstock which is waste cooking oil because this will lower the cost of the feedstock and at the same time creates less pollution. Restaurants, cafeterias, and home kitchens all have waste cooking oil (WCO) on hand (Gebremariam & Marchetti, 2018). The current study focused on converting WCO into biodiesel. WCO is two to three times less expensive than vegetable oils, and it also saves money on waste removal and treatment (Phan & Phan, 2008). The usage of WCO will also reduce the requirement of vast lands to produce the crops which will be used as the feedstock for biodiesel production (first generation). The FFA content of the WCO has been divided into two groups, first one is known as yellow grease (FFA content less than 15%) and brown grease (FFA content more than 15%) (El-Araby et al., 2018). The current price of waste cooking oil is approximately $110-$160 per metric ton which is considered cheaper than normal vegetable oil (Alibaba, 2022).

The separation of fatty acid esters and glycerol, as well as the development of dimeric and polymeric acids and glycerides, are some of the negative effects of using WCO for biodiesel synthesis (Talebian-Kiakalaieh et al., 2013). Because of the high levels of FFAs in waste cooking oils, some undesired side reactions during biodiesel manufacturing are accelerated, WCO viscosity rises, while the saponification process lowers molecular mass and iodine value (Sodhi et al., 2017). As a result, WCO was first processed with mineral acids to reduce FFAs before being transesterified in the presence of a base as a catalyst (Sahar et al., 2018). Meanwhile, saponification reaction uses up some of the catalysts, lowering the final yield of biodiesel. Water contamination results from the amount of WCO poured down drains, which is exacerbated by the lack of a systematic procedure for collecting waste cooking oils from residences (Farid et al., 2020). WCO is created in households to the tune of more than 80%, and managing its disposal necessitates significant investments, such as waste oil disposal and expensive water treatment costs (Phan & Phan, 2008).

According to Mohammadshirazi et al (2014), the best way for making biodiesel is the transesterification of vegetable oils with alcohol. There are two types of transesterification: (a) with homogenous catalyst (b) with heterogeneous catalyst and (c) without a catalyst. In this paper, we will be focused on homogenous catalysts which are taken from the case study.

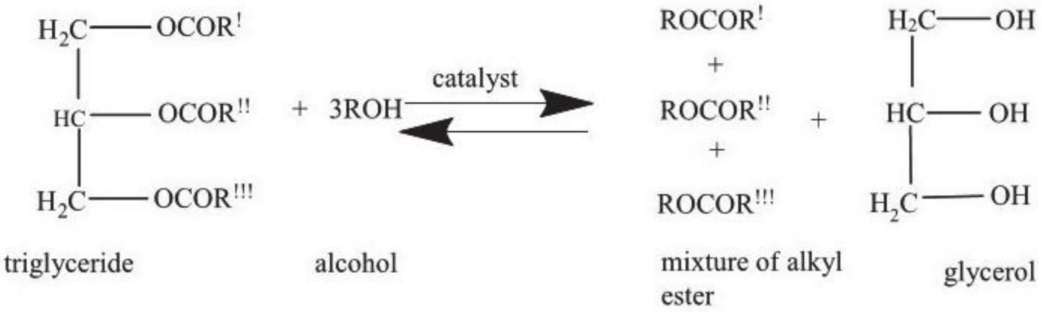


Figure 2.1: Production of biodiesel through transesterification of triglyceride (Edeh, 2020)

Mostly, the manufacturing process used in traditional biodiesel production relies on homogenous catalysts and operates in batch or continuous modes. These methods are hampered by catalyst separation from the product, which involves additional downstream purification and biodiesel recovery. The homogeneous alkali-catalyzed transesterification process also requires many heat exchangers such as a heater, process exchanger and coolers to increase or decrease the temperature of the stream. The temperature of the CSTR is also needed to be kept at their desired value in order to maintain the WCO conversion.

In a study done by Aboelazayem et al (2018b), he stated that the FFA concentration and water content of the feedstock are highly sensitive in base catalyzed process technology. A saponification reaction between the base-catalyst and the FFA in the feedstock could occur and generate soap, preventing biodiesel separation and so decreasing yield. In a study done by Semwal et al (2011), to cut the cost of catalyst separation, a heterogeneous base-catalyzed approach was adopted. However, due to its sensitivity, heterogeneous catalysts require specific facilities for catalyst synthesis and feedstock with very low water concentrations.

Non-catalytic supercritical methanol technology was used in the study by Aboelazayem et al (2018b) where he stated that the method is not subjected to any mentioned restrictions. Pre-treatment was required by WCO for either homogeneous or heterogeneous base-catalyzed processes, however, it was not necessary for supercritical methanol processes. The best parameters for biodiesel generation inside the super-critical methanol process, according to Ghoreishi & Moein (2013) are 271 degrees Celsius, 231 bar, 20.4 min, and 33.8:1 Methanol:Oil molar ratio, yielding 95.7%.

2.3 Energy Analysis in Biodiesel Plant

It is critical to improve the energy efficiency of the processes in order to increase the economic viability of biodiesel production by optimizing heat recovery and minimizing energy degradation. Based on the study done by Talebian-Kiakalaieh et al (2013), alkali catalysts (KOH, NaOH, CH3-ONa) have been utilized to produce biodiesel since they are inexpensive and easily available. However, there are certain drawbacks to the process, such as high energy consumption, which leads to a significant increase in capital equipment costs and safety concerns.

According to the study done by di Serio et al (2006), the energy consumption of two biodiesel manufacturing procedures was compared. The comparison was done for the processes which are catalyzed by homogeneous and heterogeneous catalysts are 754.8 and 153.0 kWh/ton biodiesel, respectively. In a similar study done by Hou & Zheng (2009), a biodiesel factory with a capacity of 8000 tons/annually required 2300 MJ/h of hot utility, 1920 MJ/h of cold utility, and 197 MJ/h of electricity. They also suggested that if the plant uses the solar utility to supply steam and electricity, 4676 tons of CO_2 released can be reduced annually.

Based on the study done by Joda & Ahmadi (2019), a biodiesel production plant with a 10 million gallon per year capacity was simulated using Aspen Plus simulation. Both processes, as well as the integrated combined power plant, are individually simulated in Aspen Plus to conduct thermodynamic and economic studies. The gas and steam turbines generate 37320 and 4358 kW of power, respectively, in this integrated system. Because the integrated unit's pumps and compressors utilize a total of 23331 kW, the net power generated by the integrated unit is 18346 kW. The minimum required utility amount has been calculated. The biodiesel production segment requires 2393.05 kW of hot and 2041.55 kW of cold utility, respectively. After integrating with this combined power plant, these numbers change to 0 kW and 19255.18 kW, respectively. After power plant integration, according to GCC, the simulated unit needs just 19255.18 kW of cold utility supplied from the cooling water.

Sakai et al (2009) conducted a study on the economic assessment of batch biodiesel production processes using homogeneous and heterogeneous alkali catalysts. The basis of a biodiesel production capacity is 1452 tons/year (5000 l/day). 2743 MJ of low-pressure steam and 880 kW h of electric power are used in the KOH-W process. 2743 MJ of low-pressure steam, 3274 MJ of hot oil, and 1075 kW h of electric power are used in the KOH-D process. 3280 MJ of low-pressure steam and 880 kW h of electric power are used in the CaO-W process. 3280 MJ of low-pressure steam, 3274 MJ of hot oil, and 1075 kW h of electric power are used in the CaO-D process.

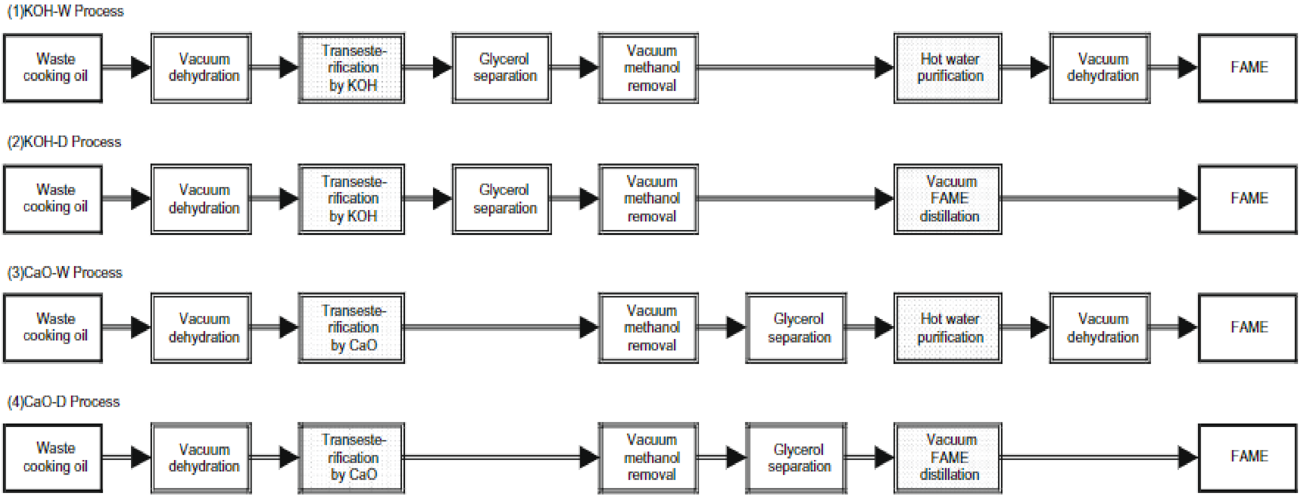
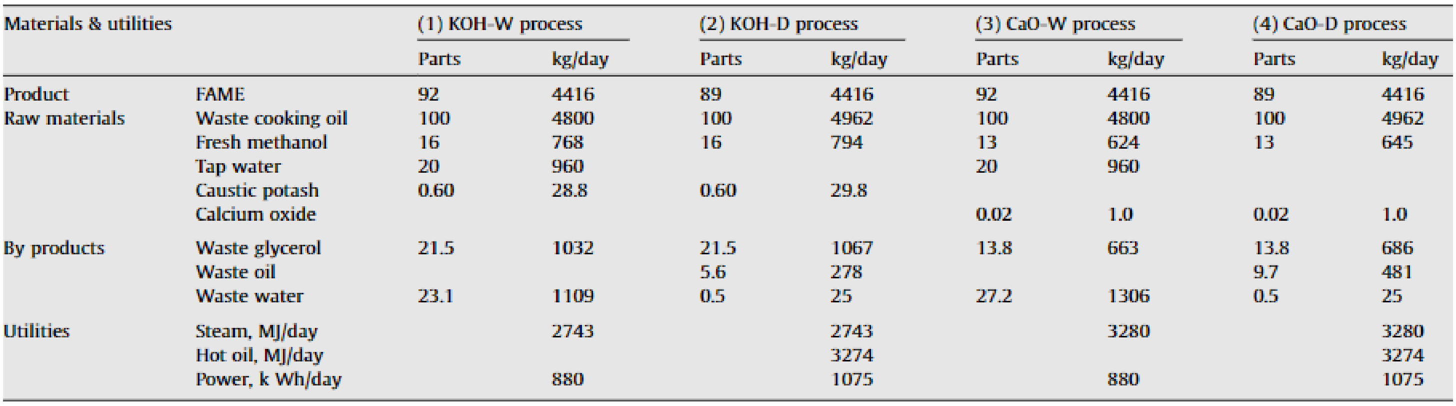


Figure 2.2: Process block flowsheets of four batch processes to produce biodiesel from WCO (Sakai et al., 2009)

Table 2.1: Summary of material balance and energy balance for the four batch processes (Sakai et al., 2009)



Materials & utilities		(1) KOH-W process		(2) KOH-D process		(3) CaO-W process		(4) CaO-D process	
		Parts	kg/day	Parts	kg/day	Parts	kg/day	Parts	kg/day
Product	FAME	92	4416	89	4416	92	4416	89	4416
Raw materials	Waste cooking oil	100	4800	100	4962	100	4800	100	4962
	Fresh methanol	16	768	16	794	13	624	13	645
	Tap water	20	960			20	960		
	Caustic potash	0.60	28.8	0.60	29.8				
	Calcium oxide					0.02	1.0	0.02	1.0
By products	Waste glycerol	21.5	1032	21.5	1067	13.8	663	13.8	686
	Waste oil			5.6	278			9.7	481
	Waste water	23.1	1109	0.5	25	27.2	1306	0.5	25
Utilities	Steam, MJ/day		2743		2743		3280		3280
	Hot oil, MJ/day				3274				3274
	Power, k Wh/day		880		1075		880		1075

2.4 Pinch Analysis and HEN Design

Pinch and exergy analysis are two extensively used methodologies for process energy optimization. Both approaches can be used to increase the energy efficiency of processes on an industrial scale. Pinch technology which is readily available can be used to solve this energy demand problem. Aboelazayem et al (2018a) stated that pinch technology is recognized as one of the most effective methods used to assess the efficiency of energy utilization for production processes. Linnhoff & Hindmarsh (1983) further developed the aspects of pinch analysis. Smith (1912) has explored the pinch analysis principles, which have been used in mass and energy integration applications, as well as in heat recovery.

Pinch analysis reduces energy usage by determining the most efficient heat exchanger network (HEN) for heat recovery within operations. It's frequently utilized for process integration, which is a crucial phase in the process design that aims to reduce utility costs by increasing heat recovery. Heat integration, on the other hand, does not always result in an increase in the processes' exergetic efficiency (Chew et al., 2015). The most inefficient units in the processes are identified using exergy analysis (Angsutorn et al., 2014). If the causes of exergy degradation on these inefficient units can be identified, improvements to improve exergetic efficiency and reduce exergy loss could be proposed.

In order to reduce the process's reliance on external energy and fresh resources, energy and mass integration techniques can be utilized. The graphical pinch approach can be used to design and build a new optimal HEN that reduces the amount of energy required for heating and cooling.

On a study conducted by Aboelazayem et al (2018a), heat integration was used for biodiesel production from waste cooking oil via supercritical methanol. Aspen energy analyser was used in this study to the pinch temperatures, minimum heating and cooling energy requirement and composite curve plotting for all process streams. The minimum energies necessary for heating (Qh) and cooling (Qc) are 4,108 kW and 5,400 kW, respectively. After that, the graphical pinch analysis method is utilized to develop the HEN which consists of 5 heat exchangers in total. The developed HEN was able to achieve 100% of both minimum heating and cooling energy requirements.

Based on the study carried out by Kastritis et al (2012), heat integration techniques are applied to an integrated biodiesel biorefinery in order to reduce the expense and improve the economic performance. Heat integration alternatives are determined by extracting the overall biorefinery's thermodynamic findings from Aspen Plus simulations. A new heat exchanger network (HEN) was developed using pinch analysis and stochastic optimisation approaches. When compared to the initial plant, the HEN optimization results in a 17.2% reduction in TAC and 62.3% and 64.2% reductions in hot and cold utilities, respectively.

2.5 Finding/Summary

In general, through the aforementioned observations from section 2.3 and 2.4, it can be summarized that there is an abundance of information available on the pinch analysis method and heat exchanger network (HEN) in biodiesel production from previous studies and literature. As days go, these methods and models increased with many publications emerged implementing the use of the pinch analysis method to find the optimum heat exchanger network. The process might seem different in all the studies but the fundamental is more or less the same.

One of the keys to sustainability and the prevention of pollution in the process sector is the efficient use of energy. Based on the study done by Anantharaman (2011), a methodical approach based on thermodynamic principles for integrating energy intensive operations was developed as an insight for solving industrial sized HEN problems. Energy level composite curve (ELCC) which is a graphical tool is utilized in this work. This approach gives physical understanding of how to integrate energy sources and sinks. From this finding, the composite curve can also be obtained from Aspen Plus which contains similar graphical tool.

Based on the findings from section 2.3, biodiesel production is an energy intensive process and it does require huge amount of energy to satisfy the heating and cooling energy requirement alone without including other utilities such as electricity. To reduce the external energy dependency, heat integration is done in a plant so that the energy from the process streams can be utilized thus reducing the dependency on utilities. This will result in less external energy usage and reduce in operating cost.

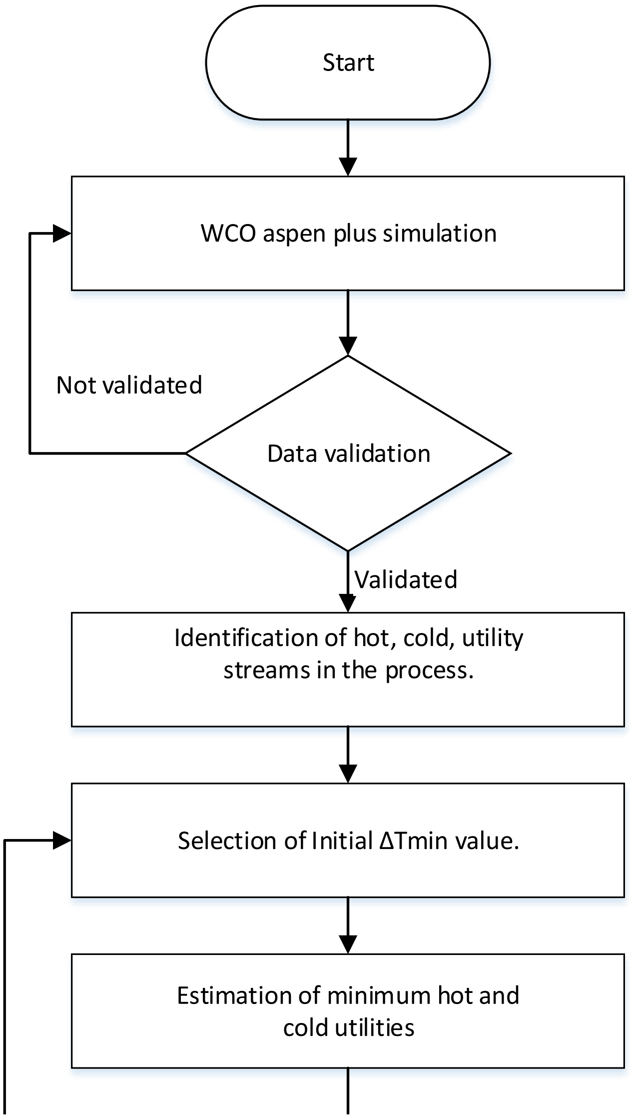
From section 2.4, pinch analysis is an effective method used to assess the efficiency of energy utilization for production processes. By using pinch technology, heat integration can be done and new heat exchanger network can be proposed. Even while the network's heat exchanger count will eventually rise, increasing the plant's capital cost, in the long term, the money saved through reduced utility bills will not only cover the plant's capital costs but also lower its operating costs.

Based on analysis and observation, the heat composite curve is much more preferred rather than the problem table algorithm for the pinch temperature identification because of its simplicity. In this case, Aspen Energy Analyzer (AEA) is a powerful tool that employs the pinch analysis method to build the best HEN for the least amount of money. By importing stream data from an excel sheet or the modelling software, AEA can work independently from Aspen Plus and Aspen HYSYS. AEA is also available as a tool in Aspen Plus and Aspen HYSYS under the name Energy Analysis.

CHAPTER 3 : MATERIAL AND METHODS

3.1 Introduction

The overall modelling features of the final year project are detailed in this chapter. The procedure for using the obtained aspen modelling of the WCO biodiesel production plant, the application of Aspen Energy Analyzer software to perform the pinch analysis and designing of the heat exchanger network (HEN), and finally the evaluation of model performance using statistical methods in which the equations used are introduced are all included. The flowchart for the project sequence can be seen below in Figure 3.1.



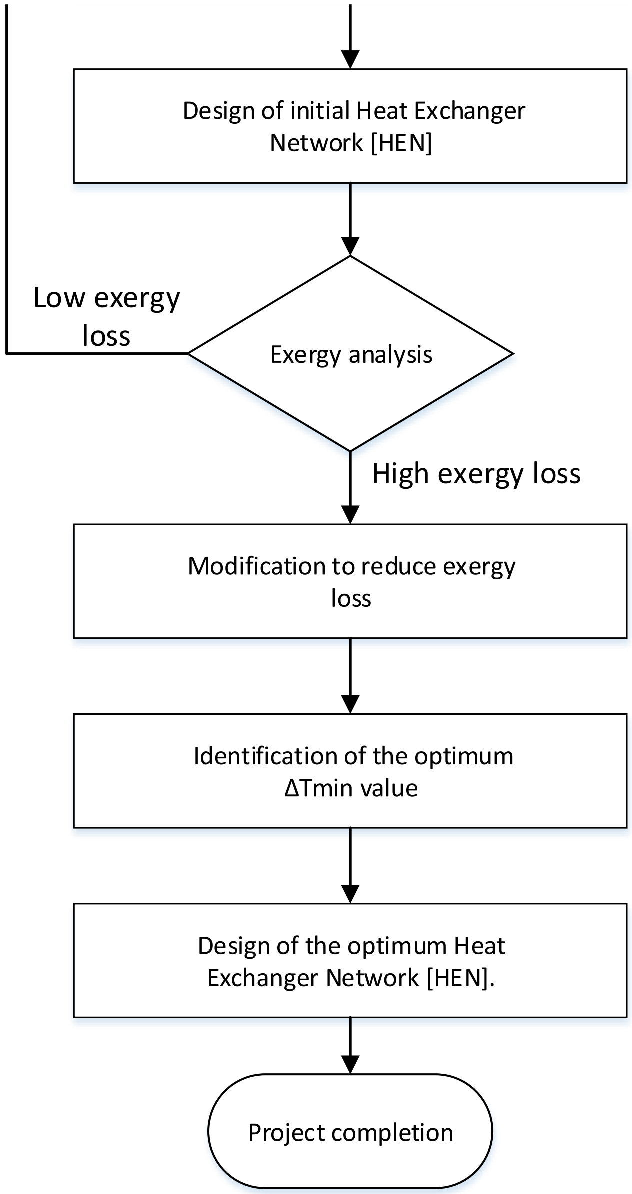


Figure 3.1: Flowchart on the general framework of the overall research sequence

3.2 Case Study: Process Development and Process Simulation for Biodiesel Production from Waste Cooking Oil (WCO)

For this study, biodiesel plant capacity is assumed to be 120 kt/annum per annum (Patle, Sharma, et al., 2014). This capacity is chosen as the plant with a similar capacity already exists. For instance, in Malaysia, a plant is designed to produce 100 kt of biodiesel per annum with infrastructure to expand capacity to 200 kt/annum (PlantBiofuels, 2013). Sharma & Rangaiah (2013) assumed a plant capacity of 20 kt/annum based on the potential WCO availability in Singapore, as estimated by Chua et al. (2010). Making a similar assumption, in Malaysia, having a population of about six times that of Singapore and having a similar food culture, the potential WCO will be around 120 kt/annum. Also, with biodiesel available in 3 states involving around 1,150 petrol stations in Malaysia, potential biodiesel consumption is 155.44 kt/annum (USDA, 2013). The plant capacity considered in this study is comparable to this potential biodiesel consumption.

3.2.1 Steady State Process Development

The feed is considered to be waste cooking palm oil (WCPO) as palm oil is extensively used in Malaysia for cooking. However, the processes presented below can process WCO as well as crude palm oil (CPO) as they have similar FFA content. So, the actual feed can be either WCO or CPO, depending on their availability and costs.

Both the process alternatives use alkali-catalyzed transesterification, which is more efficient and also used in industrial practice (Lurgi, 2007). The alternative for the complete biodiesel process, studied in this work, is discussed below.

3.2.2 Steady State Process Simulation

Figure 3.2 shows a process schematic for biodiesel production from WCO, where products separation is followed by water washing (Sharma and Rangaiah, 2013). WCO with a flow rate of 15,000 kg/h (stream ‘OIL’ in Figure 3.2) is processed in the esterification reactor (RFFA), where FFAs react with methanol in the presence of acid catalyst to yield FAMEs. The OIL stream is pre-heated in a heat exchanger with the esterification reactor products (stream ‘RFFA1’). The esterification is performed at 60ºC, 4 bar pressure, methanol (stream ‘MEOH’) to FFAs molar ratio of 10:1 and with 10% (w/w) of sulfuric acid relative to FFAs (Noureddini and Zhu, 1997). The esterification products (stream ‘RFFA1’), after cooling via pre-heating of WCO, are mixed with glycerol and then sent to the phase separator ‘W-1’, where sulfuric acid and water are separated from the reaction mixture. Glycerol forms two phases with reaction mixture, and acid catalyst is removed in heavy phase. Stream ‘W-1-2’ containing mainly glycerol, methanol, water and acid catalyst, from the phase separator ‘W-1’ goes to a distillation column (FRAC-1) where most of the unreacted methanol is recovered and recycled (stream ‘FRAC-1-1’). FRAC-1 column has 8 theoretical stages and operates at reflux ratio of 1. The recycled methanol is then fed back to the esterification reactor (RFFA). Glycerol and sulfuric acid leave the FRAC-1 column in the bottom stream (FRAC-1-2), which is then fed to a neutralization reactor (R-CAO), where sulfuric acid reacts with calcium oxide to produce calcium sulphate (stream ‘CAO’). The calcium sulphate produced in the reactor is then removed in a gravity separator (S-1). The glycerol stream (S-1-1) leaving the separator S-1 is further purified in a flash evaporator (F-1), where the remaining methanol and water are removed from the top stream (ME-WAT-1) and treated as a waste stream due to small methanol flow rate of 8.53 kg/h. Finally, glycerol is recycled back and mixed with fresh glycerol, which forms two liquid phases in phase separator W-1. The light phase from separator W-1 includes oil, biodiesel, methanol and water while the heavy phase contains glycerol, catalyst, methanol and water. The pre-treated WCO feed stream (W-1-1) is fed to a distillation column (FRAC-2 with 10 theoretical stages and operating at reflux ratio of 1), where most of the unreacted methanol (stream 'FRAC-2-1') is recovered in the distillate stream and recycled to the esterification reactor 'RFFA'.

The bottom stream 'FRAC-2-2' containing FAMEs and unreacted oil is processed in the transesterification reactor (RTRANS1 in Figure 3.2) at 50^{o}C. Excess methanol is advantageous as transesterification is a mass-transfer controlled reaction (No ureddini and Zhu, 1997). So, methanol to oil molar flow ratio of 6 is maintained in each transesterification reactor (Morais et al., 2010). Transesterification section mainly contains continuous stirred tank reactors (CSTRs), distillation columns, phase separators, a neutralization reactor and a washing column. Three CSTRs are placed in series, and treated oil mixed with methanol and NaOH catalyst is charged to the first CSTR (i.e. RTRANS1). The effluent streams from RTRANS1 and RTRANS2 are individually sent to phase separators, where glycerol and NaOH with some methanol are separated as the heavy phase (i.e. streams 'D-1-2' and 'D-2-2'). The light phase (i.e. streams 'D-1-1' and 'D-2-1') from D-1 and D-2 separators goes to RTRANS2 and RTRANS3 reactors, respectively. This phase mainly contains biodiesel, oil and methanol with some NaOH. Finally, stream 'R-3' is charged to a distillation column (FRAC-3) having 11 theoretical stages and operating at reflux ratio of 1, where 98% methanol is recovered and reused in the transesterification reactors.

Bottom product from FRAC-3 column contains mainly biodiesel, and is treated in a neutralization unit to remove NaOH using phosphoric acid. A gravity separator 'S-4' is then used to separate precipitated salt from stream 'NA3PO4-2'. It is followed by a water wash column (WASH-2). As the recycled methanol should be free of water, water wash column is used after separating methanol from the reaction mixture. From WASH-2 column, the stream BIO-D containing FAMEs (i.e., Methyl-oleate, Methyl-palmitate, Methyl-myristate, Methyl-stearate, Methyl-linoleate) and having a flow rate of 15167.3 kg/h with more than 99% purity, is taken out.

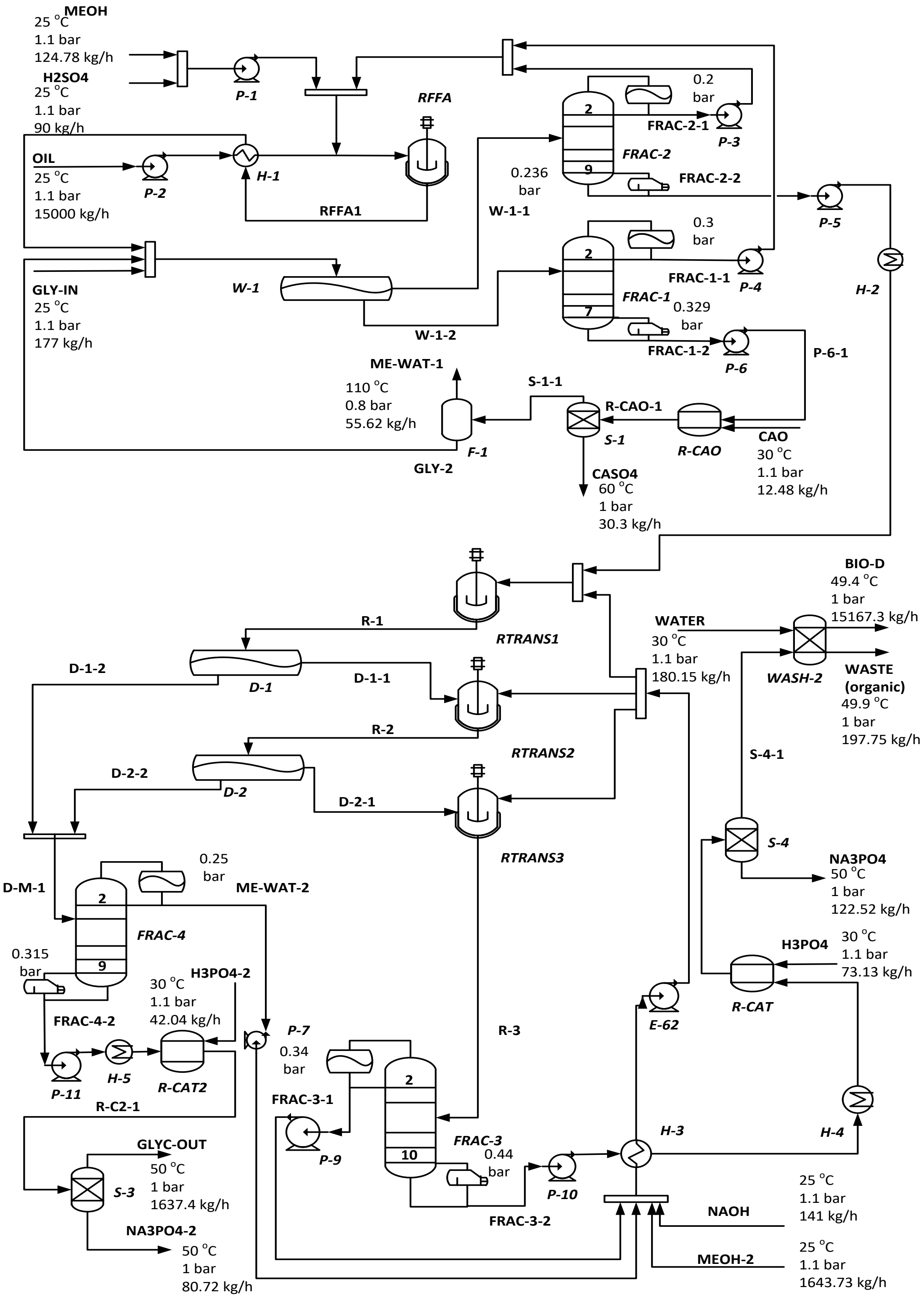


Figure 3.2: Biodiesel production process involving esterification (top section) and transesterification (bottom section): methanol removal is followed by water washing.

The remaining unreacted oil, methanol, glycerol, etc. are removed from stream ‘WASTE’ with a flow rate of 197.75 kg/h. Glycerol streams (i.e. streams ‘D-1-2’ and ‘D-2-2’) are mixed together and charged to a distillation column (FRAC-4), where most of the methanol (stream ME-WAT-2) is separated and recycled. The bottom stream (FRAC-4-2) is mainly glycerol and NaOH, and is charged to the neutralization reactor (R-CAT2) to neutralize NaOH present in the streams using phosphoric acid. The Na_3PO_4 formed in the neutralization reactor is separated using the gravity separator (S-3) from stream NA3PO4-2. The top stream ‘GLYC-OUT’, having more than 96% glycerol, is taken out at a flow rate of 1637.4 kg/h. Figure 3.2 shows temperature, pressure and flow rate of all inlet and exit streams of Process.

3.2.3 Process Simulation in Aspen Plus

This section discusses the simulation of the biodiesel processes. The biodiesel production processes using WCO (shown in Figure 3.2) have been simulated in the Aspen Plus V-10. The palm oil is a mixture of triglycerides of oleic, linoleic, myristic, palmitic, stearic and other acids. Unlike many earlier studies, detailed composition of palm oil is considered in this study. As the detailed composition of waste cooking palm oil is not available in the literature, the detailed composition of refined, bleached and deodorized (RBD) palm oil is taken from Aspen Technology (2022), and adjusted to include 6 percent FFAs. The detailed fatty acid distribution in diglycerides (DG) is not given. Therefore, all the diglycerides in the feed are represented as the PP molecule. DG such as 1-3-dimyristin, 1-3-dipalmitin, 1-3-diolein and monoglycerides (MG) including 1-monomyristin, 1-monopalmitin, 1-monostearin, 1-monoolein and 1-monolinolein are the intermediates of the transesterification reaction. Methyl-Oleate, Methyl-Palmitate, Methyl-Myristate, Methyl-Stearate and Methyl-Linoleate are the biodiesel products. NaOH is used as the catalyst, and is removed by adding H_3PO_4 to precipitate Na_3PO_4. As the