RAZOR SHELL AS HETEROGENEOUS CATALYST SUPPORT FOR CONVERSION OF WASTE COOKING OIL TO BIODIESEL

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B092010103

BACHELOR OF MECHANICAL ENGINEERING TECHNOLOGY WITH HONOURS

2024

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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**A thesis submitted
in fulfillment of the requirements for the degree of
Bachelor of Mechanical Engineering Technology with Honours**

Faculty of Mechanical Technology and Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2024

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

TAJUK: **Razor Shell As Heterogeneous Catalyst Support For Conversion Of Waste Cooking Oil To Biodiesel**

SESI PENGAJIAN: **2023-2024 Semester 1**

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Date : 24/01/2024

DEDICATION

This project is specially dedicated for my parents HUSSIN BIN BABA and SUZIEANTY BINTI MD SHARIF, my supervisor, MAHANUM BINTI MOHD ZAMBERI, for their guidance and encouragement to complete this project.

ABSTRACT

This research aims to examine the biodiesel production using waste cooking oil (WCO) and derived catalyst from razor clam shells. The objective is to investigate sustainable feedstock and catalyst alternatives for the production of catalyst. The biodiesel production from waste cooking oil is designed to minimize the disposal costs and pollution levels. It is challenging to dispose of used oil, so using it as a feedstock for biodiesel is a beneficial process. For this study, biodiesel is produced through the process called transesterification. Process by investigating the critical variables such as reaction time, reaction temperature, molar ratio and catalyst loading on the overall production performances in order to meet the standard of ASTM D6751 and EN 14214. In addition, by using razor clam shell as a catalyst source, the effectiveness of razor clam shell to produce biodiesel will be evaluated. The catalyst that achieves the best catalytic performance is the one that has been calcined at a temperature of 900°C. These results were evaluated through the use of a Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectroscopy (EDS) machine. The critical variable that gave the best results was a methanol (MeOH) to oil ratio of 9:1, with a percentage catalyst loading of 9wt% and a reaction time of 90 minutes at 65°C reaction temperature. Additionally, razor clam shell is readily accessible, thereby reducing the cost of catalyst production.

ABSTRAK

Penyelidikan ini bertujuan untuk mengkaji pengeluaran biodiesel menggunakan sisa minyak masak (WCO) dan pemangkin terbitan daripada cengkerang pepahat. Objektifnya adalah untuk menyiasat bahan suapan dan alternatif mangkin yang baik untuk pengeluaran mangkin. Pengeluaran biodiesel daripada sisa minyak masak direka untuk meminimumkan kos pelupusan dan tahap pencemaran. Adalah mencabar untuk melupuskan minyak terpakai, jadi menggunakannya sebagai bahan mentah untuk biodiesel adalah proses yang bermanfaat. Untuk kajian ini, biodiesel dihasilkan melalui proses yang dipanggil transesterifikasi. Proses dengan menyiasat pembolehubah kritikal seperti masa tindak balas, suhu tindak balas, nisbah molar dan pemuatan mangkin pada keseluruhan prestasi pengeluaran untuk memenuhi piawaian ASTM D6751 dan EN 14214. Tambahan pula, dengan menggunakan cangkerang pepahat sebagai sumber pemangkin, keberkesanan cengkerang pepahat untuk menghasilkan biodiesel akan dinilai. Pemangkin yang mencapai prestasi pemangkin terbaik ialah pemangkin yang telah dikalsinkan pada suhu 900 °C. Keputusan ini dinilai melalui penggunaan mesin Mikroskop Elektron Pengimbasan (SEM) dengan penggabungan Spektroskopi Sinar-X (EDS) Penyebaran Tenaga. Pembolehubah kritikal yang memberikan keputusan terbaik ialah nisbah metanol (MeOH) kepada minyak 9:1, dengan peratusan pemangkin memuatkan 9wt% dan masa tindak balas 90 minit pada suhu tindak balas 65 °C. Selain itu, cengkerang pepahat mudah diakses, sekali gus mengurangkan kos pengeluaran pemangkin.

ACKNOWLEDGEMENTS

In the Name of Allah, the Most Gracious, the Most Merciful

First and foremost, I would like to thanks the praise Allah the Almighty, my creator, my Sustainer, for everythong I received since the beginning of my life. I would like to extend my appreciation to the Universiti Teknikal Malaysia Melaka (Utem) for providing research platform. Thank you also to the Malaysian Ministry of Higher Eductaion (MOHE) for the financial assistance.

My utmost appreciation goes to my main supervisor Mahanum Binti Mohd Zamberi from Faculty of Mechanical and Manufacturing Engineering Technology for all her support, advice and guidance. His constant patience for guiding and providing priceless insights will forever be remembered.

Last but not least, from the bottom gratitude to my family and friends. Finally, thank you to all the individuals who had provide me the assistance, support and inspiration to embark on my study.

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CHAPTER 1

INRODUCTION

1.1 Background

Waste, described by Thurlow (2022) as something no longer useful, is found in various places, including homes, landfills, factories, oceans. It exists in households, landfills, factories, oceans. Waste cooking oil may come from plants like coconut, palm, olive, and canola, as well as fats or oils derived from animal sources like butter and ghee (Yaakob et al., 2013). The Food and Agriculture Organization (FAO) stated that urbanization has increased the use of cooking oil worldwide where the main use of cooking oil is for frying purposes.

Typically, waste cooking oil arises from the frying process, wherein cooking oil, the byproduct of frying with animal or plant fat processed in the oil, becomes the end product. Singhabhandhu and Tezuka (2010) documented that in 2004, Tango and Kyoto collectively gathered approximately 50kg of cooking oil waste, equivalent to around 132 tonnes. This translated to a noteworthy 20% reduction in carbon dioxide emissions. This has caused cooking oil to become one of the biggest contributors to pollution in the world.

The production of cooking oil by manufacturers is increasing which directly leads the amount of waste cooking oil to increase aggressively which can threaten the environment and human health. Using waste cooking oil is linked to potential cancer risks because of toxic substances from fried foods (Yaakob et al., 2013). Alias et al., (2018) says dumping waste cooking oil into water harms aquatic life by disrupting oxygen levels. Improperly disposing of it in sewer pipes and drains, according to Li et al., (2023), causes blockages, leading to flooding or sewer overflow.

1.2 Problem statement

Improper disposal of waste cooking oil (WCO) can jeopardize the environment by releasing oxidation products into the ecosystem, posing significant threats (Lombardi et al. 2018). Other than that, according to Khodadadi et al. (2020). The stringent standards regarding the reprocessing and disposal of heating oil result in a significant increase in WCO production, which presents numerous challenges for its effective management. Annually, food industries and households produce more than 16,500,000 tonnes of WCO. Research conducted by Yaakob et al. (2013) suggests that dumping waste cooking oil in landfills can contaminate water and soil, disrupting the ecosystem. Similarly, pouring it into sewage systems may reduce pipeline diameter, causing blockages and potential economic and environmental consequences.

Employing waste cooking oil as a feedstock in the production process of biodiesel, it can successfully minimise the problem of environmental pollution and turn the waste into a resource that can be used to generate useful and sustainable energy. This strategy leads to the decrease of waste creation, landfill use, and the environmental concerns that are linked with these factors.

The catalysts that are currently employed in a variety of industrial processes are not very successful in terms of efficiency, sustainability, or cost-effectiveness. There is a pressing need to create an innovative catalyst that not only overcomes these problems but also provides improved performance. In addition, in order to minimize the adverse consequences to environment at the same time make the most efficient use of resources, it is essential to discover new sources of catalyst production that are also sustainable.

The impetus for this investigation was derived from the razor clam shell (Ensis Arcuatus). In its initial phase, a razor clam shell was crafted to provide several advantages. Primarily, the utilization of the discarded razor clam shell as a byproduct of the seafood industry was imperative, given its ready availability. This eliminates the need for extra raw materials and significantly cuts down on the amount of trash produced. Razor clam shells, composed of calcium carbonate, exhibit distinct characteristics such as a high surface area and a porous structure. These characteristics have the potential to make catalytic reactions even more efficient. By using these qualities, razor clam shells have the potential to function as an efficient catalyst material, and they may even be able to overcome more conventional catalysts in terms of their efficiency and selectivity

1.3 Research objective

This project aims to create an eco-friendly and effective method for producing biodiesel from waste cooking oil, incorporating razor shell waste as a catalyst.

1. To investigate the physicochemical properties of waste cooking oil and determine if its potential as a source of feedstock for biodiesel production.
2. To investigate the effect of different process variables, such as catalyst type and concentration, reaction temperature, molar ratio of oil to alcohol, and reaction time in producing clean biodiesel production.

1.4 Scope of study

1. Identify the raw oil, type of catalyst and alcohol.
2. Producing catalyst from razor clam shell through the process of cleaning and crushing the razor clam shell into small particles.
3. Perform catalyst characterization by using SEM-EDS to determine the elements present in the produced catalyst.
4. Examining the waste cooking oil properties to ensure that it complies with the established standards.
5. Produce biodiesel using conventional transesterification process.
6. Verifying biodiesel properties for conformity with ASTM D6751.

1.5 Significant of study

The biodiesel production research has the potential to enhance our understanding of the several feedstock options, catalysts, and transesterification approaches used in the production process. By researching and analysing these variables, researchers can obtain valuable insight into the most efficient combinations that produce high-quality biodiesel. Additionally, this study serves as a roadmap for devising techniques to enhance the quality and features of biodiesel, leading to improved performance and compatibility with conventional diesel engines. In addition, by identifying the key parameters that contribute to the highest biodiesel yield, this research enables the optimization of production processes, thereby reducing costs and enhancing efficiency. As a result, this research functions as a valuable resource for future studies and industrial applications, laying the groundwork for additional advances in biodiesel production and utilization.

CHAPTER 2

LITERATURE REVIEW

.

2.1 Biodiesel overview

According to Adipah (2018), Biodiesel is non-toxic, oxygenated, sulfur-free, biodegradable, and environmentally beneficial. A renewable resource, it can serve various purposes such as animal lipids, vegetable fats, waste cooking oil, and transportation fuel. This versatility stems from its composition of mono-alkyl esters of long-chain fatty acids, meeting standard requirements such as ASTM or EU standards. Transesterification is a key step in biodiesel production. The elevated viscosity of biodiesel can be attributed to the injection and atomization characteristics associated with vegetable oil and to enhance the efficiency of diesel engines, the viscosity of vegetable oil can be reduced through the conversion of vegetable oil into biodiesel. Addressing the challenge of elevated fuel viscosity can be accomplished through four primary methods such as dilution, micro emulsification, pyrolysis, and transesterification.

Biodiesel is a substance made from animal fat or vegetable oil. Materials like these emit minimal amounts of carbon dioxide, soot, and particulates. To produce biodiesel, there are two sources which are conventional or non-conventional sources. There are three types of raw materials to produce biodiesel. The initial category comprises crude food oils like coconut oil, palm oil, and peanut oil. The second category involves inedible vegetable oils, including mahua oil, castor oil, and pongamia oil. Lastly, the third type encompasses alternative feed materials such as waste cooking oil, microalgae, animal fat, and pyrolysis oil, as outlined by Rao et al. (2018).

2.1.1 History of biodiesel

According to Rizwanul Fattah et al. (2020), the notion of utilizing vegetable oils as a fuel source has historical roots dating back to the late 19th century. Rudolf Diesel, the inventor of the diesel engine, conducted experiments with peanut oil as a potential fuel during this period. However, the widespread adoption of biodiesel gained traction in response to the energy crisis of the 1970s and growing concerns about environmental sustainability. Subsequently, in the 1980s, research and development efforts intensified, primarily focusing on identifying suitable raw materials and refining technologies to facilitate larger-scale biodiesel production.

Originally, the primary focus was on employing vegetable oils, such as soybean, rapeseed, and sunflower oil, as feedstocks for biodiesel production. These oils underwent a process known as transesterification, wherein they were transformed into esters (biodiesel) through a reaction with alcohol, typically methanol, in the presence of a catalyst. This procedure was employed to generate biodiesel.

Next, Adipah (2018) state that in the 1990s, biodiesel gained foothold as an alternative fuel in Europe, notably in Germany, where government regulations and subsidies backed its production and usage. In addition, biodiesel gained traction in the United States as an alternative fuel. It has come to people's attention that biodiesel can cut emissions of greenhouse gases, advance the cause of energy independence, and provide a market for agricultural goods. As a direct consequence of this, biodiesel manufacturing facilities and distribution networks were set up, and biodiesel blends were readily accessible for purchase in the marketplace.

At the beginning of the 20th century, biodiesel continued to attract the attention of people all over the world and experienced a rise in its use in many nations. To encourage the production of biodiesel and its usage, governments have established renewable fuel regulations and financial incentives. Concerns about sustainability, feedstock supply, and consequences on land usage were the primary focuses of research and development activities. These activities aimed at improving the productivity of biodiesel production techniques, investigate new feedstocks, and solve these issues.

2.2 Global biodiesel

Biofuels, including bioethanol and biodiesel, are fuels derived from biomass. Presently, about 60% of ethanol is sourced from corn, 25% from sugarcane, 2% from molasses, 3% from wheat, and the remaining percentage from other cereals, cassava, or sugar beets. Around 75% of biodiesel is produced from vegetable oils, including 20% from rapeseed oil, 25% from soybean oil, 30% from palm oil, or 20% from used culinary oils. Advanced technologies that utilize cellulosic feedstocks, such as agricultural residues, dedicated energy crops, and biomass, constitute a relatively small proportion of total biofuel production. The global biofuel sectors are significantly influenced by national policies with three primary objectives: supporting farmers, reducing greenhouse gas emissions, and/or enhancing energy independence.

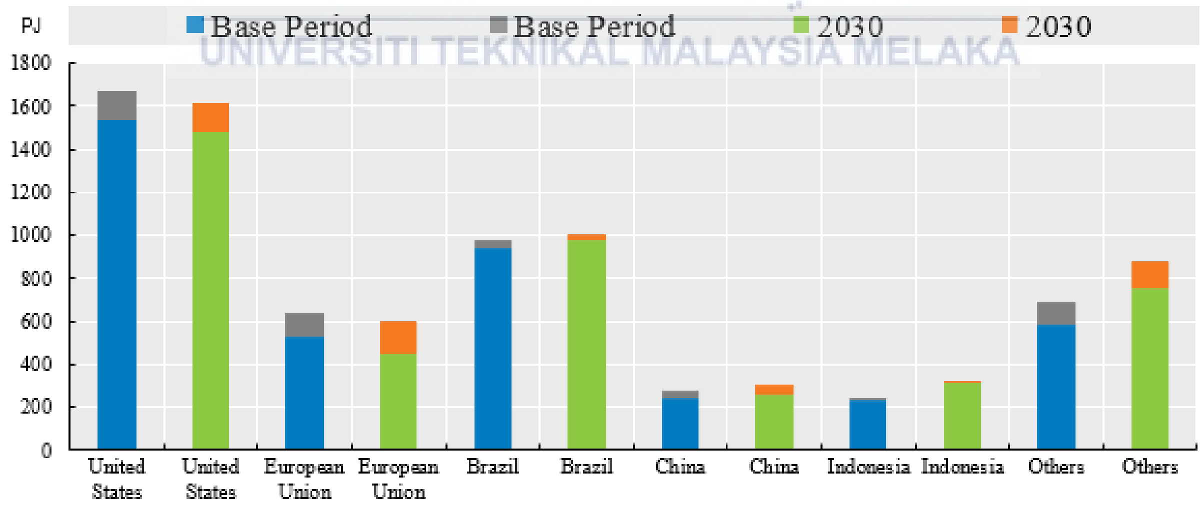


Figure 2.1: Graph of the world production of biofuel from traditional and advanced feedstock in countries around the world OECD/FAO (2021)

Traditional feedstocks, in this context, refer to biofuels derived from food and feed crops. The values are measured in Petajoules. As depicted in Figure 2.1, the United States exhibits higher values than all other countries in the base period for both traditional and advanced biofuels, as well as in the projections for 2030 in both **categories.**

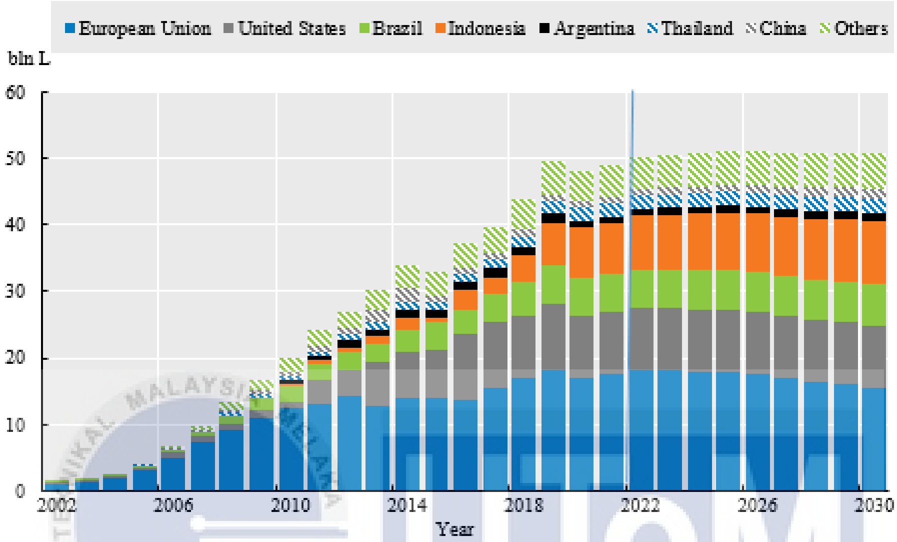


Figure 2.2: Graph development of the world biodiesel consumption OECD/FAO (2021),

Based on the Figure 2.2, European Union has highest biodiesel consumption from year 2002 until 2030 followed by United States as the second highest biodiesel consumption. Other than that, China is the lowest biodiesel consumption. In conclusion, diesel fossil resources are scarce in Europe. As a result, they are investing more in biodiesel production to reduce their reliance on fossil diesel. China has a low biodiesel production because diesel fossil resources are abundant.

2.3 Biodiesel advantages and disadvantages

In the search for sustainable energy alternatives, it is important to give serious attention to both the benefits of biodiesel and its potential drawbacks. Biodiesel is a fossil fuel alternative that is renewable and more environmentally friendly than conventional fossil fuels. Table 2.1 illustrates the pros and cons of biodiesel production.

Table 2.1: The advantage and disadvantage biodiesel production (Firoz, 2008)

Advantage	Disadvantage
Biodiesel was a useful fuel due to its demonstrated power generation, efficacy, and low cost.	Biodiesel fuel is currently around 1.5 times costlier than petroleum diesel fuel.
Biodiesel contributes to the reduction of pollution and improvement of health by lowering CO_2 emissions, thereby reducing the impact of global warming.	Producing biodiesel fuel from soy crops requires energy, in addition to the energy required for planting, fertilising, and harvesting.
Biodiesel is considered safer to manage due to its lower toxicity and ease of storage compared to petroleum.	Several engines' rubber housings may be harmed by biodiesel
No modification to the vehicle or additional fuelling equipment is required.	The impurities that biodiesel cleans from the engine may accumulate in the fuel filter, necessitating regular replacement of the filters to prevent blockages.
Biodiesel reduces reliance on imported fuels.	An area requiring enhancement within the biodiesel fuel framework is the distribution infrastructure, representing another drawback of biodiesel fuel.

2.4 Type of feedstock

Biodiesel can be produced from diverse feedstocks, such as plant matter, phytoplankton, microbial oil, and animal lipids, each yielding biodiesel with distinct purity and chemical composition. According to Sitepu et al. (2020), a crucial initial step in biodiesel production involves choosing the feedstock, a decision that impacts variables like biodiesel purity, cost, composition, and yield. The classification of biodiesel into edible, non-edible, and waste-based categories is primarily determined by the nature and availability of feedstocks. Additionally, geographical location plays a significant role in the selection of feedstocks for biodiesel production. Factors such as the country's availability and economic considerations are pivotal in the decision-making process before settling on a specific feedstock.

Digambar et al. (2020) reported that in Canada, biodiesel feedstock comprises canola oil, while Brazil and the United States predominantly use soybean oil. Indonesia and Malaysia rely on coconut and palm oils for biodiesel production, and Italy, Germany, Finland, and the United Kingdom favor rapeseed oils. In India, karanja and jatropha are being explored as potential biodiesel feedstocks. Despite past utilization of sunflower oil, rapeseed oil, soybean oil, and mustard oil as biodiesel feedstocks, concerns about adverse effects on food crops have hindered their continued use.

The utilization of edible oils as biodiesel feedstocks poses challenges due to its direct impact on the food chain. In contrast, using non-edible oils as biodiesel feedstock offers several advantages, such as biodegradability, low sulfur content, no adverse effects on the food chain, low aromatic content, and increased availability. Biodiesel production can be derived from various sources, including tallow oil, animal lipids, fish oil, microalgae, and others, as indicated by Athar and Zaidi (2020). The classification of biodiesel feedstocks for production is outlined in Table 2.2 per the same source.

Table 2.2: Classification of feedstock for the production of biodiesel (Athar & Zaidi, 2020)

Vegetable oil		Animal fats	Microbial feedstcok	Waste oil
Edible oils	**Nonedible oils**			
Sunflower	Nagchampa (Calophylluminophyllu)	Beef tallow	Fungi	Waste cooking oil
Palm	Coffee ground (Coffea arabica)	Fish oil[	Microalgae	Date pit oil
Safflower (Helianthus annuus)	Croton megalocarpus	Poultry fat	Chlorellavulg	Leather tanning waste
Coconut	Mahua (Madhuca indica)	Pork lard	Chlamydomonas	
Barley	Kusum(Schleichera triguga)		Nostoc	
Peanut	Castor (Ricinus communis)		Botryococcus braunii	
Wheat	Linseed (Linum usitatissimum)		Crypthecodiniumcohnii	
Corn	Mexican prickly poppy(Argemone mexicana)		Cylindrothec	
Sorghum	Persian lilac(Melia azedarach)		Dunaliella primolecta	
Canola	Yellow oleander (Thevetia peruviana)		Isochrysis	
Rice bran (Oryza sativum)	Karanja or honge (Pongamia pinnata)		Monallanthus salina	
Soybeans (Glycine max)	Jatropha		Nannochloropsis etc	
Sesame (Sesamum indicum L.)	Cotton seed (Gossypium hirsutum)			
Palm kernel	Camelina (Camelina Sativa)			
Rapeseed(Brassica napus L.)	Abutilon muticum			
Hazelnut	Jojoba (Simmondsia Chinensis)			
Walnut	Cynara cardunculus			
	Cumaru			
	Neem (Azadirachta indica)			
	Tobacco Seed(Nicotiana tabaccum)			
	Passion seed (Passiflora edulis)			
	Tall (Carnegiea gigantean)			
	Moringa (Moringa oleifera)			
	Rubber seed tree (Hevca brasiliensis)			

In Table 2.2, the highest feedstock source is in category vegetable oil. In vegetable, there is two type which is edible oils and nonedible oils. The nonedible oils has many source to be a feedstock compared to edible oils. At the table, the lowest feedstock source is come from waste oil.

2.4.1 First generation feedstocks (edible oil)

As per Singh et al. (2020), first-generation biodiesels are produced using food feedstocks like rapeseed oil, soybean oil, coconut oil, corn oil, palm oil, mustard oil, olive oil, rice oil, and similar sources. A variety of materials were employed in the production of the initial version of biodiesel.

2.4.2 Second generation feedstock (non edible oil)

As stated by Singh et al. (2020), second-generation biodiesels are crafted from non-edible feedstocks, including neem oil, jatropha oil, nagchampa oil, karanja oil, calophyllum inophyllum oil, rubber seed oil, and mahua indica oil. Researchers are inclined towards non-edible feedstocks due to the limitations observed in first-generation feedstocks. However, it's worth noting that primary non-edible plants like karanja oil, jojoba oil, and jatropha oil exhibit lower yields compared to other prominent non-edible plants, constituting a drawback in the production of second-generation fuels. Despite this, these raw materials can be cultivated on relatively small areas.

2.4.3 Third generation feedstock

Fish oil, animal fat, microalgae, used cooking oil, and various other sources serve as the primary raw materials for third-generation biodiesel. These resources, characteristic of third-generation biodiesel, surpass the feedstocks of previous generations in terms of availability, adaptability to environmental constraints, and economic viability. Notably, microalgae exhibit potential as a source for third-generation biodiesel due to their high lipid content and resilience in harsh conditions. Waste cooking oil, waste fish oil, and waste animal tallow oil are all considered sources of third-generation biodiesel within the category of waste oils. Moreover, this approach helps alleviate pressure on waste treatment facilities and contributes to the reduction of water contamination. Currently, animal fats from diverse sources like pig, cattle, goat, and chicken are emerging as reliable and viable sources for biodiesel generation, as highlighted by Roick et al. (2021).

2.4.4 Fourth generation feedstock

Employing genetic and metabolic engineering to improve the characteristics of oil-producing microbes becomes a feasible approach when the naturally isolated species fail to meet industrial requirements. The major goals of microalgal modification are to increase lipid and carbohydrate metabolism, nutrient utilisation efficiency, hydrogen generation, photosynthesis efficiency, stress tolerance, cell disintegration, and flocculation. Additionally, genetic manipulation may help in oil extraction from microalgal biomass by causing autolysis and product secretory systems. Although the fourth generation of biodiesel is still in the early stages of research, it may one day overcome the drawbacks of the prior three generations and outperform fossil fuel (Pikula et al., 2020).

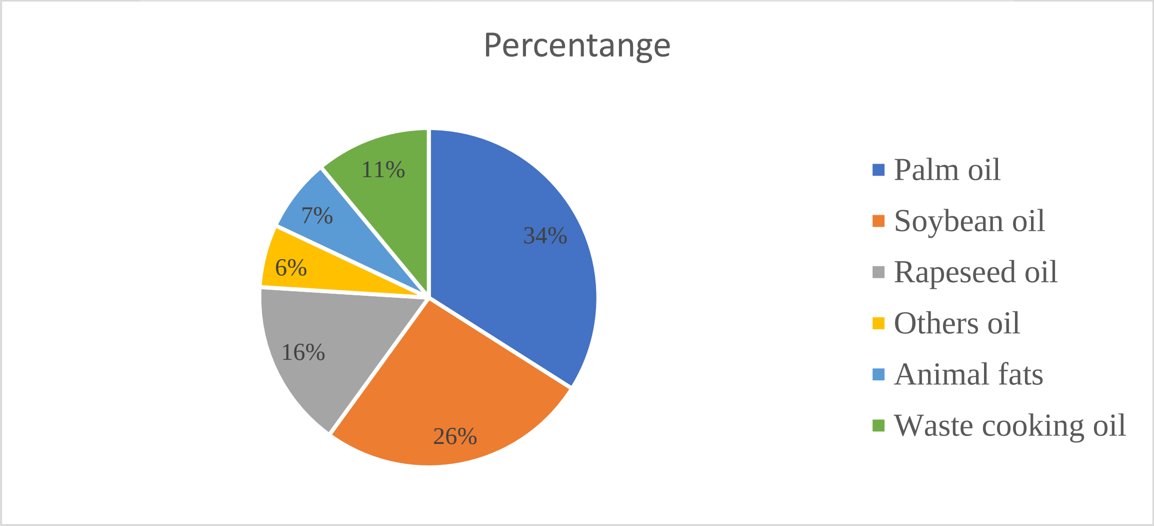


Figure 2.3: Distribution of oil types in the production of biodiesel by percentage. (Singh et al., 2020)

Pie chart illustrated in Figure 2.3 shows distribution of oil types in the production of biodiesel by percentage. around the world. The data shows that highest percentage is come from palm oil that the value is 34%. However, the low percentage that appear on the graph is come from others oil which is 6%.

2.4.5 Advantages and disadvantages 1st, 2nd, 3rd and 4th generation feedstock

Table 2.3: Advantages and disadvantages 1st, 2nd, 3rd and 4th generation feedstock

Feedstock	**Source**	**Advantage**	**Disadvantage**	**Reference**
1st generation	-Rapeseed oil, -Soybean oil -Coconut oil	-Crops are easy to grow, and the change process is relatively easy. -Low emission with greenhouse gases	- Expensive -Not many places to growth -Cause food shortage	Singh et al., (2020),
2nd generation	-*jatropha* oil -*nagchampa* oil -*karanja* oil -*calophyllum inophyllum* oil -rubber seed oil -*mahua indica* oil	-Food waste as feedstock -Low production cost - Utilisation of non-agricultural land for limited crop production.	-Pre-treatment cost highly -Used sophisticated technology to transform biomass into fuel	(Razealy Anuar et al., 2021)
3rd generation	-Waste cooking oil -Animal fat -Fish oil -Algae	-Can reduce greenhouse gases -Less harmful and biodegradable -No competition for the use of food crops	-Low lipid level or biomass accumulation in algae -More resource usage for algae -Requires a hard purification procedure, which increases effort, time, and cost.	(Roick et al., 2021)
4th generation	-Genetically optimised phytoplankton as feedstock for biodiesel	-Free straightforward conversion -Higher in calorific value and natural lipids.	-The accumulation of deposits during storage is facilitated by an increase viscosity -Conta in metal have a putrid colour and toxic	(Pikula et al., 2020)

Table 2.3 show the feedstock advantage and disadvantage for 1^{st}, 2^{nd}, 3^{rd} and 4^{th} generation feedstock. Because 4^{th} still new, the advantage and disadvantage will increase time by time from the research.

2.4.6 Waste Cooking Oil

In this research, the feedstock that use was Waste Cooking Oil (WCO). Hence, the focus of the feedstock was on WCO. The major sources of energy in the world are petroleum, coal, and natural gas. But if nations continue to rely on them without switching to other sources, their fossil fuel stocks will swiftly run out. These resources are diminishing every day. Continuous sources of greenhouse gas (GHG) emissions from these typical sources contribute to global warming and climate change. The industrialised world has already reached its goals for GHG emissions reduction and is seriously contemplating doing so it will be difficult to reach other goals, such cutting domestic emissions by 40% by 2030.

In order to safeguard the environment and human life on the earth, this should be taken seriously everywhere. Diesel fuel plays a crucial role in the industrial economy of a growing nation that is directly involved in energy generation and consumption. It powers construction and agricultural machines as well as industrial transportation. The source from which it is obtained, namely fossil fuel reserves, is the issue since they lead to environmental contamination and adversely harm the ecosystem (Bhatia et al., 2020).

Waste cooking oil (WCO), the oil left over after deep-frying, is an acceptable alternative for the creation of biodiesel. Almost 16.5 million tonnes of WCO are generated annually, according to a paper that was recently published (Loizides et al., 2019). Due to WCO's poorer solubility in water, its disposal in open spaces has an adverse impact on flora and wildlife

(Singh-Ackbarali et al., 2017). The gathering of WCO and its transformation into biodiesel may assist in resolving its disposal issue and will benefit the energy industry.

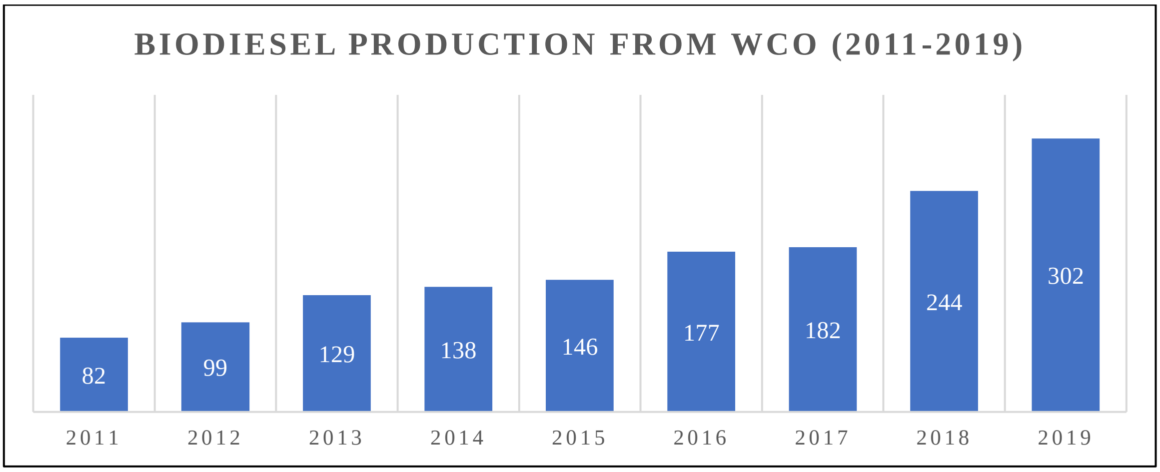


Figure 2.4: WCO biodiesel production and use in Compression Ignition (CI) engines from 2011 to 2019 (Singh et al., 2020)

From the Figure 2.4, the data occur show the seqeuence biodiesel production that use in Compression Ignition (CI) engines was increased year by year. The lowest biodiesel production is at year 2011 and the highest is in 2019.

Achieving compatibility with petroleum diesel is crucial before incorporating waste cooking oil (WCO) into an engine, as differences in key physical properties, such as viscosity and acid number, pose challenges. Direct utilization is hindered by WCO's higher viscosity and incompatible acid properties but preheating beyond 100°C and dilution with solvents or microemulsions can mitigate these issues, facilitating use in compression ignition engines. Alternatively, blending WCO with petroleum diesel in various ratios is an option, but this approach may lead to operational issues, including clogged filters, coked injector nozzles, sticking piston rings, contaminated lube oil, acidity-related corrosion, and increased engine wear. Another avenue involves pyrolyzing WCO, yielding more bio gasoline than biodiesel, as demonstrated by Yaqoob et al. in 2021.

Table 2.4: Physicochemical properties of waste cooking oil biodiesel blended with diesel fuel in diesel engines. (Yaqoob et al., 2021)

Topic	Findings
Cetane number	• The cetane number serves as a standardized measure to assess the ignition delay and combustion efficiency of diesel fuel. • Higher cetane number values are indicative of superior diesel fuel, contributing to enhanced cold start performance and a reduction in the formation of white smoke.
Viscosity	• Blends with over 20% waste cooking oil (WCO) biodiesel can increase viscosity, impacting atomization during fuel injection in compression ignition (CI) engines without modifications. To maintain optimal engine performance, it is advised to limit biodiesel blends to 20%. • Mixing waste cooking oil (WCO) with n-propanol effectively reduces its viscosity, offering a potential solution to viscosity-related challenges in biodiesel. • Biodiesel's higher viscosity reduces injection velocity, mass flow rate, and discharge coefficient, increasing penetration depth but decreasing atomization during injection. To counter these effects, biodiesel is injected at a temperature approximately 60 K higher than petroleum diesel.
Density	• Compression ignition (CI) engines can generate increased power when utilizing denser fuels; however, higher-density fuels are associated with an elevated level of soot emissions.
Calorific value	• The presence of oxygen in the molecules of waste cooking oil (WCO) biodiesel results in a calorific value approximately 12% less than that of diesel. This reduced calorific value contributes to a decrease in the thermal efficiency of an engine powered by biodiesel compared to one fuelled by petroleum diesel.
Liquid length	• The liquid length or penetration depth of biodiesel exceeds that of petroleum diesel, attributed to its elevated viscosity.

Table 2.4 show the physicochemical properties when oil biodiesel blended with diesel fuel. The properties must be monitored and investigated to fulfil the criteria that follow the standard of ASTM D6751 and EN 14214.

2.5 Catalyst

A catalyst is a material that speeds up a chemical process without changing the reaction itself. The pace at which thermodynamic responses are carried out may be altered by motivations, and they can also control the rate at which experiments advance. The equilibrium constant of the reaction is unaffected by the catalyst is presence since it affects it uniformly. In order to give the reaction enough time to complete, the stimulus quantity should be employed in a lesser amount during the first phase of the response. (Zailan et al., 2021)

Other than that, increasing the stimulus quantity might result in a drop in biodiesel production owing to diffusion reactions. As state Mares et al., (2021) by increasing the catalyst concentration further causes the production of emulsions, which raises viscosity and complicates biodiesel yield. Water is a byproduct of the esterification process used in the case of free fatty acids (FFA). Water reduces the catalytic reactivity of the reaction, lowering the yield of biodiesel.

There are three main categories of catalyst are homogeneous, heterogeneous, and biocatalyst as shown in Figure 2.5. These categories are further broken down into acid and base catalyst. Table 2.5 indicates the advantages and disadvantages of catalyst according to Changmai et a. (2020).

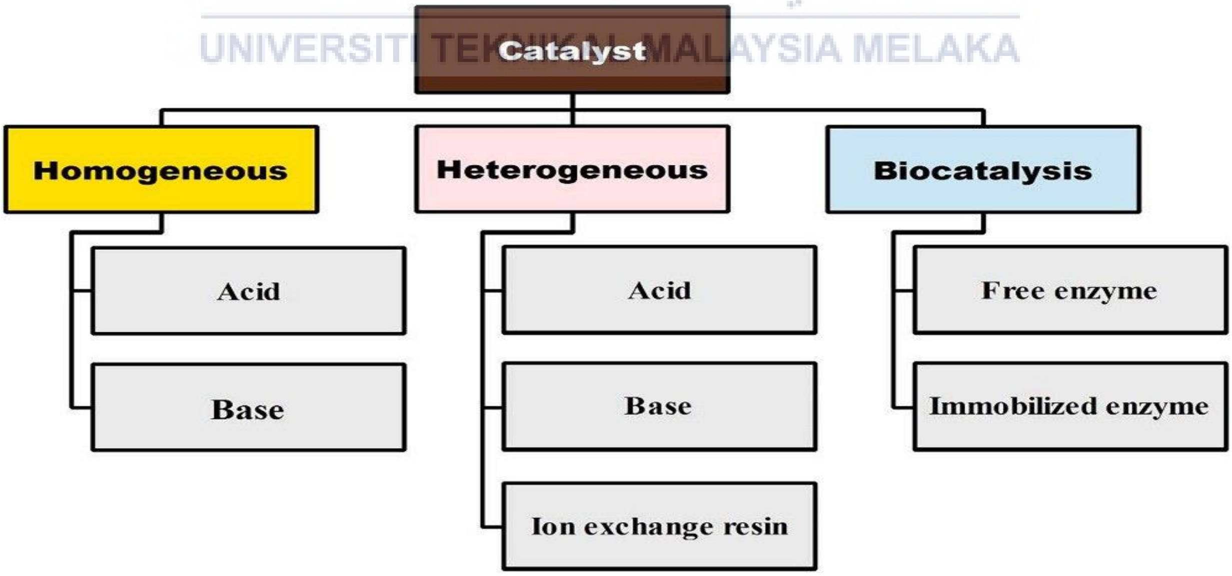


Figure 2.5: Catalyst classification for homogeneous, heterogeneous and biocatalyst (Jayakumar et al., 2021)

Table 2.5: The advantage and disadvantage of catalyst (Changmai et al., 2020)

Catalyst Types	Examples	Advantages	Disadvantages
Homogeneous Alkali	NaOH, KOH	- Elevated reactivity - Accelerated reaction rate - Optimal cost efficiency - Promoting favourable kinetics - Moderate operational conditions	- Not suitable for elevated levels of free fatty acids (FFA) in feedstocks - Becomes deactivated in the presence of both moisture and FFA - Necessitates a significant volume of wastewater - Saponification as a byproduct - Non-recyclable and possesses corrosive properties
Acid	H_2SO_4, HCl, HF	- Shows no reactivity towards moisture and free fatty acid (FFA) content in oil. - Conducts catalyzed simultaneous esterification/transesterification reactions. - Prevents the formation of soap.	- Extended reaction duration - Equipment susceptibility to corrosion - Elevated requirements for reaction temperature and pressure - High alcohol-to-oil ratio necessity - Limited catalytic efficiency - Challenges in recycling the catalyst
Heterogeneous Alkali	CaO, SrO, MgO, mixed oxide and hydrotalcite	- Non-corrosive - Environmentally friendly - Capable of recycling - Reduced issues with disposal - Easy to separate - Improved selectivity - Extended catalyst lifespan	- Slower reaction rate when compared to the homogeneous alternative - Low free fatty acid (FFA) requirement in the feedstock (<1 wt%) - High susceptibility to water and FFA - Saponification occurring as a secondary reaction - Formation of soap - Substantial wastewater generation - Leaching of active catalyst sites - Diffusion limitations - Elaborate and costly synthesis pathway - Elevated expenses associated with catalyst synthesis
Acid	ZrO, TiO, ZnO, ion-exchange resin, sulfonic modified Mesostructured silica	- Unaffected by free fatty acid (FFA) and water content in the oil - Facilitates catalyzed simultaneous esterification and transesterification reactions - Recyclable and environmentally friendly - Non-corrosive to reactor and its components	- Moderate reaction rate - Extended reaction time - Elevated reaction temperature and pressure - Substantial alcohol-to-oil ratio necessity - Limited catalytic activity - Low presence of acidic sites - Insufficient micro porosity - Leaching of active catalyst sites - Diffusion limitations - Elaborate and costly synthesis pathway - High expenses associated with catalyst synthesis

2.5.1 Homogeneous catalyst

In the biodiesel production process, as described by Sree et al. (2019), the initial standard method employs homogeneous catalysts, where both acid and alkali catalysts exist in liquid form. The decision to use either basic or acidic catalysts is contingent upon the free fatty acid (FFA) concentration in the oil, influenced by factors such as the oil's origin, production method, processing method, and storage method. The application of highly efficient base catalysts is constrained in the presence of substantial FFA levels in non-edible oils.

Typically, it is recommended to use base catalysts for oils with FFA content below 0.5 wt%. The interaction of free fatty acids in the feedstocks with alkaline catalysts leads to soap formation, reducing fatty acid alkyl ester (FAAE) output, causing catalyst depletion, and complicating the separation process. Consequently, the use of alkaline homogeneous catalysts like sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH_3ONa) is more suitable for biodiesel production from low FFA oils, as highlighted by Athar and Zaidi (2020).

2.5.1.1 Homogeneous alkaline catalyst

In the commercial process of transesterification for biodiesel production, homogeneous alkaline catalysts are favoured and commonly employed. Sodium hydroxide (NaOH), Potassium hydroxide (KOH), and alkoxides such as Sodium methoxide (CH_3ONa), Potassium methanolate (CH_3OK), and Sodium ethoxide ($NaOC_2H_5$) are frequently used in industrial settings due to their ability to facilitate a rapid reaction at moderate conditions, as highlighted by Hsiao et al. (2021).

The purity and yield of biodiesel are influenced by factors such as the initial catalyst concentration, feedstock oil quality, molar ratio of feedstock oil to alcohol, and reaction temperature. A higher catalyst concentration can lead to soap formation, causing biodiesel to mix with glycerol and prolonging the reaction time. Mandari and Devarai (2022) demonstrated this by initially achieving a 70% biodiesel yield with a 0.13 g NaOH catalyst, but as the catalyst concentration was progressively increased to 0.18 g, the yield consistently declined to 49%.

2.5.1.2 Homogeneous acid catalyst

According to Mohiddin et al. (2021), the use of homogeneous alkali catalysts in biodiesel production has notable drawbacks, particularly the generation of soap when employing premium extra-pure edible oils and dealing with higher free fatty acid (FFA) levels in feedstock oil. To address these issues, homogeneous acid catalysts can be employed. Acid catalysts exhibit indifference to the presence of FFA in the input oil, enabling them to concurrently catalyse esterification and transesterification processes. This makes acid catalysts suitable for cost-effective utilization of raw materials such as non-edible oils, spent cooking oil, and animal fats with high FFA content.

FFA is less susceptible to strong acids like sulfuric acid (H_2SO_4), sulfonic acid (H_2SO_3), hydrochloric acid (HCl), and ferric sulfate ($Fe_2(SO_4)_3$). Among these, H_2SO_4 is frequently utilized due to its effectiveness at medium temperatures and atmospheric pressure. Mandari and Devarai (2022) demonstrated the conversion of Chlorella pyrenoids algal oil with 90% water content into biodiesel using a 0.5% H2SO4 solution, achieving a biodiesel yield of 93.2% at 120 °C for 180 minutes.

2.5.2 Heterogeneous catalyst

Effective and cost-efficient heterogeneous catalysts play a vital role in reducing the overall expenses associated with biodiesel production. Particularly in challenging conditions like high temperatures and pressures, heterogeneous catalysts are considered indispensable. These catalysts exhibit resilience during water treatment stages, are easily recoverable from reaction mixtures, and can be customized to enhance activity, selectivity, and catalytic lifespans. The development of heterogeneous catalysts may involve techniques to facilitate the grafting and trapping of active molecules on the surface or within the pores of a solid support, such as silica, alumina, or ceria, as emphasized by Thangaraj et al. (2019).

2.5.2.1 Heterogeneous alkaline catalyst

Heterogeneous alkali catalysts primarily comprise alkaline oxides, alkaline earth metal oxides, hydrotalcite, metallic salt, anion exchange resins, and zeolites supported on a substantial surface area. Alkaline earth metal oxides, owing to their economical nature and robust basic strength, are commonly employed as solid alkali catalysts in biodiesel production. Single metal oxides have proven effective in catalysing biodiesel production, as highlighted by Rabie et al. (2019).

Enhanced catalytic efficacy can be achieved by incorporating dopants, leading to an increased surface area and improved catalyst properties. While CaO and BaO generally exhibit greater potency than MgO, it is noteworthy that BaO is toxic and readily soluble in ethanol and methanol. CaO stands out as an excellent heterogeneous catalyst due to its selectivity, superior activity, widespread availability, low solubility in methanol, and compatibility with moderate reaction conditions. Its accessibility and affordability further contribute to its prominence in biodiesel production, as emphasized by Goli & Sahu (2018).

2.5.2.2 Heterogeneous acid catalyst

Heterogeneous acid catalysts offer a viable alternative to homogeneous acid catalysts in the synthesis of biodiesel through esterification and transesterification. The presence of Brønsted and Lewis acid active sites on solid heterogeneous acid catalysts positions them as superior catalysts in industrial applications compared to their homogeneous counterparts. Unlike homogeneous acid catalysts, heterogeneous acid catalysts demonstrate resistance to vessel corrosion and exhibit lower toxicity. Moreover, these catalysts are robust against high free fatty acid (FFA) and water content in feedstock oils, enabling the production of biodiesel from low-quality and cost-effective feedstocks without the need for acid pretreatment, as highlighted by Tang et al. (2020).

2.5.3 Razor clam shell

In this research, the catalyst used was heterogeneous alkaline base that was Calcium oxide (CaO) that come from razor shell. Razor shells have a fragile, elongated carapace with openings on both ends. The exterior of the shell is smooth and white, with vertical and horizontal reddish-brown or purplish-brown markings that are separated by a diagonal line. The periostracum is olive green in colouration. The inner surface is white with a faint purple hue, and the foot is a delicate reddish-brown colour. The presence of razor shells in the sand is indicated by keyhole shaped apertures created by the short, united syphons that extend just above the substrate surface during suspension feeding (Donovan, 2007). Locals in Malaysia refer to these organisms by a variety of dialect-specific names. In Kuching, they are known as "ambal," in Kuala Selangor as "siput buluh," and in Sabah as "pahatpahat," as documented by Hassan and Laiping (2008).

Figure 2.6: Razor clam shell

Figure 2.6 show the razor clam shell that will be a catalyst product for biodiesel production.

Several substances have been proposed as possible catalysts for biodiesel production. The nature of fundamental sites influences the efficacy of these materials as catalysts. The most researched catalyst is calcium oxide. In addition to its fundamental properties, it has several additional benefits, including its widespread availability, ease of recycling, low cost, and lack of toxicity. However, like many other catalysts, CaO is susceptible to lixiviation, which inevitably results in a decline in performance. In addition, calcium oxide reacts with water and carbon dioxide to form lime and calcium carbonate, which are substantially less active than the oxide itself (Freire et al., 2008).

2.6 Free fatty acid

Triglyceride hydrolysis produces free fatty acids (FFA) in vegetable oils. In consumable oils, their formation predominantly occurs during the oil's production and storage processes, as well as during the processing of the basic materials. Lipid degradation processes are additional sources of FFA. Short chain FFA, for instance, can result from both the secondary oxidation of unsaturated aldehydes and the cleavage of lipid hydroperoxides. The FFA concentration in vegetable oils is determined by a number of factors, including the quality and variety of the source material, the conditions of collection, processing, storage, the age of the oil, and its state of deterioration. Even more FFA is found in waste cooking oils (WCO) due to the hydrolysis and oxidation of triglycerides that occurs during frying as a result of high temperature and air exposure. This increases the FFA content of the oil (Di Pietro et al., 2020).

The waste cooking oil (WCO) is rich in both water (humidity) and free fatty acids (FFA). In the presence of water, triglyceride can be hydrolyzed to form FFA through a hydrolysis reaction. The FFA is a significant disadvantage when using a base catalyzed transesterification process because it reacts with the base catalyst to produce detergent through saponification. These reactions lead to loss of catalyst and ester and increase production processing costs.

Table 2.6: Fatty acid composition in waste cooking oil (Awogbemi et al., 2019)

Property	Fatty acid composition (wt%)
Myristic (C14:0)	0.9
Palmitic (C16:0)	20.4
Palmitoleic (C16:1)	4.6
Stearic (C18:0)	4.8
Oleic (C18:1)	52.9
Linoleic(C18:2)	13.5
Linolenic(C18:3)	0.8
Arachidic (C20:0)	0.12
Eicosenic (C20:1)	0.84
Behenic (C22:0)	0.03
Erucic (C22:1)	0.07
Tetracosanic (C24:0)	0.04
Mean molecular wt (g/mol)	856

Table 2.6: Shows the fatty acid composition in waste cooking oil. All property has the different carbon ratio value. The low fatty acid composition value is 0.03 wt% which is come from behenic (C22:0) and the highest is mean molecular wt (g/mol) that is 856 wt%.

2.7 Methods to produce biodiesel

There are a few different routes that may be used to create biodiesel. There is the traditional approach, the method including microwave irradiation, ultrasonic heating, transesterification.

2.7.1 Microwave Irradiation Method

The selective heating mechanism of microwave irradiation is also well-known. In general, all interactions between materials and microwaves fall into three categories which is absorption, transmission, and reflection. Naturally, in a reaction mixture irradiated with microwaves, the microwaves will be absorbed by polar substances and heat will be produced within them. At the same time, the nonpolar substances in the reaction mixture that do not absorb microwaves are not heated. This selective mode of heating has been utilized and studied by numerous researchers in a variety of disciplines, and it can be categorized into three categories such as solvents, catalysts, and reagents (Nomanbhay & Ong, 2017).

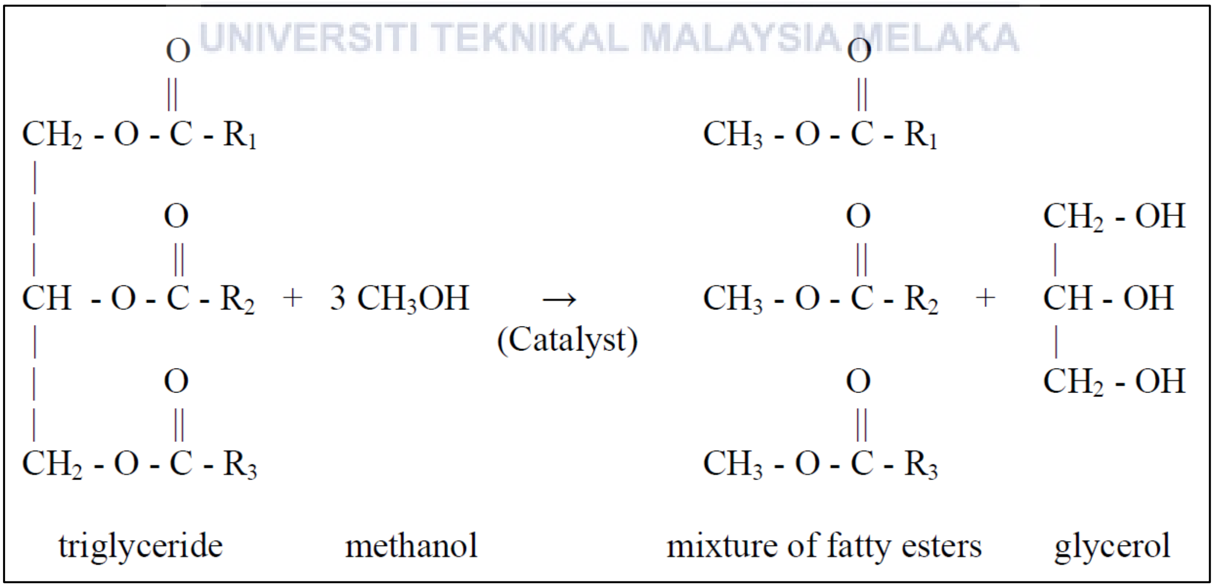
2.7.2 Ultrasonic Heating Method

It can be used directly to mix the immiscible reactants as they are introduced into a reactor with continuous flow. This method is highly effective because the ultrasonic transducer can come into direct contact with the reacting mixture. The desired ultrasonication effects are then transferred directly to the reacting mélange. Additionally, ultrasonic cavitation will result in a localised increase in temperature at the phase boundary, leading to a faster reaction rate. However, it also stresses the ultrasonic system unnecessarily, as elevated temperatures can interfere with its normal operation (Razealy Anuar et al., 2021).

2.7.3 Transesterification process

According to Transesterification is essential to the production of biodiesel, a renewable and sustainable alternative to conventional fossil fuels. The transesterification reaction converts vegetable oils or animal lipids, also known as triglycerides, into fatty acid alkyl esters, which are the primary components of biodiesel such in Figure 2.7. This reaction requires a catalyst, typically sodium or potassium hydroxide, to accelerate the conversion process (Nayab et al., 2022).

Transesterification is the reaction between a lipid or oil and an alcohol that results in the formation of esters and glycerol. Alcohol and triglycerides combine to create glycerol and esters. Typically, a catalyst is used to increase the reaction rate and yield. Transesterification consists of three reversible reactions occurring in succession. First, triglycerides are converted to diglycerides, then diglycerides are converted to monoglycerides, and lastly monoglycerides are converted to glycerol, yielding one ester molecule from each glyceride at each step (Najafpour et al., 2008)



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-R_1 \\ | \\ CH\ -O-\overset{\overset{O}{\|}}{C}-R_2 \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array} + \ 3\,CH_3OH \ \xrightarrow[\text{(Catalyst)}]{} \ \begin{array}{l} CH_3-O-\overset{\overset{O}{\|}}{C}-R_1 \\ \\ CH_3-O-\overset{\overset{O}{\|}}{C}-R_2 \\ \\ CH_3-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array} + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Figure 2.7: Transesterification reaction (Najafpour et al., 2008)

2.8 Variable involved

Biodiesel, a renewable and environmentally friendly alternative to conventional diesel fuel, has received a lot of attention in recent years because of its potential to decrease greenhouse gas emissions and reliance on fossil fuels. Biodiesel is made from a variety of feedstocks, including vegetable oils, animal fats, and even algae. There are various techniques for biodiesel production, which vary in the kind of feedstock utilised, the catalyst used, and the process parameters. Microwave irradiation, ultrasonic heating, and the transesterification process are some typical biodiesel production processes.

2.8.1 Reaction time

Freedman et al. (1986) observed that as the reaction time increases, the conversion of fatty acid esters also increases. Due to the initial mingling and dispersion of alcohol and oil, the reaction is initially sluggish. The reaction then proceeds at a rapid rate. Nonetheless, the maximal ester conversion occurred within 90 minutes. According to Okwundu et al., (2019) report that extending the reaction time does not improve the yield of biodiesel or monoalkyl ester. Moreover, due to the reversible reaction of transesterification, which results in the loss of esters and the formation of detergent, a prolonged reaction time reduces the yield of the final product biodiesel.

2.8.2 Reaction temperature

In addition to reaction temperature, yield of biodiesel is also affected by reaction temperature. Due to the decreased viscosity of lubricants, for instance, a rise in reaction temperature increases the reaction rate and shortens the reaction time. However, Leung and Guo (2006) and Eevera et al. (2009) discovered that an increase in reaction temperature above the optimal level results in a decrease in biodiesel yield because a higher reaction temperature accelerates the saponification of triglycerides.

2.8.3 Catalyst Concentration

Catalyst concentration also influences the formation of biodiesel. Sodium hydroxide (NaOH) and Potassium hydroxide (KOH) are the most typical catalysts for biodiesel production. Freedman et al. (1984) determined that sodium methoxide would be more potent than sodium hydroxide because combining sodium hydroxide with methanol produces a small quantity of water, which inhibits the formation of the final product (Biodiesel) due to the hydrolysis reaction (Guo, 2005). This is one of the reasons why the catalyst is mixed with methanol before being introduced to the oil or fat. In addition, the conversion of triglycerides into biodiesel increases when the concentration of catalyst in oil samples is increased.

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2.9 Biodiesel properties

In the making of biodiesel, oils must conform to ASTM D6751 and EN 14214 standards. Some countries base their biodiesel requirements on US and EU standards. B100 biodiesel is diesel fuel combined with a feedstock that is renewable. Biodiesel is characterized by ASTM D6751 as long-chain fatty acid mono-alkyl esters produced from vegetable oils and animal lipids. Table 2.7 show the European biodiesel standard (EN 14214) while for Table 2.8 show the biodiesel standard ASTM D6751. The major distinction between these two standards is that the European Union requires cold start properties. This EN 14214 standard is only applicable in four-season countries. Due to the lack of four distinct seasons in this country, the ASTM D6751 standard will be used to evaluate the necessary properties, including density, viscosity, flash point, water content, iodine value, and acid value

Table 2.7: European biodiesel standard (EN 14214) (Singh et al., 2019)

Property	**Test method**	**Limits**		**Unit**
		Min	**Max**	
Ester content	EN 14103	96.5	-	% (m/m)
Density at 15°C	EN ISO 3675, EN ISO 12185	860	900	kg/m^3
Viscosity at 40°C	EN ISO 3104, ISO 3105	3.5	5.0	mm^2/s
Flash point	EN ISO 3679	120	-	°C
Carbon residue (in 10% dist. residue)	EN ISO 10370	-	0.30	% (m/m)
Sulfur content	EN ISO 20846, EN ISO 20884	-	10	mg/kg
Cetane number	EN ISO 5165	51	-	-
Sulfated ash	ISO 3987	-	0.02	% (m/m)
Water content	EN ISO 12937	-	500	mg/kg
Total contamination	EN 12662	-	24	mg/kg
Copper strip corrosion (3 hours, 50°C)	EN ISO 2160	-	1	class
Oxidative stability, 110°C	EN 14112	6.0	-	hours
Acid value	EN 14104	-	0.50	mg KOH/g
Iodine value	EN 14111	-	120	g I/100 g
Linolenic acid content	EN 14103	-	12	% (m/m)
Content of FAME with ≥4 double bonds	-	-	1	% (m/m)
Methanol content	EN 14110	-	0.20	% (m/m)
Monoglyceride content	EN 14105	-	0.80	% (m/m)
Diglyceride content	EN 14105	-	0.20	% (m/m)
Triglyceride content	EN 14105	-	0.20	% (m/m)
Free glycerine	EN 14105; EN 14106	-	0.02	% (m/m)
Total glycerine	EN 14105	-	0.25	% (m/m)
Alkali metals (Na + K)	EN 14108; EN 14109	-	5.0	mg/kg
Earth alkali metals (Ca + Mg)	EN 14538	-	5.0	mg/kg
Phosphorus content	EN 14107	-	10.0	mg/kg

Table 2.8: Biodiesel standard ASTM D6751 (United States) (Singh et al., 2019)

Property	**Test**	**Limit**		**Unit**
		Min	**Max**	
Calcium & Magnesium, combined	EN 14538	-	5	ppm (µg/g)
Flash Point (closed cup)	D 93	93	-	°C
Alcohol Control (one to be met): 1.Methanol Content EN 14110 2.Flash Point	EN 14110 D93	- 130	0.2 -	% (m/m) °C
Water & Sediment	D 2709	-	0.05	% (v/v)
Kinematic Viscosity, at 40 °C	D 445	1.9	6.0	mm^2/sec.
Sulfated Ash	D 874	-	0.02	% (m/m)
Sulfur: S 15 Grade S 500 Grade	D 5453 D 5453	- -	0.0015 0.05	% (m/m) %(m/m)
Copper Strip Corrosion	D 130	-	3	No.
Cetane	D 613	47	-	-
Cloud point	D 2500	report	report	°C
Carbon Residue, 100% sample	D 4530	-	0.05	%(m/m)
Acid number	D 664	-	0.05	% (m/m)
Free Glycerin	D 6584	-	0.020	% (m/m)
Total Glycerin	D 6584	-	0.240	% (m/m)
Phosphorus Content	D 4951	-	0.001	% (m/m)
Distillation-Atmospheric equivalent temperature 90% recovery	D 1160	-	360	°C
Sodium/Potassium, combined	EN 14538	-	5	ppm (µg/g)
Oxidation Stability	EN 15751	-	3	hours
Cold Soak Filtration For use in temperatures below -12 °C	D7501 D7501	-	360 200	Seconds second

CHAPTER 3

METHODOLOGY

3.1 Introduction

This project employed razor clam shell (RCS) as a catalyst for the transesterification process of biodiesel. Catalysts played a pivotal role in enhancing the reaction rate between methanol and waste cooking oil during the transesterification process. RCS functioned as a base catalyst due to the presence of calcium oxide (CaO), derived from the decomposition of calcium carbonate ($CaCO_3$) at elevated temperatures ranging from 700 ℃ to 1000 ℃. Specifically, this study focused on temperatures of 800℃, 900℃, and 1000℃ to ascertain which among these produced a higher percentage of CaO.

In the transesterification process, certain parameters such as reaction time and reaction temperature remained constant at 90 minutes and a temperature range of 60℃ to 70℃, respectively. Conversely, variable factors like the methanol-to-oil ratio and catalyst loading were systematically adjusted. The objective was to identify an optimal combination that aligned with specified parameter requirements, including acid value (AV), flashpoint, free fatty acid (FFA), water content, and density. This approach aimed to optimize the biodiesel production process, ensuring adherence to stringent quality standards while focusing on the influence of varying catalyst preparation temperatures on the resulting catalytic activity.

3.2 Preparation of raw materials

The raw material employed was waste cooking oil, recognized as 3rd generation feedstock. The residual cooking oil utilized in this study was sourced from the Department of Dietetics and Serving at Malacca Hospital. The Dietetics and Catering Department bore complete responsibility for delivering food services to patients in the ward, physicians, and qualified paramedics at Melaka Hospital.

3.3 Preparation of catalyst (razor clam shell)

This research utilized a heterogeneous alkaline catalyst as the reaction catalyst. This was attributed to the fact that razor clam shell (RCS), produced calcium oxide, also known as CaO. The transformation of RCS into a catalyst involved several stages or procedures. Among them included the utilization of a wire brush and a knife to clean the outside of the RCS, while a toothbrush was used to clean the inside of the RCS. When the RCS was soaked in water, cleaning work was performed on it so that any dirt or impurities that might have been present on it could be readily removed.

Following that, the RCS was exposed to the sun for several days to eliminate the foul odor produced by the RCS. This was done since the production of biodiesel was negatively impacted whenever the RCS emitted a scent. Afterward, the RCS was baked in an oven at a temperature of one hundred degrees Celsius for twenty-four hours, causing the RCS to become brittle. This made the subsequent procedure, in which the RCS would be crushed into little bits, as well as the subsequent processes of calcination and characterization, run much more smoothly.

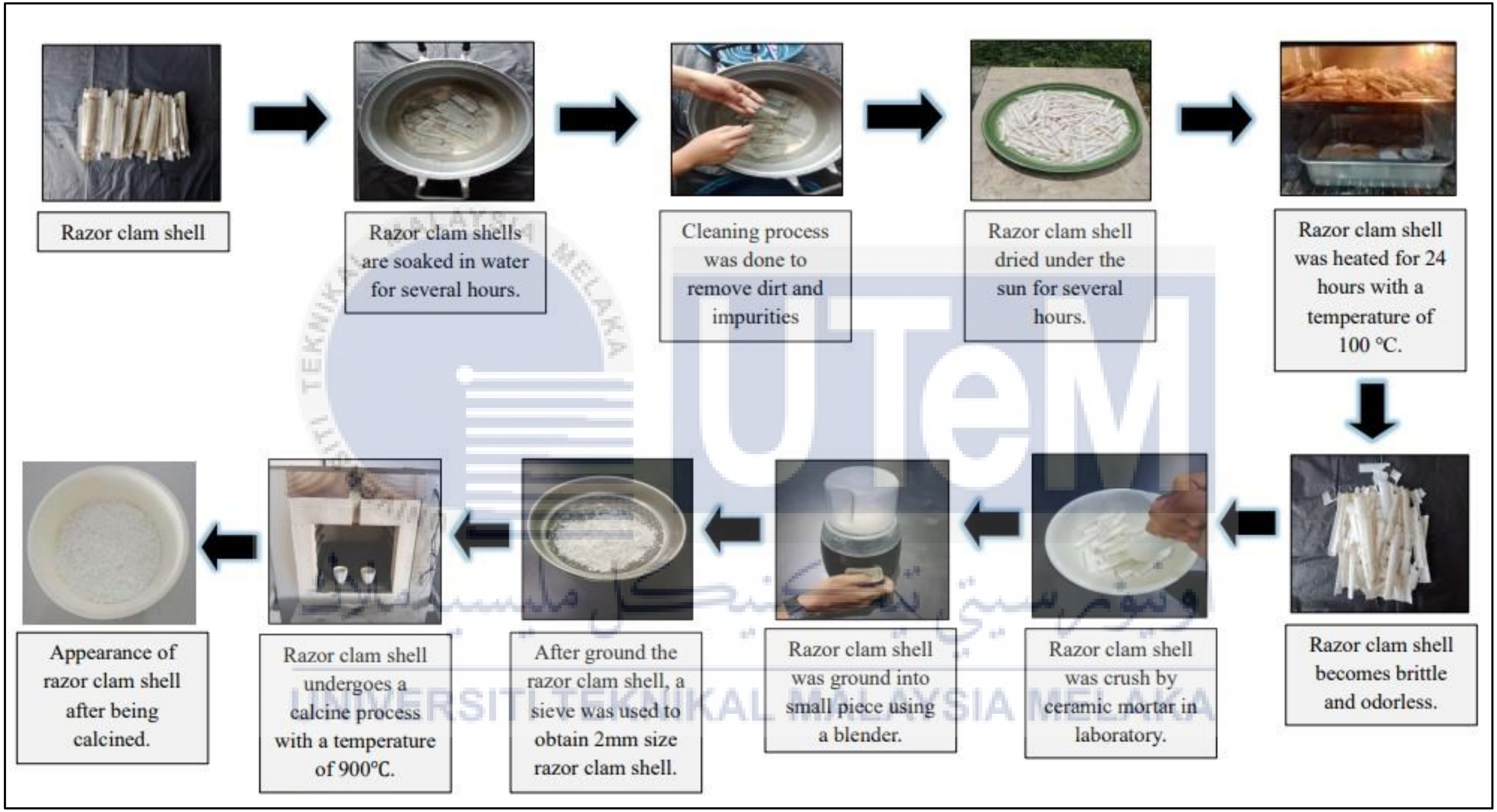

Figure 3.1: Flowchart catalyst preparation process

3.4 Apparatus preparation

To produce biodiesel, it was imperative to have adequate equipment to ensure the successful execution of the experiment. The tools for biodiesel production were available at the Technical University of Malaysia Melaka, Faculty of Mechanical Engineering and Manufacturing Technology. Among the apparatus or instruments necessary for conducting biodiesel production experiments using the transesterification method were a thermometer, a hot plate, a magnetic stirrer, a beaker, a conical flask, a separating funnel, a retort stand, filter paper, and a laboratory or analytical balance.

3.5 Biodiesel production flowchart

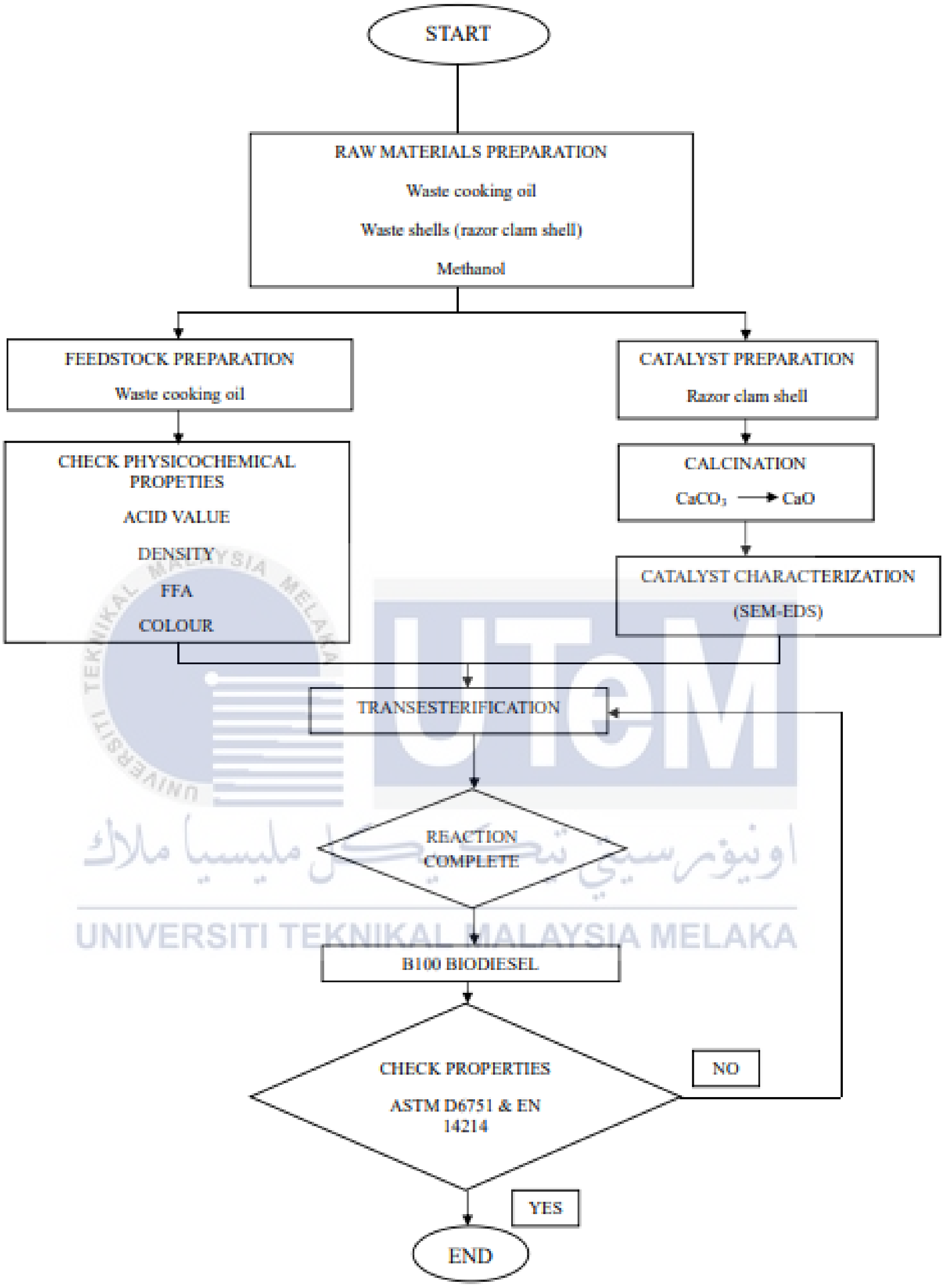

Figure 3.2: Flowchart of biodiesel production

Figure 3.2 shows the process flow for biodiesel production. This process was making the production of biodiesel more efficient. Properties such as density, acid value, free fatty acid value was determined to make sure follow the standard ASTM D6751 and EN 14214.

3.5.1 Biodiesel production process

The process began by preparing all the apparatus and materials, such as waste cooking oil, catalyst, and methanol. The remaining cooking oil was heated on a hot plate using a beaker with a temperature between 100℃ to 120℃ for 1 hour to remove the water content and contaminants. The weight of methanol and razor clam shell needed was determined through calculation. The molar ratio for alcohol: oil was 9:1, and the weight percentage of the catalyst was 9%. The weight of waste cooking oil used was 95.43 g, with the weight for methanol (MeOH) being 33.05 g and for the catalyst being 8.59 g.

After determining the weight of methanol and razor clam shell, these two ingredients were combined with the waste cooking oil. Then, heating was performed for 90 minutes, maintaining the temperature between 60 ℃ to 70 ℃. This was done to prevent the volatilization of methanol into the air, as the boiling point of methanol cannot exceed 70 ℃. Once the mixture was heated, it was transferred to a separation funnel and left for 24 hours. After 24 hours, the mixture had separated into three distinct layers, namely methanol, oil, and fat as shown in Figure 3.3.

The filtration process was carried out to separate oil from methanol and fat. The separated oil mixture was heated at a temperature of 100 ℃ to 120 ℃ for 30 minutes to eliminate the remaining water content and excess methanol that might still be mixed with the oil. After heating, the oil underwent a titration process to determine the value of free fatty acid (FFA) in the oil mixture. The oil mixture was titrated together with Potassium hydroxide (KOH) solution. When the titration was completed, a mild pink solution appeared in the oil mixture. Upon the solution becoming fully pink, the titration was halted. The reading from the pipette was then taken to calculate the acid value.

The KOH value obtained from the titration was 0.433 ml. By applying the formula, the acid value for this experiment was calculated to be 0.486 mg/KOH. Before starting the transesterification, the equipment was arranged as shown in Figure 3.4.

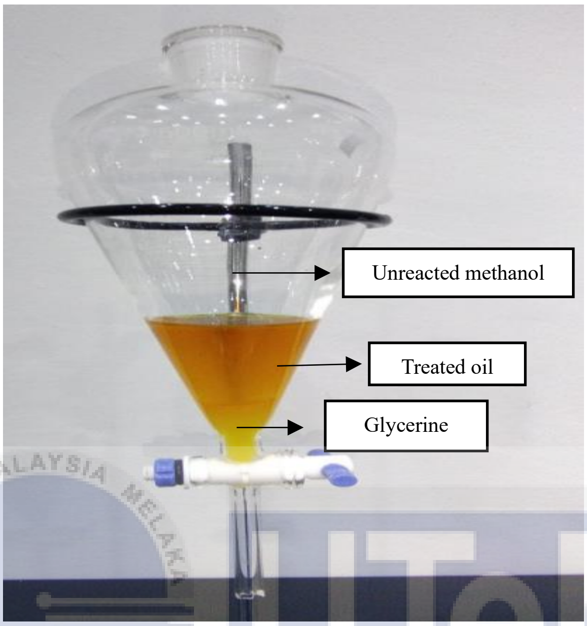

Figure 3.3: The separation of the mixture after 24 hours

Figure 3.4: Arrangement equipment for the transesterification process.

3.6 Waste cooking oil properties testing

The quality testing of waste cooking oil was conducted to ascertain its condition and physicochemical properties. Among the physicochemical parameters examined were the acid value and density. The tools utilized to assess the properties of waste cooking oil are detailed in Table 3.1.

Table 3.1: Waste cooking oil properties testing equipment

NO	Properties	Unit	Standard	Method
1	Acid value	mg KOH/g	ASTM D974	Titration
2	Density	g/cm^3 (15℃)	AOCS Cc 10-95	Pycnometer

3.7 Biodiesel properties testing

Biodiesel produced through the transesterification process was required to adhere to specific physicochemical properties outlined in ASTM D6751, including parameters such as acid value, density, and flashpoint. Consequently, various methods and tools were employed to verify the characteristics of the produced biodiesel oil.

3.7.1 Acid value and free fatty acid

The total acid number test (TAN) was the approach that was used for the purpose of determining the acid value (AV) of waste cooking oil (WCO). The quantity of potassium hydroxide (KOH), measured in milligrams, that must be used to neutralize the amount of free fatty acid (FFA) that is present. To find the percentage of the free fatty acid (FFA), the acid value (AV) must be determined first by using formula. When the AV was determined, the value of AV must be inserted into the formula to find percentage of (FFA). The equation (3.1) is formula to find acid value while for equation (3.2) is formula to determine percentage of free fatty acid.

$$Acid\ Value = \frac{(volume\ of\ KOH\ xNormality\ of\ KOHxEquivalent\ weigh\ of\ KOH\ )}{weight\ of\ oil} = mg/KOH \qquad 3.1$$

$$\text{Percentage of FFA (\%)} = \text{Acid value x 0.503} \qquad 3.2$$

3.7.2 Density

The density of biodiesel was assessed through the application of the AOCS Cc 10c-95 and AOCS Cd 1d-92 methods at the Biodiesel Laboratory of Universiti Teknikal Malaysia Melaka (UTeM) as shown in Figure 3.5. The anticipated outcome was a value below 880 kg/m3. The measurement was conducted utilizing precise tools such as the Bomex Pycnometer with a 50 ml capacity. The formula employed to derive the density value involved deducting the weight of the Bomex Pycnometer with oil from the weight of the Bomex Pycnometer devoid of oil, followed by dividing the result by the volume of the Bomex Pycnometer, which is 50 ml.

Figure 3.5: Bomex Pycnometer

3.7.3 Flash Point

The determination of the flash point, which is the lowest temperature at which the vapors of a substance ignite when exposed to an open flame or another ignition source, plays a pivotal role in evaluating the flammability and fire hazard associated with liquids, including fuels. This flash point analysis is conducted employing the Pensky-Martens Closed Cup test (NORMALAB NPM 131) at the Oil Analysis Laboratory of Universiti Teknikal Malaysia Melaka (UTeM) as shown in Figure 3.6. The protocol involves carefully filling the oil into a designated cup, ensuring it reaches a benchmark line for accurate thermometer insertion. Subsequently, the cup is sealed with a lid equipped with a fan and a hole for thermometer placement. The closed cup is then placed into a heating apparatus, where gas is released through a designated pipe hole. The controlled ignition of this gas, achieved using a lighter, is crucial, and the ensuing flame is modulated by regulating the gas flow within the machine. Simultaneously, the fan on the lid is activated to ensure uniform oil temperature, thus facilitating consistent conditions within the cup.

Throughout the procedure, meticulous control is exercised over variables such as gas flow and fan operation to achieve precision in temperature regulation. The flash point is reached as the vapors from the oil briefly ignite upon exposure to the controlled ignition source. The temperature at which this ignition event occurs is diligently recorded, providing a quantitative measure of the flash point for biodiesel. This methodical process is essential for acquiring accurate data on the ignition characteristics of the substance, aiding in comprehensive safety assessments and facilitating informed decision-making in the handling and utilization of such materials.

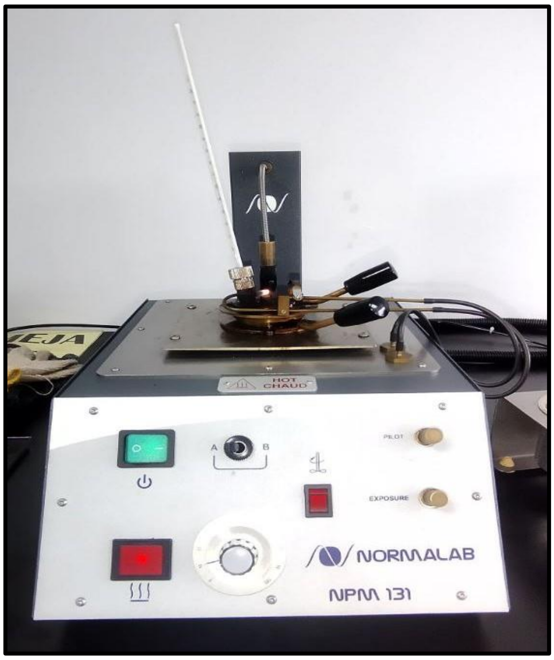

Figure 3.6: Pensky-Martens Closed Cup

3.8 Scanning Electron Microscope

SEM-EDS (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) constituted an advanced analytical method that integrated two pivotal functions. A focused electron beam was directed onto a material in scanning electron microscopy (SEM), yielding signals like secondary electrons and backscattered electrons. These signals were subsequently identified and translated into high-resolution images, providing comprehensive insights into the topography and composition of the sample's surface. The SEM functioned as an imaging tool, delineating the microstructural details of the specimen.

SEM was complemented with energy dispersive X-ray spectroscopy (EDS), facilitating elemental analysis. When an electron beam interacted with a sample, it induced the emission of distinctive X-rays associated with the material's elemental makeup. The EDS system captured and analysed these X-rays, generating a spectrum that depicted the sample's elemental composition. SEM-EDS enabled researchers to attain comprehensive insights into the morphological and elemental characteristics of various materials at the microscale by mapping the spatial distribution of these elements and quantitatively analysing their concentrations.

For the razor clam shell (RCS), being a non-conductive material with limited electron conductivity, it was imperative to address potential issues related to charge accumulation during SEM-EDS analysis. Therefore, prior to conducting the SEM-EDS examination, the RCS specimens were meticulously coated with a layer of carbon. This precautionary step was undertaken to guarantee the production of clear and artifact-free images. The application of carbon coating not only served to dissipate any accumulated charge, ensuring accurate imaging, but also contributed to an enhancement in specimen conductivity. This measure effectively prevented the penetration of the electron beam, thereby averting signal loss and maintaining optimal imaging resolution throughout the analysis. SEM-EDS was carried out at the Materials Science Laboratory at the Faculty of Mechanical Engineering, UTeM. SEM-EDS output was received from a JEOL machine (JSM-6010PLUS/LV) shown in Figure 3.7.

Figure 3.7: SEM-EDS machine (JEOL JSM-6010PLUS/LV) (Material Science laboratory)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In the course of this project, various tests were conducted to attain the targeted outcomes, encompassing catalyst preparation, characterization, and the transesterification process. The results were obtained through a comprehensive examination that included the sedimentation of waste cooking oil (WCO) over an extended duration. As a consequence of this prolonged sedimentation process, the acid value (AV) observed in the oil was relatively high, aligning with the free fatty acid (FFA) value. Unlike employing a two-step transesterification to diminish the FFA value, the chosen methodology involved elevating the efficacy of the catalyst, derived from razor clam shells (RCS), employed in the production of biodiesel.

Following the completion of the transesterification process, a series of tests were conducted to analyze the properties of the fuel, aiming to ascertain its compliance with the parameters outlined in ASTM D6751. The primary focus of scrutiny was directed towards the acid value, with the intention of identifying the biodiesel oil exhibiting the lowest acid value. Subsequently, the selected oil underwent further examination, encompassing tests for density, flashpoint, and Free Fatty Acids (FFA). This systematic approach was employed to ensure a meticulous evaluation of the biodiesel oil's quality and conformity to the prescribed standards.

In the biodiesel production conducted, various factors influencing the produced oil were examined. The set parameters encompassed the reaction temperature and time, while the manipulated variables included the methanol-to-oil molar ratio and the concentration of the catalyst. The objective of the project was to attain oil that adheres to the ASTM D6751 standard, thereby necessitating a comprehensive investigation into the impact of the methanol-to-oil molar ratio and catalyst concentration on the overall success of the biodiesel production process. The study was designed to provide insights into the efficacy of these specific variables in achieving the desired biodiesel quality, aligning with the ASTM D6751 standard.

4.2 Catalyst characterization of razor clam shell

In the pursuit of comprehending the characterization of the razor clam shell, a multitude of analytical methods were undertaken. Specifically, Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS). The comprehensive understanding garnered from these characterization methods played a crucial role in the selection of a suitable catalyst for the transesterification process.

4.2.1 Scanning electron microscopy (SEM)

In this study, Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) was employed to characterize the catalyst derived from razor clam shell. The catalyst, measuring 2 mm in size, underwent calcination at three distinct temperatures, 800℃, 900℃, and 1000℃, with the aim of assessing its performance in a given reaction. The investigation focused on determining the optimal temperature, at which the catalyst exhibited the highest calcium (Ca) content.

During the calcination process, the 2 mm shell, originating from razor clam shells, was subjected to high temperatures, leading to the decomposition of calcium carbonate ($CaCO_3$) into calcium oxide (CaO). The SEM-EDS results revealed that after being heated at 800℃, 900℃, and 1000℃, the catalyst contained calcium oxide, indicating the successful decomposition of calcium carbonate throughout the calcination process.

The SEM-EDS analysis further indicated that the temperature of 900°C yielded the highest elemental content of calcium as shown in Figure 4.1. Consequently, it can be concluded that 900°C is the optimal temperature for the calcination of razor clam shell, based on the highest calcium content observed in the SEM-EDS results.

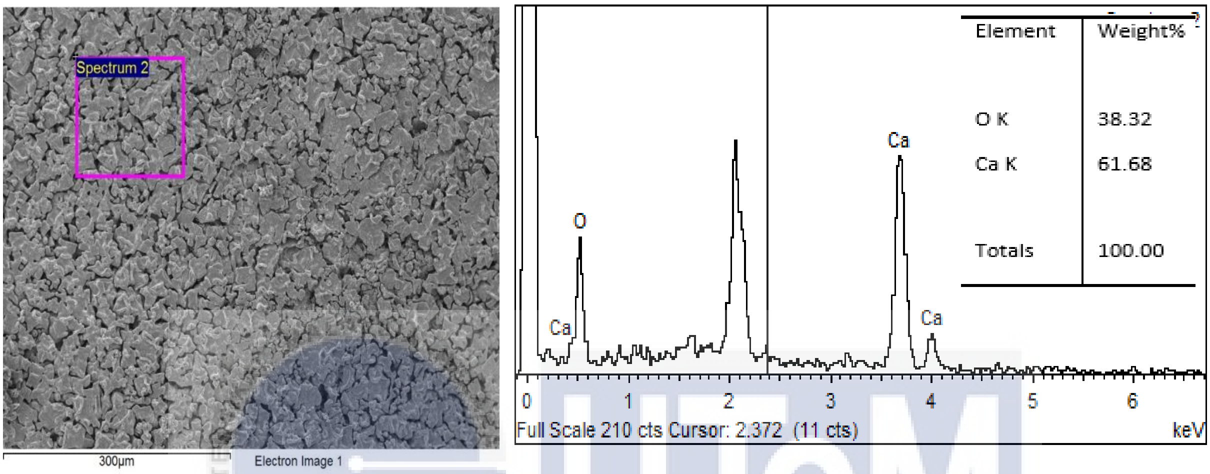

Figure 4.1: SEM-EDS of calcined razor clam shell at 900°C

4.3 Properties of raw waste cooking oil

Several properties of cooking oil needed to be identified, with a particular focus on an acid value below 0.5 mg KOH/g for optimal use, as the resulting biodiesel oil was required to maintain an acid value below 0.5 mg KOH/g as well. However, the acid value obtained from this specific cooking oil was 9.76 mg KOH/g. Table 4.1, shows the properties of the waste cooking oil that will be used in this research.

Table 4.1: Properties of raw cooking oil

Properties	Unit	Standard measure	Result
Acid Value	mgKOH/g	ASTM D644	9.76
FFA	%	-	4.91
Density	Kg/m^3	ASTM D6751	894
Colour	-	-	Dark brownish

4.4 Conventional transesterification method

The transesterification process involved several key variables, including the methanol-to-oil molar ratio, catalyst concentration, reaction time, and temperature. The parameters for reaction time and temperature were predetermined, set at 90 minutes and within the range of 60℃ to 70℃ respectively. As for the methanol-to-oil ratio, four distinct ratios 9:1, 15:1, 18:1, and 24:1 were examined. Simultaneously, the catalyst concentration was varied across five levels 3%, 5%, 7%, 9%, and 12%.

The primary objective throughout the transesterification process was to achieve a biodiesel acid value (AV) below 0.5 mg KOH/g. At a methanol-to-oil molar ratio of 9:1, coupled with a catalyst concentration of 9%, and utilizing a reaction time of 90 minutes at a temperature range of 60℃ to 70℃, the lowest achieved acid value (AV) was 0.486 mgKOH/g. Table 4.2 presents the data utilized and obtained from the standard transesterification procedure that contain catalyst concentrations (wt%), reaction time (min), reaction temperature (℃), methanol to oil molar ratio and acid value (AV) of biodiesel.

Table 4.2: Data transesterification process

Catalyst (wt%)	Reaction time (min)	Reaction temperature (℃)	Methanol to Oil Molar Ratio	Acid Value (mgKOH/g)
3	90	65	9:1	1.047
			15:1	1.685
			18:1	5.648
			24:1	6.582
5	90	65	9:1	0.598
			15:1	6.208
			18:1	5.386
			24:1	5.236
7	90	65	9:1	0.523
			15:1	1.871
			18:1	1.609
			24:1	1.945
9	90	65	9:1	0.486
			15:1	1.683
			18:1	2.020
			24:1	3.516
12	90	65	9:1	0.487
			15:1	1.945
			18:1	1.758
			24:1	2.469

4.5 Effect of variables on biodiesel production

Several variables influence the outcomes of transesterification products. Four categories of variables played a crucial role in ensuring that the produced oil adhered to the ASTM D6751 standard. The catalyst derived from this project, specifically razor clam shell (RCS), facilitated the determination of variable values through SEM-EDS results. This is significant, as the catalyst exerts a substantial impact on the successful attainment of biodiesel oil that complies with the ASTM D6751 standard.

4.5.1 Effect of methanol to oil molar ratio

The methanol-to-oil molar ratio constitutes a pivotal parameter in the biodiesel production process, specifically within the transesterification procedure. This ratio assumes significance in ameliorating the free fatty acid (FFA) value and augmenting the overall yield percentage. In order to address these critical parameters effectively, a heightened methanol-to-oil ratio is often employed, such as 9:1, 15:1, 18:1, and 24:1 with catalyst concentration 3%, 5%, 7%, 9% and 12%. Based on the study done by Aitlaalim et al., (2020), the parameters used are 6:1, 9:1, 12:1, 15:1, and 18:1 with a catalyst of 1.5%, 2.5%, 3.5%, and 5.0% as which is shown in graph Figure 4.2 which is the graph of biodiesel yield versus methanol to oil molar ratio. The ratio used is considered high for the specific type of catalyst shear under investigation.

The evaluation of the effect of methanol to oil molar ratio on the transesterification process was conducted without considering biodiesel yield (%) due to the absence of corresponding yield calculations. Instead, the impact of methanol to oil molar ratio was assessed through acid value measurements (mgKOH/g). A fixed catalyst concentration of 9% was employed for simplicity.

Figure 4.2 illustrates the molar ratios examined, namely 9:1, 15:1, 18:1, and 24:1, in conjunction with a 9% catalyst, plotted against acid value (mgKOH/g). Contrary to expectations, the graph indicates a noteworthy increase in acid value as the methanol to oil molar ratio rises. The conventional understanding suggests that higher methanol amounts should lead to decreased acid values by facilitating the transesterification reaction, thus reducing free fatty acid (FFA) content in the oil (Rabie et al., 2019).

Observations, however, reveal that the 9:1 ratio stands out as the optimal methanol value for the 9% catalyst. Excessive methanol quantities result in diminished reaction performance. The molar ratios of 15:1, 18:1, and 24:1 show this behaviour, where an abundance of methanol leads to the formation of undesired by-products, including soap, monoacylglycerol, and diacylglycerol. These by-products interfere with the transesterification process by affecting catalyst performance, ultimately impeding the complete conversion of triglycerides into biodiesel. Consequently, the expected decrease in free fatty acid content and acid value does not occur (Ismail et al., 2017).

It is noteworthy that the observed trend is not consistent across all catalyst concentrations, as tabulation by Table 4.2. For instance, the 7% catalyst exhibits a low acid value at molar ratios of 9:1 and 18:1 but registers a high acid value at ratios of 15:1 and 24:1. While the acid value is anticipated to continue increasing after the 15:1 ratio, an unexpected decrease and subsequent increase occur. This underscores the intricate interplay of factors in achieving an acid value below 0.5 mgKOH/g. Catalyst concentration, reaction time, and temperature are identified as critical factors influencing the transesterification reaction optimally.

In the context of this study, a molar ratio of 9:1 with a 9% catalyst concentration and 12% catalyst concentration yielded oil with acid values of 0.486 mgKOH/g and 0.487

mgKOH/g, respectively. Furthermore, the study's observations revealed that the augmentation in methanol resulted in an excess production of glycerol, as depicted in Figure 4.3. The surplus glycerol posed challenges during the separation process with oil

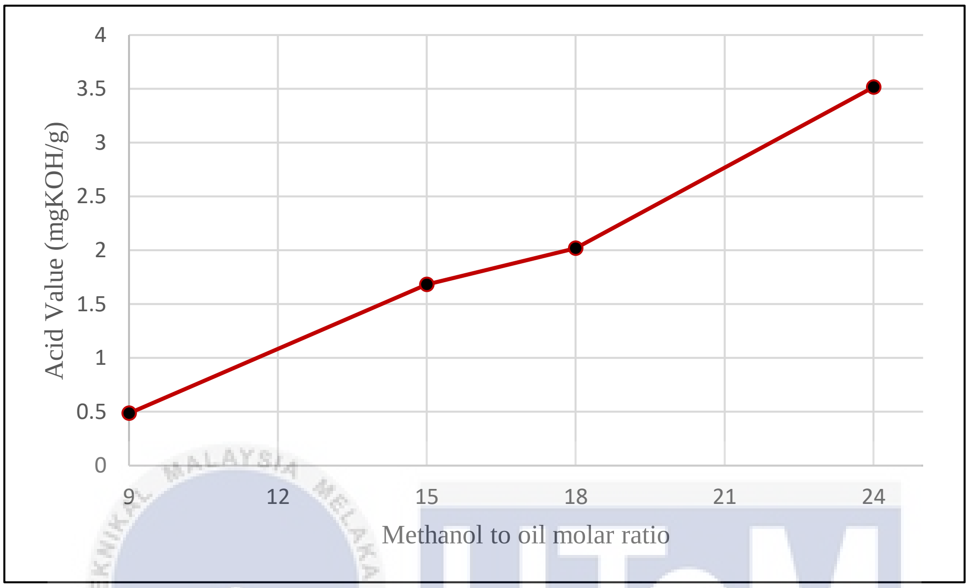

Figure 4.2: Graph for different methanol to oil molar ratio (9:1, 15:1, 18:1 and 24:1) with catalyst 9% versus acid value mgKOH/g

Figure 4.3: Glycerol produced from methanol to oil molar ratio 24:1 with 9% catalyst.

4.5.2 Effect of amount catalyst

In this study, catalyst concentrations of 3%, 5%, 7%, 9%, and 12% were employed. The selection of higher percentage values was undertaken to ensure the adequacy and completeness of the transesterification process for the given ratio. This decision was informed by the observation, as revealed by Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) results, that the calcium (Ca) percentage in the razor clam shell (RCS) did not exceed 70%. When electrons were targeted at an area on the catalyst, the catalyst value was 61.8%.

Moreover, the determination of the catalyst amount (wt%) was grounded in the efficacy of prior investigations utilizing a 2mm catalyst size. According to Soria-Figueroa et al. (2020), for a catalyst size of 2mm, a total concentration of 6wt% was employed for a ratio of 6:1, and 9wt% for a ratio of 15:1, yielding corresponding high percentages of 95.21% and 94.40%, respectively. However, biodiesel yield (%) data was not provided, precluding a direct comparison with previous studies.

Nonetheless, the data acquired in this study suggests that a high biodiesel yield indicates successful conversion of oil into biodiesel. This success is closely tied to the free fatty acid (FFA) value, which diminishes when the transesterification reaction is thorough, converting all triglycerides into fatty alkyl methyl ester (FAME). This implies that a higher catalyst quantity contributes to a reduced acid value due to enhanced reaction efficiency. Consequently, the catalyst concentrations employed in this study were comparatively high at 3%, 5%, 7%, 9%, and 12%. Figure 4.4 presents the acid value results obtained from this study.

Due to the relatively low calcium value, it was imperative to employ a higher catalyst concentration to achieve an oil product with an acid value of less than 0.5 mgKOH/g. The rationale behind this approach lies in the fact that a higher catalyst concentration is necessary to compensate for the low calcium content, which, in turn, affects the reaction rate. It is anticipated that a longer reaction time would be required if a lower percentage of catalyst concentration were employed. The efficiency of the reaction is intricately linked to the catalyst amount insufficient catalyst for the specified ratio may result in an incomplete reaction between waste cooking oil and methanol (Sahar et al., 2018).

Based on the results obtained in this study, a consistent methanol to oil molar ratio of 9:1 was employed across various catalyst concentrations, namely 3%, 5%, 7%, 9%, and 12% as shown in Figure 4.5. Consequently, the trend graph illustrates a declining gradient in the acid value. At a catalyst concentration of 3%, the acid value measured 1.047 mgKOH/g, which subsequently decreased to 0.598, 0.523, 0.486, and 0.487 mgKOH/g for catalyst concentrations of 5%, 7%, 9%, and 12%, respectively. The successful achievement of an acid value of 0.5 mgKOH/g for the oil was observed at catalyst concentrations of 9% and 12%. Thus, this study effectively demonstrated that higher catalyst concentrations contribute to a reduction in the acid value of the oil.

Nevertheless, elevating the catalyst concentration for alternative molar ratios did not yield analogous data to that of the 9:1 ratio for the acid value. This discrepancy may be attributed to several factors, and it suggests that an excess concentration of catalyst (wt%) can also disrupt the transesterification process. Based on Hsiao et al., (2021), an excess of catalyst can result in the production of undesired by-products and the breakdown of biodiesel, leading to a reduction in biodiesel yield. Furthermore, an excessive amount of catalyst can induce the reverse reaction, converting biodiesel back into triglycerides. Because of that, it is possible that the FFA value in the oil does not decrease due to less biodiesel production.

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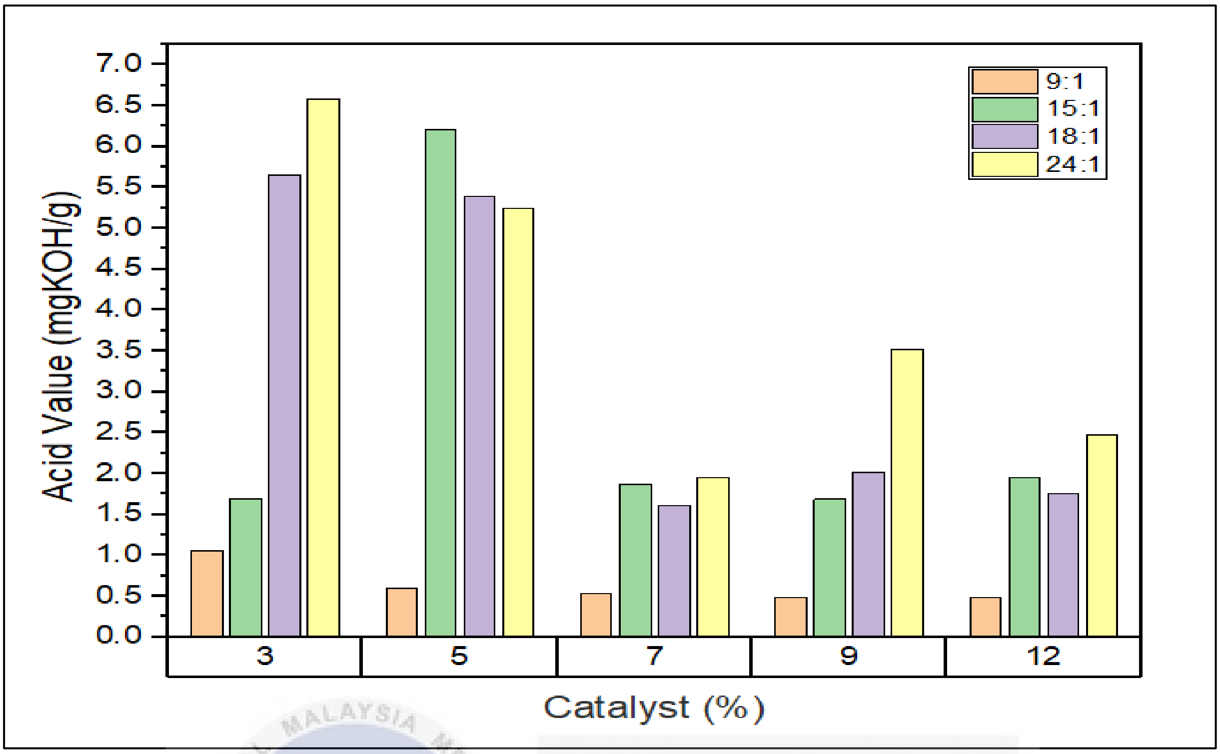

Figure 4.4: Acid value from process transesterification for molar ratio 9:1, 15:1, 18:1 and 24:1 with catalyst 3%, 5%, 7%, 9% and 12%

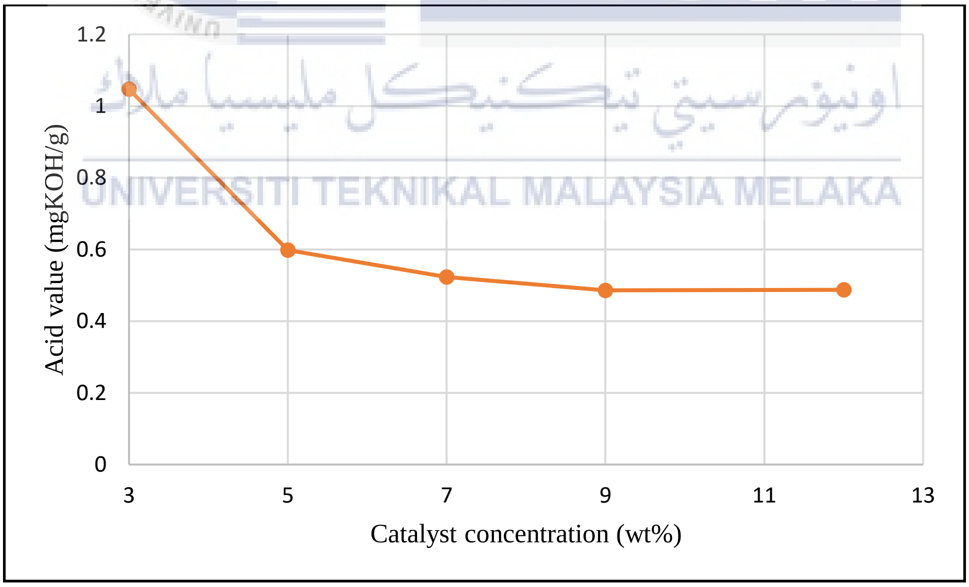

Figure 4.5: Graph for different catalyst concentration (3wt%, 5wt%, 7wt%, 9wt% and 12wt%) for 9:1 molar ratio versus acid value

4.5.3 Effect of reaction time

The time duration selected for the transesterification process was 1 hour and 30 minutes, equivalent to 90 minutes. This specific time interval was chosen with the intention of facilitating the comprehensive completion of the transesterification reaction. The rationale behind this decision was grounded in the recognition that an extended reaction time is essential for achieving thorough conversion of triglycerides in the oil feedstock into fatty alkyl methyl ester (FAME), which constitutes biodiesel. In the absence of a catalyst, the reaction time could potentially extend up to 3 or 4 hours (Yeom & Go, 2018). Even when utilizing a catalyst that may not be well-characterized, the reaction time remained elevated, albeit below the duration required in the absence of a catalyst. The overarching objective was to ensure a reaction time sufficient to guarantee the successful transformation of triglycerides into biodiesel, emphasizing the critical role of catalysts in expediting the transesterification process.

4.5.4 Effect of reaction temperature

In the conducted research, the transesterification process was carried out at temperatures ranging from 60℃ to 70℃. This variation in temperature indicates an inherent instability in the applied values during the transesterification process. The elevation of the reaction temperature was observed to have a direct impact on the transesterification reaction, influencing the conversion of oil into biodiesel, as elucidated by (Negm et al., 2018).

According to (Negm et al., 2017), an escalation in temperature resulted in an increased reaction rate, fostering more collisions between the utilized methanol and triglyceride molecules. This, in turn, facilitated a faster conversion reaction at higher temperatures, aligning with the findings of. However, caution was exercised not to exceed a temperature of 70°C. This precautionary measure was attributed to the potential evaporation of methanol at elevated temperatures, leading to a reduction in the methanol-to-oil molar ratio during the conversion reaction. Additionally, concerns were raised regarding the reverse behaviour of the transesterification reaction at temperatures exceeding 70℃ (Negm et al., 2018).

It is noteworthy that the inability to maintain a fixed temperature for this study was attributed to the use of a conventional, non-digital heating plate. The manual control of the hot plate introduced challenges in temperature regulation. The implementation of a digital hot plate would have ensured a more consistent and optimal temperature, such as the temperature of 65℃, which could have been precisely maintained across experiments.

4.6 Biodiesel Properties

In this biodiesel analysis, two distinct sets of standard specifications, namely ASTM D6571 and EN 14212, were considered. The physicochemical properties outlined in these two standards exhibited variations. In the scope of this study, ASTM D6751 served as the benchmark for assessing the efficacy of the oil. In this study, four parameters were initially designated for testing, encompassing acid value, flash point, density, and water content. However, only three parameters were tested such as acid value, flash point, and density were ultimately assessed due to the unavailability of materials and tools required for the water content test

4.6.1 Acid Value

The acid value (AV) stands out as the pivotal parameter in determining the successful conversion of oil into biodiesel. According to ASTM D 6751 specifications, the AV value should not have surpassed 0.5 mgKOH/g. The pivotal criterion for considering the oil as successfully transformed into biodiesel is that the acid value of the produced oil must not exceed 0.5 mgKOH/g. This stringent requirement is stipulated due to the potential implications associated with elevated acid values, which may signify an excess of free fatty acids capable of detrimentally affecting the stability and combustion characteristics of the biodiesel product, as articulated by (Zhang et al., 2018).

Throughout the transesterification process, a significant reduction in acid value was achieved, decreasing from an initial 9.761 mgKOH/g to a final value of 0.486 mgKOH/g. This successful reduction in acid value prompted the continuation of testing for other parameters, including density and flash point.

4.6.2 Density

In the ASTM D6751 table utilized in this study, no predetermined range or limit for biodiesel density parameters was specified. In contrast, EN 14214 establishes a standard range for biodiesel density. This differentiation arises from the recognized association between density and cold start performance. Density significantly influences the flow characteristics of biodiesel at lower temperatures, contributing to easier engine starting in cold conditions (Zare et al., 2021). The biodiesel oil produced in the conducted study exhibited a density of 881 kg/m³. Notably, this density falls within the defined range stipulated by EN 14214, which spans from 860 to 900 kg/m^3.

According to Zare et al., (2018) Biodiesel characterized by an elevated density is inclined to exhibit a correspondingly higher cloud point, delineating the temperature at which visible crystals commence formation within the fuel. In chilly climates, these crystals possess the capacity to precipitate filter plugging, obstructing the unimpeded fuel flow through the engine system. Such hindrance holds the potential to pose challenges during engine initiation or compromise the overall performance of the engine, particularly in the context of cold starts.

Consequently, the produced oil is deemed satisfactory owing to its high density, approaching nearly 900 kg/m³.

4.6.3 Flashpoint

Flash point parameters, adherence to ASTM D6751 standards necessitated a flash point temperature above 93℃, and the obtained biodiesel oil surpassed this requirement with a flash point temperature of 222℃. According to Álvarez et al., (2019), The criticality of flash point lies in its representation of the temperature at which biodiesel vapor can ignite when exposed to an open flame or spark. A higher flashpoint is considered desirable to mitigate the risk of accidental ignition during the various stages of handling, transportation, and storage, as emphasized by (Liu & Liu, 2010). Table 4.3 shows the result from the test for biodiesel properties.

Table 4.3: Biodiesel properties result

Property	**Unit**	**Prepared biodiesel**	**ASTM D6751**	**EN 14214**
Acid value	mgKOH/g	0.486	<0.5	0.5max
Flashpoint	℃	222	>93	>120
Density	kg/m^3	881	NA	860-900

CHAPTER 5

CONCLUSION AND RECCOMMENDATIONS

5.1 Conclusion

Biodiesel production is a meticulously evaluated process, wherein each parameter, including catalyst concentration, methanol-to-oil molar ratio, reaction temperature, and reaction time, significantly influences the success of oil production. In this transesterification process, a heterogeneous base catalyst, namely calcium oxide (CaO), derived from razor clam shells, was employed to expedite the reaction. It is well-established that various types of shells can be utilized for catalyst production, as they typically contain calcium carbonate ($CaCO_3$), which undergoes decomposition during the calcination process, yielding CaO.

Diverse shells possess varying concentrations of calcium (Ca) and oxygen (O) elements. Therefore, for the purposes of this study, razor clam shells were selected to investigate the catalyst's performance. Surface morphology and elemental composition data were acquired through Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) tests. Distinct data values were obtained from the calcination process conducted at temperatures of 800℃, 900℃, and 1000℃. Optimal data values were observed at a temperature of 900 ℃, leading to the selection of razor clam shells calcined at this temperature as the catalyst for the subsequent transesterification process.

The properties of the waste cooking oil (WCO) obtained were determined based on acid value and density. The acid value of WCO was found to be 9.761 mgKOH/g, while the density measured at 894 kg/m3. The elevated acid value was attributed to prolonged storage in a bottle, leading to sedimentation processes. Consequently, the sedimentation process resulted in an increase in Free Fatty Acid (FFA) values, concurrently elevating the acid content in the oil.

Before undertaking the transesterification process, oil with a high acid value needed to undergo treatment through the acid esterification method. However, in cases where the pre-treatment method was omitted, the risk was managed by elevating the catalyst amount to a significant level, thereby enhancing the reaction process. With the intensification of the reaction, the resultant oil exhibited reduced fat content, subsequently diminishing the Free Fatty Acid (FFA) levels. Key variables such as methanol-to-oil molar ratio, catalyst concentration, reaction time, and temperature were considered in this analysis. Methanol-to-oil molar ratio and catalyst concentration were particularly emphasized to determine the optimal combination conducive to the production of high-quality and effective biodiesel.

Out of the twenty oil production runs conducted, only two successfully met the primary parameter, which is the acid value. Both oils shared the same methanol-to-oil ratio of 9:1, with catalyst concentrations set at 9% and 12% which is 0.486 mgKOH/g and 0.487 mgKOH/g. Other parameters which are density and also flashpoint managed to pass the set standards which are 881kg/m3 and 222°C. The conclusive findings of this study established that Waste Cooking Oil (WCO) as the feedstock and razor clam shell as the catalyst type achieved successful compliance with the requisite biodiesel properties.

5.2 Recommendations

Several recommendations were made to enhance the quality of biodiesel production, with particular attention to the environment where the transesterification process takes place. Considerations were given to factors such as humidity and temperature in the working space. Biodiesel is known to be susceptible to water, and elevated humidity within the room was observed to result in increased moisture absorption, consequently raising the acid value during the separation process.

This research was conducted in a room exposed to varying temperature conditions, leading to constant fluctuations in humidity levels. Furthermore, the influence of wind on the transesterification process was acknowledged. The wind was identified as a factor causing the volatilization of methanol mixed with oil. Ensuring precise control was crucial to maintaining the calculated amount of methanol reacting with the oil.

Additionally, temperature effects was found to introduce particles from the surrounding environment, potentially compromising the cleanliness of the produced biodiesel. Contamination, especially in small-scale biodiesel production, emerged as a significant concern. As a preventive measure, it was determined that the biodiesel production process should be conducted in an enclosed space with a controlled room temperature ranging from 24℃ to 29℃.

The second recommendation involved employing methods, including diatomite utilization, deposition-precipitation, and impregnation, to enhance the performance of the catalyst. These methods were implemented to impart favourable characteristics to the catalyst, aiming to augment the efficiency of the transesterification process.

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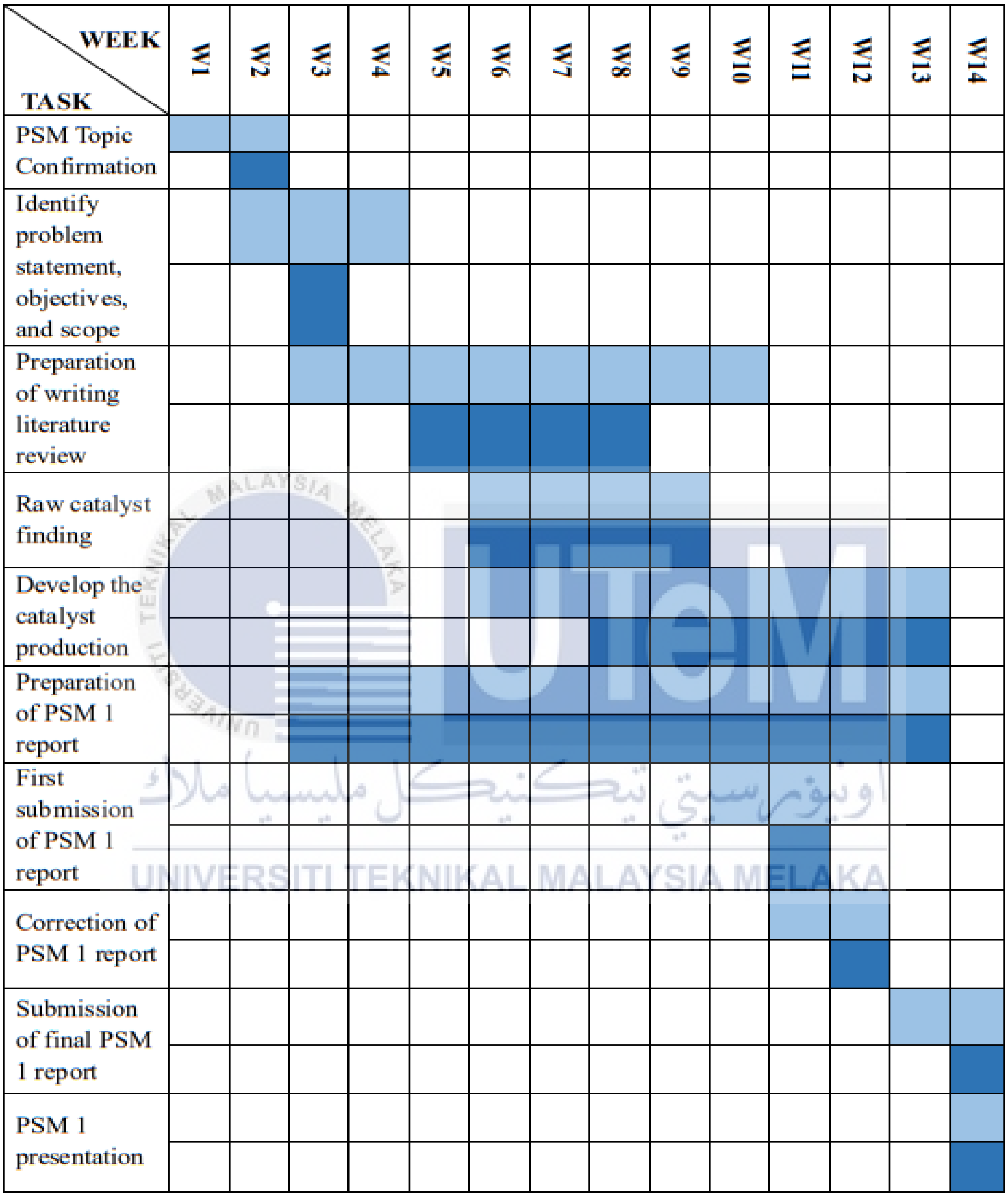
APPENDIX

Appendix A: Gantt Chart PSM 1



WEEK / TASK	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14
PSM Topic Confirmation	▒	▒												
		█												
Identify problem statement, objectives, and scope		▒	▒	▒										
			█											
Preparation of writing literature review			▒	▒	▒	▒	▒	▒	▒	▒				
					█	█	█	█						
Raw catalyst finding						▒	▒	▒	▒					
						█	█	█	█					
Develop the catalyst production						▒	▒	▒	▒	▒	▒	▒	▒	
								█	█	█	█	█	█	
Preparation of PSM 1 report			▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
			█	█	█	█	█	█	█	█	█	█	█	
First submission of PSM 1 report										▒	▒			
											█			
Correction of PSM 1 report											▒	▒		
												█		
Submission of final PSM 1 report													▒	▒
														█
PSM 1 presentation														▒
														█

NOTE:

▒ Plan

█ Actual

Appendix B: Gantt Chart PSM 2

WEEK TASK	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15
Raw Material preparation	▨	▨	▨	▨											
	■	■	■	■	■										
Catalyst preparation				▨	▨	▨	▨	▨							
				■	■	■									
Biodiesel production						▨	▨	▨	▨	▨					
							■	■	■	■					
Biodiesel properties testing						▨	▨	▨	▨	▨	▨	▨			
							■	■	■	■	■	■			
Preparation of PSM 2 report		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		
		■	■	■	■	■	■	■	■	■	■	■	■		
First submission of PSM 2 report												▨			
												■			
Correction of PSM 2 report													▨	▨	▨
													■		
Submission of final PSM 2 report														▨	▨
														■	■
PSM 2 presentation															▨
															■

NOTE:

▨ Plan

■ Actual