A Review on Sustainable Approach for Production of Biodiesel from Waste Cooking Oil: A Case Study of Brunei Darussalam

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Received: April 2022; Revised: June 2023; Published: July 2023

Abstract

Biofuels like biodiesel and bioethanol are the latest technologies to meet the rising energy demand and to replace depleting petroleum supplies. Biodiesel, which is made from vegetable oils, can be used to replace diesel fuel. Vegetable oils are a sustainable energy resource with a similar energy content to diesel fuel. In the proposed process, the main product from the reaction is biodiesel, whereas the by-products consist of glycerol and fertilizer. Biodiesel is mainly used in automotive diesel engines for various reasons, such as having a greater oxygen content, a higher cetane number, a higher viscosity, a lower aromatic content, and very little sulfur. These properties are essential in engine performance, combustion, and emissions. This review provides a comprehensive analysis of recent literature on biodiesel production methods from waste cooking oil, where the methods are grouped systematically and assessed. A decision table on process selection is provided to screen the most suitable technology for biodiesel production from waste cooking oil. The properties and application of potential products and by-products are also discussed. Finally, the case study of supplying biodiesel for B5 fuel in Brunei Darussalam is also provided.

Keywords: Biodiesel; Waste cooking oil; Sustainable engineering; Circular economy; Resource recovery; Sustainable Development Goals


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INTRODUCTION

Due to the shortage of traditional fossil fuels, rising emissions of combustion-generated pollutants, and rising prices, biomass sources will become increasingly appealing (Şensöz et al., 2000). On the other hand, biomass usage has the features of being interesting as both biomass and carbon-neutral source (Dowaki et al., 2007). Biofuels such as biodiesel and bioethanol are at the forefront of alternative technologies to fulfill growing energy demand and replace dwindling petroleum sources.

Biodiesel, derived from vegetable oils, can be used to substitute diesel fuel. Biodiesel comprises methyl esters of long-chain fatty acids such as lauric, palmitic, stearic, and oleic acids, among others. The most common biodiesel sources are soybean, rapeseed, and palm oils. Other biodiesel sources include almond, barley,
camelina (*Camelina sativa*), coconut, copra, cumaru (*Dipteryx odorata*), *Cynara cardunculus*, fish oil, groundnut, *Jatropha curcas*, karanja (*Pongamia glabra*), laurel, *Lesquerella fendler* (Pinto et al., 2005), and wheat. B100, or "neat" fuel, is called when the biodiesel is 100 percent pure. A biodiesel blend is a mixture of pure biodiesel and petrodiesel. BXX is the abbreviation for biodiesel blends. The XX represents the percentage of biodiesel in the mix (i.e., a B80 blend is 80 percent biodiesel and 20 percent petrodiesel).

Biodiesel is the best candidate fuel for diesel engines. Furthermore, biodiesel has a lot of potential for compression-ignition engines. Biodiesel may be characterized as a domestic, sustainable diesel engine fuel that meets ASTM D 6751 criteria. Biodiesel offers some possible benefits when used as an extender for combustion in the engine, including lowered exhaust emissions (Dunn, 2001).

Vegetable oils are a sustainable energy resource. They have lately gained popularity due to their environmental benefits and because they are created from renewable resources with a similar energy content to diesel fuel. Since the commencement of diesel engines, the idea of utilizing vegetable oils as a fuel has been recognized. However, the viscosity of vegetable oil is too high to be used as a direct replacement fuel oil in most current diesel engines. Vegetable oils can be made more viscous in a variety of methods. The four procedures used to tackle difficulties with high fuel viscosity are dilution, micro emulsification, pyrolysis, and transesterification, all will be discussed in this paper. Transesterification is one of the most frequent processes used in biodiesel to lower oil viscosity.

Transesterification is the chemical process of converting oil into its equivalent fatty ester (Bala, 2005). The interaction of a fat or oil triglyceride with alcohol to create esters and glycerol is known as transesterification (alcoholysis). The transesterification of triglycerides is shown in Figure 1. To boost the reaction rate and yield, a catalyst is frequently used. Since the reaction is reversible, excess alcohol shifts the equilibrium to the product side.

\[
\begin{align*}
\text{Triglyceride} & \quad \text{Alcohol} & \quad \text{Esters} & \quad \text{Glycerol} \\
\text{CH}_3\text{OOC-R}_1 & + 3\text{ROH} & \xrightarrow{\text{Catalyst}} & \text{R}_2\text{COO-R} & + \text{CH}_2\text{OH} \\
\text{CH}_3\text{OOC-R}_2 & + 3\text{ROH} & \xrightarrow{\text{Catalyst}} & \text{R}_3\text{COO-R} & + \text{CH}_2\text{OH} \\
\text{CH}_3\text{OOC-R}_3 & + 3\text{ROH} & \xrightarrow{\text{Catalyst}} & \text{R}_4\text{COO-R} & + \text{CH}_2\text{OH}
\end{align*}
\]

*Figure 1. Transesterification of triglycerides.*

Although, the production of biodiesel from renewable resources is vastly growing. However, there are some challenges faced during the manufacturing of biodiesel. The profitability of biodiesel production is questionable in terms of its high cost of raw materials, inadequate supply of feedstocks, environmental impacts, the product’s viscosity, and high emission of nitrogen oxides. As an example of the raw materials, oil palm is extensively used to produce biodiesel in certain countries across Asia, such as Malaysia and Indonesia. The profitability of the produced biodiesel is caused by the high cost of the feedstocks, which are far from the value of normal Petro diesel.

A study analyzed the cost of the feedstocks for both biodiesel and Petro diesel from 2015-2020; the market price for palm oil ranges from USD 430-USD 778 per ton,
while for crude oil, the range of the cost is USD 73.3-USD 623 per ton. Moreover, it can pose an issue concerning the availability of the feedstocks. To grow oil crops, specific conditions and locations are required to get the best and ample supplies, including relative humidity, rainfall regime, etc. The effects of first and second-generation biodiesel on land utilization and frequent deforestation are concerning. It may lead to increased carbon dioxide emission due to carbon sequestration’s value of the oil crops being far lower than the forest (Syafiuddin et al., 2020).

Furthermore, considering the high viscosity of biodiesel, when compared with pure petrodiesel, it is said to generate much lower energy which could highly affect the productivity of vehicle engines. It exerts detrimental impacts such as high corrosion of copper-strip, cold-start problems, and difficulty pumping fuel (Yusuf et al., 2011). The increase in the high viscosity of biodiesel also poses an increased emission of nitrogen oxide (NO\textsubscript{x}). However, high viscosity is not the only factor contributing to this nitrogen oxide emission from its high density, low cetane number, and other conditions (Syafiuddin et al., 2020).

Petroleum, coal, and natural gas contribute significantly to the world’s energy supply (Yaqoob, Teoh, Goraya, et al., 2021). These resources, however, are depleting daily (Yaqoob, Teoh, Jamil, et al., 2021), and if countries continue to rely on them without diversifying their sources, they will shortly run out of fossil fuel reserves (Demirbas, 2005). The depletion of nonrenewable fossil fuels will impact future generations (Martins et al., 2019). These sources constantly release greenhouse gas (GHG) which causes climate change, such as global warming (Norman et al., 2006).

The developed countries are actively considering lowering emissions of GHG, and they have already met their goals (Al-Juboori et al., 2020). However, the rate of emissions reduction would decline beyond 2020. It has posed a problem as it is more difficult to reach their other targets, such as lowering the domestic emissions by 40 percent by the year 2030 compared to the emissions level in the 1990s. As a result, all parts of the world should take this seriously to protect the environment and save human lives (European Environment Agency., 2018). Due to global warming, researchers are looking for ways to produce suitable alternative fuels to petroleum oil.

The alternative fuel should be technically practical, environmentally friendly, economically competitive, and easily accessible. Hence, biodiesel is becoming an alternative fuel to diesel oils which can be produced from waste cooking oil (WCO) to reduce raw material costs (Lakshmi S. et al., 2019). When cooking oil is used for frying, it undergoes oxidation, polymerization, and hydrolysis reactions. These reactions reduce the nutritional value of the cooking oil, form polar compounds and decompose some products such as polymeric triglycerides (Karakaya & Şimşek, 2011; Sánchez-Gimeno et al., 2008). Waste of this resource can result in various disposal issues, including the degradation of soil quality, water pollution, economic loss and most importantly, it can also threaten human health (N. Banerjee et al., 2014).

Additionally, it is a typical practice in developing countries to dispose of WCO in commercial water bodies or home drainage systems. Toxic compounds transported underwater eventually reach human bodies and cause significant health problems. Furthermore, it also causes eutrophication, which occurs when an oil coating forms on the water’s surface, disrupting the water's oxygen supply and leading fishes or other marine animals to suffocate (El-Fadel & Khoury, 2001).

Chemically, WCO-based biodiesel refers to the lower alkyl ester of long-chain fatty acids (Meher et al., 2006). Its chemistry is determined by temperature, agitation
rate, the duration and pressure of the reaction, the catalyst used, the types of alcohol used, alcohol to oil ratio, moisture content, and the concentration of free fatty acid in raw oil (A. Banerjee & Chakraborty, 2009). To study the performance of the biodiesel on an engine, a diesel engine test was conducted utilizing WCO-based biodiesel fuel. The results showed increased specific fuel consumption and a loss in thermal efficiency for biodiesel blends when 20% WCO-based biodiesel is added by volume (Lakshmi S. et al., 2019; Shahid et al., 2012). When used in diesel engines, vegetable oils create operational and durability issues. These issues are related to the vegetable oils’ high viscosity and low volatility. Transesterification successfully decreased vegetable oil viscosity while also solving operational and durability issues (Abed et al., 2018).

In recent years, multiple countries have been implementing laws and regulations on the use of biodiesel in their countries as part of their strategies to reduce GHG emissions. Brazil has implemented strategies concerning biodiesel. In 2005, Brazil introduced the Programme for the Production and Use of Biodiesel. The program has the vision to achieve an increase in domestic production and the use of biodiesel while lowering the socio-economic inequality between and within regions. In addition, this program also introduces biofuels in the Brazilian energy matrix, which has a minimum requirement for blending and lowers the tax on biodiesel production. The law also stated that at the beginning of January 2005, a 2% of biodiesel (B2) must be blended throughout Brazil. The number had raised to 5% (B5) in January 2013 (Hajjari et al., 2017). In 2017, the legislation required diesel fuel to include 8% biodiesel (B8) (Hajjari et al., 2017).

Another example of a country that implemented strategies concerning biodiesel is China. In November 2015, China’s State Council published the 13th Five-Year Plan for Economic and Social Development from 2016 to 2020. The plan mainly concentrated on energy consumption reduction, environmental protection, and renewable and biomass energy utilization. The State Council also issued ‘The Energy Development Strategy Action Plan (2016-2020)’, which intended to curb yearly energy use and set a target of 15% non-fossil fuel-based energy usage in the country by 2020. Biofuels are seen as an essential component of this strategy (Worledge, 2019). Over the first six months of the year 2021, China’s biodiesel imports nearly doubled to 55,000 tonnes, most of which arrived in May and June as palm oil-based grades. The imports were mainly from Malaysia and Indonesia (Parmar, 2021).

There are various conversion methods to produce biodiesel. One of the methods to convert WCO into biodiesel is through micro-emulsion. Micro-emulsion is a technique for combining and dispersing two or more immiscible liquids into homogeneous systems with the help of surfactants and cosurfactants (Leng et al., 2018). The three components of the fluid formed during the process are the oil phase, aqueous phase, and surfactant. The micro-emulsion process improves biodiesel's spray characteristics while increasing its cetane number. The problem of high biodiesel viscosity can be solved using a solvent like methanol or ethanol during micro-emulsion (Yusuf et al., 2011). However, using micro-emulsified diesel in diesel engines has some drawbacks, including nozzle failure, incomplete combustion, and the formation of carbon deposits (Koh & Mohd. Ghazi, 2011).

Aside from microemulsion techniques, an alternative method to generate biodiesel is through the pyrolysis process. Generally, pyrolysis involves heating the biomass to a specific temperature ranging from 400-500°C without oxygen via a
thermochemical process, along with undergoing hydrotreating and hydrocracking to acquire the properties of biodiesel for transportation fuel (Hsu, 2012). The pyrolysis process is beneficial for its simple, efficient conversion and easy functioning (Wei et al., 2020). However, the disadvantages are more apparent in its low-quality production, including high acidity, low stability at high temperature, and low heating value of biodiesel. There was a reduction in the application for this process as it lacks assets (X. Hu & Gholizadeh, 2019).

From analyzing the two process techniques mentioned, it is evident that, generally, the techniques are unsuitable and feasible to produce biodiesel from WCO as they pose significant problems with its production quality. In that sense, implementing other process techniques, such as transesterification, is more beneficial as it is widely and commonly implemented to produce better fuel quality.

In contrast to diesel, biodiesel is a source of renewable energy that will not deplete over time. It is less polluting than diesel as it hinders the production of sulfur, smoke, hydrocarbons, and carbon dioxide. Instead, it produces less carbon monoxide and zero particulate matter (Mishra & Goswami, 2017). When fossil fuels are burned, GHGs are released into the atmosphere, raising the temperature and causing global warming. Nearly one million species could become extinct, and hundreds of millions of people could lose their lives if the average global temperature increases by more than 2°C (Ahmad et al., 2011). Various countries are converting to using a demand-driven product, biodiesel, as a prevention action towards the calamity of the climate. In addition, biodiesel can reduce the reliance on expensive oil products imported and supplied from other countries as it can be manufactured locally using domestic raw materials.

Moreover, biodiesel as an alternative fuel from Petro diesel constitutes an improvement in its economic impacts. As reported by various studies, countries such as Japan (Yang et al., 2016) and Brazil (Miranda et al., 2018) have implemented biodiesel usage and showed positive economic impacts due to the selected feedstock of WCO. Valente et al. (Valente et al., 2011) reported a significant cost reduction of 60-70 percent of biodiesel when WCO is used. As biodiesel is relatively cleaner than petroleum-based diesel, it gradually improves air quality, significantly reducing air pollution in the future and posing positive environmental effects.

Specifically, for WCO production, land utilization is not needed as it is commonly collected for domestic and commercial use. The two have no conflict regarding their energy and food security (Awogbemi et al., 2021). Undoubtedly, biodiesel is a much safer alternative than commercial diesel fuel due to its flammability compared to its difference in flashpoint values. Additionally, this biodegradable fuel is characterized by its high-octane number, low viscosity, and high lubricity, which without requiring any modifications, it can be employed in conventional compression-ignition engines (Rabie et al., 2019). From the practicality of biodiesel production, it can be shown great interest in manufacturing WCO to produce biodiesel.

The demand for fossil fuels, such as diesel, rapidly increases as the world's population grows. It is because fossil fuels are the primary source of energy generation (Shafiee & Topal, 2009). With the growing concern about climate emergencies and the depletion of global crude oil, which could lead to decreased diesel production, there has been a rising demand for alternative renewable energy sources. Biodiesel, a high-
potential alternative to conventional diesel fuel, has been considered a vital substitute (Xu et al., 2016).

To strive to tackle the occurrence of the climate crisis, the International Energy Agency (Net Zero by 2050, n.d.) has established a policy concerning reaching Net-Zero by 2050. The carbon dioxide emission will be lowered to zero percent by 2050 to complement the declining usage of fossil fuels and to become more dependent on low-emission fuels, inclusive of the utilization of biofuels. The commencement of the respective policy provides the determination to manufacture better and highly sustainable products, such as biodiesel. Consequently, biodiesel has been known for its relatively faster biodegradability, high sustainability, and non-toxicity characteristics. Moreover, it has a higher cetane number, improving the ignition quality even when blended with petroleum diesel (Bhatia, 2014; Roberts & Patterson, 2014; Sharmeen et al., 2019). Besides, due to its higher oxygen content, it was reported that biodiesel blending significantly reduced carbon monoxide and hydrocarbon emissions compared to diesel fuel (Abedin et al., 2016).

Biodiesel has been of great interest to researchers. According to the electronic database (ScienceDirect), the number of publications on biodiesel-related studies has constantly increased for the past decade (2010-2021), as shown in Figure 2. The publications mainly range from the various types of synthesis processes, the challenges encountered, the exploration of potential feedstocks, and the current and future developments of the global biodiesel industry.

![](image)

**Figure 2.** The number of publications on biodiesel-related studies from 2010-2021 on ScienceDirect.

The biodiesel industry has been continuously growing with its rising demand. According to the International Energy Agency, global biodiesel and Hydrotreated Vegetable Oil (HVO) production reached 48 billion liters globally in 2019, and it is anticipated to increase by 30 percent to 63 billion liters over 2023-2025 (IEA, 2020). Though, the high cost of edible feedstock has been a significant concern of biodiesel (Mohiddin et al., 2021). Therefore, a rise in exploration for non-edible, sustainable feedstock is seen to reduce food-energy competition.

Due to the lack of recycling companies dealing with WCO currently, most of the WCO in Brunei Darussalam is improperly disposed of. It could pose risks to the environment and human health. An estimation provided by Zhang et al. (H. Zhang et al., 2012) showed that approximately 40-60 percent of WCO in China illegally flowed back to dining tables, posing health hazards to consumers. Moreover, over 60 percent
of WCO is improperly handled in Europe, causing water drainage clogs, and increasing wastewater treatment costs and energy consumption (Bhuiya et al., 2016). Additionally, fat, oil, and grease (FOG) are also responsible for sewer blockages in many countries such as Malaysia (70 percent), the United States (50 percent), and the United Kingdom (50 percent). Approximately USD 25 billion is associated with removing these sewer blockages in the US annually (Zhao et al., 2021). WCO-based biodiesel is an outcome of the problem mentioned above. The conversion of WCO into biodiesel is a multiple-advantage solution that can enhance energy security, promote a circular economy, minimize waste and environmental pollution, and safeguard food safety (Zhao et al., 2021). Therefore, this study is conducted to assess biodiesel production potential based on WCO in Brunei Darussalam and the specifications required for the synthesis process.

PROPERTIES OF POTENTIAL PRODUCTS AND BY-PRODUCTS OF WASTE COOKING OIL TRANSESTERIFICATION

Biodiesel

Biodiesel is a liquid biofuel made from vegetable oils or animal fats and an alcohol that can be used alone or combined with diesel oil in diesel engines (Fukuda et al., 2001; Knothe et al., 1997; Van Gerpen et al., 2004b, 2004a). In contrast to traditional diesel derived from petroleum, the prefix bio indicates renewable and biological nature, while diesel fuel refers to its use in diesel engines. Biodiesel can be obtained from the transesterification process. Transesterification converts triglycerides in oils such as soybean, palm oil, rapeseed, castor, and sunflower oil into methyl or ethyl esters. Each triglyceride molecule's three chains of fatty acids react with an alcohol in the presence of a catalyst to produce ethyl or methyl esters, as shown in Figure 3 (F et al., 2011). Biodiesel is defined by ASTM (American Society for Testing and Materials) International as a blend of long-chain mono alkyl esters derived from renewable fatty acids for use in diesel engines. "Bx " is the percentage of biodiesel in a blend with diesel fuel, where "x" is the percentage of biodiesel in the blend. "B5", for example, denotes a blend of 5% biodiesel and 95% diesel fuel; B100, on the other hand, denotes pure biodiesel.

Biodiesel typically has long-chain carbon molecules containing hydrogen atoms, with an ester functional group (-COOR) at the end of the long chain (Ruhul et al., 2015). Biodiesel with 17 or 16 carbons and ester groups is depicted below. There is a difference between the structure of biodiesel and petrol diesel in terms of the presence of the ester group (The Chemistry of Biodiesel | Biodiesel Project | Goshen College, n.d.). Aside from that, both of them have a relatively similar chemical structure.

![Figure 3. The molecular structure of biodiesel (top) and petroleum diesel (bottom)](image-url)

As biodiesel is an attractive alternative energy source for diesel, it has similar combustion properties and even an improved class of its physical properties. Biodiesel
produces a higher flash point, ultra-low sulfur content, higher cetane number, enhanced lubricity, and low carbon footprint, and it is highly biodegradable (Ismail & Ali, 2015). The biofuel specification must follow the registered requirement for fuel by the Environmental Protection Agency (EPA). In addition, satisfying the specification authorized in the European Standard (EN 14214) along with the American Society for Testing and Materials (ASTM D6751) (Jariah et al., 2021), both are compared in Table 1.

Table 1. The comparison between two different standards, adapted from (Rajamohan et al., 2017).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>EN 14214</th>
<th>ASTM D6751</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flashpoint</td>
<td>°C</td>
<td>Min 130</td>
<td>Min 101</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>Min 47</td>
<td>Min 51</td>
</tr>
<tr>
<td>Density at 15°C</td>
<td>kg/m³</td>
<td>880</td>
<td>860 - 900</td>
</tr>
<tr>
<td>Kinematic viscosity @ 40°C</td>
<td>mm²/s</td>
<td>1.9 - 6.0</td>
<td>3.5 - 5.0</td>
</tr>
<tr>
<td>Acid number</td>
<td>mg.KOH/g</td>
<td>Max 0.5</td>
<td>Max 0.5</td>
</tr>
<tr>
<td>Cold filter plugging point</td>
<td>°C</td>
<td>Max +5</td>
<td></td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>h</td>
<td></td>
<td>Min 3h</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>%m/m</td>
<td>Max 0.05</td>
<td>Max 0.3</td>
</tr>
<tr>
<td>Copper corrosion</td>
<td></td>
<td>Max no. 3</td>
<td>Max no.1</td>
</tr>
<tr>
<td>Sulfated ash content</td>
<td>%mass</td>
<td>Max 0.002</td>
<td>Max 0.02</td>
</tr>
<tr>
<td>Water and sediment</td>
<td></td>
<td>0.005 vol%</td>
<td>500 mg/kg</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>%mass</td>
<td>Max 0.02</td>
<td>Max 0.02</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>%mass</td>
<td>0.24</td>
<td>0.25</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>%mass</td>
<td>Max 0.001</td>
<td>Max 0.001</td>
</tr>
<tr>
<td>Total contamination</td>
<td>mg/kg</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>

Glycerol

Glycerol, also known as propane-1,2,3-triol, has a stable chemical structure with three hydroxyl groups, and it is known as a multi-functional organic molecule having hydrophilic and hydrophobic properties (Rodrigues et al., 2017). Its physical properties are summarized in Table 2. Due to its thermal stability, it requires high energy availability to break the bond and form other compounds. With a mass yield of 10%, the glycerol obtained as a byproduct from biodiesel synthesis is known as crude glycerol, which contains methanol, free fatty acids (FFA), or fatty methyl esters from the transesterification process (H. W. Tan et al., 2013). Despite its low cost, glycerol purification is an expensive process, especially for small and medium-sized businesses; as a result, researchers have looked at new ways to incorporate crude glycerol into numerous industries, maybe with a straightforward purification phase. Due to the low price of crude glycerol, there is a potential for crude glycerol to be used in biorefineries that produce high-value-added products. Glycerol has over 1500 end products. The oversupply of unprocessed glycerol may allow novel applications of this feedstock to compensate for the cost difference between biodiesel and fossil diesel while lowering the energy needs for biodiesel production. In 2012, global crude glycerol output was over 4 mtons (Okoye & Hameed, 2016). In 2020, the global glycerol market will be worth roughly 2.52 USD, with biodiesel as the primary feedstock (He et al., 2017). Crude glycerol can be refined into value-added goods, such as cosmetics and pharmaceuticals, via distillation.
Glycerol is made up of three carbon (C) atoms, eight hydrogens (H) atoms, and three oxygen (O) atoms (Hernandez & Garcia, n.d.). As seen in Figure 3, the glycerol molecule is composed of a three-carbon chain with three hydroxyl groups (OH) connected to each (Glycerol Formula - Structure, Formula, Information, Molecular Weight of Glycerol, n.d.). The molecule has free rotation around all bonds as every carbon atom is in an sp3 configuration (John, 2021).

Generally, pure glycerol is in the liquid phase, portraying a colorless or pale-yellow liquid and odorless. Though it is soluble in both water and alcohol medium, it is insoluble in ether, chloroform, and in oils of volatile state. The stability of glycerol depends on the compounds it reacts with, where it is not compatible with lead oxide, perchloric acid, nitrobenzene, acetic anhydride, peroxides, chlorine, strong acids, and bases (Cormier, 1991).

**Table 2. The physical properties of glycerol.**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>92.09 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>1.25 g/mL at 25°C</td>
</tr>
<tr>
<td>Storage temperature</td>
<td>Store 5°C to 30°C</td>
</tr>
<tr>
<td>Form</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>Color</td>
<td>Colorless or pale yellow (APHA color)</td>
</tr>
<tr>
<td>Melting point</td>
<td>17.8°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>290°C</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in water</td>
</tr>
<tr>
<td>Water solubility</td>
<td>&gt;500 g/L at 20°C</td>
</tr>
<tr>
<td>Stability</td>
<td>Stable</td>
</tr>
</tbody>
</table>

**Fertilisers (Tripotassium phosphate, K₃PO₄)**

Tripotassium phosphate, also known as tribasic potassium phosphate (Potassium Phosphate Tribasic Reagentgrade, =98 7778-53-2, n.d.), is a colorless crystal, usually in the form of white powder. Its other physical properties are summarized in Table 3. It is water-soluble but insoluble in alcohol. When mixed with water, the solution is alkaline, has a pH value of 11.8, is corrosive, and has a high moisture absorption rate (TongVo Chemicals Limited, 2008). Tripotassium phosphate can be used as a food additive, an emulsifier, a foaming agent, and a whipping agent. When mixed with fatty acids, it has the potential to be an antibacterial agent in chicken processing. Tripotassium phosphate is commonly used to create N, P₂O₅, and K₂O fertilizer compounds (TongVo Chemicals Limited, 2008).

**Table 3. The physical properties of fertilizers.**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>212.27 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>2.564 g/mL at 25°C</td>
</tr>
<tr>
<td>Storage temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Form</td>
<td>Solid</td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
</tr>
<tr>
<td>Melting point</td>
<td>1340°C</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in water, clear, colorless</td>
</tr>
<tr>
<td>Water solubility</td>
<td>50.8 g/100mL</td>
</tr>
<tr>
<td>Stability</td>
<td>Stable</td>
</tr>
</tbody>
</table>
Potassium phosphate is formed by combining three potassium K\(^+\) cations and one phosphate PO\(_4^{3-}\) anion. The phosphate ion, PO\(_4^{3-}\) is composed of one phosphorus atom (P) and four oxygen atoms (O), with phosphorus having an oxidation state of +5 and oxygen having a valence of -2 \((\text{Potassium Phosphate (K}_3\text{PO}_4), \text{n.d.})\). The crystal structure of K\(_3\)PO\(_4\) appears to be composed of layers and blocks. The blocks are made up of octahedrally coordinated K(2) and tetrahedrally coordinated P atoms, with eight-coordinate K(1) atoms layer in between \((\text{Voronin et al., 2006})\).

The production of tripotassium phosphate from the potassium hydroxide and phosphoric acid of 3:1 stoichiometric ratio is in solid-state. It is white, has no odor, and tends to become liquid. In terms of its solubility, it is highly soluble in water, whether in hot or cold conditions—however, lower solubility rate in cold water and low solubility in ethanol medium. The aqueous solution of the product shows to be in an alkali state, and it is highly insoluble in alcohol. Moreover, even though it is stable, it is said to be a strong oxidizing agent \((\text{Potassium Phosphate Tribasic | 7778-53-2, n.d.})\).

The summary of the chemical properties of biodiesel, glycerol, and fertilizer is provided in Table 4.

### Table 4. Summary of the chemical properties of the potential products.

<table>
<thead>
<tr>
<th>Products</th>
<th>Biodiesel (B2-B20)</th>
<th>Glycerol, C(_3)H(_8)O(_3)</th>
<th>Fertilizer, K(_3)PO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxicity (to human)</td>
<td>Acute toxicity when inhaled; unharmful for dermal and oral</td>
<td>Very low oral toxicity in nature; TDLo (oral): 1428 mg/kg</td>
<td>ADI 0 to 70 mg/kg (generally safe, acute toxicity, oral and dermal)</td>
</tr>
<tr>
<td>Flammability</td>
<td>N/A; Fl. P: 52-82°C; AP: 611°C; EL: 0.3-10.0</td>
<td>Flammable; Fl. P: 176°C (open cup)/160°C (closed cup); AP: 393°C; EL: 2.6-11.3</td>
<td>Non-flammable; Fl. P: N/A; AP: N/A; EL: N/A</td>
</tr>
<tr>
<td>The heat of formation, (\Delta_f H^0) (298.15K, 1 atm, kJ/mol)</td>
<td>N/A</td>
<td>-669.6 (l)</td>
<td>-1988 (s)</td>
</tr>
<tr>
<td>The heat of combustion, (\Delta_c H^0) (298.15K, 1 atm, kJ/mol)</td>
<td>N/A</td>
<td>-1654.3 (g)</td>
<td>N/A</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>Stable under normal ambient conditions; incompatible with strong oxidizing and reducing agents and heat</td>
<td>Stable; incompatible with strong oxidizers, heat, and chemicals ((\text{H}_2\text{O}_2, \text{KMnO}_4, \text{K}_2\text{O}_2, \text{NaH, AgClO}_4 \text{etc.}))</td>
<td>Stable under normal conditions; incompatible with strong oxidizing agents, heat, and moisture</td>
</tr>
<tr>
<td>Products</td>
<td>Biodiesel (B2-B20)</td>
<td>Glycerol, C₃H₈O₃</td>
<td>Fertilizer, K₃PO₄</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Reactivity with other chemicals</td>
<td>Not chemically reactive</td>
<td>Reacts with acetic acid, K₂O₂, Na₂O₂, HCl, C₂H₄O, HClO₄, PI₃, (HNO₃+HF) and (HClO₄+PbO)</td>
<td>Explosive with KClO₃</td>
</tr>
<tr>
<td>pH</td>
<td>N/A</td>
<td>Weakly acidic or neutral to litmus</td>
<td>11.5~12.3 (1% aqueous solution); strong inorganic base</td>
</tr>
</tbody>
</table>

**References**

- (Safety Data Sheet: No. 2 Biodiesel Blend, 2018)

Note: ADI - Acceptable Daily Intake, TDLo - Toxic Dose Low

**APPLICATION AND USE OF WASTE COOKING OIL CONVERSION PRODUCTS IN THE INDUSTRY**

**Biodiesel**

*Fuel in Automotive Diesel Engines*

More and increasingly individuals fear that petroleum supplies can be depleted as the constraints of oil reservoirs become more apparent and the peak of world oil output approaches (Rajaeifar et al., 2016). Transportation accounted for 50% of world oil output as early as 2010. CO₂ emissions from the transportation sector account for more than 20% of global emissions, with road vehicle emissions accounting for more than 70% (“Policies to Reduce Fuel Consumption, Air Pollution, and Carbon Emissions from Vehicles in G20 Nations,” n.d.). These significant causes have resulted in dwindling oil sources and a rising greenhouse effect. Biodiesel has steadily gained traction as a viable alternative to petroleum fuel, leading to increasing interest and study. Without any modifications to the engine, biodiesel is often utilized in vehicle engines in either plain or mixed form (Man et al., 2016; Özener et al., 2014). Biodiesel uses a variety of feedstocks, unlike standard fossil fuels. Raw vegetable oil (palm oil, corn oil, etc.), animal fat (tallow, lard, etc.), non-edible oil (algae oil, jatropha oil, etc.),
and waste vegetable oil may all be utilized as biodiesel raw materials under present conditions (Aghbashlo & Demirbas, 2016). To form monoalkyl esters, WCO must undergo transesterification reactions with alcohols using acidic or alkaline catalysts (Knothe & Razon, 2017). The biodiesel's viscosity will be substantially lowered following transesterification, making it easier to use as fuel in the engine (How et al., 2014).

Biodiesel has a greater oxygen content, a higher cetane number, a higher viscosity, a lower aromatic content, and very little sulfur (Das et al., 2018). These unique qualities will impact engine performance, combustion, and emissions. Furthermore, biodiesel is non-toxic, non-harmful, and aids in reducing carbon emissions. Plants can partially recover carbon emissions from biodiesel generated from some crops, reducing greenhouse gas emissions (DeCicco et al., 2016). It's no secret that biodiesel reduces emissions more effectively than other fuels. Many studies have demonstrated that biodiesel-fueled diesel engines produce lower levels of controlled pollutants such as carbon monoxide (CO), hydrocarbon (HC), nitrogen oxide (NOx), and particulate matter (PM). Several other gases, including certain uncontrolled gases like volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs), will be decreased in most circumstances (excluding NOx). There are also full-cycle risk analyses of biodiesel, which reveal that only a small quantity of hazardous gases are generated before the biodiesel feedstock is cultivated and manufactured (Curran, 2013; Milazzo & Spina, 2015). Although most VOC and PAH components are harmful and may affect the natural environment and organisms, research on these exhaust pollutants produced by biodiesel-fueled engines is currently restricted (Ballesteros et al., 2010; N. Hu et al., 2017). The influence of biodiesel on VOC and PAH emissions has to be summarized and supplemented further.

The use of biodiesel in combustion will directly impact engine performance and indirectly impact engine noise and vibration, an essential component of in-vehicle comfort (Uludamar et al., 2016). Noise is the sound created by irregular vibrations, and it is a severe health hazard second only to air pollution. It may have negative consequences for various activities and create physical ailments such as neurological and cardiovascular disease (Theakston & Weltgesundheitsorganisation, 2011). As a result, competitive alternative fuels should fulfill both exhaust and noise pollution standards (Kirk-Othmer Encyclopedia of Chemical Technology, 2000). Many studies have examined the noise and vibration of engines powered by various biodiesel, but a follow-up study is still needed.

Although biodiesel has attributes comparable to diesel, the compatibility of the fuel and fuel system will directly impact the engine's regular functioning and longevity. Fuel injectors and oil pumps require lubricity, and it aids in reducing fuel system friction loss under high temperature, high pressure, and high-speed circumstances (Vriesema & Terlingen, 2013). The lubricity of the gasoline in fuel injectors promotes smooth movement of the plungers, tappets, and needle valves. Although most researchers claim that biodiesel has good lubricity, it also has oxidative deterioration and corrosion issues. Degradation of biodiesel can produce oxidation products such as acids, alcohols, aldehydes, and polymers, which can clog tiny holes in filters and nozzles and strain the fuel delivery system's corrosion resistance. It, however, indicates biodiesel's superior degradability. The precise impact of biodiesel compatibility on automobile engines is primarily based on laboratory testing, and real-world, long-term road tests are still sparse.
Glycerol

Glycerol is employed in almost all industries. The most common application is in pharmaceuticals and oral care items such as toothpaste, mouthwash, and oral rinses. Its application in tobacco processing and urethane foams has been relatively consistent. However, its usage in foods is rapidly increasing.

Foods

Although it is found in mixed form in all vegetable and animal fats, glycerol as a nutrient is readily digested and harmless, and its metabolism positions it with carbs. Glycerol is a solvent in flavoring and coloring compounds; its viscosity gives the product body. When raisins with glycerol are blended with cereals, they stay soft. It's utilized as a solvent, a moistening agent, and a vehicle ingredient in syrups. Glycerol prevents sugar crystallization in sweets and icings. Glycerol is a lubricant in food processing and packing machines and a heat-transfer medium in direct contact with foods during fast freezing (Kirk-Othmer Encyclopedia of Chemical Technology, 2000).

Drugs and cosmetics

Glycerol is a constituent in many tinctures and elixirs in medications and remedies, and glycerol of starch is used in jellies and ointments. It's used in cough medications, anaesthetics, and bacteriological culture medium and glycerol–phenol solutions for ear treatments. Its compounds (e.g., glyceryl guaiacolate) are employed in tranquillisers, and nitroglycerin is a vasodilator in coronary spasm. Glycerol is used in numerous cosmetic creams and lotions (qv) to maintain the skin smooth and restore moisture. It's commonly used in toothpaste to keep its smoothness, viscosity, and shine (Kirk-Othmer Encyclopedia of Chemical Technology, 2000).

Tobacco

Glycerol is a key component of the casing solution sprayed on tobacco leaves before they are shredded and packed in the tobacco processing industry. It is applied at a rate of ca 2.0 wt percent of the tobacco, along with other flavoring agents, to prevent the leaves from becoming friable and thus crumbling during processing; by remaining in the tobacco, glycerol helps to retain moisture and thus prevents the tobacco from drying out, and influences the tobacco's burning rate. It's also utilized as a plasticizer in cigarette papers and in the production of chewing tobacco to enhance flavor and avoid dehydration (Kirk-Othmer Encyclopedia of Chemical Technology, 2000).

Fertilisers (Water-soluble sertilisers, WSF)

There are many types of phosphate fertilizers, namely, $\text{K}_3\text{PO}_4$, $\text{KH}_2\text{PO}_4$ and $\text{KHPO}_4$. $\text{K}_3\text{PO}_4$, a by-product, could be utilized as fertilizers instead of eliminating. One or more aspects of the present invention relate to improved water-soluble fertilizer ("WSF") compositions. More particularly, they relate to solid fertilizer compositions having rapid dissolution times and high water-solubility. The WSF compositions also provide stable, precipitate-free stock and feed solutions and excellent dry-storage characteristics. One or more aspects of the present invention also relate to methods of using improved WSF compositions (Vriesema & Terlingen, 2013).

Fertilizer compositions can be provided in many forms, including dry granulated or free-flowing compositions intended for dispersion or dissolution in an aqueous solution before delivery to plants or crops. Advantageous, dry fertilizer compositions can be provided in many forms, including dry granulated or free-flowing compositions intended for dispersion or dissolution in an aqueous solution before delivery to plants or crops.
compositions provide for quick release (high water-solubility) when the production of stock solution is desired. In other contexts, dry fertilizer compositions are advantageous when they provide for slow release (as by low water-solubility or by encapsulation), such as when the steady or controlled delivery of nutrients over time is desired (Vriesema & Terlingen, 2013).

The invention provides, in one or more embodiments, a water-soluble, solid fertilizer composition comprising one or more acidic fertilizer components such as the acid urea phosphate, said acid being solid at ambient temperature, and one or more basic fertilizer components such as tripotassium phosphate (Vriesema & Terlingen, 2013).

METHOD OF PRODUCTION OF BIODIESEL FROM WCO

Multiple existing production technologies and processes of biodiesel have been introduced throughout the years for the conversion of useful energy products. The production methods include supercritical, microwave-assisted, transesterification, and pyrolysis. This report highlights the esterification and transesterification process and presents further justification. Transesterification is the most commonly used method in biodiesel production. However, pretreatment is necessary for an optimal and feasible production process. It will be further discussed later.

Transesterification Process

In any plant that manufactures biodiesel, the transesterification reaction is considered the primary process of the whole production process (Kuen et al., 2010). It is very critical to regulate and maintain the transesterification reactor, as any deviation in the operating conditions might affect the production quality of biodiesel (Shi et al., 2013).

Transesterification is a catalyzed chemical process that combines vegetable oil and alcohol to produce fatty acid alkyl esters, that is, biodiesel and glycerol, as the by-product (Y. Zhang et al., 2003). The equation below represents the typical transesterification reaction (Figure 4).

\[
\text{Triglyceride} + 3 \text{MeOH} \xrightarrow{\text{catalyst}} \text{Fatty Acid Methyl Esters (Biodiesel)} + \text{Glycerol}
\]

**Figure 4.** Transesterification reaction of vegetable oil (triglyceride) and methanol to fatty acid methyl esters (biodiesel) and glycerol.

Vegetable oil has a higher viscosity and lower volatility than diesel fuel. Due to these reasons, issues such as lubricating oil thickening, engine deposits, piston ring sticking, and injector coking are common when vegetable oil is utilized as fuel (Colucci et al., 2005). These problems can be lessened or eradicated by transesterifying vegetable oil.
To optimize the production of biodiesel, it is recommended that refined vegetable oils should have a free fatty concentration of less than 0.5 percent, that is, an acid value of \(< 1\), and a water content of \(< 0.06\) percent (van Kasteren & Nisworo, 2007). The presence of water in vegetable oils has a more damaging impact than free fatty acids as it causes ester saponification to occur. Since crude oils, WCO, and animal fats typically contain free fatty acids and water; this makes them inefficient in becoming feedstock sources for biodiesel production. Most industries usually include a pre-treatment step before the transesterification reaction to lower the free fatty acid and water content.

**Esterification Process**

The esterification reaction is a chemical reaction between fatty acid and alcohol with an acid catalyst support (Vieira et al., 2013). The esterification reaction is considered as a substitute process for the production of biodiesel, where it is utilized as a pretreatment before transesterification to reduce the FFA content to a lower value, especially when the FFA value is greater than 2% and to prevent the production of saponification reaction (Aranda et al., 2008). Not limited to the only undesired formation of soap but also inclusive of yield loss and complex product separation in the later stages of biodiesel production as the soap acts as an emulsifier (Chai et al., 2014).

Raw materials of high fatty acids can be converted into high-yield biodiesel. Waste vegetable oils, coconut oil, cottonseed oil, chicken fat, pork fat, and residues from various industries are examples of these raw materials mentioned (Pisarello et al., 2010). Aside from other types of fatty acids used in the respective method, WCO as feedstock is attractive. Various articles reported on biodiesel production WCO due to its beneficial traits in terms of its cost and availability. WCO consists of various types of fatty acids and different compositions. Table 5 shows the composition of fatty acids in WCO following the EN 14103 standard (Bautista et al., 2009). The significant fatty acid in the WCO is usually oleic acid (Chai et al., 2014; Y. Zhang et al., 2003).

**Table 5.** The composition of fatty acids in waste cooking oil, adapted from (Bautista et al., 2009).

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Formula</th>
<th>Composition (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic</td>
<td>C14:0</td>
<td>0.13</td>
</tr>
<tr>
<td>Palmitic</td>
<td>C16:0</td>
<td>8.8</td>
</tr>
<tr>
<td>Stearic</td>
<td>C18:0</td>
<td>4.2</td>
</tr>
<tr>
<td>Oleic</td>
<td>C18:1</td>
<td>45.15</td>
</tr>
<tr>
<td>Linoleic</td>
<td>C18:2</td>
<td>39.74</td>
</tr>
<tr>
<td>Linolenic</td>
<td>C18:3</td>
<td>0.2</td>
</tr>
<tr>
<td>Arachidic</td>
<td>C20:0</td>
<td>0.43</td>
</tr>
<tr>
<td>Behenic</td>
<td>C22:0</td>
<td>0.75</td>
</tr>
<tr>
<td>Erucic</td>
<td>C22:1</td>
<td>0.3</td>
</tr>
<tr>
<td>Lignoceric</td>
<td>C24:0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Moreover, it is necessary to consider its operational conditions where it can greatly impact the esterification reaction. It includes the moisture in the material, its alcohol-to-oil ratio, temperature, contact time, type of catalyst and type of enzyme if any (Chongkhong et al., 2012). Furthermore, for both esterification and transesterification reactions, methanol is used explicitly for the alcohol medium as it...
is widely used in both reactions. It is due to its cheap cost and favorable physicochemical properties (Al-Hasan, 2013).

**Pyrolysis Process**

The pyrolysis process, also known as thermal cracking, is a well-known thermochemical process to produce biochar (solid), bio-oil (liquid), and non-condensable gas with an option of with or without catalyst (Rajalingam et al., 2016). This pyrolysis is highly crucial, especially from the perspective of utilizing vegetable oil as the feedstock of the process, as the direct use of vegetable oil as fuel is unachievable due to some of the oil’s undesired properties. It includes the absence of aromatics in vegetable oil when diesel fuel has between 15-37% (Bartlett et al., 1992). Besides that, this process utilizes high temperatures above 350°C and without air or oxygen. Hence, with the high temperature, the process uses raw materials such as biomass and vegetable oil and breaks down the respective complex structure of the hydrocarbons into a more straightforward structure for fuel transportation applications.

In the case of vegetable oil, the triglycerides must be broken down into more minor compounds because the average number of carbon atoms in the compound is 57 (Mazur & Maier, 2016). For diesel/biodiesel for fuel, the required number of atoms usually are around 12 to 20 (Richards, n.d.). Furthermore, high temperature breaking bigger molecules into simpler molecules decreases the biodiesel's density and viscosity. Decreased density and viscosity are both advantageous and important alterations as the bio-oil produced by pyrolysis can be directly utilized in diesel engines without further adjustments or treatments.

This pyrolysis process consists of simultaneous and successive reactions when heated organic material (Bartlett et al., 1992). In this process, organic components’ solid decomposition and thermal decomposition occur at the starting range of 350–550 °C and extend to 700–800 °C without air/oxygen (Jahirul et al., 2012). The long chains of organic compounds such as Carbon, Oxygen, and Hydrogen in the organic matter disintegrated into smaller molecules in different forms such as solid charcoal, gases, and condensable vapors (tars and oils) (Bartlett et al., 1992). The rate and extent of decomposition of each of these components depend on the process parameters such as reactor (pyrolysis) temperature; heating rate; pressure; reactor configuration; feedstock; etc.

Depending on the operating condition, pyrolysis can be classified into three main categories: slow/conventional, fast, and Ultra-fast/flash pyrolysis (Basu, 2013). Slow pyrolysis is generally utilized to alter the solid material, thus limiting the amount of oil produced. This slow pyrolysis is the opposite of fast and ultra-fast pyrolysis, as the two processes prioritize the gas and oil produced as products. The main products, therefore, are mainly gases, char, and bio-oil (tar).

Fast pyrolysis works on the principle of rapid thermal decomposition in an oxygen-free environment and with moderate and high-temperature conditions. It is the most common type of pyrolysis, with the significant product being bio-oil. One of these fast pyrolysis characteristics is an endothermic reaction, dry and more minor feedstock particles. The expected yield of products from this fast pyrolysis is thinner bio-oil, gases, and char (Meier et al., 2013).

Ultra-fast pyrolysis uses thermal decomposition significantly faster than fast pyrolysis and utilizes a high-temperature rate. This pyrolysis mainly produces gases
and biochar. The temperature required for the process can exceed 10,000°C. The standard products yield from this flash pyrolysis are gases and bio-oil (Sui, 2013).

The complexity of the reaction mechanisms of pyrolysis can be simplified in three main steps (Demirbas, 2004; Pourkarimi et al., 2019).

1. organic matter → Water + unreacted residue
2. Unreacted residue → (Volatile + Gases)\(_1\) + (Char)\(_1\)
3. (Char)\(_1\) → (Volatile + Gases)\(_2\) + (Char)\(_2\)

The first stage is biomass decomposition, where few chemical changes occur in the organic matter that yields water and unreacted residue. The first chemical change is the internal rearrangement, such as moisture and volatiles loss. The second chemical change is breaking the bonds with the aid of temperature. The other chemical change that takes place is the appearance of free radicals due to the bond-breaking phenomenon that then yields a formation of carbonyl compounds, carboxyl compounds, carbon dioxide, and carbon monoxide. Charred unreacted residue, basically the remaining organic compound, is also produced in this first stage and will be brought into the second step of the pyrolysis process.

In the second process, the unreacted residue, the primary product in the first step, will undergo secondary reactions such as cracking, dehydration, and polymerization. Thus, this converts the unreacted residue to components such as gases, tar, and secondary char. Increasing the temperature causes the long-chain molecules to decompose into smaller segments. Finally, the primary char will react differently in the final stage to produce secondary volatiles, gases, and secondary char.

**Supercritical Method**

Supercritical biodiesel production is an exciting alternative to catalytic transesterification. The strategy proposed by Saka and Dadan (2001), provides some distinct advantages over other techniques. One advantage is that biodiesel production through a supercritical method does not require a catalyst throughout the reaction. Moreover, it has a fast reaction rate of about a few minutes. It allows for triglyceride transesterification and FFA esterification to coincide. Hence, it improved production efficiency and fewer processing steps (more straightforward purification and separation) (Saka & Kusiana, 2001). Furthermore, compared to other methods, supercritical methods can tolerate high FFA content and the presence of water, and the operations can be run continuously (Farobie & Matsumura, 2017).

Methanol has a critical temperature of 239.2 °C and a pressure of 8.09 MPa (Farobie & Matsumura, 2017). When methanol reaches its critical temperature and pressure, its mass density changes significantly, affecting its solubility and mass-transfer properties (Farobie & Matsumura, 2017). Due to a rise in methanol density and a drop in its dielectric constant, triglyceride and methanol form a single phase in supercritical methanol (Saka & Kusdiana, 2001). Additionally, the polarity of methanol decreases as density rises due to the presence of hydrogen bonding. As a result, in supercritical circumstances, the nonpolar triglyceride dissolves better in methanol, forming a homogenous phase. According to Glisic and Skala (2010), triglyceride solubility rises when the temperature and pressure increase.

Glisic and Orlovic (2012) investigated the phase behavior of triglyceride methanolysis in subcritical and supercritical circumstances. The distribution of methanol, triglyceride, biodiesel, and glycerol during methanolysis was shown to
vary depending on temperature and pressure. They split the phase transition into three regimes (Glisic & Orlovic, 2012). Below 170 °C and 1.5 MPa, the first regime occurs. The second regime corresponds to phase change at subcritical temperatures and pressures (170-220 °C and 1.55-5 MPa), whereas the third regime occurs near the critical point.

Kusdiana and Saka (2004a) were the first to suggest a chemical mechanism between triglycerides and methanol under supercritical circumstances. Methanol clusters attack the carbon atom of the carbonyl group in triglycerides when they break into free monomers at high temperatures and pressures. As a result, an intermediate is formed via the transfer of a methoxide moiety, as illustrated in Figure 5. The intermediate is then rearranged to form more stable molecules, such as biodiesel and diglyceride. Diglyceride combines with another methanol molecule to generate biodiesel and monoglyceride similarly. Biodiesel and glycerol are produced when monoglycerides and methanol combine.

![Figure 5. The proposed reaction mechanism between triglyceride and methanol under supercritical conditions (adapted from (Kusdiana & Saka, 2004a)).](image)

The necessity for high oil-to-alcohol molar ratios and heightened temperature and pressure are some of the drawbacks of supercritical biodiesel synthesis. Cosolvents and catalysts have been presented as solutions to these issues. Figure 6 illustrates a two-step method developed by Kusdiana and Saka (2004b). The triglycerides are first digested in subcritical water to create FFA and glycerol, followed by supercritical esterification of FFA in lower oil-to-methanol molar ratios. Due to the softer operating temperatures (270°C, 7 MPa) compared to one-step biodiesel synthesis (350°C, 2050 MPa) and a significantly enhanced oil-to-methanol molar ratio, two-step processing significantly decreases energy usage.

A co-solvent has been proposed to make the conditions for supercritical biodiesel production in methanol less severe. Adding a co-solvent can increase the reciprocal solubility of triglycerides and methanol. As a result, biodiesel may be generated in a more temperate environment. Propane, carbon dioxide, ethane, n-butane, n-hexane, n-heptane, and tetrahydrofuran (THF) have all been explored as co-solvents. Cao et al. (2005) found that reducing the propane-to-methanol molar ratio to 0.1 could decrease the reaction temperature to 280 °C from 350 °C, resulting in full biodiesel conversion. Also, CO₂ inclusion as a co-solvent enhanced the biodiesel throughput in the methanolysis of canola oil, according to Imahara et al. (2009). However, the yield declined when the molar ratio was increased over 0.1 CO₂/ methanol. Furthermore, Trentin et al. (2011) used a microtube reactor to study the influence of CO₂ injection...
on biodiesel output under supercritical conditions. They discovered that a CO₂-to-substrate mass ratio of 0.2:1 was ideal. Tan et al. (2010) found that n-heptane substantially influenced palm oil conversion to biodiesel in supercritical methanol when the n-heptane-to-oil molar ratio was 0.2. Muppaneni et al. (2012) investigated n-hexane as a co-solvent and found that an n-hexane-to-oil volume ratio of 0.2 was ideal for biodiesel output.

Catalysts have also been suggested to boost biodiesel production under supercritical circumstances. Demirbas (2007) explored the effect of adding calcium oxide (CaO) to sunflower oil as a feedstock in biodiesel output. With the addition of CaO, he found that the biodiesel output increased. Furthermore, with an oil-to-methanol molar ratio of 1:41 and the addition of 3 wt percent CaO, the maximum biodiesel output was seen within 6 minutes at 525 K. SrO, CaO, ZnO, TiO₂, and ZrO₂ were used as metal oxide catalysts on biodiesel synthesis in supercritical methanol (Yoo et al., 2010). They demonstrated a yield of about 95% by adding 1 wt% of ZrO₂ at 250 °C and a 1:40 oil-to-methanol molar ratio within a 10-minute reaction period. Most heterogeneous catalysts, on the other hand, are unstable in supercritical conditions. Only a few heterogeneous catalysts, such as zinc aluminate and zirconia-supported metal oxide catalysts, are stable under these circumstances (Kim et al., 2012; Pugnet et al., 2010). The use of trace amounts of homogeneous catalysts at subcritical settings was also investigated due to the unfavorable stability of heterogeneous catalysts (Liu et al., 2017).

Figure 6. Two-step processing for supercritical biodiesel production (Farobie & Matsumura, 2017).

Microwave-assisted process

Microwave heating is one of the heating methods used to manufacture biodiesel from WCO. Microwave irradiation consists of electromagnetic rays ranging from 0.01 to 1 m wavelengths and frequencies varying from 0.3 to 300 GHz (Khan et al., 2021). The frequency of microwave irradiation is greater than that of radio waves but considerably lower than that of x-rays (Orchard et al., 2007).

There is a difference in the heating mechanism between a conventional and a microwave. The heating mechanism in a microwave is far more complex than others. An experiment to determine the difference between the two heating mechanisms was conducted. The solvent temperature was rapidly increased and cooled under microwave irradiation compared to conventional heating, in which an oil bath was utilized. Moreover, the thermal behavior of the same experiment was observed as
well. It can be seen that the temperature was increased simultaneously and evenly throughout the total solvent, while it is not the case for conventional heating (Gude et al., 2013).

The microwave-assisted method conserves more energy (Lin & Chen, 2017) compared to transesterification via conventional heating. The microwave process uses 23 times less energy than conventional methods (Talebian-Kiakalaieh et al., 2013). It tremendously cuts the overall cost of producing biodiesel.

Production of biodiesel via microwave irradiation-assisted enables rapid optimization of transesterification processes and boosts the product yield (Varol et al., 2021, p. 3). The optimal microwave power is 750W when WCO is used as feedstock in a lab-scale setup (Chen et al., 2012). Since microwave energy is directly transferred to the reactants, the microwave-assisted approach reduces the time to produce biodiesel with high conversion (Qu et al., 2021). It was reported by Khan et al. (2021) that in the usage of heterogeneous catalyzed microwave-assisted transesterification, there is a significant decrease in the reaction time, which simultaneously improves the catalytic activity by greater than 90% compared with conventional heating.

The microwave technique can increase the production of higher-quality biodiesel (Rokni et al., 2022). The advantages of producing biodiesel by microwave heating include a reduced oil-to-methanol ratio, reduced by-product output, and simplicity of operation (Sathyamurthy et al., 2021). Though it exhibits some benefits, its limitations in applying microwave irradiation exist. The occurrence of enzyme deactivation is possible due to exposure to microwave radiation during the process, which decreases its catalytic activity (Kapilan et al., 2014). In addition, one of the primary disadvantages of using microwave processes on a wide scale in the industry is that the high microwave output or power may harm organic molecules, such as triglycerides (Saifuddin & Hua, 2004).

Some scientific reports have been published on various methods for biodiesel production by converting WCO as the primary raw material. The summary of those methods, including the decision consideration for process selection, is provided in Table 6.

Table 6. Decision table for process routes selection for waste cooking oil conversion into biodiesel and other by-products

<table>
<thead>
<tr>
<th>Types of transesterifications</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic transesterification (in general)</td>
<td>• Presence of a catalyst increases the reaction rate, hence the yield of the reaction.</td>
<td>• Relatively time-consuming</td>
<td>(Baskar et al., 2019)</td>
</tr>
<tr>
<td>Chemical catalytic transesterification General</td>
<td>• Reaction conditions can be well controlled • Large-scale production • Cheap production cost • The methanol produced in the process can be recycled • High conversion of the production</td>
<td>• Reaction temperature is relatively high • Complex reaction process • The later disposal process is complex • Higher energy consumption • Needs an installation for methanol recycling</td>
<td>(Quader &amp; Ahmed, 2017)</td>
</tr>
<tr>
<td>Types of transesterifications</td>
<td>Advantages</td>
<td>Disadvantages</td>
<td>References</td>
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<tr>
<td>-------------------------------</td>
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</tr>
<tr>
<td>Homogeneous catalyst</td>
<td></td>
<td>• The wastewater pollutes the environment</td>
<td>(Thangarasu &amp; Anand, 2019)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>• Soap formation during the process</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Expensive catalyst removal after the process</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Great yield loss due to washing step</td>
<td></td>
</tr>
<tr>
<td>Heterogeneous catalyst</td>
<td>• Can be used to convert feedstock with high FFA</td>
<td>-</td>
<td>(Athar &amp; Zaidi, 2020; Thangarasu &amp; Anand, 2019)</td>
</tr>
<tr>
<td></td>
<td>• Easier and cheaper separation process</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Easy purification</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Recoverable and reusable</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Fewer hazards</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>• Non-corrosive</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Environmentally friendly</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Less disposal problem</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>• Good catalytic activity</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Long life span</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Neutralisation process not required</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homogeneous acid catalyst</td>
<td>• Able to catalyze esterification and transesterification simultaneously</td>
<td>• Presence of water content in feedstock may affect the transesterification process</td>
<td>(Buchori et al., 2016; Nasreen et al., 2018)</td>
</tr>
<tr>
<td></td>
<td>• Insensitive to FFA and water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heterogeneous acid catalyst</td>
<td>• Insensitive to FFAs</td>
<td>• Low catalytic activity</td>
<td>(Buchori et al., 2016, p.; Faruque et al., 2020; Sani et al., 2013)</td>
</tr>
<tr>
<td></td>
<td>• Suitable for low-grade feedstocks with high FFA content</td>
<td>• Usually requires high reaction temperature (&gt;350°C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Able to catalyze esterification and transesterification simultaneously</td>
<td>• Long reaction time (8-20h)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Easier purification, the washing step can be eliminated</td>
<td>• Leaching of active components of catalyst, hence the need of purification step</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Easy separation of catalyst from reaction products</td>
<td>• Generates waste solvent, hence increasing production cost and decreasing catalyst activity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High biodiesel yield</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High reusability of the catalyst</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Non-corrosive</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Environmentally friendly</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>• Insensitive to FFAs and water in WCO</td>
<td>• Lower catalytic activity in some catalyst</td>
<td>(Faruque et al., 2020;</td>
</tr>
<tr>
<td>Types of transesterifications</td>
<td>Advantages</td>
<td>Disadvantages</td>
<td>References</td>
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</tr>
</tbody>
</table>
| solid acid catalyst          | • Suitable for low-grade feedstocks with high FFA content  
                              • Able to catalyze esterification and transesterification simultaneously  
                              • Less or no saponification  
                              • (Acid) pretreatment process not required  
                              • Easy separation of catalyst from reaction products  
                              • High biodiesel yield  
                              • Easier purification of the product  
                              • High catalytic activity  
                              • Highly stable catalyst performance  
                              • Less contaminant; environmentally friendly  
                              • Consists of numerous acid sites with different strengths of Bronsted or Lewis acidity  
                              • Promising yield could be obtained at the relatively low reaction temperature, hence lower energy consumption  
                              • High reusability and regeneration of the catalyst  
                              • Attain the necessary specifications of ASTM standards in biodiesel production  
                              • Less susceptible to leaching  
                              • Less cost  
                              • High selectivity (for catalyst selection) | • Requires elevated reaction temperature and prolonged time to attain the highest conversion rates due to lower catalytic activity  
                              • Slow reaction  
                              • Complex procedures in the development of some catalyst  
                              • Poor thermal or hydrothermal stability  
                              • Difficult to calculate the number of the active site and to determine reaction rates  
                              • Less prone to catalyst deactivation | Mansir et al., 2017; Peng et al., 2008; Sani et al., 2013 |
| Homogeneous base catalyst     | • Fast reaction (10min to 2h)  
                              • Mild reaction temperature (25-70°C) and atmospheric pressure  
                              • High biodiesel yield than the acidic catalyst  
                              • High conversion in short reaction time  
                              • High availability and cheap  
                              • Faster reaction than homogeneous acidic catalyst (~4000 times faster) | • High energy consumption  
                              • High sensitivity to feedstock purity  
                              • No water content in the feedstock  
                              • Needs high-quality feedstock to avoid undesired reactions such as hydrolysis and saponification  
                              • Pretreatment required for FFA/water containing feedstocks | Buchori et al., 2016; Kuo et al., 2015; Ling et al., 2019; López et al., 2005; Sani et al., 2013 |
<table>
<thead>
<tr>
<th>Types of transesterifications</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Heterogeneous base catalyst</em></td>
<td>- The catalyst is reusable and recyclable</td>
<td>- Occurrence of the saponification process</td>
<td>(Faruque et al., 2020; Ling et al., 2019)</td>
</tr>
<tr>
<td></td>
<td>- Separation process from the product is easier</td>
<td>- Hence difficult post-production separation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- The life span of the catalyst is long</td>
<td>- Low catalytic activity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- The reaction happened at mild reaction which eventually minimizes the energy utilization</td>
<td>- The catalyst is poisonous during exposure to ambient air</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- The reaction happened at mild reaction which eventually minimizes the energy utilization</td>
<td>- The transesterification process will require more molar ratio of methanol to oil</td>
<td></td>
</tr>
<tr>
<td><em>Heterogeneous bifunctional (solid) catalyst</em></td>
<td>- Able to catalyze esterification and transesterification simultaneously</td>
<td>- -</td>
<td>(Faruque et al., 2020)</td>
</tr>
<tr>
<td>(Relatively new)</td>
<td>- Consists of both active acid and base sites, so would not be affected by water content in feedstock as well as those produced during biodiesel production</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Lower production cost</td>
<td>- -</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Can be modified to achieve required catalyst characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Acid-base two-step catalyzed</em></td>
<td>- Can be applied to any feedstock oils, including high FFA containing oil</td>
<td>- -</td>
<td>(Thoai et al., 2019)</td>
</tr>
<tr>
<td></td>
<td>- Can be a transesterification-transesterification (T1 + T2) process or an esterification-transesterification (E + T) process depending on the FFA content in the feedstock</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Does not lead to saponification</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Types of transesterifications</td>
<td>Advantages</td>
<td>Disadvantages</td>
<td>References</td>
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<tr>
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</tr>
<tr>
<td>Base- acid two-step catalyzed</td>
<td>Moderate reaction condition • Small amount of methanol is required in the reaction • Environmentally friendly • Cost-effective • Neutral pH, so less saponification</td>
<td>Limitation of enzyme in the conversion of short-chain of fatty acids • Chemicals that exist in the process of production are poisonous to enzyme • Usually use lipases - expensive, low yield, slower than the chemical catalyst • Slow reaction &amp; low productivity</td>
<td>(Clifford, 2020; Faruque et al., 2020; Manirafasha et al., 2020; Quader &amp; Ahmed, 2017)</td>
</tr>
<tr>
<td>General</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enzymatic-catalyzed transesterification (biocatalyst)</td>
<td>Able to catalyze esterification and transesterification simultaneously • No complex operation is needed • Environmentally friendly • Lower energy input • Does not cause undesirable side reactions such as saponification of free fatty acid. • Low reaction temperature • Give high purity product (esters) • Reusable immobilized enzyme</td>
<td>Complicated recovery, purification, and immobilization processes for industrial application • High cost • High reaction time • Inactivation of lipase enzyme caused by methanol and glycerol</td>
<td>(Faruque et al., 2020; Gebremariam et al., 2017)</td>
</tr>
<tr>
<td>Using lipase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Notes for the catalyzed process:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• When FFA&lt;1mg of KOH/g of oil - better conversion efficiency of homogeneously catalyzed transesterification</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• When FFA&gt;1mg of KOH/g of oil - two-step transesterification process required</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Studies report heterogeneous and enzymatic catalysts are best for conversion of TG into methyl esters</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>• Examples of catalysts:</td>
<td></td>
<td></td>
<td>(Demirbas, 2009; Thangarasu &amp; Anand, 2019)</td>
</tr>
<tr>
<td>• Homogeneous alkali: NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Homogeneous acid: H₂SO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Heterogeneous alkali: CaO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Heterogeneous acid: Fe₂(SO₄)₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Two-step transesterification methods: NaOH+H₂SO₄ or H₂SO₄+NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Solid acid: sulfonated saccharides, tungsten oxides, sulfated zirconia (SZ), and National resins</td>
<td></td>
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<tr>
<td>• Presence of free fatty acids and water causes saponification, consumes catalyst, and reduces catalyst effectiveness. Hence, water content should be kept below 0.06%</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Types of transesterifications</td>
<td>Advantages</td>
<td>Disadvantages</td>
<td>References</td>
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</tr>
</tbody>
</table>
| **Non-catalytic transesterification** | • No catalyst required  
• Washing step is not required  
• Short reaction time  
• Environmentally friendly  
• Pre-treatment of impurities in the feedstock because it does not affect the reaction strongly  
• Easy to be controlled  
• Insensitive to both water and FFA; FFA in WCO is transesterified simultaneously  
• Tolerates water and free fatty acids in the system, and the soap formation that is common in the traditional process is eliminated  
• Simpler purification and less energy-intensive | • High-cost apparatus  
• High operation temperature (250-400 °C)  
• High operation pressure (40-45 MPa), therefore not feasible in the large scale industry  
• High molar ratio of alcohol to oil (more than 40:1) or very high methanol consumption  
• Wastes energy | (Buchori et al., 2016; Demirbas, 2008, 2009; Farm Energy, 2019; Mofijur et al., 2021; Quader & Ahmed, 2017) |
| **Supercritical transesterification** | • In the conventional transesterification process, heating of material takes place by conduction. Whereas microwaves heat by means of thermal radiation and it is a very efficient mode of heat transfer.  
• Microwave energy is delivered directly to the reacting molecules which undergo a chemical reaction | • Biodiesel produced by this process has reduced performance due to comparative high viscosity.  
• Smoke opacity, HC, and CO emissions increase. | |
| **Microwave-assisted transesterification** | • Easier purification of biodiesel  
• No catalyst required hence prevents soap formation/saponification  
• Easy to be controlled  
• Environmentally friendly  
• Safe and faster overall reaction | • High temp and pressure in reaction condition leading to high equipment/production cost and waste | (Baskar et al., 2019; Quader & Ahmed, 2017; Thangarasu & Anand, 2019) |
| **Biox process** | • Able to handle feed with high FFA  
• Short reaction time  
• Can be carried out under ambient temperature and pressure | • Co-solvent must be completely removed due to its hazardous and toxicity natures (creates an economical barrier) | |
<table>
<thead>
<tr>
<th>Types of transesterifications</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
</table>
| Ultrasonically assisted transesterification | • Less amount of catalyst  
• Lower molar ratio of oil to methanol (1:6)  
• Faster reaction  
• Lower reaction temperature  
• Higher biodiesel yield  
• Increase mass transfer | • Produces high pressure | |
| Extra info:  
• Lower frequency is more efficient than high frequency  
• Enzyme catalyzed transesterification is enhanced with ultrasonic radiation. | | (Buchori et al., 2016) |
| Plasma-electro catalysis transesterification (without catalyst) | • Very short reaction time  
• Does not require a catalyst  
• No saponification | • Difficult to control the reaction mechanism due to the action of high energetic electrons  
• Difficult to control the bond that will be excited or ionized  
• Difficult to prevent continuing reactions due to the action of high energetic electrons | (Buchori et al., 2016) |
| Nanocatalysts transesterification | • Relatively short reaction time  
• Catalyst can be reused many times  
• Catalyst has a high surface area, less amount of catalyst required | • More alcohol is required than other processes for an effective yield  
• High cost preparing appropriate catalyst (some cases) | (Mofijur et al., 2021) |
| Ionic liquid transesterification | • High catalytic performance  
• Easy and safe to handle  
• Steady reusability | • Lack of complete characterization of physical parameters (this research topic is relatively new). | (Panchal et al., 2020) |
| In-situ transesterification | • One step for integrated lipid extraction and transesterification of lipids to biodiesel  
• No need for hazardous chemical extraction solvent, such as hexane  
• Reduced processing time  
• Production and recovery of FAME can be done within 90 minutes | • Longer sonication times (Inefficient)  
• More losses of methanol and biodiesel  
• Overheating of the reaction mixture | (Farag & Elmoraghy, 2014) |
Based on the table above, the group has decided to use a homogeneous base-catalyzed transesterification process for the WCO-based biodiesel production, with potassium hydroxide (KOH) selected as the main catalyst due to its high availability and economic feasibility. The WCO in Brunei Darussalam typically has a high FFA content (more than 2 wt%), which can lead to saponification when catalyzed by the alkali. Therefore, the WCO will first undergo an acid-catalyzed pretreatment process to lower the FFA level. Here, the FFA-water-insensitive acid catalyst will esterify the FFAs into desired fatty acid methyl esters (FAME) and water before entering the alkali-catalyzed transesterification process.

**REACTOR SELECTION**

Batch reactors and continuous reactors are the two types of reactors available. Batch reactors are enormous stirred tanks that can accommodate the whole inventory of a batch cycle. Batch reactors can sometimes be run in a semi-batch mode, where one chemical is charged to the vessel and a second chemical is slowly added. Continuous reactors are smaller than batch reactors and process the product continuously. Continuous reactors can be constructed as pipelines with or without baffles or as a sequence of linked stages. The benefits of continuous reactors are discussed below (Changcheng, 2019).

The concentration of reactants determines the rate of many chemical reactions. Due to their greater heat transfer capacity, continuous reactors can often handle significantly larger reactant concentrations. Plug flow reactors provide the added benefit of a superior concentration profile due to the larger separation between reactants and products (Changcheng, 2019).

Continuous reactors' tiny size allows for higher mixing speeds (Changcheng, 2019). Changing the run time of a continuous reactor can change the output. Manufacturers will have more operational freedom due to this (Changcheng, 2019). Continuous flow processing methods evolved as a result of technological improvements as well as the inherent constraints and limits of batch reactors. The latter thoroughly investigates variables like time, temperature, order, and reactant type. If more product is required, bigger vessels are used, resulting in inefficiencies due to process optimization problems and vessel/process scaling. Reduced yields and higher costs are all consequences of inefficiency (Anderson, 2021).

Continuous flow reactors have come a long way in development and use, especially for small-scale chemical synthesis. In many situations, the financial benefits exceed the practical hurdles, and the technique is gaining traction in pharmaceutical drug development. Regarding safety, quality control, and throughput, continuous flow techniques may benefit batch reactor processing (Anderson, 2021).

**PRODUCTION FEASIBILITY IN BRUNEI DARUSSALAM**

This section provides a quick justification of the feasibility of the WCO-to-biodiesel plant will be feasible to be applied in Brunei Darussalam. With several countries that have successfully implemented biodiesel, this review also provides good insight into the possibility of implementing biodiesel in Brunei Darussalam. The most common and main application of biodiesel throughout different countries is fuel in the automotive industry as a diesel oil replacement in the mixture of 5% biodiesel and 95% diesel. Hence, the application of biodiesel as fuel is also plausible in Brunei
as fuel for all of its road transport runs on petrol or diesel. This report highlights the implementation of biodiesel in Brunei for most existing cars.

In 2020, out of Brunei’s average production of 110-kilo barrels per day of oil (Brunei Darussalam Department of Statistics, 2021, p. 20), 33-kilo barrels per day is estimated to be for local usability, by which 689 metric tonnes out of the total is diesel for various applications (Brunei Darussalam Department of Statistics, 2021, p. 20). Since 18% of the total diesel consumption is consumed by vehicles (ERIA & BNERI, 2020), this yields 124 tonnes per day or 45,260 tonnes per year of diesel consumed in 2020. To produce biodiesel from WCO, Brunei Darussalam can rely on edible oils for domestic food and beverage consumption. Brunei imported edible oils >BND 21.1 million in 2020 (Brunei Darussalam Department of Economic Planning and Statistics, 2020) from in forms of palm oil (as the main ingredient) from Indonesia and Malaysia and rapeseed and soybean oils as secondary ingredients (Wong, 2019).

Assuming 90% of the WCO is recycled annually within Brunei Darussalam and a conversion rate of 75% in the reaction, it would yield 8499 tonnes or 8,499,000 kg of biodiesel. Furthermore, since the estimation was aimed at B5 blend (5% biodiesel, 95% petroleum diesel), it is expected to yield 169,980 tonnes B5 blend biodiesel annually. The amount of diesel consumed by automobiles is about 45,260 tonnes per year. It shows great potential in replacing diesel with biodiesel for automotive fuel in Brunei, as the supply tripled the demand. This WCO to biodiesel process can be extremely valuable and feasible for application in Brunei to reduce the amount of disposal of WCO and simultaneously implement reliance on biodiesel for vehicles.

Production - B5 blend biodiesel

Some considerations to approximate the estimated annual cost of diesel supplied locally to prepare B5 blend biodiesel have been presented below:
- Actual cost of diesel to consumers: 0.31/L
- Agreed cost of diesel supply: 0.18/L
- Estimated amount of diesel required: 164,106,705L
- Total cost of diesel supply: BND$29,539,207

Table 7. Estimated annual revenue for the WCO to biodiesel production.

<table>
<thead>
<tr>
<th>Type of product</th>
<th>Quantity (L)</th>
<th>Unit Price (BND/L)</th>
<th>Amount (BND)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCO</td>
<td>11,516,260</td>
<td>0.2</td>
<td>2,303,252</td>
</tr>
<tr>
<td>B5 biodiesel production</td>
<td>172,743,900*</td>
<td>a. 1.15 without government subsidy**</td>
<td>198,655,485</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b. 0.50 with government subsidy***</td>
<td></td>
</tr>
<tr>
<td>Glycerol</td>
<td>8,000,000</td>
<td>2.2</td>
<td>17,600,000</td>
</tr>
<tr>
<td>Fertilizers</td>
<td>110,000</td>
<td>3</td>
<td>536,800</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>219,095,537</td>
</tr>
</tbody>
</table>

*Assuming a minimum of 75% conversion of WCO to biodiesel. The actual conversion is estimated to be in the range of 90-95%.
** vs $0.81/L diesel without government subsidy
*** vs $0.31/L diesel with government subsidy
Table 7 summarizes the assumptions and estimation of the annual revenue for biodiesel production from MDPI. The producers would be subjected to pay BND 0.20 per litre of WCO. Through a rough estimation, the possible amount of WCO recycled would be 11,516,260 litres and a total revenue of BND 2,303,252.

**Production of glycerol**

Glycerol is a by-product of the WVO-to-biodiesel production process. This can be utilized as an additional profitable product of the company which can be sold to a local pharmaceutical company for multipurpose uses such as raw materials for cosmetics and medicines. The expected production of glycerol in the process is 8,000,000 litres per year. Furthermore, through brief research on the potential market value of glycerol, this subchapter will take BND 2.2 per litre of glycerol as a selling price. This yields a total annual sale of BND 17,600,000 of glycerol.

**Production - K₃PO₄ fertilisers**

In addition to glycerol, a solid fertilizer, K₃PO₄, is another by-product of the WCO-to-biodiesel production process. It can also be utilized as another product. The expected production of K₃PO₄ in the process is 178,000 kilograms per year. Furthermore, through brief research on the potential market value of local fertilizers, this subchapter will take BND 3 per kilogram of K₃PO₄ as a selling price. It yields a total annual sale of BND 536,800 K₃PO₄ fertilizers.

**CONCLUSION AND RECOMMENDATIONS**

Production of biodiesel from WCO is plausible to be implemented in Brunei Darussalam. It is because petrol and diesel are primarily used as fuel for transportation and Brunei has been relying on edible oils for domestic purposes. It was roughly estimated that Brunei has an annual consumption of 12,591 tonnes of vegetable oil. Assuming a 75% conversion of WCO to produce the B5 blend biodiesel would result in 169,980 tonnes annually. This volume exceeds the current demand for petroleum diesel by a factor of three. With the total amount of diesel consumed in the country, biodiesel can replace petro-diesel. Glycerol and fertilizer by-products can also be sold locally.

**Author Contributions**

Conceptualization, MRB; writing — original draft preparation, MFA, AMBAM, FKNH, HHT, MHWMH and WYS; writing — review and editing, MRB. All authors have read and agreed to the published version of the manuscript.

**Funding**

This research received no external funding.

**Conflict of interests**

The authors declare no conflict of interest.

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