

Fatima Yahya Amer Al-Marani

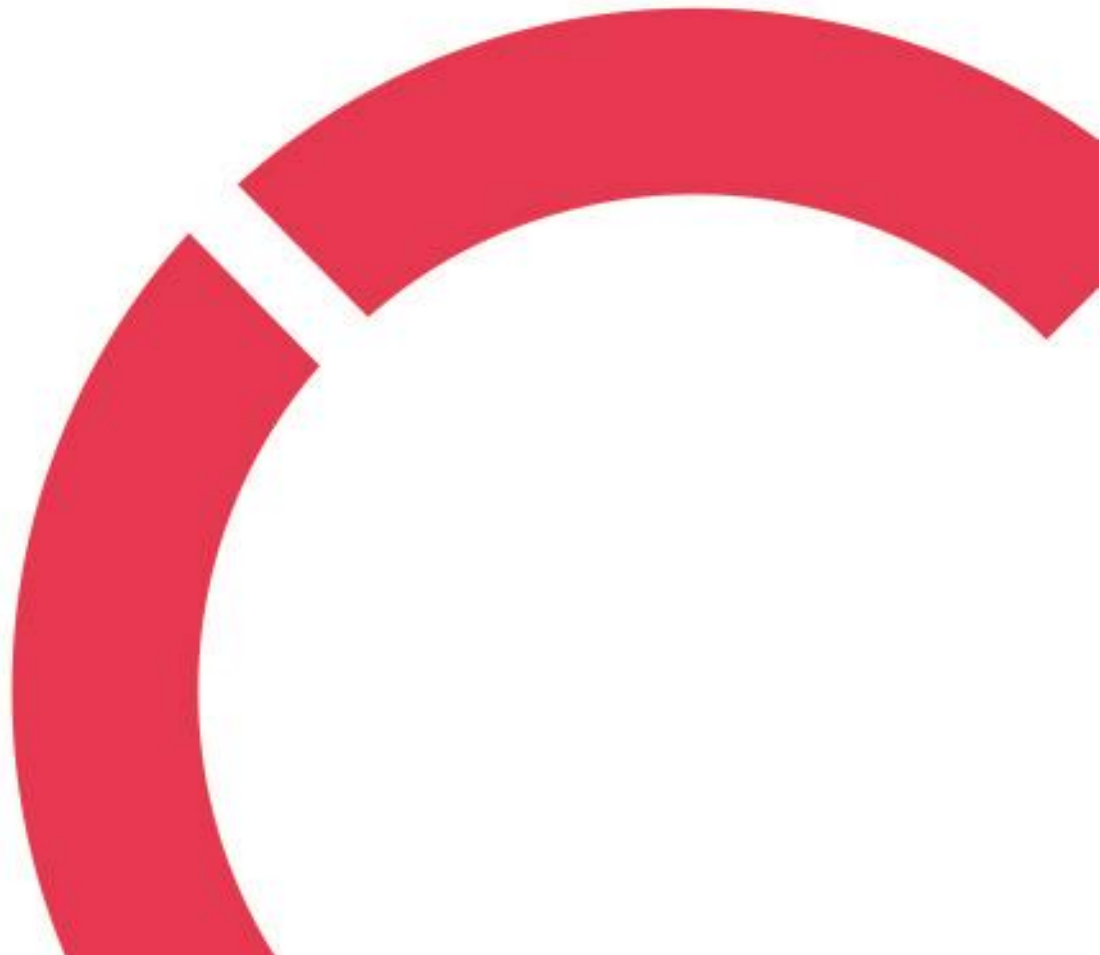
BIODIESEL PRODUCTION FROM WASTE COOKING OIL: PROCESSING, CHALLENGES AND OPPORTUNITIES IN YEMEN

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ABSTRACT

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<p>Biodiesel is a renewable, clean, environmentally safe energy that can replace conventional diesel effectively. Its potential contributes to reducing the great demand for petroleum-based fuel as well as covers the market needs. Fuel price is a real concern nowadays; therefore, it is important to find cheaper raw materials and components (catalyst and alcohol) for the production process to minimize the cost. Biodiesel production using waste cooking oil (WCO) is ideal, not only because of its low in cost but also it is a good step towards environmental protection and economic efficiency. However, it requires additional pre/post-treatment. To get around the drawbacks of the traditional transesterification approach, researchers have developed a variety of homogeneous and heterogeneous catalyzed transesterification reactions. Additionally, the final conversion, yield, and in particular the product quality has been considerably impacted by the use of innovative technologies such as membrane reactors, reactive distillation columns, reactive absorption, and ultrasonic and microwave irradiation. Biodiesel is a suitable alternative fuel for the diesel crisis in Yemen specifically. Its potential has been proven but the production on a large scale is still challenging.</p>		

Key words Alkali catalysed transesterification, biodiesel, Transesterification, WCO

CONCEPT DEFINITIONS

FAME: Fatty Acid Methyl Ester

FFA: Free Fatty Acid

WCO: Waste Cooking Oil

WFO: Waste Frying Oil

USD: Used Cooking Oil

CN: Cetane Number

ASTM The American Society for Testing and Materials

ABSTRACT
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1 INTRODUCTION

Energy consumption and demand correlate with population growth. The increase in population number increases the demand. According to the BP Statistical Review of World Energy, the total amount of petroleum-based diesel consumed worldwide increased in a decade, rising from 3.5 million tons in 2010 to 3.9 million tons in 2019 (Suzihaque, M., Alwi, H., Kalthum Ibrahim, U., Abdul-lah, S. & Haron, N. 2022). The world energy demand will increase by 53% by the year 2030 (Talebian-Kiakalaieh, A., Amin, N. A. S. & Mazaheri, H. 2013). Diesel fuel - a source of fossil fuel - is widely utilized in the engines of trucks, railroads, and the majority of military, agricultural, and construction equipment and vehicles due to its range of performance and efficiency. As projected by 25% of total energy consumption in 2021, the transportation industry in the United States utilized around 46.82 billion gallons of distillate fuel, or essentially diesel fuel (EIA,2022). Relying on traditional energy sources like fossil fuel results in disturbance of the climate and other environmental threats such as biodiversity loss, and greenhouse gas emission (GHG) brought on by its overuse. (Grönman, Pajula, Sillman, Leino, Vatanen, Kasurinen, Soininen, & Soukka 2019).

The depletion of global petroleum reserves, rising oil prices, environmental concern about vehicle pollution, and local atmospheric changes have necessitated searching for alternative clean, renewable energy sources. Significant desirable chemical properties such as being safe and non-toxic, biodegradable (Amin 2011), and carbon neutral (Mohamed 2011) defers biodiesel from non-renewable diesel. Biodiesel, fatty acid methyl ester FAME, produced from renewable sources, vegetable oils, or fats, is one of the most appealing alternative fuels that have minimal emissions as well as is compatible with regular engine injection (Hosseini, Nikbakht & Tabatabaei 2012). Biodiesel formation occurs mostly through a transesterification reaction between triglycerides and alcohol.

Vegetable oils such as sunflower oil, corn oil, and palm oil contain lipids that are converted to biodiesel by modification processes like pyrolysis, micro-emulsion, or transesterification. Transesterification is the most popular and effective process in terms of good-quality biodiesel production. However, food source utilization in biodiesel production is associated with food insecurity concerns. Therefore, a great interest is gained in using non-edible vegetable oils like waste/ used cooking or frying oil WCO as biodiesel production feedstock. Since the greatest issue in biodiesel industrialization is the cost, WCO is preferable because it reduces the cost by 60%-90% (Zhang, Dube, McLean, & Kates 2003). However, this type of feedstock involves impurities such as free fatty acids FFA due to cooking

processes. These impurities influence the yield and quality of biodiesel if not pre-treated. Saponification and equipment corrosion are some consequences of them if carried out using typical alkali-catalyzed transesterification. Therefore, alkali and acid-catalyzed in two-step trans-esterification is the solution to reduce FFA and obtain better conversion yield (Zahan, Zafar Iqbal, Reza Selim & Shahidur 2018)

Homogeneous (alkali and acid catalyzed) transesterification, heterogeneous catalyzed transesterification using solid (acid and alkali) catalysts as well as enzymatic and non-enzymatic catalysts are processes utilized to convert WCO to biodiesel (Mata, Martins, & Caetano 2010). However, each type of process has advantages and disadvantages as well as key factors that influence the yield of production. FFA in feedstock, temperature, molar ratio, reaction, type and amount of catalyst as well as intensity mixing are the major effecting factors in biodiesel production specifically in the base transesterification process according to researchers. (Suzihaque et.al 2022; Gude, Patil, Grant & Deng 2012). A clear effort is paid to find solutions and new techniques to overcome the drawback of conventional processes and maintain high-quality biodiesel at lower prices. For that, novel processes such as non-catalytic transesterification or supercritical methods and techniques such as reactive distillation, absorption, membrane, continuous flow, microwave, and ultrasonic are investigated and utilized.

Yemen is among the countries that heavily depend on fossil fuels with marked disability of fuel production to cover the demand. (Binhweel, Bahadi, Sambo, Hossain & Ahmed 2022) The only two refineries can only cover 23 % of the demand (Yemen Times Newsletter 2014). The huge shortage of diesel and price raise especially during the current political situation necessitate to search for proper alternative fuel. Biodiesel is found to be among the best candidate fuels to fulfill the needs. (Al-Weshali, Bamaga, Borgia, van Steenberg, Al-Aulaqi, & Babaqi 2015.) Its production in Yemen is promising in terms of feedstock availability like palm oil and Jatropha. ((Baggash & Abdulrahman 2010) However, for low-cost biodiesel production, WCO feedstock is much preferable which could reduce the incredible fuel price raise. On the other hand, production on a large scale is still challenging due to a lack of investment, technology, and infrastructure.

In this thesis work, an overview of biodiesel production from WCO is outlined. The study will provide an overview of biodiesel production processes particularly transesterification process and its different types, the advantages and disadvantages of biodiesel as fuel, benefits and challenges of biodiesel production from WCO, and the various production methods and new emerging techniques such as continuous flow, reactive and dual reactive distillation methods, reactive absorption, membrane reactor,

ultrasonic and microwave. The research will also assist and examine the biodiesel production potential and challenges in Yemen.

2 BIODIESEL

Biodiesel - non-petroleum-based diesel- is a renewable biofuel produced from vegetable oils or animal fats that has similar physical properties as petroleum distillate fuel (EIA,2020). It is an environmentally friendly alternative fuel for diesel that is being widely used in different applications including agriculture, transportation, and industrial applications. It is utilized in engines of trucks, railroads, and the majority of military, agricultural, and construction equipment and vehicles. Biodiesel utilization contributes to the environmental and health hazards reduction that is associated with the usage of conventional diesel. In the following sub-chapter, the chemistry and properties of biodiesel, as well as its advantages and disadvantages, are presented.

2.1 Biodiesel chemistry and properties

A typical biodiesel molecule consists of a long chain of carbon atoms with hydrogen atoms linked and what is known as an ester functional group at one end as seen in the lower part of Figure 1 (Goshen College; Muley & Boldor 2018). The process of transesterification, or ester exchange, of vegetable oils and animal fats produces a combination of fatty acid alkyl esters known as biodiesel (Mata et.al 2010). Unlike biodiesel, diesel consists of a long chain of hydrocarbons, but the ester group does not exist (see Figure 1 upper part) (Goshen College; Muley & Boldor 2018). According to the American Society for Testing and Materials (ASTM) biodiesel is defined as a monoalkyl ester of fatty acids, or a fatty acid methyl or ethyl ester (FAME) derived from plant/animal-based having the same chemical and physical properties as petroleum-based fuels. Biodiesel is commonly produced by transesterification where triglyceride reacts with alcohol in the presence of a catalyst to form alkyl ester and glycerol as by-products.

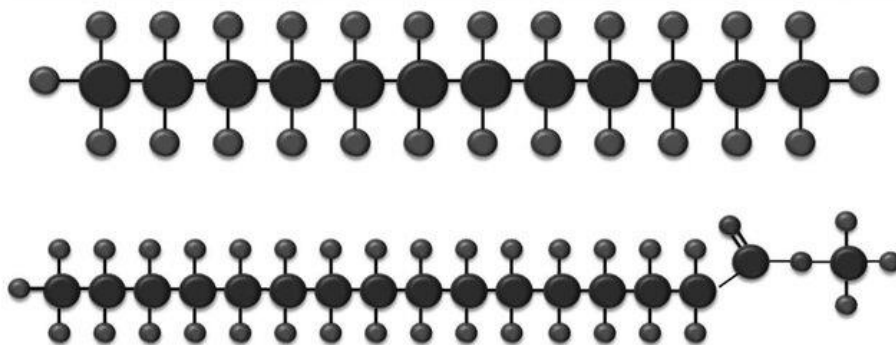


FIGURE 1: Biodiesel and diesel molecule structures. (Muley & Boldor 2018).

For biodiesel to be approved as a diesel alternative and utilized in ground transportation, its fuel characteristics must satisfy the requirements of ASTM D6751 or EN 14214 criteria such as density, liquid's kinematic viscosity, composition of fatty acid esters, iodine value, acid value, cloud and pour points, flash point, volatility, cetane number, water content, carbon residue, ash, and sulphur. (Mata et.al 2010.) Table 1 lists some physical properties for biodiesel. Based on the ASTM standard, table 1 compares the properties of biodiesel and diesel. According to the table, sulphur, ash, and carbon values of biodiesel are apparently less than those of diesel which emphasize its environmentally friendliness. Cetane number is higher in the case of biodiesel which proves its ignition ability. Other properties such as viscosity, density and flash points are still high compared to diesel, but they can be reduced and improved by blending.

Flashpoint is a property that increases the needed temperature for fuel ignition when it increases. For combustion purposes, lowering the flashpoint is preferable. However, the fuel is safer to transport because of the greater flash point. The flash point of biodiesel is ten times higher than that of regular diesel because it contains unsaturated long chains C18:1 (Catoire & Naudet 2004). Whereas pour point, the temperature at which a liquid begins to lose its fluidity and solidify, as well as cloud point are correlated with the quantity of fatty acid, increasing with the increase of saturated fatty acid (Tyson & McCormick 2006). In comparison to regular fuel, biodiesel typically has higher cloud and pour points (Al-Mashhadani & Fernando 2017.)

The liquid's kinematic viscosity, which essentially gauges how thick the fuel would be, is the resistance to flow. A complete combustion may not be possible with low viscosity and the fuel injection system would become clogged with high viscosity. The feedstock and measurement technique, however, may affect viscosity. Compared to fossil fuel, biodiesel has a higher viscosity, according to reports (Dhar, Kevin & Agarwal 2012.). Cetane number is another important property for fuel quality identification. When fuel is pumped into a diesel engine, its ability to ignite is measured by the cetane number (CN). The fuel gets more efficient and quicker to ignite or burn the higher the CN. Accordingly, if the CN is higher, the fuel will ignite faster. Typically, saturated, longer carbon chains have higher CN values. Therefore, the CN will be higher than the feedstock's hydrocarbon concentration. (Al-Mashhadani & Fernando 2017.)

Sulfur increases the discharges of particulate matter into the exhaust, increasing pollution (Sirviö et al. 2016; Kalghatgi 2014). The engine cylinder will corrode as a result of the increased sulfur in the

gasoline pollution (Sirviö et al. 2016). Long-term exposure to sulfur gaseous emissions will result in cardiac illnesses and eventual mortality pollution (Sirviö et al. 2016). Exposure to sulfur gaseous emissions can also induce respiratory difficulties. Therefore, the better the fuel, the lower the sulfur content (Sirviö, Niemi, Heikkilä et al. 2016). One of the more frequently accepted explanations for the decrease in emissions of CO, CO₂, hydrocarbons, SO₂, particulates, and smoke is the presence of sufficient oxygen in biodiesel. Compared to diesel, which has no oxygen, biodiesel has 10% more oxygen (Agarwal & Das 2000). As shown in Table 1, biodiesel outperforms gasoline and diesel in a number of categories, including higher cetane number, low ash content, and low carbon residue, while the other characteristics can be improved through blending. Environmental friendliness is by far biodiesel's biggest advantage over petroleum diesel. Benefits of using biodiesel as a diesel fuel include portability, accessibility, renewability, improved combustion efficiency, and low sulfur and aromatic content. (Cordero-Ravelo & Schallen-berg-Rodriguez 2018; Suzihaque, Alwi, Kalthum Ibrahim, Abdullah, & Haron 2022.)

TABLE 1: Diesel and Biodiesel properties comparison. (Sakthivel, Ramesh, Purnachandran, & Mohamed Shameer 2018)

Properties	Biodiesel	Diesel
Flash point (°C)	130 minimum	60–80
Pour Point (°C)	–15 - –16	–35 - –15
Kinematic viscosity at 40°C (mm ² /s)	1.9 – 6.0	2.0–4.5
Density at 15°C (kg/m ³)	880	820–860
Cetane number	47 minimum	46
Ash content (%)	-	100 maximum
Carbon residue (%)	0.05 maximum	0.2 maximum
Sulphur content (%)	0.002 maximum	-
Water content (%)	0.005 vol% maximum	0.05 maximum
Higher heating value (MJ/kg)	42.65	46.48

2.2 Biodiesel pros and cons

Basically, biodiesel is a renewable, biodegradable, environmentally friendly, and nontoxic fuel which makes it a good replacement for fossil fuel. This type of biofuel has advantages in terms of manufacture, environment, and human health, however, it has also some disadvantages. In this chapter, the cons and pros will be discussed. Starting with the advantages of biodiesel, in terms of the environment, biodiesel has almost no sulfur and lowers the generation of ozone, carbon monoxide, nitrogen oxides, and hydrocarbon emissions. In terms of human health, at any concentration, biodiesel minimizes engine particulate emissions that contribute to respiratory issues including asthma. (UWA; Teresa, Alleman and Robert; Chozhavendhan, Vijay, Fransila, Praveen Kumar, & Karthiga 2020)

Biodiesel can still operate in regular diesel engines without modification, although new diesel engines feature design adjustments to maximize performance with biodiesel. Also, Petro-diesel is frequently combined with biodiesel to enhance its lubricating characteristics (Chozhavendhan et.al 2020), which are impacted by sulfur removal. Lubricity can rise by up to 50% when biodiesel is added to Petro-diesel at a rate of just 2%. As a global standard, biodiesel can now be mixed up to 20% with Petro-diesel. However, especially with new, upgraded engines, any percentage mix up to 100% can be employed. Additionally, biodiesel can aid in the dissolution of engine sediments when mixed with Petro-diesel. Furthermore, using a production and refining process, biodiesel can be created from any source of fatty acids, including animal fats. Domestically produced, renewable oilseed crops including soybeans, canola, cottonseed, mustard seed, and palm can be used to make biodiesel. Besides that, some waste materials, like chicken fat, are recyclable and can be converted into biodiesel. Finally, large-scale manufacturing of biodiesel becomes more economically feasible as Petro fuel prices climb. (University of West Alabama (UWA))

Although biodiesel has many advantages as mentioned, but it also has some drawbacks. Biodiesel has subpar cold flow characteristics. This suggests that a diesel engine may need to be modified to warm the fuel before starting, or that a dual-fuel vehicle may be created where Petro-diesel is used to warm biodiesel first. Also, compared to Petro-diesel, biodiesel has a calorific value of 33 MJ/L, which is 9% less. When a substance burns, the calorific value describes how much heat is generated (UWA). Over time, biodiesel causes rubber and elastomers to soften and degrade, which has an impact on the fuel hose and fuel pump. Consequently, engines must be adjusted. And it is possible for fuel to enter motor

oil with greater biodiesel ratios, leading to the production of sludge. As well as it may dissolve the paint. Some biological growth is also possible because biodiesel has about six months shelf life. Concerning the environment, a huge space of land is required for biodiesel production to replace fossil fuels. For instance, to replace the US usage of fossil fuels with biodiesel, soybeans would take double the size of the country's area to be produced. Moreover, in order to make room for biofuel crops, vast areas of Southeast Asian rainforests, mainly in Sumatra and Kalimantan, have been devastated. Finally, choosing to grow crops for biodiesel instead of food has a number of repercussions such as the rise of food crops cost (OECD 2007).

3 BIODIESEL FEEDSTOCK

It is possible to produce biodiesel from a variety of raw sources, most of which are edible (Kansedo, Lee, & Bhatia 2009) waste cooking oils (Meng, X., Chen, G. & Wang, Y. 2008) and animal fats (Encinar, Sánchez, Martínez, & García 2011), such as tallow, yellow grease (Bhatti, Hanif, Qasim, & Ataur-Rehman 2008), lard (Shin, Lee, Ryu, & Bae 2012) and chicken fat (Gürü, Metin, et al. 2010) as well as leftovers from the fish oil industry's manufacturing of omega-3 fatty acids., (Costa, Al-meida, Alvim-Ferraz, & Dias 2013). Because they may grow in ponds, sewage, or shallow ocean water without disturbing agricultural land, algae are another viable feedstock for biodiesel and have a great potential to replace edible oil. (Chen, Liu, Zhang, Chen& Wang 2012)

31% of biodiesel generated globally is made from palm oil, 27% from soybean oil, and 20% from rapeseed oil (Changmai, Vanlalveni, Ingle, Bhagat, & Rokhum 2020). However, the main raw materials for the production of biodiesel in the United States are vegetable oils, primarily soybean oil (FIGURE 2). Other significant U.S. biodiesel feedstocks come from restaurants' yellow grease and used/recycled cooking oil as well as animal fats from slaughterhouses. Rapeseed, sunflower, and palm oils are common feedstocks used to make biodiesel in various countries. Additionally, algae are a potential source for biofuel production. (Eia 2021). Figure 2 illustrates the major used biofuel feedstock in the US.

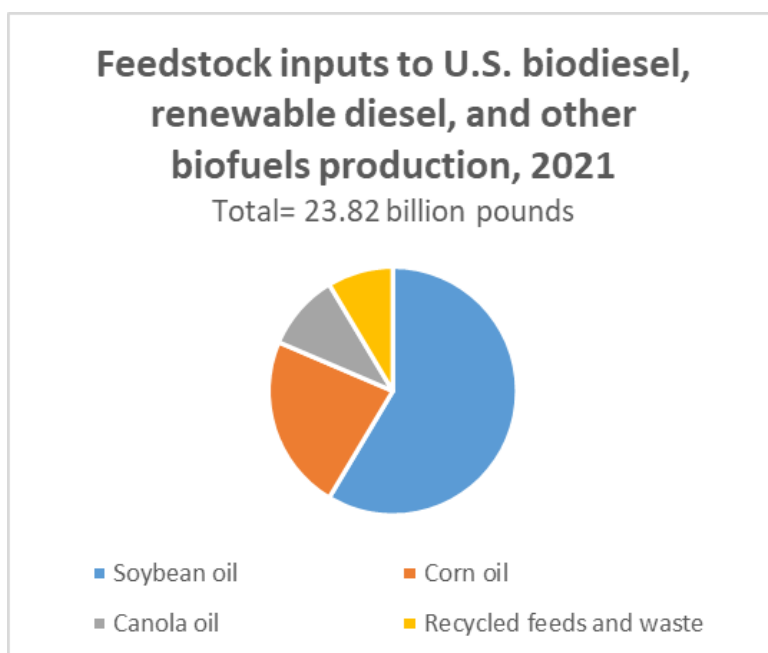


FIGURE 2. Feedstock inputs to for biofuel production in US (eia 2021)

3.1 Waste cooking oil (WCO)

Waste cooking oil (WCO) used cooking oil (UCO) and frying oil (WFO) are terms referring to oils or fats that have been used in cooking or frying. They are leftovers or wastes collected from restaurants or household to be recycled or treated to be further used in different applications including biodiesel production. In terms of global vegetable oil consumption as well as WCO production, it is stated that more than half of the world's consumption of vegetable oil is accounted for by China, India, the United States (US), and EU nations (Teixeira, Nogueira, Nunes 2018). Consequently, 5 million tonnes of WCO are thought to be produced in China per year (Chen, Liu, Yao, Qi, Yan 2017), from 0.1 to 0.5 million tonnes/per year in Japan (Teixeira et al. 2018), and 1,660,000 tones/year in EU countries combined (EWABA 2016).

3.2 WCO structure

Basically, the primary constituents of vegetable oils are combinations of triglycerides with varying substitution patterns such as fatty acids (Colón 2001) while WCOs are long-chain fatty acids mixtures (mostly linoleic, linolenic, and oleic), in the form of tri-, di-, and mono-glycerides, and a variable fraction of free fatty acids (FFA) resulting from the frying process. These fatty acids are utilized as raw materials for different industries (Singhabhandhu & Tezuka, 2010.) An example of a vegetable oil molecule is shown in FIGURE 3. The carbon and hydrogen atoms are arranged in long rows, but the size of the molecule is nearly three times that of a typical diesel molecule. Similar to biodiesel (in blue), it also contains ester functional groups.

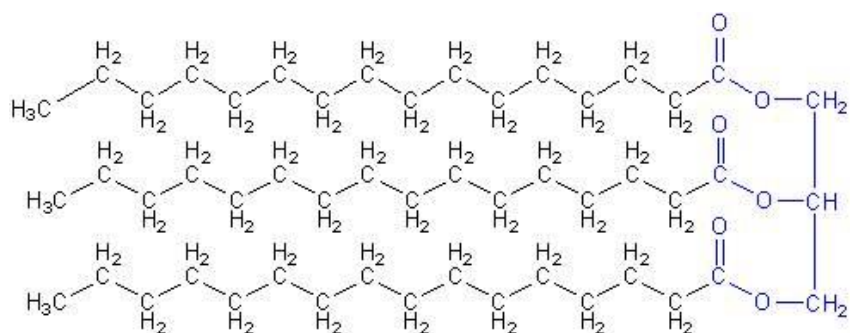


FIGURE 3. Vegetable oil molecule structure (triglyceride). (Goshen College).

In terms of WCO conversion, they can be used as primary raw materials in a variety of industrial processes, such as the manufacturing of bio-lubricants (Karmakar, Ghosh, & Sharma 2017) or fuel (Hazrat,

Rasul, Khan, Ashwath, & Rufford 2019; Chattopadhyay, Singh, & Prakash 2018; Chry-sikou, Dagonikou, Dimitriadis, & Bezergianni 2019), or as additives for asphalt (Ahmed, & Hossain 2020) animal feed and biodiesel production. The existence of triglycerides structure in WCO made it possible to be converted to biodiesel using a transesterification process. However, the main drawback of this raw material is that WCO involves some impurities like FFA which requires pre-treatment process, otherwise biodiesel production is restricted by saponification formation. (Cai, Wang, Teng, Chong, Wang, Zhang, & Yang 2015).

3.3 Benefits of WCO utilization as raw material

WCO is harmful to consume (Ganesan, Sukalingam & Xu, 2019), a drainage issue, and a significant water and soil contaminant. WCO has a significant potential to be converted to biodiesel in order to prevent the environmental harms of disposal while still using it effectively (Cao, Ruan, Chen, Hong & Cai, 2017). WCO is triglycerides in structure which makes it easy to convert to biodiesel through a transesterification reaction. Therefore, it creates renewable, biodegradable, and non-toxic fuel. Recycling wasted cooking oil results in the production of biodiesel fuels. Because biodiesel fuels are clean, they reduce pollution overall and greenhouse gas emissions. (Cordero-Ravelo, V. & Schallenberg-Rodriguez, J. 2018.). Restaurant owners who recycle spent cooking oil lessen the country's dependency on imported oil. Dependence on indigenous biodiesel resources lessens possible risks to the country's economic health and national security, particularly in the event of an oil embargo. By recycling waste cooking oil, the plumbing in the kitchen will last longer and cost less to replace. Furthermore, working with an oil collection firm is essential to maintain compliance with local laws and avoid paying fines for improper disposal (Mahoney Environmental). WCO as feedstock for biodiesel production is cheaper compared to other raw materials, therefore the expenses for the production process reduce, and the price of the product becomes affordable (Yaqoob, Teoh, Sher, Farooq, Jamil, Kausar, Rehman 2021). In addition, it is a great replacement for clean vegetable oils as feedstock for biodiesel production.

3.4 Challenges

Prior to producing biofuel, it is crucial to ascertain the oil characteristics in the case of WCO. This is due to the variation in WCO properties brought on by factors like the type of fried food, sugar and protein content, frying time, oil reuse, and utilization mode, which would result in the formation of polymers, dimers, oxidized triglycerides, and free fatty acids. Therefore, it is crucial to ascertain whether the WCO

includes a high acid value in order to increase the yield and efficiency of biodiesel production (Ben Hassen Trabelsi, Zaafour, Baghdadi, Naoui, & Ouerghi 2018.). The high free fatty acid content of WCO presents the main obstacle to its application in the production of biodiesel; as a result, two-step catalytic conversion is frequently employed. Therefore, the production expenses increase. The impurities involved in WCO could cause corrosion to equipment and post-treatment such as the separation of emulsion formed by saponification. Consequently, cooking oil's viscosity increases while its molecular mass and iodine levels drop throughout the saponification process (Alemayehu, & Teshita 2014). In the meantime, soap formation uses up some of the catalysts and lowers the overall yield (APPENDIX 1).

4 BIODIESEL PRODUCTION PROCESS

Typically, biodiesel is made utilizing four basic methods from vegetable oils and animal fat. The techniques are the transesterification process which is the most commonly used method, pyrolysis, and micro-emulsion, as well as it can be directly used and blended. Vegetable or animal fat can be used as fuel in direct injection engines since it has a sufficient amount of power and a decent heating value. However, because of its unfavourable characteristics, it has some issues and cannot be utilized in a DI engine without being modified. As a solution for this issue, blending it with fossil fuel is applied to improve fuel quality as well as reduce fossil fuel consumption. (Rajalingam, Jani, Senthil Kumar, & Adam Khan 2016.)

Thermal cracking or pyrolysis is another biodiesel production method that aims to convert complex hydrocarbons into simpler structures with or without a catalyst. Thermal cracking, which produces biodiesel at temperatures between 250°C and 350°C, uses three different materials as catalysts: alumina, zeolite, and red mud (Parawira, 2010). The density and viscosity of oil, which are two essential engine atomization qualities, decrease as a result. Also, the process that works to improve the viscosity and atomization properties of the oil is known as micro-emulsion. Basically, an isotropic mixture of liquid, water, and surfactant is used to lower the surface tension of a liquid (Abhishek 2014; Yusuf, Kamarudin, & Yaakub, 2011). Alcohol is also used to increase the volatile property of an oil to reduce smoke and alkyl nitrate is used to increase the cetane number. Despite the mentioned improved characteristics that this process provides, the micro-emulsified diesel can interface some problems if used in diesel engine like incomplete combustion, carbon deposit, and nozzle failure. (Rajalingam, Jani, Senthil Kumar, & Adam Khan 2016).

In addition to the previous biodiesel production methods, conventional transesterification is the most commonly used process to produce biodiesel. In essence, it is a reaction between triglycerides in vegetable oils and alcohol to produce mono alkali ester (biodiesel) and glycerol as by-product (Raghuvanshi; Singh 2014). A catalyst is also involved in the process to fasten the reaction. Among other methods, transesterification is giving better fuel quality and yield and is cost-efficient. (Rajalingam et al, 2016). There are several ways to make biodiesel from used cooking oil using transesterification method, which can be categorized into three basic categories: homogeneous, heterogenous, and non-catalytic transesterification. (Talebian-Kiakalaieh et.al 2013)

4.1 Homogeneous catalysed transesterification

Homogeneous catalytic transesterification utilizes homogeneous catalysts. Alkali (NaOH, KOH, CH₃ONa), acid (sulfuric acid, phosphoric acid, sulfonated acid, and hydrochloric acid) catalysts or both can be utilized separately or as a two-step process. The table in APPENDIX 3 represents the condition for the best yield of conversion for each type of process. Alkali catalyzed process is commonly used due to the catalyst's low cost and faster reaction time. On the other hand, the process consumes energy and is highly sensitive to water and FFA involved in the feedstock which requires pre-treatment. Unlike the alkali-catalyzed process, acid catalysts are unaffected by free fatty acids and perform better with vegetable oils that have an FFA content above 1% (Freedman, Pryde, & Mounts 1984). But acids can result in numerous salt interactions, which lead to corrosion. So, the esterification of feedstock above 2% FFA using an acid catalyst is preferable as a first-step process (Meng, Chen, Wang, 2008) followed by alkali-catalyzed transesterification to avoid saponification and accelerate the reaction time. Acid catalysts are slower than base, thus the reaction time increases.

In the case of waste cooking oil WCO base-catalyzed transesterification to biodiesel, the production process stages follow the methodology in Figure 4. The first stage is feedstock collection, waste cooking oil WCO is chosen as feedstock for biodiesel production. The residue of cooking known as waste cooking oil (WCO) can be found in homes, restaurants, and other eating places. This step can be challenging in absence of collection systems as it is in many countries including Yemen. Since the feedstock is a residue, it requires treatment to remove impurities such as water and FFA before moving to the conversion process.

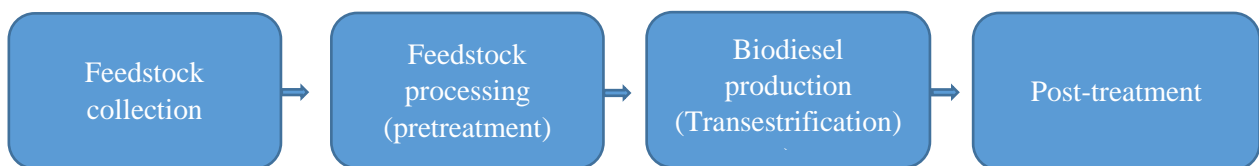


FIGURE 4. Biodiesel production chain stages (Mata, & Martins, 2010)

4.1.1 Pre-treatment process

The existence of triglycerides structure in WCO makes it possible to be converted to biodiesel using a transesterification process. However, WCO undergoes oxidation, hydrolysis, and polymerization reactions during the frying process which makes it different from fresh cooking oil. Values of properties such as density, kinematic viscosity, acid value, and iodine value are very high in WCO, so they are restricted to a standard limit for maximizing biodiesel production yield. (Cordero-Ravelo, Schallenberg-Rodriguez 2018). One obstacle to WCO usage as feedstock for biodiesel production is that it contains undesired components like (free) fatty acids, water, phospholipids, and other suspended impurities that effects negatively the reaction performance and therefore minimize the production yield. (Cordero-Ravelo, Schallenberg-Rodriguez 2018)

Free Fatty Acids are chains of hydrogen terminating a carboxyl group that are unbound and therefore less stable than neutral fatty acids (FIGURE 5). They are therefore more likely to oxidize and get rancid. (Di Pietro, Mannu, & Mele 2020). The normal FFA content in waste oil and animal fat is 2% (Watanabe et al. 2001), typically 15%, and can be higher than 40% (Van Gerpen et al. 2004; Canakci, 2007). Different kinds of oils contain various fatty acids, typically with carbon chains ranging from C12 to C20 with a majority of C16 and C18 molecules. Vegetable oil typically contains the following five fatty acids: oleic (C18:1), linoleic (C18:2), palmitic (C16:0), and linolenic (C18:3).(Di Pietro.M, et.al, 2020.)

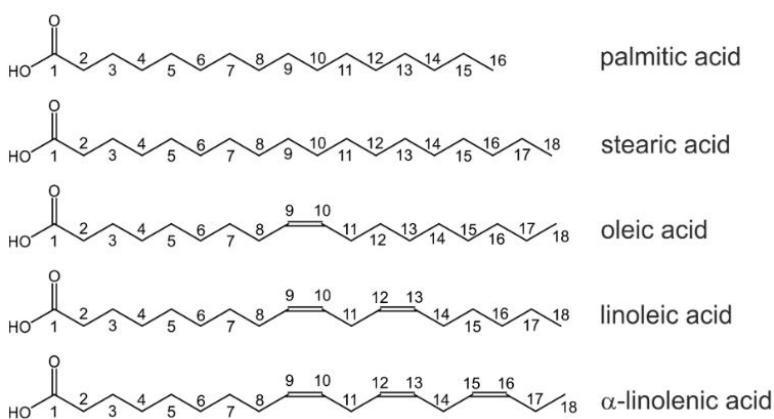


FIGURE 5. Chemical structure of free fatty acids in WCO. (Di Pietro.M, et.all, 2020)

The transesterification process is sensitive to feedstock purity. Free fatty acid (FFA) limits the reaction rate by orders of magnitude, as well as water (Cai, Wang, Teng, Chong, Wang, Zhang, & Yang 2015; Guo 2006; Canakci, 2007). High FFA content also leads to saponification instead of conversion to biodiesel (ester) since it reacts very fast with the (base) catalyst resulting in catalyst consumption (Gerpen et al., 2004). Additionally, the saponification reaction encourages the development of emulsions that cause issues with biodiesel purification and post-treatment procedures. Basically, the formed soap limits the mass transfer between phases, reduces the reaction rate and selectivity to biodiesel, and complicates the separation of phases at the end of the reaction (Aran-da, Santos, Tapanes, Ramos, & Antunes 2008). As a result, the yield of biodiesel production is minimized.

To ensure better production yield, a pre-treatment process is required to minimize FFA content in WCO to less than 2% before undergoing a transesterification. For that, an acid esterification reaction is conducted to convert FFA into methyl ester (Aranda et al. 2008; Issariyakul, Kulkarni, Dalai, & Bakh-shi 2007). FFA reacts with excess alcohol (methanol) to ensure full FFA conversion in the presence of an acid catalyst (H_2SO_4) producing ester and water (Meng et al. 2008). The water by-product needs to be removed or controlled in order to minimize the amount of alcohol required and avoid biodiesel production problems further downstream. A membrane reactor is one approach that could manage water removal during the reaction. (Mata et al. 2010.)

Water content in waste oils is another component that inhibits esterification and transesterification. It is reported a range of 1-5% (w/w) water in oils (Rice, Frohlich, Leonard, & Korbitz 1997). The presence of water makes the hydrolysis of triglycerides and FFA more likely, reduces the yield of esters, and makes it difficult to separate esters from glycerol and wash them out of the water. The presence of water in feedstock would also affect biodiesel quality. Consequently, a reduction in the heat of combustion, corrosion of fuel system components, and an acceleration of the hydrolytic reaction would likely happen. (Atadashi, Aroua, Abdul Aziz, Sulaiman 2012.) Therefore, the water content in the feedstock should be less than 0.06% (w/w) (Rice et al. 1997). For excess water removal, WCO is heated up to its boiling point (100-120 °C) to evaporate (Demirbas, A., 2008),

Other impurities such as solid particles and sodium chloride resulting from frying food are also undesired components that need to be eliminated. According to the feedstock characteristics, either filtration, pressing, or centrifugation can be conducted for solid particle separation. The presence of chloride causes corrosion which therefore needs to be removed or requires investment in stainless steel equipment

that is a corrosion-resistant material. (Mata et.al 2010.) After impurities removal from the feedstock, transesterification, the conventional biodiesel production process, is the next step. The pre-treated oil is suggested to be stored in a heated tank at 55-60 °C (Canakci and Van Gerpen.,1999).

4.1.2 Alkali catalyzed transesterification

In this chapter, the transesterification process of waste cooking oil for biodiesel production will be explained in more detail. The transesterification can be directly carried out at 2% FFA content without pre-treatment (esterification). Acid-catalyzed esterification is conducted otherwise if the feedstock contains more than 2% FFA. (Talebian-Kiakalaieh et.all 2013) Figure 6 shows the transesterification of triglycerides to ester and glycerol. Short-chain alcohol replaces the glycerol in triglycerides during transesterification and the catalyst accelerates the reaction. The first phase of the operation is depicted in Figure 6 as a series of three reversible steps that transform triglycerides into diglycerides, monoglycerides into glycerol, and monoglycerides into monoglycerides. Each step results in the creation of an ester, and as a result, one triglyceride molecule yields three ester molecules. These ester molecules are biodiesel. The chemical conversion of oil to biodiesel occurs as seen in Figure 6. Basically, alcohol breaks the bond (highlighted in yellow) to unwind the backbone which becomes glycerol then the methoxy group (from alcohol) is attached to the other part to be an ester (biodiesel).

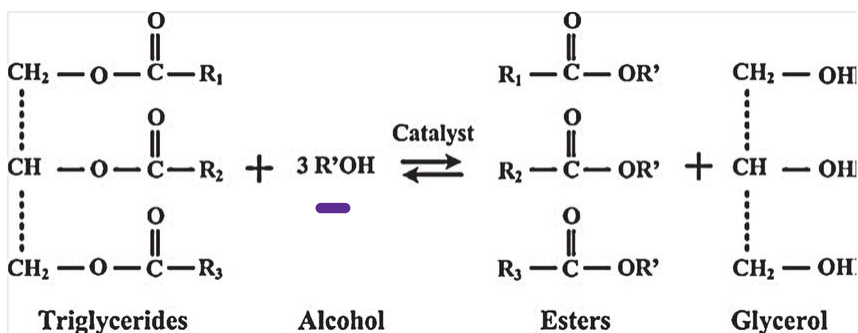


FIGURE 6. Overall transesterification of triglycerides with alcohol (Mata, Martins, & Caetano 2010)

Basically, to move the equilibrium to the product side and guarantee a complete conversion of the triglycerides, an excess of a primary alcohol is necessary. The optimum alcohol (mostly methanol or ethanol) intake will depend on the circumstances (3:1,6:1,..) (Van Gerpen, 2005). Typically, conventional transesterification is a process of mixing pre-treated oil and alcohol in the presence of a base catalyst (KOH or NaOH) to fasten the reaction, existence of heat (50-70 °C) in a reactor and allowed it to react for a certain time. Two essentially immiscible phases are created after the chemicals are combined: one

non-polar phase, which contains triglycerides and esters, and the other polar phase, which contains glycerol and alcohol. As soon as the reaction is complete, the glycerol is eliminated by allowing the two phases to develop and settle. The excess alcohol that did not undergo a reaction and the catalyst is then taken out of both phases (of esters and glycerol) and recycled back into the reactor (Mata et.al 2010.) (see FIGURE 7).

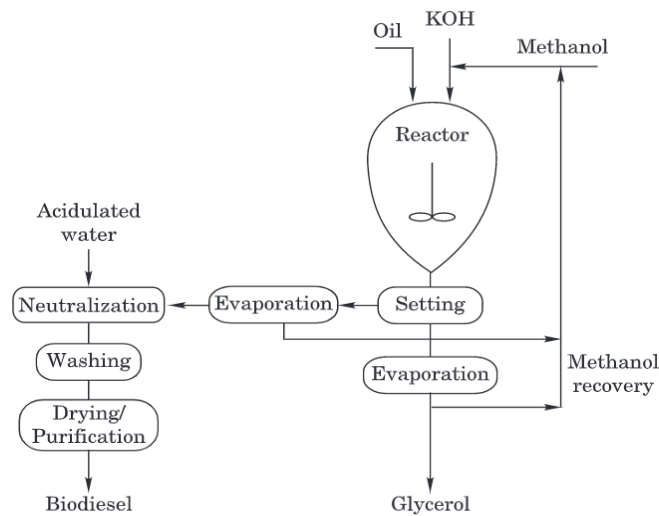


FIGURE 7: Flow chart for biodiesel production flowchart with alkaline catalysis (Mata, & Martins, 2010)

4.1.3 Process considerations

The transesterification process causes a significant change in the viscosity of the vegetable oil. The product has low viscosity like fossil fuels. After transesterification, the biodiesel's flash point decreases and its cetane number rises. The output of biodiesel during the transesterification process depends on a variety of variables, including the catalyst, moisture content, the presence of free fatty acids (FFA), and the molar ratio of the alcohol to the oil (Gude, Patil, Grant, & Deng 2012; Highina, Bugaje, & Umar 2012). Biodiesel production increases with the increase in temperature and time. Oils become less viscous as the temperature rises, which speeds up the reaction process and cuts down on reaction time. Lower temperature results in insufficient mixing and the viscosity of oil remains high, but also high temperature leads to alcohol evaporation (Anitha, & Dawn 2010) and speeds up the saponification of

triglycerides (Mathiyazhagan, & Ganapathi 2011). In order to prevent alcohol from evaporating, the temperature of the transesterification reaction should be kept below the boiling point of alcohol. So, the temperature should be at the optimum 60 °C. (Anitha, & Dawn 2010)

The oil-to-alcohol ratio is another important factor in transesterification. Due to the reversibility of the esterification process, it is recommended to either use excessive alcohol or remove one of the products from the reaction mixture in order to move the reaction to the right and increase the amount of biodiesel produced. Methanol is a preferable alcohol due to its low price and is polar and has the shortest chain. Compared to methanol, ethanol is the preferred alcohol since it can be produced from agricultural products, is renewable, and has biologically less harmful environmental effects. Alcohol to oil ratio is affected by the type of catalyst by which the acid catalyst necessitates a greater ratio than the base (1:15 for acid, 1:6 for base). Lower ratio results in reverse to reactant since transesterification is reversible. Therefore, biodiesel will not be produced. (Reddy, Saleh, Islam, & Hamdan 2017.)

Catalyst type and concentration are essential in transesterification. The quality of the oil or fat, the alcohol, and the process method is generally what determines the type and quantity of catalyst required. Acid catalysts are used for high FFA content in feedstock and base catalyst is used in low FFA (Suzihaque et.al 2022). Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the two most often utilized catalysts for the manufacture of biodiesel. The pure raw material prefers to use base catalyst because it is 4000 times faster than acid (Suzihaque et.al 2022). As more active sites are made available by the addition of more catalyst during the transesterification process, the yield of esters typically increases. However, because the catalyst is so expensive, this method is not practical. Therefore, it is crucial to establish the ideal concentration of the catalyst required for the transesterification process (Jagadale, & Jugulkar 2012). On the other hand, high catalyst concentration reduced biodiesel yield by forming slurry, increasing viscosity, and then increasing soap formation (Korkut, & Bayramoglu 2018).

The conversion of fatty acid esters has been reported to increase with an increase in reaction time. The ideal transesterification reaction period depends on the feedstock, catalyst, and concentration. Similarly, the time given should be sufficient to allow good mixing but not so long that the ester is hydrolyzed and saponified (Suzihaque et.al 2022). Due to the transesterification reaction's reversible nature, this causes the production of biodiesel to decline. (Reddy et.al 2017). The optimal time is 60 minutes-5 h (Eevera, Rajendran, & Saradha 2009). As oils and alcohols are not totally miscible and reaction can only occur in the interfacial region between the liquids, transesterification reaction becomes a lengthy process, mixing is crucial to the process. Depending on how much mixing is needed for the transesterification

process, the intensity can be altered. (Jagadale et al. 2012.) When using feedstocks with high viscosities, such as vegetable oils, the intensity of the mixing is typically increased to ensure adequate and uniform mixing of the feedstock (Jagadale et al. 2012).

On the transesterification of glycerides with alcohol employing a catalyst, the free fatty acid and water contents have a significant impact. The low yield of the biodiesel product is caused by the high free fatty acid (FFA) concentration, which is greater than 1% w/w and makes soap generation and product separation very difficult (Shereena, & Thangaraj 2009). The separation of glycerol from biodiesel is further complicated by the development of gels and foams (Mathiyazhagan, Ganapathi 2011). The presence of water in WCO accelerates the hydrolysis reaction while reducing the amount of ester formation (Shereena et al. 2009). The transesterification of the glycerides is hampered by the production of ester and water as a result of the FFAs' conversion of waste cooking oil to biodiesel and alcohol, respectively. (Berchmans, Hirata 2008) Therefore, water content should not be more than 0.5% in order to get a biodiesel yield of 90%, and it is riskier for an acid-catalyzed process than a base-catalyzed reaction (Arun, Sampath, Siddharth, & Prasaanth 2011).

4.1.4 Post-treatment

The most commonly used biodiesel production method at an industrial scale is the homogeneous alkali-catalyzed process (transesterification). The mixture is allowed to separate after the transesterification procedure into an upper layer of methyl esters and a lower layer of glycerine that has been diluted with methanol. The methanol that has not yet reacted is removed by air stripping or vacuum distillation and added back into the process. Depending on the procedure, water can be used to re-move sodium soaps and catalyst remnants from the methyl esters. To further break down catalyst residues and sodium soaps, modest volumes of concentrated phosphoric acid (H_3PO_4) can be added to the raw methyl esters. The by-product of making biodiesel, glycerol, can be financially valued by being used as a raw material in the pharmaceutical, cosmetic, or food industries, for example. However, the growth of bio-diesel has flooded the market with glycerine, driving down the price. Therefore, alternate methods of glycerol valorization must be found. Since it is not economically feasible to further process or purify glycerol in order to meet the requirements mandated for its usage in other applications, many bio-diesel companies are currently burning glycerol for heat production in the biodiesel production process (Mata & Martins 2010).

4.2 Heterogeneous catalyzed transesterification

Different techniques for producing biodiesel have used various kinds of heterogeneous catalysts. These catalysts are ion exchange resins (Marchetti, & Errazu 2008; Furuta, Matsushashi, & Arata 2006; Park, Lee, Kim, Lee, & Lee 2008), sulfated oxides (Sakai, Ka-washima, & Koshikawa 2009; Holser Ronald, Doll Kenneth, & ErhanSevim 2006; Alba-Rubio, Vila, Alonso, Ojeda, Mariscal, & Granados 2010), heterogeneous base/acid catalysts and waste material based heterogeneous catalyst (Deka, Basumatary, & Lee 2011; Chakraborty, Bepari, Banerjee 2011), carbon-based heterogeneous catalyst (Shu, Gao, Nawaz, Liao, Wang, & Wang 2010; Dekhoda, West, Ellis 2010), and heterogeneous catalysts based on enzymes (Hama, Yamaji, Kaieda, Oda, Kondo, & Fukuda 2004; Du, Xu, Liu, & Zeng 2004). Biodiesel production by heterogeneous solid catalysts instead of conventional homogeneous catalysts leads to economical production costs due to the catalyst's ability to recycle and be reusable (Suppes, Dasari, Doskocil, Mankidy, & Goff 2004), the possibility for transesterification and esterification to occur simultaneously (Furuta, Matsushashi, & Arata 2004), and catalyst (solid base) consumption reduction. Mbaraka and Shank (Mbaraka, & Shanks 2006) reported that 88 tons of homogeneous catalyst (NaOH) was necessary for 8000 tonnes biodiesel production.

Contrarily, Dossin et al. (2006) employed just 5.7 tons of heterogeneous solid catalyst (supported by MgO) (Dossi, Reyniers, Berger, & Marin 2006) for 100,000 tonnes of FAME production. However, the main drawback of solid catalyst application is the formation of three phases mixture (catalyst, oil, and alcohol). There are two key solutions for the mass transfer problem. The first is the application of cosolvents such as n-hexane, dimethyl sulfoxide (DMSO), ethanol, and tetrahydrofuran (THF) that improve the miscibility of alcohol and oil. The second is catalyst support utilization which increases the catalyst activity by providing a larger specific surface area and pores (Zabeti, Daud & Aroua 2009). So, to overcome the drawbacks of homogeneous reactions, researchers have concentrated on the heterogeneous reaction with solid (acid, base) catalysts and enzymatic catalysts. In the following part of the thesis, an overview of heterogeneously catalyzed processes and their features will be presented.

4.2.1 Solid catalyzed

The solid-catalyzed method is a type of heterogeneous catalyzed transesterification process which uses solid catalysts. It is utilized for biodiesel production to eliminate the drawbacks of the homogeneous catalyzed process which requires pre-treatment or purification processes. A solid catalyst should have a network of large pores (Brito, Mello, Cesar, Macedo, Meneghetti, Suarez, et al. 2008; Islon, MacRae,

Smith, & Bosley 1994), strong acid sites with a medium to high concentration, and a hydrophobic surface (Dalai, & Meher 2006). It should also be able to control the surface's hydrophobicity to halt the deactivation process (Miao, & Shanks 2009). Solid catalysts are categorized to acid and base solid catalysts as described in the coming sub-chapters.

4.2.2 Solid acid catalyzed

Using WCO as feedstock, Gardy et.al (2017) reported that utilizing sulfonated solid acid catalyst $\text{TiO}_2/\text{PrSO}_3\text{H}$ in transesterification resulted in 98.3% biodiesel yield (see APPENDIX 3). The conditions used are a 15 : 1 molar ratio, and a 4.5 catalyst load, at 60 °C, for 540 minutes. In addition to its higher yield conversion, the solid acid catalysts method is preferable because it is not sensitive to FFA in feedstock which makes it a good choice for WCO conversion. The esterification and transesterification reaction occurs simultaneously which would reduce equipment cost as well as eliminate acid wastewater thus reducing corrosion. This method does not require a product washing process which makes it environmentally friendly. Finally, it requires a lower amount of catalyst and is easy to remove afterward. (Talebian-Kiakalaieh et.al 2013.)

4.2.3 Solid base catalyzed

Heterogeneous base catalysts that have been used in biodiesel production through transesterification are cheap and have high yields. These are some types of solid base catalysts: transition metal oxide and derivatives (Sreeprasanth, Srivastava, Srinivas, & Ratnasamy 2006; Antunes, Veloso, & Henriques 2008), boron group base heterogeneous catalyst (Umdu, Tuncer, & Seker 2009; Xu, Yang, Yu, Guo, & Maynurdader 2008), alkaline earth metal oxides and derivatives (Wang, & Yang 2007; Lopez, Bruce, Lotero 2005), metal oxides mix and their derivatives (McNeff, Yan, Nowlan, Rasmussen, Gyberg, et al 2008; Xu et. all 2008) alkali metal oxides and derivatives (Ebiura, Echizen, Ishikawa, Kazuhito & Baba 2005). However, the best catalysts for the manufacture of biodiesel are supported solid base catalysts. As seen in the table in APPENDIX 3, Taslim et.al (2018), reported that utilization of base-supported catalyst in WCO transesterification resulted in 96% biodiesel yield. The conditions applied are 12 : 1 molar ratio, %wt catalyst load, at 60°C, for 120 minutes. 12 : 1, 3, 60, 120. The experiment indicates that this method used a lower catalyst and less time.(Taslim, Bani, Iriany, Aryani, & Kaban 2018.)

4.2.4 Enzymatic catalyzed

Immobilized lipase, an enzymatic catalyst, has recently been discovered to be useful in transesterification reactions (Talebian-Kiakalaieh et. al 2013). In comparison to alkali-catalyzed transesterification, enzymatic catalyzed is tolerant to water and FFA in the feedstock WCO (Robles-Medina, Gonzalez-Moreno, Esteban-Cerdan, & Molina-Grima 2009). Therefore, the downstream processes are reduced or not required. According to Ranganathan et. al (2008) using a biocatalyst can result in very high FAME purity. This method eliminates by-product formation, removes the product simply, and the catalyst can be reused without any separation steps, and it also requires lower operating temperatures (Robles-Medina et al. 2009).

In addition to the process benefits, it is possible to utilize immobilized lipase repeatedly without suffering a substantial loss of activity. However, it is discovered to be extremely expensive and time-consuming (Shimada, Watanabe, Sugihara, & Tominaga 2002). Generally, the number of cycles, kinds of alcohol, the ratio with oil, and the kind of lipase are some variables that have a big impact on the production of biodiesel with lipase (Talebian-Kiakalaieh, Amin, & Mazaheri 2013). For example, ethanol utilization in transesterification is resulting in (84–94%) conversion yield which is higher compared to methanol n (47–89%) (Talebian-Kiakalaieh et. al 2013).

4.2.5 Non-enzymatic

These catalysts ZrO_2 , ZnO , SO_4^{2-}/SnO_2 , SO_4^{2-}/ZrO_2 , KNO_3/KL , zeolite, and KNO_3/ZrO_2 are used in this relatively novel approach. This method requires high temperature and pressure for better efficiency. These catalysts' key benefits include less corrosion and greater environmental friendliness. The price of producing biodiesel may be decreased by these characteristics. Additionally, they can lessen soap production even with inferior oils (Ranganathan, Narasimhan, & Muthukumar 2008.). However, for best efficiency, this type of reaction was conducted at 200 °C and 50 bar pressure, with a 6:1 molar ratio of methanol to oil and 3% catalyst weight (Ranganathan et.al 2008).

4.3 Non-catalytic

Researchers have looked for new, catalyst-free ways to reduce or eliminate these kinds of production-related barriers for biodiesel (Niza, Tan, Lee, & Ahmad 2013). The supercritical process is a non-catalytic process approved to make biodiesel by Saka (Saka, & Kusdiana 2001). The supercritical process

can accomplish conversion in a short amount of time without the need for a catalyst. However, this process is maintained at high pressure and temperature to produce biodiesel. Therefore, this technology cannot be used for industrial-scale manufacturing. These factors significantly raise equipment and manufacturing costs. The majority of studies have focused on creating new techniques in order to reduce the reaction temperature and pressure. The use of co-solvents like CaO, CO₂, and hexane is crucial for overcoming these challenges (Han, Cao, & Zhang 2005; Demirbas 2007). Hexane was added to the mixture to address the issue that alcohol and oil do not combine to create a single phase. (Han et.al 2007)

The supercritical method has a number of benefits, such as the following: no catalyst is used, a high molar ratio of methanol to oil can produce higher conversion in short reaction time, as enzymatic catalyzed, this method accepts a large amount of water in the feedstock.; glycerides and free fatty acids react at the same rates, and the homogeneous phase eliminates the diffusive problems. On the other hand, the high pressure (25–40 MPa) and temperature (350–400 °C) involved in this process adds additional costs for cooling and heating processes. Consequently, the alcohol evaporates, and thus the cost increases due to the high molar ratio of methanol to oil. (Talebian-Kiakalaieh et al 2013.)

4.4 New techniques

There are new techniques have been followed to enhance biodiesel production either by improving the quality, increasing conversion yield, or to eliminate some steps and reduce operation costs. Example of these techniques are continuous flow, reactive and dual reactive distillation methods, reactive absorption, membrane reactor, ultrasonic and microwave utilization. These processes have features that affect the production yield. The continuous flow techniques ensure continuous flow/operation. Therefore, the continuous process lowers expenses and speeds up response time while increasing productivity and profit. This method came to overcome the drawbacks of batch operations. Batch operations are used in the traditional transesterification process, which has some drawbacks including labor-intensive, laborious, and poor automation adaptation. (Talebian-Kiakalaieh et al 2013.) Continues flow method showed higher quality biodiesel per unit of work (Noureddini, Gao, & Phil-kana 2005). The ideal conditions yielded the greatest conversion of 97.3% ester: 0.72 min of reaction duration, 900 rpm mixing intensity, a 6:1 molar ratio of alcohol to oil, 3%w/w catalyst weight, and 60 °C reaction temperature (Komers, Skopal, & Čegan 2010).

Reactive distillation is a single piece of equipment used to handle chemical reactions and distillation separation at the same time. Therefore, the process cost and expenses are minimal. One feature of

reactive distillation is that it carries out different reactions involving catalytic (homogeneous and heterogeneous) and non-catalytic processes. Also, it is continuously removing products from the reaction zone which contributes to product conversion elimination, thus saving cost. Furthermore, the use of a re-boiler is also unnecessary with this method since exothermic processes generate heat through vaporization rather than reaction heat. (Talebian-Kiakalaieh et al. 2013.)

Dual or catalytic reactive distillation is a multi-purpose reactive distillation device with increased operational flexibility (Talebian-Kiakalaieh et al 2013). Its integrated design contributes to lower equipment costs (Dimian, Omota, & Kiss 2007). It works to remove water for solid catalyst protection to prevent deactivation. Therefore, the recovery cost of alcohol is avoided. Increased process productivity of between 5 and 10 times compared to traditional units is the first benefit of this approach. Alcohol excess is avoided since it is supplied in a stoichiometric ratio. It eliminates catalyst neutralization, saltwater treatments, and soap production as well as removes sulfur from the product. Additionally, it is highly acceptable to a wide range of alcohols and fatty acids. As a result, the investment cost and energy consumption are reduced (Talebian-Kiakalaieh et al. 2013.)

A new biodiesel production technology called reactive absorption has greater benefits than traditional ones. It has high conversion, and selectivity and operates at normal atmospheric pressure and temperature. According to Kiss (2009), this method results in a 99.9% yield of conversion under a reaction condition of 160C and 1 bar pressure (Kiss 2009). This method is high tolerance to FFA in the raw material, so it is the best choice for waste cooking oils, waste vegetable oils, and animal fats with up to 100% FFA. Other benefits include the following: a straightforward and reliable process, no thermal product degradation, the omission of routine catalyst-related procedures, and the absence of waste streams therefore no additional separation steps are needed. (Talebian-Kiakalaieh et al 2013.)

Since vegetable oils and methanol cannot mix, the membrane reactor makes use of this immiscibility to improve the purification process. The main role of membrane reactors in biodiesel production is to remove impurities involved throughout the process (Talebian-Kiakalaieh et al 2013). The impurities are free glycerol, catalyst, unreacted methanol, bound glycerol, unreacted triglycerides (TG), diglycerides (DG), and monoglycerides (MG), as well as minute amounts of soap and water (Saleh, Tremblay, & Dubé 2010). These impurities are serious obstacles in biodiesel production that needs to be eliminated to achieve good FAME conversion and reduce the capital cost. Another way to eliminate these impurities is to drive the reaction as near to total oil conversion as possible. However, because TG transesterification is an equilibrium reaction, it can never be completed completely. (Talebian-Kiakalaieh et al 2013.)

Another traditional solution for this problem is the multiple water washing (hot water) of the product, although it necessitates wastewater treatment (Karaosmanoglu, Cigizoglu, Tuter, & Ertekin 1996). The key advantage of this technique is the integration of reaction and separation steps, thus reducing production costs. It also eliminates undesirable reactions as well as controls contact between incompatible reactants. (Talebian-Kiakalaieh et al 2013.)

The ultrasonic process using sound waves affects the reaction by cavitation bubbles created by a liquid breakdown caused by substantial negative pressure gradient application in liquid. (Talebian-Kiakalaieh et al 2013) Micro-bubble creation and collapse are where ultrasonic vibrations have the most impact on chemical reactions (Kumar, Kumar, Poonam & Singh 2010). The cavity collapse caused by the liquid jet effect, which disturbs the interfacial boundary layers, enhances mass transfer. The reaction rate, mass transfer, and catalytic surface areas can all be significantly increased by these waves' high temperature (>4726.85 °C) and pressure (>1000 atm) (Yu, Tian, Wu, Wang, Wang, Ma, & Fang 2010). The role of the ultrasonic technique in the biodiesel production process is to mix alcohol with oil by low-frequency ultrasonic waves to achieve a better yield. Compared to a normal stirring system (340 nm by 1000 rpm), ultrasonic irradiation produces smaller droplets (146-148 nm by 50–70 W), which enhances the contact area between the oil and alcohol (Mikkola, & Salmi 2001). Ultrasonic radiation decomposes the catalyst, so a solid catalyst is recommended to be used with. Parameters such as ultrasonic power, frequency effect, catalyst type, and alcohol type influence the process, so they need to be controlled. The benefits that made this technique suitable for industrial scale are many. The process is fast, energy-efficient, and cost-effective since it lowers the molar ratio and catalyst. It provides a higher reaction rate, therefore enhancing the conversion and improving the yield. In addition to its simple setup, it operates simple purification and separation processes. Furthermore, it produces high-quality glycerol. On the other hand, the process drives higher reaction temperatures and consumes more catalysts than traditional methods (Talebian-Kiakalaieh et. al 2013.)

The feature of microwaves is their ability to transfer energy to samples directly which drives the reaction to completion. Microwaves cannot alter the chemical composition of a molecule like breaking bonds or forming energy, rather it interacts with a material to produce heat. (Talebian-Kiakalaieh et al 2013.) Biodiesel production from WCO, with high FFA, possibility using a microwave is demonstrated by Refaat, El Shel-tawy, & Sadek (2008.). According to the data, microwaves can easily transport fuel while also boosting the reaction reactant and enhancing the separation and purification process. According to Talebian-Kiakalaieh et. al (2013), microwave utilization in biodiesel production has various advantages although it faces some challenges when maintained on an industrial scale. These challenges are

safety-regarding issues and the risk of organic molecules (triglycerides) damage due to microwave power (Saifuddin, & Chua 2004). The microwave utilization benefits are summarized by: high quality and production yield, environmentally safe, lower molar ratio, and fewer by-product production. Additionally, it is fast, energy efficient (23 times less), and does not require preheating. Furthermore, Motasemi and Ani (2012.), reported that a kilogram of biodiesel may provide an average of 2.1277 kWh of electrical energy while only requiring 0.47 kWh of power when heated in a microwave. As a result, the microwave method has the potential to generate an additional 1.6596 kWh/kg of electrical energy.

5 BIODIESEL PRODUCTION OPPORTUNITIES AND CHALLENGES IN YEMEN

Yemen is a developing nation whose economy is mainly dependent on oil exports. The Yemeni Ministry of Oil and Minerals' records show that the year 2001 saw the highest oil output, with 438,501 barrels per day. In 2015, oil production decreased to roughly 142,264 bbl/d as a result of intensive extraction (Yemeni Ministry of Oil and Minerals 2021). However, the ongoing conflict and political instability have caused a significant drop in oil production and export, which has affected the country's economy negatively. In contrast to the nation's monthly consumption of 250,000–300,000 tons of diesel, the combined production capacity of the two refineries in Yemen is only 50,000–70,000 tons per month. The government distributes funds from its budget to pay for fuel imports at import parity rates and then sells the petroleum to customers at lower costs, in order to meet the remaining requirements to meet these needs. (Yemen Times Newsletter 2014.)

Beginning in February 2011, a serious political crisis gripped Yemen. Conflicts turned violent as a result of the crisis, and government authority over oil pipelines and roadways was eroded. As a result of the security issues, local refineries have either been shut down entirely or partially, and fuel imports have stopped. Thus, the diesel crisis swiftly materialized in the form of both severe price increases and supply shortages. The government was forced to entirely remove the fuel subsidy due to a string of record-breaking fiscal deficits and the potential for a swift collapse of the national economy. The diesel price was initially raised to about 50% of its parity price in 2012, then more recently, in July 2014, the price was fixed to be equal to the parity price. Diesel prices have increased by 95% as a result of the latest price increase, which has led to unprecedented political instability and rallies spearheaded by the Houthi movement. (Al-Weshali, Bamaga, Borgia, van Steenberg, Al-Aulaqi, & Babaqi 2015.)

Diesel fuel is utilized in different applications and machinery such as powering trucks, construction equipment, and transportation, and is mostly used in agriculture and electricity generation in Yemen. To generate electricity, Yemenis typically use diesel generators independently as an alternative source to cover their needs outside governmental farmwork. As a consequence of the diesel crisis and a scarcity of fuel to pump groundwater for irrigation, farmers reported losses in yields, product quality, income, and irrigated areas (Al-Weshali et. al 2015). For electricity generation, it is stated in 2020 to be 3.3 BKW/year from fossil fuels including coal, natural gas, and oil, and only 0.36 BKW/ year from solar energy (GlobalPetrolPrice 2020).

Environmentally, Yemen's CO₂ emissions increased to 10.9 million tons in 2019 from 10.5 million tons the year before, a rise of 3.25 percent, placing the nation 97th in the world (REN21 2019). Domestic, agricultural, and commercial usage of diesel and kerosene accounts for 15.2% of emissions whereas the power plant is accounting for 69,3% (Emission Database for Global Atmospheric Research 2021).

5.1 Biodiesel production potential

As a result of the country's fuel crisis, a strong need for alternative fuel to cover the needs existed. Similarly, the environmental concern created an increased interest in renewable energy sources, such as biodiesel. Therefore, biodiesel is considered a potential solution to the country's challenges. The country can develop a sustainable biodiesel industry that can create jobs, reduce the reliance on fossil fuels, therefore, reduce environmental hazards, and contribute to the country's economy. In Yemen, biodiesel production is still in its early stages, but no biodiesel production plant exists so far although the country has vast potential for biodiesel production, given its abundant sources of feedstock, such as palm oil, jatropha, and other oilseeds (Baggash & Abdulrahman 2010). Two industrial projects were set up for the manufacturing of biodiesel from used cooking oil by the non-governmental group Small and Micro Enterprise Promotion Service (SMEPS). To take advantage of the scarcity or absence of biodiesel plants, the competition will decrease, and thus the market will be exclusively for investors in this field.

A few studies were done on Yemeni biodiesel fuel production using different feedstock, extracted Jatropha, frying oil, and waste cooking oil. Al-attab et al. (2017), conducted a techno-economic study on Yemen's generation of biodiesel from WCO. 87.2% was the biodiesel's highest output. The results were obtained using 166.5 ml of methanol and 5 g of sodium hydroxide for every liter of re-fined waste cooking oil (Al-attab, Wahas, Almoqry, & Alqubati 2017). According to Fozy Binhweel et al (2022) the analysis found that it is technically possible to produce biodiesel from used cooking oil and that doing so will only be financially viable if the manufacturing line can produce at least 2000 liters per day.

Mohammed, Badiea, & Moad (2016) employed frying oil as opposed to extracting oil from the vegetative feedstock, in contrast. Yemen consumes 113,182.64 tons of cooking oils annually, per their analysis. The study samples were taken from Taiz state, where around 1,799 liters of used cooking oil are

collected every day. 96% was the highest biodiesel yield. It was produced using the idealized reaction conditions of 25% wt methanol, 0.78% wt catalyst NaOH, and 70 °C.

Jatropha curcas is another possible and promising source for biodiesel production. It was used as a feedstock by Baggash & Abdulrahman (Baggash & Abdulrahman 2010) to make biodiesel. The research was conducted to confirm the viability of producing biodiesel from *jatropha curcas* on an industrial scale to meet some of the world's energy requirements. According to their research, *jatropha curcas* has the advantages of quick growth, high oil output, and appropriateness for the Yemeni environment, making it a good prospective supply of the fatty acids needed for the manufacturing of bio-diesel in Yemen. Traditional methods were used to extract the oil from the *jatropha curcas* plant before it was further processed by the base-catalyzed transesterification reaction with alcohol and methanol. The cloud point (- 10 °C) and flash point (167 °C) were used to define the biodiesel conversion percentage, which was 80%. (Baggash & Abdulrahman 2010.)

5.2 Challenges

Although the aforementioned data such as the urgent need for an alternative fuel to diesel to cover the needs, provide job security and environmental safety, as well as the availability of raw materials and the ease of the conversion process suggest that biodiesel production is the ideal solution for the current crisis, However, biodiesel production in Yemen remains limited. The production process in Yemen faces some challenges and difficulties such as lack of investment, technology, and infrastructure. Biodiesel production requires significant investment in infrastructure, technology, and human resources. However, the country receives little foreign investment as a result of the continuous conflict and political unrest, which restrains the growth of the biodiesel sector. Lack of technology is also a challenging factor. Yemen lacks the necessary technology to produce biodiesel on a large scale. The country needs to import technology, equipment, and expertise, which increases the cost of production.

Feedstock availability is another reason for biodiesel production limitation. Although Yemen has abundant sources of feedstock, such as palm oil, *jatropha*, and other oilseeds, the availability of these feedstocks is not consistent throughout the year and the lack of laws related to the environment and health in terms of the number of times allowed to use cooking oil and the appropriate disposal methods makes it difficult to establish a steady supply chain. Additionally, Yemen lacks the necessary infrastructure to support the biodiesel industry, such as storage facilities, transportation networks, and blending facilities. To develop a sustainable biodiesel industry in Yemen, the government and private sector should take these factors into consideration. Yemen must also adopt measures and policies to

support and advance renewable energy projects, including filling in some of the power gaps and adhering to the global movement toward environmentally friendly energy, as well as ensuring Yemen has investment opportunities for both domestic and international investors. (AL-wesabi, Zhijian, Bosah, & Dong 2022.)

6 CONCLUSION

Finding a new fuel that is environmentally friendly, affordable, broadly accessible, and technically feasible is necessary to replace or reduce the demand for fossil fuel. The depletion of fossil fuel resources, the volatility of crude oil and other fossil fuel prices, and environmental concerns necessitated searching for alternative fuels. Research and investigations are concentrated on biodiesel as one of the greatest fuel options, considering minimizing the cost with outstanding fuel qualities. For biodiesel production, the transesterification method and its different approaches such as homogeneous catalyzed, heterogeneous catalyzed non-catalytic are the most suitable and widely used rather than pyrolysis and micro-emulsion.

Transesterification is conducted using fresh or waste vegetable oils, and animal fats as feedstock mixed with alcohol (typically alkali catalyst) or without catalyst at a certain temperature for a certain time. Temperature, molar ratio, type and amount of catalyst, and the most important factor feedstock are the main factors to influence biodiesel production. In order to achieve biodiesel at a lower price, WCO is utilized as feedstock. However, WCO is associated with impurities left from cooking processes that change its chemical properties. Free fatty acids, water, and solid particles are the common impurities involved in the feedstock therefore, a pre-treatment is required otherwise the cost of separation (due to saponification) and purification downstream of biodiesel production increases.

In the case of WCO as biodiesel production feedstock, the traditional method alkali catalyzed transesterification is applied, but this approach has significant issues with purification since it is so sensitive to the presence of FFA and water in the raw material. In contrast to base catalysts, the acid-catalyzed reaction is not affected by the presence of FFA or water, but the reaction is much slower. The use of enzymatic catalysts produced excellent results, but they are expensive, and this is unacceptable for the commercial synthesis of biodiesel. Additionally, the supercritical or non-catalyst approach calls for high pressure and temperature, which is apparently not affordable. Therefore, researchers concentrate on using heterogeneous acid and base catalysts to produce biodiesel because catalysts may be reused numerous times. The most crucial characteristic of catalysts that might make them cost-effective for industrial production in a continuous process is their ability to be reused. A variety of techniques have been applied in transesterification reactions to decrease production costs, reaction times, and catalyst and alcohol needs, including membrane reactors, reactive distillation, reactive absorption, microwave,

and ultrasonic. Without modifying the engine in any way, these techniques can improve FAME for applications to diesel engines.

Yemen has vast potential for biodiesel production, given its abundant sources of feedstock such as Jatropha and palm oil as well as the increasing fuel needs to cover and overcomes the fuel price raise. However, the biodiesel industry in the country faces significant challenges. To develop a sustainable biodiesel industry in Yemen, the government and private sector should take steps to attract investment, transfer technology, develop feedstock, and invest in infrastructure. If these steps are taken, biodiesel production in Yemen can contribute to the country's economy, create jobs, and reduce the reliance on fossil fuels.

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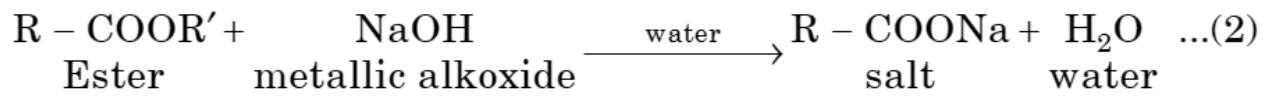
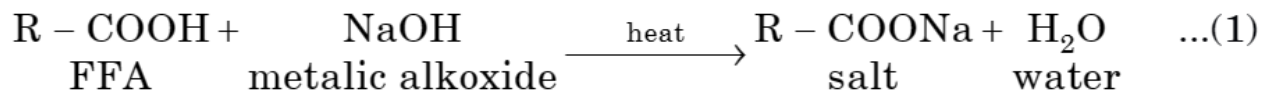
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APPENDIX 1.

Saponification reaction

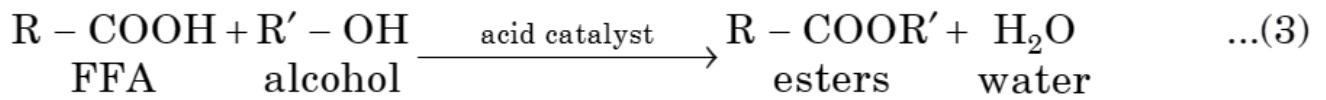
The following equations represent respectively the saponification reactions of FFA and esters when reacting with alkali catalysts. (Mata et.al 2010; Van Gerpen et al. 2004)



APPENDIX 2

Acid-catalyzed esterification reaction

The acid-catalyzed esterification can be used as a pre-treatment for basic transesterification reaction to convert the FFA into methyl esters (Aranda et al., 2008; Issariyakul et al., 2007)



APPENDIX 3.

Table of conversion yield of biodiesel using different catalysts.

The table lists the reaction conditions for the best conversion yield for each catalyst type using either waste cooking oil (WCO), waste frying oil (WFO) or used cooking oil (UCO) as feedstock. (a) on table represents methanol-to-oil (M/O) molar ratio, catalyst loading (wt%), temperature (°C), reaction time (min). * means ethanol to oil.

For example, according to 56, transesterification of WFO using homogeneous base catalyst KOH leads to 96.61 % biodiesel under conditions of 6:1 molar ratio, 1 wt% catalyst loading, at 65 C temperature for 60 minutes.

Type of catalyst	Catalyst	Feed-stock	Condition (a)	Yield %	Method	References
Homogeneous (base)	KOH	WFO	6 : 1,1 65,60	96.1 5		Refaat, A. A., Attia, N. K., Sibak, H. A., El Sheltawy, S. T. & El Diwani, G. I. 2008
	NaOH	WFO	4.8 : 1, 0.6, 65, 60	98		Felizardo, P., Neiva Correia, M. J., Raposo, I., Mendes, J. F., Berkemeier, R. & Bordado, J. M. 2006
	NaOCH ₃	WCO	4.8 : 1, 0.6, 65, 60	96.6	by using sodium methoxide and a microwave heating system	Chen, K., Lin, Y., Hsu, K. & Wang, H. 2012
	NaOH	WCO	6 : 1, 1, 50, 90	89.8		Meng, X., Chen, G. & Wang, Y. 2008
Homogeneous (acid)	H ₂ SO ₄	WCO	20 : 1, 4, 95, 600	90	Two-steps	Wang, Y., Ou, S., Liu, P., Xue, F. & Tang, S. 2006
Heterogeneous (base / Alkaline earth metal oxides)	CaO	WCO	(1:3, 1:4, 1:6), (0, 1 1.5) (40 50 , 60), 60	93	Ultrasonic irradiation	Topare, N. S., Patil, K. D. & Khedkar, S. V. 2021

Heterogeneous (base/ Transition metal oxides)	SrO– ZnO/Al ₂ O ₃	WCO	10:1*, 15, 75, 5h	95.7	Simultaneous trans-esterification and esterification	Al-Saadi, A., Mathan, B. & He, Y. 2020
Heterogeneous (base /zeolite)	KOH/zeolite	WSO	11.5 : 1, 6, 50, 120	96.7		Al-Jammal, N., Al-Hamamre, Z. & Alnaief, M. 2016.
Heterogeneous (base /Solid supported catalyst	KOH/AC	WCO	12 : 1, 3, 60, 120	96,65		Taslim, Bani, O., Iriany, Aryani, N., & Kaban, G.S. 2018
Heterogeneous (base / Hydrotalcite)	Mg–Al HT	WCO	6 : 1, 1.5, 80, 150	95,2		Ma, Y., Wang, Q., Zheng, L., Gao, Z., Wang, Q. & Ma, Y. 2016
Heterogeneous (base/Mixed metal oxides)	TiO ₂ –MgO	WCO	50 : 1, 10, 160, 360	92.3		Wen, Z., Yu, X., Tu, S., Yan, J. & Dahlquist, E. 2010
Biomass-based (waste shell/egg shell)	CaO	WCO	24 : 1, 4, 60, 240	100		Niju, S., Begum, K.M.M.S., & Anantharaman, N. 2015
Biomass-based (waste shell/egg shell)	CaO/KF/Fe ₃ O ₄	WCO	24 : 1, 4, 60, 240	97		Oladipo, A. S., Ajayi, O. A., Oladipo, A. A., Azarmi, S. L., Nurudeen, Y., Atta, A. Y. & Ogunyemi, S. S. 2018.
Biomass-based	CaO/Ba	WCO	6 : 1, 1, 65, 120	>98		BORO, J., KONWAR, L. J., THAKUR, A.

(waste shell/ Turbonilla stri- atula shell)						J. & DEKA, D. 2014
Biomass-based (Ash / Musa bal- bisiana Colla peel)		WCO	6 : 1, 2, 60, 180	100		Gohain, M., Devi, A. & Deka, D. 2017
Heterogeneous (Acid / ion ex- change resin)	Amberlite gel resin	WCO	7 : 1, 60, 120	85.95		Hartono, R. , Mulia, B., Sahlan,M., Utami, T.S., Wijanarko & Hermansyah, H. 2017
Heterogeneous (Acid / Sul- phated catalyst)	TiO ₂ /PrSO ₃ H	WCO	15 : 1,4.5, 60, 540	98.3		Gardy, J., Hassanpour, A., Lai, X., Ahmed, M. H. & Rehan, M. 2017
Heterogeneous (Acid / Mixed metal oxides)	Fe–Mn– MoO ₃ /ZrO ₂	WCO	25 : 1, 4, 200, 300	95.6 ± 0.15		Alhassan, F. H., Rashid, U. & Taufiq- Yap, Y. H. 2015
Heterogeneous (Acid / Sul- fonated carbon- based catalyst)	C–SO ₃ H	WCO	20 : 1, 10, 60, 180	93.6		Nata, I. F., Putra, M. D., Irawan, C. & Lee, C. 2017.
Enzyme catalyst	Lipase	WCO	3 : 1, 1.5, 65, 240	88		Jayaraman, J., Alagu, K., Appavu, P., Joy, N., Jayaram, P. & Mariadoss, A. 2020
Bifunctional solid catalysts	Mg/MCM-41		8 : 1, 10, 80, 180	94		Pirouzmard, M., Anakha- toon, M. M. & Ghasemi, Z. 2018