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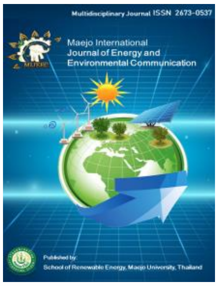

ARTICLE

Biodiesel (Methyl Esters)

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ABSTRACT

Biodiesel, an environmentally friendly biomass-based fuel, is gaining popularity globally as a cost-effective way to meet rising fuel demand. However, the high cost of raw materials and catalysts continues to drive up biodiesel production. An alternative feedstock with a heterogeneously catalyzed reaction could be the most cost-effective way to stabilize industrial biodiesel growth. Understanding these issues led to the idea of using waste palm oil as a feedstock for biodiesel production. While using waste materials as feedstock for biodiesel is an elegant solution, converting high free fatty acids (FFA) directly into methyl esters has some drawbacks. High FFA processes (acid esterification, then base transesterification) are costly. The commercial processes currently use a homogeneous system with sulfuric acid to catalyze both esterification and transesterification. However, heterogeneous solid acid catalysts are preferred over hazardous mineral acids for high FFA esterification because they are less corrosive, produce less waste, and are easier to separate from reactants and products by filtration, recovery, and reusability. Heterogeneous acid catalysts can also simultaneously catalyze transesterification and esterification reactions. Thus, new waste-based support for heterogeneous catalysts (solid acid catalysts) is required to convert waste oils into biodiesel.

1. Introduction

Nowadays, energy has fallen into three basic economic needs: electric power technologies, process heating for industries and consumers, and private and cargo transportations (Ashnani et al., 2014; Reynolds, 2014; Abd Malek et al., 2020). As a result, the advancement of sustainable alternative fuels, particularly biodiesel, is crucial. Biodiesel, also known as fatty acid methyl ester (FAME), is made from renewable sources such as vegetable oils and animal fats through transesterification or esterification (Ahmad et al., 2021; Ramaraj et al., 2021; Nithin et al., 2020). Biodiesel may be blended with petroleum diesel in any proportion to generate

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a more stable biodiesel blend. Due to its minimal emissions, exceptionally low sulfur content, and highly renewable nature, it is also characterized as a clean-burning fuel with low pour point and viscosity, biodegradable, and ecologically beneficial.

The history of biodiesel existed more than 100 years ago when Dr. Rudolph Diesel invented a diesel engine that ran on vegetable oil on August 10, 1893 (Shay, 1993). In remembrance of this scene, August 10 has been declared as 'International Biodiesel Day'.

1.1. History of biodiesel development

In the 1920s, vegetable oils for fuel were nearly abolished due to lower prices, more availability, and government subsidies for fossil-based diesel. The diesel engine has been adapted to run on petroleum fuel known as "diesel," which has a lower viscosity (Agarwal, 2007; Khazaai et al., 2021). Unfortunately, in the 1970s, fossil fuels were scarce, and safety concerns prompted a renewed interest in producing vegetable oils as an alternative energy source. However, the upgraded diesel engine is no longer suitable for using high viscosity, low volatility vegetable oils. High viscosity results in poor fuel atomization, causing deposits and coking in the injector, combustion chamber, and valves (Lin et al., 2011). As a result, the transesterification process has emerged as the most practical method for converting vegetable oils to alkyl esters and lowering viscosity to diesel fuel levels, allowing them to be utilized in current engines without modification. Transesterification of vegetable oil existed for many years before developing the first diesel engine in 1853 by scientists E. Duffy and J. Patrick. After G. Chavanne, a Belgian chemist was awarded a patent for a "Procedure for the transformation of vegetable oils for their applications as fuels" in 1937, the notion of "biodiesel" was initially suggested (Knothe, 2001). After that, another grant, 'industrial process for biodiesel', was applied by a Brazilian scientist, Expedito Parente, in 1977 (Parente, 2007). Actively in 1979, South Africa led research on biodiesel from sunflowers. By 1983, the engine-tested biodiesel was completed and published globally to have fuel quality (SAE, 1983).

Meanwhile, an Austrian firm, Gaskoks, constructed the first biodiesel pilot plant and the first industrial-scale biodiesel facility in 1987 and 1989, respectively. Biodiesel manufacturing began to increase commercially in the late 1990s, owing to increased concerns about environmental sustainability and a narrowing cost disparity (Lim and Teong, 2010). Many European nations had built biodiesel facilities at the time, including France, which introduced biodiesel made from rapeseed oil, dubbed "diester" locally. A series of international standards, including EN 14214 (Europe), ASTM D6751 (the USA and Canada), and DIN 51606 (Germany), were created in succession to increase the quality control needs of engines for the use of biodiesel fuels (Germany). The latest versions of EN 14214 and ASTM D6751 were documented in 2008, superseding the previous standards (EN 14214:2003) (Pahl, 2008). The detailed chronology events of the biodiesel development industries show in Table 1.

Table 1 Chronology events of the biodiesel development industries.

Year	Remarkable Event
1893 (August 10)	Rudolf Diesel's prime diesel engine model by peanut oil ran for the first time in Augsburg, Germany.
1900	Rudolf Diesel introduced his engine to the world during an exhibition in Paris, telling its engine was running on 100% peanut oil.
1937 (August 31)	'Procedure for transforming vegetable oils for their uses as fuels' patent was granted by a Belgian scientist, G. Chavanne.
1977	Expedito Parente, a Brazilian scientist, applied the first patent of the industrial process for biodiesel.
1979	South Africa has initiated the research of transesterified sunflower oil and refining it to diesel fuel standards.
1983	The process for producing fuel-quality, engine-tested biodiesel was completed and published internationally
1987	An Austrian company, Gaskoks, established the first biodiesel pilot plant.
1989	First industrial-scale plant established by Gaskoks.
1991	Austria's first biodiesel standard was raised.
1997	German standard, DIN 51606, was issued.
2002	ASTM D6751 was published.
2003	DIN EN14214 was published (Europe biodiesel standard).
2008 (October)	ASTM published new Biodiesel Blend Specifications Standard
2008 (November)	The current version of EN 14214 and ASTM D6751 were published and superseded EN14214:2003.

Source: Lin et al. (2011)

1.2. The need for biodiesel

1.2.1. World regulation/ environmental effect

Climate change concerns have raged around the globe, the prospect of a carbon-neutral fuel seemed like the magical solution to achieve deep reductions in greenhouse gases (GHGs) emissions in the transportation sector by 2050 (Bhuyar et al., 2018). Compared to fossil fuels, the use of biomass is expected to not contribute further to the increase of atmospheric CO_2. The rapidly increasing CO_2 concentration is evident from the Keeling Curve, where its current means value was escalating to 380 ppm from 315 ppm in 1958. It is worth noting that during the last 420 000 years, the CO_2 concentration fluctuates between 190 and nearly 300 ppm only (da Rosa, 2013). Because the combustion of biodiesel produced from biomass only returns the carbon dioxide absorbed from the air by feedstock crops to the atmosphere through the photosynthesis process, the surge in interest in biodiesels has highlighted biodiesel produced from biomass as having the potential to be 'carbon–neutral' over their life cycles.

Fossil fuels, on the other hand, only release carbon dioxide that has been trapped beneath the earth's surface for millions of years. Therefore, biodiesel can replace fossil-based fuels and contribute to the mitigation of GHGs emissions (Lin et al., 2011; Embong et al., 2021; Bhuyar et al., 2020c). According to the EPA's Renewable Fuel Standards Program Regulatory Impact Analysis, published in February 2010, biodiesel made from soy oil reduces greenhouse gas emissions by 57 percent (on average) when compared to fossil diesel, while biodiesel made from waste grease reduces emissions by 86 percent (EPA, 2010). According to the EPA's Renewable Fuel Standards Program Regulatory Impact Analysis, published in February 2010, biodiesel made from soy oil reduces greenhouse gas emissions by 57 percent (on average) compared to fossil diesel, while biodiesel is made from waste grease reduces emissions by 86 percent. According to reports, China emitted 29% of global carbon dioxide emissions in 2013, more than twice the amount emitted by the United States, the world's largest economy and second-largest carbon polluter. In 2009, the Chinese government pledged to reduce carbon dioxide emissions per unit of GDP by 40 to 45 percent by 2020, compared to 2005 levels. According to Chinese official data, carbon intensity has decreased by 33.8 percent from 2005 levels by late last year, demonstrating their adherence to their initial pledge (Christ, 2015). The Japanese government attempts to reduce a GHG emission of 60–80% as a target by 2050 from its current level (Matsumoto et al., 2009). China has emitted 29% of global carbon dioxide emissions in 2013, more than twice that of the United States, the world's largest economy and second-largest carbon polluter. In 2009, the Chinese government promised to reduce carbon dioxide emissions per unit of GDP by 40 to 45 percent by 2020, compared to 2005 levels. According to Chinese official data, carbon intensity was down 33.8 percent from 2005 levels late last year, demonstrating their adherence to their initial pledge.

1.3. Biodiesel around the world

1.3.1. Biodiesel in Europe and United States

Biodiesel is the second-largest category of worldwide biofuel (accounting for 6.9 billion gallons globally in 2013 — 22.6 percent of total biofuel output) and is the most widely utilized biofuel in the European Union. In 2013, the EU generated 40% of total global biodiesel, or 2.8 billion gallons of biodiesel, typically made from rapeseed oil. Even though several EU nations have decreased their biofuel mandates in recent years due to concerns that the growth of particular biodiesel feedstocks was increasing deforestation, the EU countries still maintain biofuel mandates that encourage the use of biodiesel. According to analysts, the EU now has over 120 facilities generating up to 6.1 million tonnes of biodiesel per year, with the majority of these units situated in Germany, Italy, Austria, France, and Sweden (European Biodiesel Board, 2015).

Meanwhile, the US successfully put itself as the most significant national producer of biodiesel in 2013, producing 1.4 billion gallons in 2013, produced primarily from soybeans. Germany and Brazil were behind the US, with 820 million gallons and 766 million gallons respectively in 2013. Argentina was the fourth-largest producer and the world's fifth-largest biodiesel producer, after France and the United States (Robert Rapier, 2014). The US National Biodiesel Board's goals, according to National Biodiesel Board (2012), are to reduce reliance on petroleum, enhance the local community economy, and minimize adverse environmental effects through lowering vehicle emissions, net CO_2, and risks to water and the ecosystem. Furthermore, the United States had enacted the Clean Air Act of 1990, which mandated lower sulphur content in diesel fuel and lowered diesel exhaust emissions. Biodiesel satisfies the Ultra-Low Sulphur Die because it has a low sulphur content (Biodiesel Market Outlook, 2016).

1.3.2. Biodiesel in Asia

In examining the Asia-Pacific biodiesel sector, Frost and Sullivan, a worldwide market-analysis firm, claimed that most governments in the area realize that biodiesel can cut oil imports, enhance fuel security, and promote domestic agriculture. According to the report, Indonesia, Malaysia, China, and the Philippines account for approximately 74% of regional demand (Biodiesel Market Outlook, 2016).

In early 2006, Indonesia legally created its National Energy Policy, enacting Presidential Regulation No. 5/2006 (Regulation No. 5) that codified the production of biofuels in Indonesia, including ethanol and biodiesel, and set a five percent biofuel requirement B5 by 2025. In the latter, the policy has been reinforced concerning the regulation of biodiesel utilization, National Biodiesel Standard SNI 04-7182-2006, and the Decree of the Oil and Gas Directorate General on Biodiesel Blending regulation that allows a maximum blending of 10% (Khazaai et al., 2021; Bhuyar et al., 2020a). Palm oil, jatropha oil, and coconut oil are domestically available feedstock for Indonesian biodiesel production.

China's rapid increase in energy consumption was unavoidable, owing to the country's remarkable economic expansion. By 2020, the yearly biodiesel production objective outlined in 2007's "The Medium and Long-Term Development Program for Renewable Energy" is 2 million gallons. Due to a lack of feedstock availability and volatility, China's biodiesel business is shrinking. Compared to the US or EU, which mostly use fresh vegetable oil such as soybeans as feedstock, China's plans have had to rely on salad oil waste, used oils, waste animal fats, and wild oilseed plants to generate biodiesel. Recently, initiatives have been made to grow crops like jatropha, Chinese pistache, acidification oil, and oil algae to combat this problem. Among the numerous kinds of energy trees, Jatropha is regarded as one of the best feedstock trees in China and is now the focus of efforts to expand the country's biodiesel program. In the next 10–15 years, those provinces are anticipated to have around 167 million hectares of jatropha planting on hilly and marginal regions (Qiu et al., 2012 and Yang et al., 2012).

The Philippines Biofuels Act of 2006 (Republic Act 9367) requires that biodiesel be blended at 2% in all domestically supplied diesel and gasoline, with coconut oil as the preferred feedstock. The Philippines' biodiesel success after implementing RA 9367 in 2007 is attributable primarily to its position as the world's leading producer of coconut oil. In 2012, nine biodiesel producers were operational, with a total annual capacity of 300,000 tonnes (Biodiesel Market Outlook, 2016).

1.4. Biodiesel in Malaysia

When former Malaysian Prime Minister Tun Dr. Mahathir Mohamad proposed using palm oil for fuel in 1982, Malaysia began its journey into palm biodiesel use, manufacturing, and exporting. In 1985, the National Energy Policy was adopted, emphasizing the dependability and security of biofuel supplies. Malaysian Palm Oil Board (MPOB) had led to initial research and development on the construction of a palm biodiesel pilot plant, and subsequently, a series of laboratory, engine, and road evaluations were carried out successfully so that the fuel can be used in the existing engine without significant modifications (Abdul-Manan et al., 2014; Chin, 2011; Bhuyar et al., 2019a). National Biofuel Policy (NBP) was introduced in March 2006 where highlighted the growing concern of the nation caused by the depletion of fossil fuels, environmental issues, and escalating petroleum prices. The policy focuses on blending processed palm oil with petroleum diesel and converting palm oil into biodiesel mainly for export. The Malaysian government had pledged to set aside 6 million tonnes of CPO specifically for biodiesel production. The implementation was planned to commence originally in 2010 and rolled out in phases, initially for use by selected government vehicles before a nationwide execution (Chin, 2011). Furthermore, the NBP promotes biodiesel following the country's Five Fuel Diversification Policy, which is in line with the goals of the United Nations Framework Convention on Climate Change (UNFCCC). Five strategic thrusts underpin NBP:

- Biofuel for transport – B5 diesel for land and sea
- Biofuel for the industry – B5 diesel used in firing boilers in manufacturing, construction machinery, and generators
- Biofuel technology – Research, development, and commercialization of biofuel technology, funded by the government and private sector
- Biofuel for export – Malaysia has an edge because it is the largest palm oil producer and exporter in the world
- Biofuel for the cleaner environment – minimize emissions of CO_2, CO, SO_2, and particulates

1.4.1. Malaysia biodiesel blend mandate

In the case of Malaysia, biodiesel consumption is driven mainly by blending mandates. In February 2009, the policy mandate of B5 blend of palm oil-based biodiesel into diesel in all government vehicles was implemented and expected will be increased to B10 in the future. The B5 blend mandate had fully implemented nationwide in 2014. Furthermore, the NBP promotes biodiesel usage by the country's Five Fuel Diversification Policy, which aligns with the UNFCCC's goals. Initially, the mandate was implemented in Putrajaya, followed by Malacca on July 1, Negeri Sembilan on August 1, Kuala Lumpur on September 1, and Selangor on October 1. The Malaysian government has allocated about RM43.1 million (USD 14.3 million) to finance the development of in-line blending facilities at six petroleum depots in the region owned by Petronas, Shell, Esso, Chevron, and Boustead Petroleum Marketing, through its Malaysian Palm Oil Board (Apptanaidu et al., 2014). Following the success of B5 biodiesel, the B7 biodiesel requirement (an additional 7% biodiesel and 93% normal petroleum-based fuel) was introduced across Peninsula Malaysia in November 2014, with Sabah and Sarawak following suit in December 2014. National palm oil consumption is expected to increase to 575,000 metric tonnes per year with the adoption of the B7 strategy, resulting in savings of 667.6 million gallons of diesel per year.

Malaysia's ministry believes that implementing B7 has put the country on par with other developed nations in terms of renewable energy use, such as the European Union, where B7 has been in place since 2009, Thailand has been using B7 since January 2014, Indonesia has been using B7.5 since February 2012, and Colombia is using palm-based biodiesel to implement B8 and B10 (Wahab, 2015). With a great hope to have full implementation of a B7 by 2015, 10 percent blend (B10) is expected to be introduced in October 2015, which, if successfully implemented, could further spur production to 703 million litres in 2016. Malaysia plans to introduce B15, potentially boosting biodiesel production of more than 2.17 billion litres. The recently released Eleventh Malaysia Plan (2016-2020) mentions having B15 biodiesel by 2020 (Malaysia Biofuels Annuals, 2015). Supporting the use of B10 biodiesel fuel, Mercedes-Benz Malaysia has informed its customers about the B10 biodiesel blend suitability for all Mercedes-Benz diesel vehicles currently sold by Mercedes-Benz Malaysia. The statement was relieved by the president and chief executive officer Ronald Folger after having tests conducted by the car company with service intervals of 12,000 km to ensure that their customers' vehicles have run both smoothly and safely with the B10 biodiesel blend (Malaysia Biodiesel Association, 2015). The Malaysian government's efforts to diversify the use of crude palm oil, reduce reliance on petroleum diesel, and reduce GHG emissions through environmentally friendly energy sources are demonstrated by implementing B5, B7, very soon B10 and future B15 biodiesel programs.

1.4.2. Biodiesel plant

According to the Malaysian Biodiesel Association (MBA), 60 biodiesel licenses have been issued by Malaysia's Ministry of Plantation Industries and Commodities by the end of February 2011 and new license applications have been frozen temporarily in fear of overgrowing. Even though the country has many biodiesel facilities, only a handful are operational, and biodiesel output remains at 2.13 million tonnes, much below the government's planned 10 million. Table 2 shows a list of the top biodiesel firms that are currently registered in Malaysia. Other contributors in the Malaysian biodiesel market as stated by MPOB include AJ Oleo (Segamat, Johor), Future Prelude (Port Klang, Selangor), Green Edible Oil (Sandakan, Sabah), Innovations BioFuel (Port Klang, Selangor), In track technology (M) (Rawang, Selangor), Malaysia Vegetable Oil Refinery (Pasir Gudang, Johor), Man Jang Bio (Port Klang, Selangor) and Platinum Biofuels (Seremban, Negeri Sembilan). Furthermore, Malaysia's top two CPO producers, FGV (Felda Global Ventures) and Sime Darby, have announced plans to form a biodiesel consortium known as Biodiesel Malaysia Sdn Bhd. (Johari et al., 2015; Wahab, 2015; Bhuyar et al., 2019b).

Table 2 Lists of active registered biodiesel companies in Malaysia.

Biodiesel companies	Total capacity (tonnes/year)
AM Biofuels	30,000
Carotech Bhd	200,000
Carotino Group	180,000
Genting Plantations	200,000
KL Kepong	150,000
Kumpulan Fima	60,000
Lereno BC	60,000
Mission New Energy	250,000
Plant Biofuels Corp	100,000
Senari Biofuels	120,000
Sime Darby	90,000
SPC Biodiesel	100,000
Vance Bioenergy	150,000
Weschem Technologies	120,000
Wilmar	200,000
YPJ Palm International	120,000
Total	2,130,000

Source: Johari et al. (2015) and Lim and Teong (2010)

1.5. Feedstock for biodiesel

In terms of price and availability, the feedstock used is a critical component in biodiesel production. The cost of biodiesel feedstock takes up a significant percentage of the overall production cost, accounting for more than 70% of the total (Marchetti, 2011; Trejo et al., 2021; Chandrakant et al., 2021). Biodiesel may be made from various oleochemical feedstocks, such as animal fat, vegetable oils, and algal oils, and is mainly made up of triglycerides, which are three long fatty acid chains linked to the glycerol molecule. Biodiesel feedstock may be classified into three categories, as follows:

- Plant-derived oil (soybean, oil palm, rapeseed), which is the most expensive
- Animal-derived oil (tallow, poultry fat, white and yellow grease)
- Oils and grease recycled, primarily from restaurants and food processing industries, are a cost-effective alternative.

1.5.1. Common/Commercial feedstock

Experts indicate that more than 350 different vegetable oil crops are being utilized as the traditional primary feedstocks today, depending on the climate and soil conditions (Ghazali et al., 2015). It is estimated that about 95% of biodiesel is produced from edible oils, and about 50% of biodiesel production is obtained globally by rapeseed oil, which happens to be edible oil. Similarly, other edible oils such as sunflower oil, palm oil and soybean oil are most sought as feedstock for biodiesel production. While many European countries are concerned with rapeseed oil, soybean oil is of primary interest as a biodiesel source in the United States, and tropical climates countries prefer to utilize palm oil or coconut oil. However, the use of this first-generation feedstock comes at the expense of the poor as it inevitably increases the prices of the commodities. The uses of edible vegetable oils raise competition with food materials in the long term. Eventually, the price of biodiesel produced from edible feedstock sky-rocket. As a result, non-edible vegetable oils, regarded as second-generation biodiesel feedstock, garnered international interest and will always be evaluated as possible biodiesel substitutes for conventional edible food crops. Rubber seed Jatropha (Gonzáles, 2016; Bokhari et al., 2016), karanja or pongamia, neem (Gurunatham and Ravi,2015), jojoba (Sánchez et al., 2015), cottonseed (Shrigiri et al., 2016) are among the famous non-edible biodiesel feedstock recently. The existence of the world second-generation biodiesel feedstocks is believed to eliminate competition for food, be more efficient, be more environmentally friendly, produce valuable by-products and be more economical compared to edible oils.

Fats generated from animals are another source of biodiesel feedstocks. They have comparable biological lipid components, consisting primarily of triacylglycerols with fewer diacylglycerols and monoacylglycerols (Banković-Ilić et al., 2014; Saengsawang et al., 2020). For dependable and low-cost raw materials, animal fats such as tallow (beef tallow and mutton tallow), white grease or lard, chicken fat, and yellow grease offer an economic advantage for conversion into biodiesel. For dependable and low-cost raw materials, animal fats such as tallow (beef and mutton tallow), white grease or lard, chicken fat, and yellow grease provide an economic advantage for biodiesel conversion. Unfortunately, because of the limited supply of animal fats, they will never fulfil the world's fuel demands. Aside from that, due to their high amount of saturated fatty acids, they tend to be primarily solid wax at room temperature, making biodiesel synthesis from animal fats a challenging procedure (Banković-Ilić et al., 2014 and Rojas-González and Girón-Gallego, 2011). Furthermore, because of the high fatty acid concentration in fats and the different fatty acid distributions, animal fats have not been researched as thoroughly as vegetable oils for biodiesel synthesis (Karmakar et al., 2010; Abd Malek et al., 2021).

1.5.2. Waste oil and the by-product of industry

Recently, the third category of biodiesel feedstock, which is made up of recycled oil or waste oil and grease from restaurants, households, and food processing plants, has attracted a lot of attention from the general public around the world because it makes use of waste products and eliminates the need for costly disposal. However, the collecting mechanism, particularly for waste stream feedstock like waste cooking oil and grease, might be challenging because the sources are typically dispersed and lack quality control. Various forms of waste oils, such as waste cooking oil, have been the subject of significant investigation throughout the years (Sanli et al., 2015; Cai et al., 2015; Priambodo et al., 2015 and Hindryawati and Maniam, 2014), waste oils from processing plants (Maniam et al., 2013; Cho et al., 2012a and Lokman et al., 2015a) and grease (Kim et al., 2013 and Pastore et al., 2014). The bulk of waste fats and oils, on the other hand, include substantial levels of free fatty acids (FFAs), which cause saponification and a decrease in the quantity of methyl esters generated. Furthermore, waste feedstock (particularly waste fats) contains several contaminants that need pretreatment in order to create high-quality biodiesel. Proteins, water, oxidation products, and phosphatides are among the additional components that must be eliminated or considerably reduced (de Moura et al., 2005; Bhuyar et al., 2021b,d). Due to these problems, the separation of methyl esters becomes a significant problem as the homogeneous base catalysts will be consumed in the reaction (Liu et al., 2008). Homogeneous base catalysts can ideally tolerate less than 0.05 % w/w of FFA (Marchetti et al., 2007). This paved the door for heterogeneous catalysts, which could handle FFA better than homogeneous catalysts (Liu et al., 2008).

1.5.2.1. Palm fatty acid distillate (PFAD)

Palm fatty acid distillate (PFAD) is one of the many potential alternative feedstocks presently available, and it might provide a low-cost, non-food source of feedstock for biodiesel manufacturers. Palm fatty acid distillate, which is brownish produced during the distillation process, is classed as non-edible due to its high free fatty acid (FFA) concentration of up to 85 percent (Wan and Hameed, 2014). With about 670 000 tonnes produced as a by-product of the refining process in Malaysia in 2014, the amount of conveniently available PFAD is significant (MPOB, 2015). Furthermore, Malaysia produces a considerable amount of crude palm oil (CPO) each year, estimated to be approximately 19.4 million tons (Sanjid et al., 2014 and Hashim and Ramli, 2013). The amount of PFAD produced is proportional to the amount of CPO produced.

Furthermore, the price difference between RBD palm oil and PFAD is always positive, suggesting that PFAD is always less expensive. The differential was about $700/metric tonnes in 2008, while it was just $30/metric tonnes in 2015 (MPOB, 2015 and Cheah et al., 2010). Nonetheless, the PFAD price is always lower than the RBD palm oil price. As the price of crude oil rises, so will the price of RBD palm oil, resulting in a considerably more significant price gap between RBD palm oil and PFAD at that time (Embong et al., 2016). In summary, PFAD has reduced feedstock prices for various applications, including biodiesel, soap, animal feed, oleochemical industries (cosmetics and toiletries), squalene, and vitamin E.

1.5.2.2. Decanter cake (Dc)

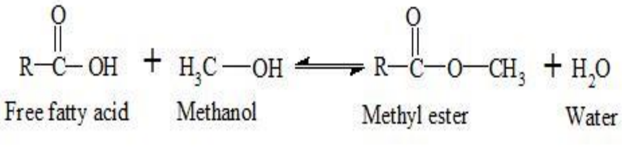
Dc is a brownish-blackish solid waste created by oil palm mills when the solid fraction is separated from wastewater generated during crude oil extraction. When crude palm oil is centrifuged for purification, the sediment is decanter cake, while the supernatant is the desired purer palm oil (Maniam et al., 2013). In reality, over 70% of the fresh fruit bunches (FFB) processed are transformed into the trash in the form of fibres (30%), empty fruit bunches (FFB, 28.5%), palm kernel shell (6%), decanter cake (Dc, 3%), and other materials (2.5 %) (Ramli, 2012). In 2014, Malaysia had roughly 5.4 million hectares (ha) of palm oil plantations, making it one of the world's leading producers and exporters of palm oil over the previous 40 years. According to MPOB figures from 2015, the overall average production of processed FFB was 18.48 tonnes per hectare (January-Dec 2015). As a result, it will generate 3.13 million tonnes of Dc (3 percent x 104.23 million tonnes of FFB) in Malaysia by processing 104.23 million tonnes of FFB yearly (18.48 tonnes/ ha x 5.64 million ha). Despite being discarded freely to the environment, this massive volume of Dc waste should be utilized and transformed into value-added goods or energy to produce more profit for the palm oil business. Otherwise, when dried, Dc creates a fire danger and increases the quantity of suspended particles near palm mills. Dc has been used as a feedstock for the manufacture of cellulose, bio-fertilizer and bio-oil, bio-butanol, and bio-surfactant, all in accordance with the waste to wealth idea (Razak et al., 2012; Dewayanto et al., 2014; Loyarkat et al., 2013 and Noparat et al., 2014). Dc has a significant quantity of oil adsorbed, suggesting that it may be used as a biodiesel feedstock. The Dc retrieved around 11.5 wt. percent oil (on a dry basis), with an acid value of 13.8 mg/KOH g, or 6.3 percent FFA as palmitic acid (Maniam et al., 2013).

1.6. Biodiesel production process

1.6.1. Esterification process of biodiesel

An alternative option to produce biodiesel compatible with raw materials rich in FFA, such as wastes and by-products of industrial biomass processing, is by direct esterification of FFA with alcohol (methanol/ethanol). In other words, esterification is another method employed to convert FFA into methyl esters, which can be accomplished by using an acid catalyst that rapidly drives the equilibrium to the products (Figure 1). There is no doubt regarding the economic transcendence that the achievement of esterification in a single step using homogeneous acid catalyst would have, but they usually are not appropriate because they are highly polar. Hence, the reaction rate is prolonged due to the preferential location of the catalyst in the alcoholic phase (Alegría and Cuellar, 2015). Therefore, homogeneous acid catalysts are not preferred because of the long reaction time, plus difficult catalyst separation due to their corrosive nature. Recently, extensive research has been done to find the most suitable heterogeneous acid catalyst to convert low-quality waste oils and fats into biodiesel (Cirujano et al., 2015; Olutoye et al., 2014; Dabbawala et al., 2013). Esterification is also affected by factors such as methanol to FFA molar ratio, catalyst type and concentration, reaction duration, reaction temperature, stirring effect, and co-solvent.

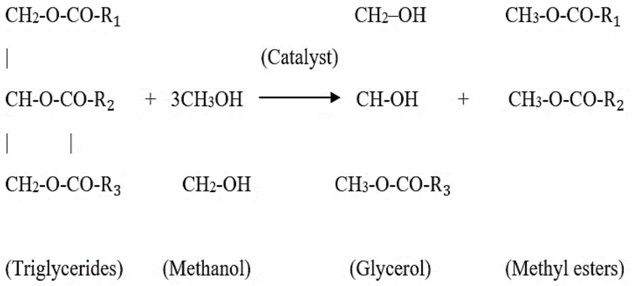
Figure 1 Esterification of free fatty acid.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H_3C-OH \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3 + H_2O$$

1.6.2. Transesterification process of biodiesel

The general term applied to describe the important class of organic reactions where an ester is transformed into another through the interchange of the alkoxy moiety is called transesterification. In oils and fats, the conversion of component triglycerides to a mixture of fatty acids, alkyl esters, and glycerol with short-chain alcohols like methanol and ethanol is achieved mainly by transesterification. Stoichiometrically, the reaction requires 1 mole of a triglyceride and 3 moles of the alcohol to produce 3 moles of methyl esters and 1 mole of glycerol (Figure 2). However, a reversible process transesterification proceeds appreciably by an excess of the alcohol to increase the alkyl esters' yields and allow its phase separation from the glycerol formed (Schuchardt et al., 1998). Other than that, the presence of a catalyst (typically a strong acid or base) accelerates the equilibrium adjustment considerably. Transesterification is the best-suited process to lower the viscosity and, at the same time, increase the volatility of the oil. It has been proven that oil conversion to methyl esters with a suitable catalyst reduces the molecular weight up to 66% (Pryde, 1983).



$$\begin{array}{lllll}
CH_2\text{-}O\text{-}CO\text{-}R_1 & & & CH_2\text{–}OH & CH_3\text{-}O\text{-}CO\text{-}R_1 \\
| & & \text{(Catalyst)} & & \\
CH\text{-}O\text{-}CO\text{-}R_2 & + \ 3CH_3OH & \xrightarrow{\hspace{2em}} & CH\text{-}OH \quad + & CH_3\text{-}O\text{-}CO\text{-}R_2 \\
| \quad | & & & & \\
CH_2\text{-}O\text{-}CO\text{-}R_3 & CH_2\text{-}OH & CH_3\text{-}O\text{-}CO\text{-}R_3 & & \\
\text{(Triglycerides)} & \text{(Methanol)} & & \text{(Glycerol)} & \text{(Methyl esters)}
\end{array}$$

Figure 2 Transesterification of triglyceride.

Several aspects like type of catalyst (alkaline or acid), alcohol to oil molar ratio, reaction temperature, stirring effect, ultrasound effect, purity of the reactants (mainly water content), and free fatty acid content influence the course of the transesterification. According to Agarwal et al. (2012), a further increase in alcohol beyond the optimal amount will not cause any further increase in methyl esters conversion. The same pattern goes to the effect of reaction time, where the rate of conversion increases until a certain period of time and reaches a plateau. This observation happened due to the reversible nature of the transesterification reaction and further increase in reaction time will eventually lead to a decrease in the methyl esters yield (Eevera et al., 2009). On the other hand, increasing the catalyst amount does increase the methyl ester yields to a certain extent where when an optimum amount is reached, no increase in methyl esters yield will be observed. The soap formation (homogeneous catalysts) and difficulty in stirring (heterogeneous catalysts) will occur if further increase in catalyst amount which eventually will decrease the methyl esters conversion (Agarwal et al., 2012; Khammee et al., 2021; Whangchai et al., 2021a,b).

1.7. Solid (heterogeneous) catalyst in biodiesel production

As a fundamental requirement for biodiesel, the choice of catalyst has always resulted into a certain level of differences in the term of producing methyl esters. Solid acid and solid base are categorized as heterogeneous catalysts. Although homogeneous catalysts are effective and feasible, they lead to serious contamination problems in terms of poor separation and product purification protocols. The low tolerance for FFA and water concentration is one of the primary disadvantages of homogenous base catalysts. Water hydrolyzes the feedstock (triglycerides) and methyl esters to create FFA, which then interacts with the base catalyst to form unwanted soap, complicating methyl ester separation. Furthermore, FFA consumes base catalyst during the reaction causing additional catalysts to need to be added to the reaction system. The removal of the catalyst and soap from the product necessitates a huge volume of water, resulting in a large amount of wastewater (Liu et al., 2008; Chu et al., 2021). Fundamental catalysts, such as sodium hydroxides and methoxides, can only tolerate FFA concentrations of less than 0.05 percent w/w (Marchetti et al. 2007) and 0.5% w/w water (Ma and Hanna, 1999). When employing a traditional base catalyst, it is critical to heat feedstocks to remove moisture content (Boey et al., 2009; Bhuyar et al., 2020b). Thus, some inexpensive oils like waste oils and animal fats which contain a high level of FFA and water content, are no longer feasible with conventional homogeneous base catalysts. The adverse effects of FFA and water in the homogeneous base-catalyzed transesterification process are as illustrated in Figure 3. Esterification of FFA with alcohols in the presence of acid catalysts is another pathway to produce methyl esters. The fact that homogeneous acid catalysts such as H_2SO_4, HF, H_3PO_4, and HCl have been used in esterification has been extensively studied over the years. However, the use of these strong acids is hazardous, generates much wastewater during product washing. The long reaction time (Lin et al., 2011), not recoverable (Vicente et al., 2004), and difficulty in catalyst separation due to the corrosive nature of the catalyst make homogeneous acid catalysts unfavourable (Wang et al., 2006; Bhuyar et al., 2021a).

Because of the problems faced with both homogeneous base catalysts and homogeneous acid catalysts, interest looms in the direction of heterogeneous catalyst systems have been seen in the area of biodiesel production. With the advent of contemporary technology such as supercritical methanol, homogeneous catalysts quickly become obsolete (Shin et al., 2012; Jayakumar et al., 2021) and heterogeneous catalysts. Heterogeneous catalysts are chosen because the method is less expensive, making large-scale production more feasible. For both transesterification and esterification, heterogeneous catalysts such as alkaline-earth metal oxides and solid acid catalysts have been investigated.

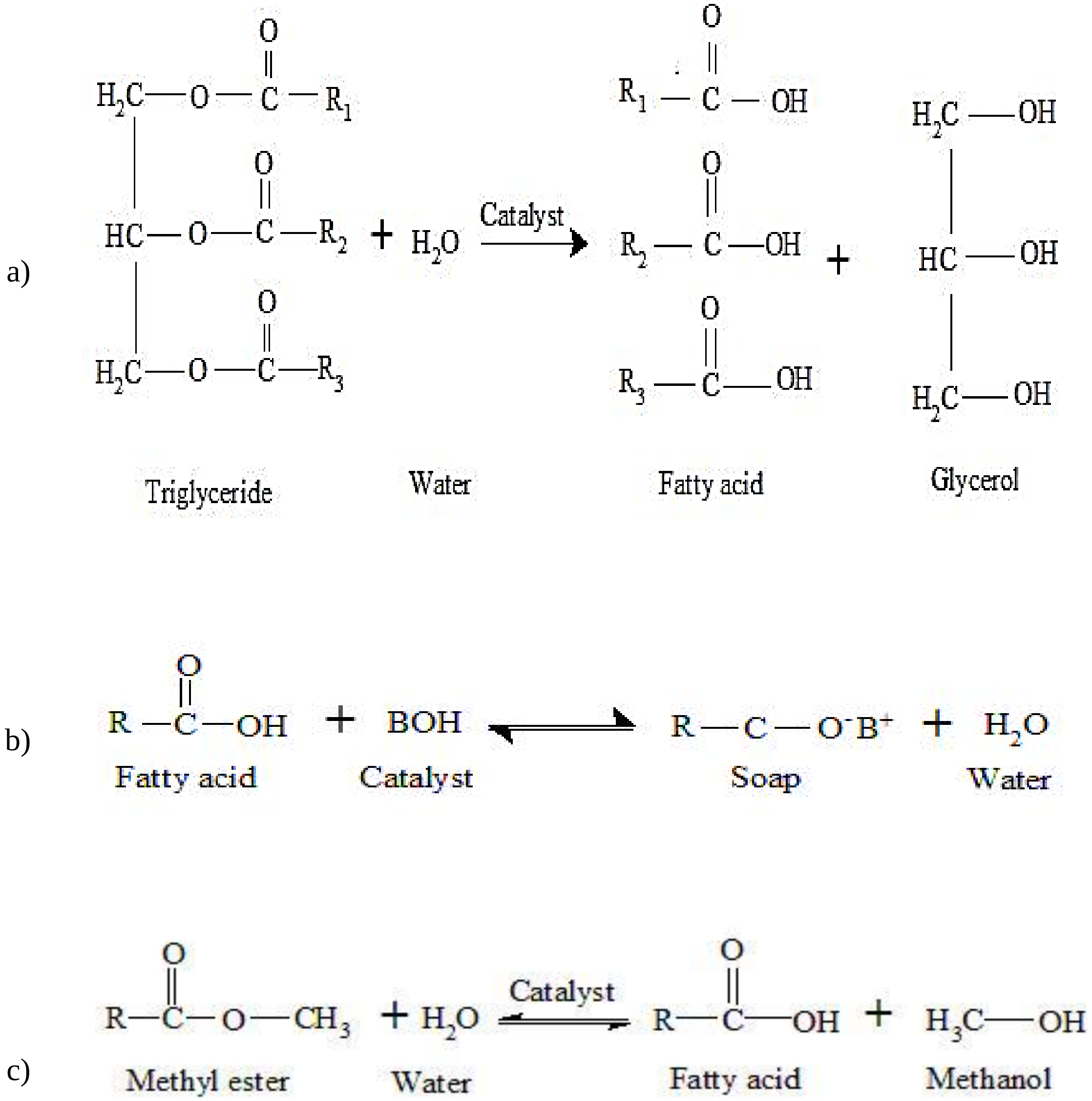


Figure 3 The effects of (a) water on triglycerides; (b) FFA on homogeneous base catalyst; (c) water on methyl esters.

Source: Su and Guo (2014)

1.7.1. Solid acid catalyst

The emergence of suitable heterogeneous acid catalysts opens the platform for using low-grade, highly-acidic, and water-containing oils feedstock in biodiesel production (Lokman et al., 2016; Olutoye et al., 2014; Shu et al., 2010 and Peng et al., 2008). Furthermore, a more environmentally friendly approach to biodiesel manufacturing has prompted the adoption of sustainable solid acid catalysts as liquid acid catalyst substitutes, avoiding the use of hazardous chemicals and the formation of toxic waste. Solid acid catalysts have lower catalytic activity, but they have higher stability than solid primary catalysts. Thus they can be used for feedstocks with high FFA without catalyst deactivation (Lotero et al., 2005). In recent years, various solid acid catalysts were developed like sulphated metal oxides, sulfonated carbon-based catalysts, heteropolyacids (HPAs), and sulfonic ion-exchange resins H-form zeolites, and sulfonic modified mesostructured silica for the sake of biodiesel production. Russbueldt and Hoelderich (2009) used sulfonic ion-exchange resins to pre-esterify FFA into methyl esters with 1 wt.% catalyst amount and FFA to methanol molar ratio of 12:1 Evaluation of sulphated zirconia towards esterification of oleic acid reported giving maximum 90% yield of methyl oleate under the mild conditions, besides able to be used as a recyclable catalyst after simple regeneration without significant loss in catalytic activity (Patel et al., 2013). Meanwhile, the sulfonated glucose-derived acid catalyst was found to be able to esterify PFAD with 92.3% methyl esters yield at a catalyst loading of 2.5 wt.%, methanol to PFAD molar ratio of 10:1, reaction temperature of 75 ºC, and reaction time of 2 h (Lokman et al., 2015a). Table 3 lists some of the diverse solid acid catalysts used in the production of biodiesel.

Table 3 Various solid acid catalysts for esterification and transesterification.

Solid acid catalyst	Feedstock	Yield (%)	References
Carbon-based solid acid from rice husk	Oleic acid	91	Zeng et al., 2016
$[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$	Palmitic acid	93	Han et al., 2015
Coconut shell char-based catalyst	PFAD	84	Hidayat et al., 2015
INDION-225H	Sal oil	97	Hajra et al., 2015
$NiSO_4/SiO_2$	Brown grease	85	Kim et al., 2013
$OMC-H_2O_2-SO_3H$	Oleic acid	80	Chang et al., 2013
Zr-PMOs	Crude palm oil	80-85	Sánchez-Vázquez et al., 2013
POVB-$[C_{1vim}][SO_3CF_3]$	Tripalmitin	93	Liu et al., 2012
$H_3PW_{12}O_{40}$/Hß	Jatropha oil	93	Patel and Narkhede, 2012
$H_3PW_{12}O_{40}.6H_2O$	Waste cooking oil	93	Noshadi et al., 2012

1.7.2. Solid acid catalysts design for biodiesel synthesis design

The ideal solid acid catalysts for the esterification and transesterification process should have strong Brønsted and Lewis' acid properties, hydrophobic surface, and unique porosity properties (morphology of the support). However, leaching of the acid site, deactivation, and poisoning during the reaction process should be avoided. The H^+ donor Børnsted acid sites are strongly polarized hydroxyl groups at the catalyst's surface, while the electron-pair acceptor Lewis acid sites are coordinately unsaturated cationic sites that leave the exposed M+ ion to interact with guest molecules. A solid acid catalyst with both Brnsted and Lewis acid sites (bifunctional) and a hydrophobic environment shielding the Lewis site from water poisoning would be the ideal choice for biodiesel synthesis. Due to their reduced catalytic activity relative to solid bases, most solid acid-catalyzed esterification or transesterification processes occur at higher temperatures and pressures (Su and Guo, 2014; Bhuyar et al., 2021c).

1.7.3 Sulphated Metal Oxide Solid Acid Catalyst

Solid acid catalysts are available in various forms, sulfated metal oxides such as SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2, and SO_4^{2-}/Ta_2O_5 are of interest for esterification and transesterification, and under moderate circumstances, they have the potential to provide economic and environmental benefits for a wide range of hydrocarbon processes. Table 4 lists the recently published works that employed the sulfated metal oxide solid acids in biodiesel production. Generally, the electronegativity of the metal element influences the Brønsted acid strength of sulfated metal oxide. The lower the electronegativity of the metal element, the weaker the M−OH bond is expected, where the release of the proton becomes more easily (Su and Guo, 2014). In addition, the existence of sulfate group modifying metal oxide could also enhance the Brønsted acidity (Hernández et al., 2013). As shown in Figure 4 in each SO_4^{2-}/TiO_2 unit, two oxygen atoms from S−O bonds are bonded to Ti atoms so that the S=O group can coordinate with a Ti atom. As a result, the acidic proton is derived from the surface hydroxyl group of TiO_2 induced by the sulfate group. The acidic proton can be released easily because S−O−Ti bonds link an SO_4^{2-} group with the TiO_2 matrix, resulting in the strong Brønsted acidic strength of the SO_4^{2-}/TiO_2. The same explanation goes for SO_4^{2-}/Ta_2O_5, SO_4^{2-}/Nb_2O_5, and SO_4^{2-}/ZrO_2 (Su and Guo, 2014).

Table 4 Recently study on sulfated solid acid catalysts in biodiesel production.

Catalyst	Experimental conditions (catalyst amount, alcohol to oil molar ratio, reaction time, reaction temperature)	Yield (%)	References
Sulphated zirconia	6 wt.%; 20:1; 5-7 h; 60 ºC	90	Saravanan et al., 2016
Sulphated Ti-SBA-15	1 wt.%; 15:1; 4 h; 200 ºC	91	Singh et al., 2018
Sulphated lanthanum oxide	6 wt.%; 5:1; 7 h; 100 ºC	96	Vieira et al., 2013
Sulphated titania	10 wt.%; 20:1; 3 h; 120 ºC	77	Shao et al., 2013
Sulphated tin oxide	6 wt.%; 15:1; 1.5 h; 150 ºC	88.2	Lam and Lee, 2010

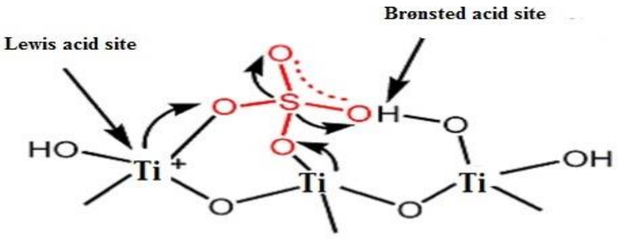


Figure 4 Illustration of the Brønsted and Lewis acid sites in SO_4^{2-}/TiO_2 acid.

2.8. Rice husk ash (RHA) as a catalyst supporter

Alumina, silica, montmorillonite, organic polymer, and zeolite are some of the supports or precursors that may be used to produce solid acids catalysts. All of these materials have a high surface area (100-1000 m^2/g) and porous structure. High surface area is necessary for any active catalyst for the reactants and products to have fast mass transfer and good active phase dispersion (Singh and Patel, 2014). Alumina and silica were well-known been used in biodiesel production. For alumina, alumina oxide, which exists in forms of porous γ-alumina and ή-alumina and nonporous crystallineα-alumina has been widely used as a support in catalysis processes, especially in general biodiesel mainly due to its high specific area, large pore size, and high thermal stability. For example, Xie et al. (2006) studied the catalytic efficiency of potassium supported by alumina as a solid base catalyst in the transesterification of soybean oil to biodiesel. The catalyst was prepared by an impregnation method of the aqueous solution of potassium nitrate on alumina. The results revealed that the catalyst was the most active when calcined at 500 °C and loaded by 35 wt.% of KNO_3 with the highest conversion of oil reached 87%, after the reaction time of 8 h with a molar ratio of methanol to soybean oil of 15:1 and 6.5 wt.% of catalyst.

However, between alumina and silica, silica is one of the upmost used cases due to its ease of handling, abundantly available, low cost, and non-corrosive (Shirini et al., 2013). Numerous studies were successfully used the amorphous silica as support in the biodiesel field. For example, Lin and Radu (2006) patented the application of sulfonic acid supported by mesoporous silica as a robust solid acid for transesterification reaction. They used Tetraethoxysilane (TEOS) was used as a precursor of silica. Shao et al. (2013) studied biodiesel production by sulfated titania supported with silica via the sol-gel method. It was observed that the sulfated titania-silica composite calcined at 450 °C and 500 °C possessed high catalytic activity for esterification of oleic acid and transesterification of waste oil.

Current research prefers to employ agricultural wastes, such as rice husk ash (RHA), as a support for catalytic materials, according to the costing-related concern. RHA is believed to be mostly made up of silica (87-99%) and a few inorganic salts (Prasetyoko et al., 2006). RHA was obtained during the milling process by burning the rice husk (outer layer of rice grain) in the air, a waste product. RHA has a high percentage of silica (87-99%), cellulose, hemicellulose, lignin, and a trace quantity of inorganic salt (Hindryawati et al., 2014, and Chakraborty et al., 2011). RHA can be economically feasible support for the manufacture of silica-based solid acids catalysts since it has a solid pozzolanic activity and a substantial quantity of silica content (Feng et al., 2004). In addition, currents biodiesel teams already showed interest in using RHA as catalytic materials (Chen et al., 2015; Hindryawati et al., 2014; Chen et al., 2013; Shirini et al.,2013).

2. Conclusion

To conclude, choosing the right feedstock is a key-driven to the success of biodiesel preparation as the feedstock makes up a significant portion of the overall production cost. Waste oil and a by-product of industry are promising biodiesel feedstock in terms of cheaper prices and availability. The potential of waste oils, especially PFAD and Dc-oil can be used as feedstock are briefly reviewed in this chapter. Even though waste feedstock has a high FFA value, it can be solved by applying a heterogeneous solid acid catalyst system. Several solid acid catalysts were used in the preparation of biodiesel which possesses high FFA and highly acidic feedstock; the results of which are reviewed and summarized. The survey shows that sulfated metal oxide solid acid catalysts offer great interest in the biodiesel field. The survey also reveals that not much effort has been undertaken to evaluate the performance of sulfated metal oxide acid catalysts in the esterification and transesterification of waste oil for biodiesel production.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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