SCUM SLUDGE FROM PALM OIL MILL EFFLUENT TREATMENT PLANT AS BIODIESEL FEEDSTOCK

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LIST OF SYMBOLS

Symbol	Description	Unit
A_S	Saponification value	mg KOH/ g biodiesel
Aa	Acid number	mg KOH/ g biodiesel
AV	Acid value	mg KOH/ g oil
G_{ttl}	Total glycerol content	%mass
$V_{titrant}$	Volume of titrant used	mL
W_{FFA}	Weight of soap converted to FFA (oil)	g
$W_{moisture}$	Weight of moisture content	g
W_{oil}	Weight of oil	g
$W_{oil,i}$	Initial weight of oil	g
$W_{oil,f}$	Final weight of oil	g
$W_{scum,i}$	Current weight of scum oil	g
$W_{scum, i-1}$	Previous weight of scum oil	g

LIST OF ABBREVIATIONS

Abbreviation	**Description**
ASTM	American Society for Testing and Materials
CN	Cetane number
CPO	Crude palm oil
EASAC	European Academies Science Advisory Council
EN	European Standards
FAME	Fatty acid methyl esters
FFA	Free fatty acid
GC-MS	Gas chromatography-mass spectrometry
GHG	Greenhouse gas
HVO	Hydrotreated vegetable oil
LBM	Liquefied biomethane
OPEC	Organization of the Petroleum Exporting Countries
OTEC	Ocean thermal energy conversion
POME	Palm oil mill effluent
SDGs	Sustainable Development Goals
SVO	Straight vegetable oil
UMN	University of Minnesota
WOO	World Oil Outlook
WWTP	Wastewater treatment plant

ABSTRAK

Bahan bakar biodiesel telah menarik perhatian pengguna sebagai alternatif lestari untuk bahan bakar diesel yang tidak boleh diperbaharui. Sementara itu, pengurusan enapcemar kumbahan yang terapung di atas permukaan lagun rawatan air buangan kilang kelapa sawit telah menjadi isu. Dalam kajian ini, potensi penggunaan enapcemar kumbahan sebagai bahan biodiesel telah dikaji. Enapcemar kumbahan daripada kolam rawatan air sisa Syarikat Hilltop Palm diperoleh di dalam bekas dan disimpan di dalam bilik sejuk. Ciri-ciri enapcemar kumbahan seperti kelikatan, kandungan kelembapan dan nilai asid telah ditentukan. Kandungan kelembapan dalam enapcemar kumbahan dikeringkan dalam oven pada suhu 105°C sementara nilai asid ditentukan dengan titrasi minyak terhadap larutan standard kalium hidroksida. Kemudian, biodiesel dihasilkan melalui transesterifikasi in-situ dan kesan parameter operasi seperti masa reaksi, dos pemangkin dan isipadu pelarut dikaji. Daripada pencirian enapcemar kumbahan, kelikatannya berkaitan secara negatif dengan suhu, purata peratusan kandungan kelembapan yang dikeluarkan adalah 0.05% dan nilai asid enapcemar kumbahan diturunkan menjadi kurang dari 2mg KOH/g minyak melalui esterifikasi yang dikataliskan oleh asid. Peratusan maksimum penghasilan biodiesel adalah 80.12% berdasarkan enapcemar kumbahan basah. Peratusan ini diperoleh melalui tindak balas 10g minyak enapcemar kumbahan yang dilarutkan dalam 70 ml pelarut n-heksana dengan bantuan katalis asid 5% H_2SO_4 dalam 100 mL metanol pada suhu tindak balas 60 ° C selama 4 jam. Daripada analisis komposisi FAME, telah ditentukan bahawa komponen utama yang terdapat dalam biodiesel yang dihasilkan adalah metil palmitat dan metil oleat yang juga terdapat dalam biodiesel yang dihasilkan dari minyak sayuran lain. Oleh itu, enapcemar kumbahan berpotensi untuk pengeluaran biodiesel.

ABSTRACT

Biodiesel fuel has gain consumers attention as a more sustainable alternative for conventional non-renewable diesel fuel. Meanwhile, the management of floating scum on the surface of the palm oil mill effluent (POME) wastewater treatment lagoon has been an issue. In this study, the potential of using POME scum as biodiesel feedstock was investigated. The scum was collected from Hilltop Palms Sdn. Bhd. wastewater treatment pond and stored in a carboy container in a cold room. The characteristics of scum oil including viscosity, moisture content and acid value were determined. The moisture content in the scum was removed by oven drying at 105°C while the acid value was determined by titration of oil against potassium hydroxide standard solution. Then, the scum-to-biodiesel was produced through in-situ transesterification and the effects of operational parameters such as reaction time, catalyst dosage and solvent volume were studied. From the characterization of POME scum, the viscosity of the scum is negatively related to temperature, the average percentage of moisture content removed is 0.05% and the acid value of scum was reduced to less than 2 mg KOH/g oil through acid-catalysed esterification. The maximum scum-to-biodiesel yield percentage is 80.12% based on wet scum oil. The reaction condition for the maximum biodiesel yield percentage is the reaction of 10g wet scum oil dissolved in 70mL of n-hexane solvent aided by 5%wt H_2SO_4 acid catalyst (based on scum oil weight) in 100mL methanol at a reaction temperature of 60°C for 4 hours. From the FAMEs composition analysis, it was determined that the major component found in the biodiesel produced is methyl palmitate and methyl oleate which is also found in biodiesel produced from other vegetable oil. Therefore, POME scum has the potential for biodiesel production.

CHAPTER 1
INTRODUCTION

Chapter 1 introduces the overview of this research and the potentiality of using scum from palm oil mill effluent (POME) wastewater treatment lagoons as biodiesel feedstock. Other important biodiesel feedstocks and the four major techniques of biodiesel production are included. This chapter summarizes the research background of scum-to-biodiesel production, the problem statements, and the objectives of this final year project.

1.1 Research Background

Scum is a waste material produced by wastewater treatment plants (WWTPs). It is a floatable material that can be found on the surface of primary and/or secondary settling tanks or lagoons in WWTP. Scum comprises mainly fats, oils, and grease. Since oils are less dense than water, most oils float on the surface and form scum by conglomeration with other wastes. Depending on the sources of wastewater, scum may contain animal fat, vegetable oil, food wastes, plastic material, soaps, waxes, and several other impurities (Bi et al., 2015). The origin of the scum may result in a high amount of biodegradable compounds including lipids, proteins, carbohydrates, and other organic materials (di Bitonto et al., 2020a). Scum, if not removed in the first place will cause detrimental effects on the operations of WWTP by clogging the treatment unit systems. A sufficient amount of lipids and fatty acid especially long-chain fatty acid can significantly impact both aerobic and anaerobic processes (Chipasa and Mędrzycka, 2006) and slow down the process of methanogenesis during anaerobic digestion (Damasceno et al., 2018, Luostarinen et al., 2009, Carucci et al., 2005). Furthermore, when scum is removed by pumping it together with the sludge to the waste sludge treatment system, it will essentially cause clogging in sludge pipes and sludge dewatering unit which then impede the operation of dewatering unit (Wang et al., 2016, Chernicharo et al., 2019). Thus, it is crucial to skim off the scum by using a grit chambers at the beginning of wastewater treatment process.

The skimmed off scum is a rich source of energy for recovery since its oil content can be as high as 60% (Bi et al., 2015). However, technology issues and considerations regarding cost and environmental consequences are a concern for the utilization, energy recovery of scum and even in the disposal of scum. The two most practised methods in managing scum waste are landfill and anaerobic digestion. Many wastewater treatment plants decided to directly dispose of scum in landfills because of the problems that emerge in scum anaerobic digestion. For instance, the floating scum on top of the digester formed a thick layer on the surface impairs the digester performance (Bi et al., 2015). Nevertheless, landfilling does not appear to be a better choice of managing scum either because of the many serious environmental problems that resulted. The percolation of rainwater through the wastes in landfill cells produced another waste which is landfill leachate. Landfill leachate is a potential source of underground water pollution (Haslina et al., 2021). Hence, another sustainable alternative is to be developed and applied for the disposal or utilization of scum waste.

Recently, new progress was developed to manage scum waste in a much environmentally friendly and economical way. The new scum-to-biodiesel process has attracted many researchers attention and as a result, different methods were approached to optimize the conversion (di Bitonto et al., 2020b). Developing this technology is like killing two birds with one stone because not only the problem of treating scum is dealt with, the issue about the high rocketing cost of biodiesel feedstock is also addressed. Biodiesel has been an attractive alternative for diesel fuel and since the 1990s, vegetable oil has been the chief source for global biodiesel production and it still is the largest feedstock now. Regardless, the inflating price of vegetable oil especially soybean oil led to the searching for other possible feedstock alternatives. In sequence, refined vegetable oils, animal fats and then waste oil such as yellow grease in particular used cooking oils are adopted as biodiesel feedstocks. As the market demands significantly rising, even the less preferred and extra difficult to process waste oil including trap greases and brown greases are used as feedstock alternatives. It is noticed that the alternative feedstock is getting ‘dirtier’ but significantly cheaper in each succeeding step. The newest potential feedstock of scum and sludge waste from WWTP is most likely the ‘dirtiest’ and yet the cheapest available feedstock for biodiesel production. However, as promising as it sounds, hurdles still exist. These ‘dirtier’ sources contained more impurities and a higher level of free fatty acid (FFA) and lipid content which requires more processes to produce biodiesel (Cobb et al., 2020).

Most implemented methods for biodiesel production comprises dilution of vegetable oil and diesel, micro-emulsion synthesis, pyrolysis or thermal cracking and modified transesterification method (Srivastava et al., 2018, Siddiquee and Rohani, 2011, Vyas et al., 2010). Among the four techniques, modified transesterification is the prevailing biodiesel production method due to its low process cost and the low viscosity biodiesel produced has superior quality (Liu et al., 2021). Under modified transesterification, several different approaches are researched for the past decade on account of different characteristics of the feedstocks. Traditional transesterification, in-situ transesterification, two-step esterification/transesterification and six-step esterification/transesterification methods are some of the approaches developed (Liu et al., 2021, Bi et al., 2015).

In this research, the concerns are the potentiality of floatable scum from palm oil mill effluent waste treatment plant as biodiesel feedstock with regards to the scum characteristics.

1.2 Problem Statement

The scum on the surface of the wastewater treatment ponds or settling tanks can cause detrimental effects due to its high biodegradable compounds level. Scum must first be skimmed off the settling tanks before the succeeding treatment process of the wastewater can proceed. The problem that arises is the management of scum waste. Traditionally, it is disposed to landfill or digested anaerobically for biogas recovery. However, these conventional methods are not ideal. Landfilling causes environmental issues such as the formation of landfill leachate while anaerobic digestion is costly, and the floating scum continuously hindered the digestion performance. On the other hand, biodiesel is an emerging renewable source for liquid fuel. However, plant-based biodiesel production is facing an issue with the availability of feedstock. Biodiesel feedstocks such as soybean and palm oil are getting expensive because of competition with the food supply hence making biodiesel production less economical. Alternative of using oily waste such as scum as the biodiesel feedstock is currently applied and this new scum-to-biodiesel method is also a promising approach to solve the issue regarding scum disposal or utilization. The efficiency of scum-to-biodiesel conversion and the quality of biodiesel produced are essentially dependent on the characteristics of the scum such as water content and acid value. The characteristics of scum as feedstocks will determine the best production route for biodiesel production. Transesterification is one of the many methods to produce biodiesel. This process has a stringent requirement of low water and free fatty acid content since the type of catalyst used in this process is highly sensitive to water and free fatty acid. Thus, the problem arises when the scum to be used as feedstock oil for biodiesel has high water and free fatty acid content. For the past years, research for the scum-to-biodiesel conversion was done by using municipal scum or municipal sewage sludge and the results are encouraging. However, the origin of scum from municipal wastewater treatment plants differs from the scum obtained from POME wastewater treatment plant. In other words, the water and free fatty acid content in the scum obtained from the POME treatment plant may be higher or lower as compared to the scum from a municipal wastewater treatment plant. Hence, this study is addressing the issue of scum management from the POME wastewater treatment plant by using it as biodiesel feedstock alternatives. The characteristics of the scum including viscosity, moisture content and acid value are first to be determined before the process of biodiesel production. The chosen biodiesel production route is in-situ transesterification. The importance of acid washing and acid-catalyzed esterification in biodiesel production are also studied. Besides, the effects of parameters on the in-situ transesterification are studied by manipulating the parameters such as solvent volume, catalyst dosage and reaction time.

1.3 Objectives

The objectives of this report are:

i. To study the viscosity, moisture content and acid value characteristics of palm oil mill effluent scum.
ii. To investigate the effect of operating conditions on biodiesel production through in-situ transesterification.
iii. To analyze fatty acid methyl esters (FAMEs) composition in the biodiesel produced.

CHAPTER 2
LITERATURE REVIEW

Chapter 2 lays out many past researches and discoveries from valid scientific records and references related to this topic. This chapter covers the overview of biodiesel as bioenergy, biodiesel feedstock, biodiesel production technologies and scum-to-biodiesel conversion.

2.1 Biodiesel the Bioenergy

Biodiesel fuel has gain consumers attention as a more sustainable alternative for conventional non-renewable diesel fuel. With the rapid and continuous growth of the world's population, urbanization, industrialization, and economy especially in developing countries, the demands for energy sources correspondingly increased. However, the aforementioned conventional energy sources are facing a shortage and are not able to meet the global demands in the future. According to the World Oil Outlook 2014 prepared by the Organization of the Petroleum Exporting Countries (OPEC), the key to increasing global oil demands is undoubtedly developing countries. The annual medium-term rise of developing countries is 1.1 mb/d (millions of barrels per day) from 2013 to 2019 (OPEC, 2014). In this report, Malaysia is grouped in the 'Other Asia' category and the average demand growth is almost 0.2 mb/d p.a. (millions of barrels per day per annum) for the same year range. It was predicted that oil demands in 'Other Asia' will increase to 10.3 mb/d in 2030 from 8.4 mb/d in 2019.

Regardless of whether the conventional energy sources are in shortage or not, it is wise to reduce the exploitation and usage of these energies since they contributed significantly to greenhouse gases (GHGs) emissions and other environmental damages. Another environmental damage is oil spillage to the watercourse which then affected marine life and later impacting human's life (Gopal and Reddy, 2015). Nevertheless, GHGs is more crucial in this generation and was paid more attention by many organisations worldwide. In 2010, the economic sector specifically the industry and building sectors consumed the most electricity and heat hence contributing eminently (more than 50%) to GHGs emissions (OPEC, 2014). In developing countries, there is no doubt that the number of industrial factories and other buildings built is increasing tremendously which results in uncontrollable high GHGs emissions. According to the BP Statistical Review of World Energy 2019, Malaysia's carbon dioxide (CO_2) emissions increased from 241.6 million tonnes in 2017 to 250.3 million tonnes in 2019, an increase of 3.6% (BP, 2019). In 2020, the CO_2 emissions remarkably reduced to 244.5 million tonnes as a consequence of the pandemic that took place in the year 2020 (BP, 2020). In light of the GHGs emissions from the utilization of non-renewable energy, alternative energy is of everyone interest and hence research on renewable energy has gotten extra attention since the last decade.

Renewable energy is an energy source derived from renewable sources that are replenished naturally. When utilized, renewable energy does not contaminate the natural environment or air and watercourse thus also called green power or clean energy (Rafiee and Khalilpour, 2019). Bioenergy is one of the many examples of renewable energy apart from tidal, wave, and ocean thermal energy conversion (OTEC). Bioenergy can be further categorized into biofuels and bioenergy for heat and power. It is available in the form of solid, liquid, or gaseous. Solid biofuels include charcoal, fuelwood, and wood pellets meanwhile the most utilized biofuel in gaseous form is biomethane gas. Some viable liquid biofuels are biodiesel, bioethanol, biomass-based Fischer-Tropsch diesel, biomethanol, dimethyl ether, hydrotreated vegetable oil (HVO), liquefied biomethane (LBM), pyrolysis oil, and even straight vegetable oil (SVO) are used for seaborne transport (IRENA, 2015). Biofuels are sought for the numerous benefits promised which related to the energy securities, environment, and economy. Even so, several hurdles must be overcome to conquer these assets. The major benefits and challenges in the production and consumption of biofuels are summarized in Table

2.1 (Nigam and Singh, 2011, Hoekman, 2009, USDA, 1999, Rafiee and Khalilpour, 2019). The challenges to be addressed including feedstock, technologies, and policy.

Table 2. 1 The benefits and challenges of biofuels.

Benefits	Challenges
Energy Security • Domestic supply • Locally distributed resources • High supply reliability • Well-connected supply-demand chain • Reduction of petroleum usage	**Feed Stock** • Source availability • Collection network • Storage facilities • Food-fuel competition
Environmental Impact • Reduce GHGs emissions • Reduce local pollution • Better waste management and usage • Decrease in landfill sites • Improve biodiversity • Wildlife habitat conservation • Biodegradable with little or no toxicity	**Technology** • Pre-treatment efficiency • Catalyst development • Enzyme production • Yield improvement • Extraction cost • Production cost • Production of value-added co-products
Economic Stability • Price stability • Employment opportunities • Development in rural areas • Reduce demand-supply gap • New industry growth	**Policy** • Research and development fund • Land usage • Pilot-scale demonstration • Policy for biofuels • Commercial-scale deployment • Tax credit on production and application of biofuels

Among the many types of liquid biofuels, biodiesel and bioethanol are most widely used mainly because of their favourable characteristics viz. suitable to replace petroleum-derived diesel, suitable to be used in most diesel engines with slightly or without modifications necessitated in the existing engine hardware and fuel delivery infrastructure, relatively easier production route and economically viable (Bora et al., 2020, USDA, 1999). Comparing the two biofuels, biodiesel is more preferable compared to bioethanol due to the limited application of bioethanol as an additive with gasoline to enhance the quality of combustion and the performance of engines (Bora et al., 2020). Meanwhile, biodiesel has properties almost similar to diesel and is hence much preferred as a fuel alternative. However, the main concern of the biodiesel characteristic is its high viscosity. High viscosity does not necessarily offer better application of biodiesel. The high viscosity is the result of the large molecular mass and chemical structure of vegetable oils (Hassan and Kalam, 2013). If significantly high viscosity biodiesel is to be used in a diesel engine, problems in pumping, combustion and atomization in the injector system may occur. Other drawbacks of biodiesel are high pour and cloud point, augmented nitrogen oxides emission, less volatility and lower energy content (Demirbas, 2008a). Regardless, biodiesel among other options is still the best alternative for the fulfilment of future energy requirements.

The effort of producing biodiesel to be utilized and commercialized will be in vain if the produced biodiesel does not meet the permissible limits stipulated by the American Society for Testing and Materials (ASTM) or European Standards (EN) depending on the origin of production. According to these standards, the quality of biodiesel is determined by measuring its properties such as acid number, cetane number (CN), density, flashpoint, iodine number, kinematic viscosity and oxidation stability. Table 2.2 shows the specifications of ASTM D 6751 and EN 14214 standards of biodiesel (Jääskeläinen, 2009).

Table 2. 2 Specification of biodiesel properties according to EN 14214 and ASTM D 6751 standards.

Parameters	**EN 14214**		**ASTM D 6751**	
	Test method	**Limits**	**Test method**	**Limits**
Ester content	EN 14103	96.5% [a]min	-	-
Monoglycerides	EN 14105	0.80% [a]max	-	-
Diglycerides	EN 14105	0.20% [a]max	-	-
Triglycerides	EN 14105	0.20% [a]max	-	-
Free glycerine	EN 14105	0.02% [a]max	ASTM D 6584	0.020% [b]max
Total glycerine	EN 14105	0.25% [a]max	ASTM D 6584	0.240% [b]max
Water	EN ISO 12937	500 mg/kg max	ASTM D 2709	0.050% [c]max
Methanol	EN 14110	0.20% [a]max	-	-
Potassium	EN 14108	5.0 mg/kg max	UOP 391	5.0 mg/kg max
Phosphorus	EN 14107	10.0 mg/kg max	ASTM D 4951	0.001% [b]max
Density	EN ISO 3675	860-900 kg/m^3 (15°C)	-	-
Kinematic viscosity	EN ISO 3104	3.5-5.0 mm^2/s (40°C)	ASTM D 445	1.9-6.0 mm^2/s (40°C)
Flashpoint	EN ISO 3679	120°C min	ASTM D 93	130°C min
Cloud point	-	-	ASTM D 2500	N/A
Sulfated ash	ISO 3987	0.02% [a]max	ASTM D 874	0.020% [b]max
Total contamination	EN 12662	24 mg/kg max	-	-
Acid value	EN 14104	0.5 mgKOH/g max	ASTM D 664	0.5 mgKOH/g max
Iodine value	EN 14111	120g I2 x 100g^{-1} max	-	-
Heating value	-	-	ASTM D 240	-
Cetane number	EN ISO 5165	51 min	ASTM D 613	47 min

[a](mol/mol)
[b](w/w)
[c](v/v)
max: maximum
min: minimum

* ester content (%-mass) = $[100(A_s-A_a-4.57G_{ttl})]/A_s$

Note:

A_s : saponification value, AOCS Cd 3-25, mg KOH/g biodiesel

A_a : acid number, AOCS Cd 3-63, mg KOH/g biodiesel

G_{ttl} : total glycerol content, AOCS Cd 14-56, %-mass

2.2 Biodiesel Feedstocks

According to the European Academies Science Advisory Council (EASAC) Report 2012, biodiesel which is also known as alkyl ester of fatty acid can be classified into four generations according to the type of feedstocks. The first-generation biodiesel is produced from edible oils, the second generation from non-edible oils, the third from wastes oil and the fourth which is still on infancy level is biodiesel drawn from man-made biological tools (Singh et al., 2019, Singh et al., 2020). Depending on the type of feedstock, the route of production and properties of the end product biodiesel varies. Nevertheless, as long as the end product characteristics comply with the aforementioned standard, it is permissible to be utilized and commercialize. The route of production either with pre-treatment or without will determine the cost-effectiveness of biodiesel conversion.

The first generation of biodiesel produced from edible oils such as cashew nut, pistachio and walnut (Tanzer et al., 2016), coconut (Aninidita et al., 2010), corn (Mahdavi et al., 2015), cottonseed (Subbarayan et al., 2016), hazelnut (Bryan, 2012), mustard and radish (Abdelrahman and Waseem, 2014), olive (Woodford et al., 2014), palm oil (Rajesh and Shakkthivel, 2013), rapeseed (Sergei et al., 2016), rice bran (Mayank et al., 2017), soybean (Daniela et al., 2016) and sunflower (Tony et al., 2016). The major oils will be soybean, coconut, corn, olive, cottonseed and sunflower (Demirbas, 2008b). In the mid-1990s, the biodiesel industry reached a commercial scale and soybean oil is the major feedstock for biodiesel production (Cobb et al., 2020). During that year, soybean farmers were producing more oil than the market demands which causes the price to decrease significantly and hence are economical to be used as biodiesel feedstock. As biodiesel manufacturing grows, the soybean oil demand increased and its price inflated to the point that it is no longer economical to use soybean as biodiesel feedstock (Anon, 2021b). To meet the increasing soybean oil demands for biodiesel production, a huge land area is required to yield more crops every year. Moreover, the major problem faced in using edible oil as biodiesel feedstock is the competition with the food supply. Hence, an alternative of non-edible oils as biodiesel feedstock led to the second generation.

The biodiesel feedstock sources broaden when non-edible oils are also utilized. There are a vast of non-edible oils including oil from *Aleutites fordii*, sea mango, hochst, *Jatropha curcas* L., *Madhuca indica*, neem, tobacco, rubber seed, soapnut and yellow oleander (Jagannath and Atul, 2014), babassu tree, jojoba, karanja, milk bush, nagchampa, petroleum nut, silk-cotton tree and tall (Tanzer et al., 2016), *Calophyllum inophyllum* (Atabani et al., 2013) and castor oil (Murat et al., 2013). The main advantage of non-edible oil is that the plant producing the crops can be grown on non-arable land thus continuous yield of crops are possible (Atabani et al., 2013). However, the biodiesel yield by some of the non-edible oils are lower as compared to edible oils and the cost-effectiveness of conversion technology is essentially low. The development of biodiesel manufacturing then moved to the third generation whereby wastes are used as feedstock and not only plant-based oil waste, but even animal wastes are also used as feedstock mainly because they possess high oil content.

In third-generation, the waste oils are animal tallow (Cengiz and Şehmus, 2009), biomass pyrolysis (Le et al., 2013), *Botryococcus brauinii*, *Chlorella vulgaris* and *Dunaliella salina* (Teresa et al., 2010), chicken fat (Metin et al., 2010), poultry fat (Paulo et al., 2015), fish (Gnanasekaran, 2016) and waste cooking oil or yellow grease (Joonsik et al., 2016). Now, the feedstock for biodiesel conversion appear to be less clean and it may contain undesirable contaminants in which needed to be handled before proceeding with biodiesel production. Nevertheless, waste oils are much cheaper as compared to the previous two generations feedstock and can be easily acquired. The available feedstock oils became 'dirtier' when the less desirable oils like trap grease and brown grease are used. Trap greases are collected from restaurants and commercial kitchens while brown greases are trap greases that have been heated to melt, decanted to remove free water, and filtered to remove food scraps or other solid materials (Cobb et al., 2020). This idea of utilizing waste oils to produce valuable product is bringing a great positive impact not only economically but also environmentally by reducing air and water pollution. For the past decade, the dirtiest waste oil available and applicable as biodiesel feedstock probably is the scum and sludge from wastewater treatment plants. Many lab's scale research has been conducted to study scum-to-biodiesel conversion, many patents available and some countries have developed a pilot system of this process for instance in St. Paul, Minnesota Wastewater Treatment Plant. St. Paul WWTP applied a portion of the pilot system design from the UMN process patent – US Patent # 9,745,530 (Ruan et al., 2017). The scum and sludge used in research are mainly acquired from municipal wastewater treatment which contain usable oils and fatty acid from kitchens, soaps and detergents from households and other unique impurities and oil like contaminants (Chen et al., 2016, di Bitonto et al., 2016, Ibrahim and Hamza, 2017, Wang et al., 2016, Bi et al., 2015, Cobb et al., 2020).

Lastly, the fourth generation comprises photobiological solar fuels and electro-fuels (Aro, 2016). The conversion of solar energy into biodiesel using raw materials from renewable sources that are broadly available, limitless and inexpensive is a new research field (Singh et al., 2020). Modern synthetic biology is a permissive technology for described transformation of solar energy to biodiesel (Cameron et al., 2014). This technology offers better promises as listed in Table 2.3 but then again, the challenge will be the high initial investment since this technology is recently developed and still require more research. Table 2.3 describes each generation's feedstocks as well as their advantages and limitations. The advantages and limitations of each biodiesel generation are summed up from different research done in the past (Deepak et al., 2006, Ejaz and Younis, 2008, Atabani et al., 2013, Devendra et al., 2015, Özer, 2014, Jagannath and Atul, 2014).

Table 2. 3 Feedstocks, benefits, and limitations for each biodiesel generation.

Generation	Feedstocks			Benefits	Limitations
First (Edible oil)	Cashew nut Coconut Corn Cottonseed Hazelnut Mustard	Olive Palm Pistachio Radish Rapeseed Rice bran	Soybean Sunflower Walnut	• Readily available feedstocks • The biodiesel conversion process is easy	• Competition with food supply • Crop yield is low • Large area required for cultivation • Crops are less adaptable to environmental changes
Second (Non-edible oil)	*Aleutites fordii* Babassu tree *Calophyllum inophyllum* Castor Hochst *Jatropha curcas* L.	Jojoba Karanja *Madhuca indica* Milk bush Neem Petroleum nut Rubber seed	Sea mango Silk-cotton tree Soapnut Tall Tobacco Yellow oleander	• Does not compete with food supply • Crops can generally grow on non-arable land • Production cost is lesser	• Less cost-effective conversion technology • Some feedstocks yield essentially less biodiesel
Third (Waste oil)	Animal tallow Biomass pyrolysis *Botryococcus brauinii* Chicken fat	*Chlorella vulgaris* *Dunaliella salina* Poultry fat Fish	Waste cooking oil Trap greases Brown greases Scum sludge	• Better management of wastes • The growth rate of algae is high • Not affecting food supply • Algae can be grown in seawater or wastewater	• Energy consumption for algae cultivation is high • Lipid content of algae in open pond system is low • The oil extraction process is expensive • Extra pre-treatment required.

Table 2.3 (continued)

Fourth (Solar biodiesel)	Photobiological solar biodiesel Electrobiofuels Synthetic cell	• Lipid content is higher • Higher carbon dioxide absorbing ability • Energy content is high • Rapid growth rate	• High initial investment • Research is still on infancy level

2.3 Biodiesel Production Technologies

Managing waste that is abundantly generated every day from different sectors by converting it into valuable products is a sustainable route for a better future in terms of environmental, economic, and social. Scum-to biodiesel is undoubtedly a sustainable approach yet to what extent does it reflects sustainability? To date, many biodiesel production technologies have been developed but four major technologies applied are dilution or blending, micro-emulsification, pyrolysis or thermal cracking, and transesterification. Table 2.4 explains the pros and cons of each major production technology based on previous findings by researchers (Zahan and Kano, 2018, Peter et al., 2015, Agarwal, 2007, Puneet and Sharma, 2016, Cherng-Yuan and Li-Wei, 2008, Cherng-Yuan and Shiou-An, 2007, Sani et al., 2012, Lin et al., 2011, Liu et al., 2021, Bora et al., 2020, Singh et al., 2020)

Table 2. 4 The pros and cons of four major biodiesel production technologies.

Technologies	Pros	Cons
Dilution (direct blending)	• Easy and simple process • No chemical process required • Non-polluting process • No technical modifications	• High viscosity • Unstable • Low volatility • Poor atomization • Incomplete fuel combustion • Difficult to handle • Improper spraying pattern
Micro-emulsification	• Easy and simple process • Pollution-free process	• Unstable • Less volatile • High viscosity • Incomplete combustion • Carbon deposition in the engine cylinder • Tendency of sticking

Table 2.4 (continued)

Pyrolysis (thermal cracking)	• Easy process • Fewer emissions • Effective process • Wasteless • Pollution-free process	• High installation cost • High carbon residue • High energy consumption • Low biodiesel purity
Transesterification	• Biodiesel produced is comparable with diesel • Mild reaction condition	• Low FFA and water content feedstock • Homogeneous catalyst is not reusable • Extensive separation and purification steps • Possibilities of side reaction to occur • Generation of a large amount of wastewater

Dilution or direct blending of preheated crude straight vegetable oil (SVO) with a certain proportion of petro-diesel within a 10-40% (w/w) ratio is the easiest route for biodiesel production (Zahan and Kano, 2018). Besides being an easy application, dilution does not involve any technical modification and is a non-polluting process as no chemical process is required (Peter et al., 2015). However, the produced biodiesel blend is difficult to be used as engine fuel due to its properties such as high viscosity, high acid value, high free fatty acid (FFA) content, and the high tendency of gum formation (Agarwal, 2007). The increasing viscosity is due to the polymerization of polyunsaturated vegetable oils while the gum formation is caused by oxidation during storage or by complex oxidative (Fangrui and Milford, 1999). Note that feedstock from the third generation ought to be treated to remove impurities before mixing with another diesel.

Next in line with the simple dilution process will be the micro-emulsion method. Instead of mixing oils with diesel, the micro-emulsion process involves the mixing of oils with suitable emulsifying agents to form emulsions. Alcohol is one of the major emulsifying agents used which includes methanol, ethanol, propanol, and butanol (Puneet and Sharma, 2016). Through micro-emulsification, some biodiesel produced almost has a similar viscosity to diesel while some results in viscosity up to three times the diesel (Cherng-Yuan and Shiou-An, 2007, Cherng-Yuan and Li-Wei, 2008). Both direct blending and micro-emulsification processes generally produced high viscosity biodiesel which causes the problem of carbon deposition and lube pollution (Lin et al., 2011). To overcome the high viscosity setback, pyrolysis technology is approached.

Pyrolysis is the thermal cracking of organic matter in the absence of oxygen supply but in the presence of a catalyst (Atabani et al., 2013). The oils are decomposed at an elevated temperature of more than 350°C (Charusiri and Vitidsant, 2017, Avhad and Marchetti, 2015). Compared to biodiesel from the dilution and micro-emulsification method, the biodiesel produced from this process has a lower viscosity, flashpoint, and pour point than diesel fuel and equivalent calorific values but lower cetane number (Sani et al., 2012). Pyrolysis managed to bring down the viscosity and enables the de-coupling of the unit operation equipment in a shorter time, place, and scale, plus it is a pollution-free process. The major demerit of this process would be high energy consumption, expensive equipment such as distillation units and low biodiesel purity (Sani et al., 2012). Moreover, pyrolysis is hard to be controlled by its reactant at high temperatures (Lin et al., 2011). Thus, for better control of the biodiesel conversion from feedstock oils, the transesterification process stands out as the most favourable method.

The transesterification process involves the reaction between triglycerides and alcohols with or without the presence of a catalyst to produce the main product of esters and by-product of glycerol as shown in Figure 2.1. One mole of triglyceride reacts with three moles of alcohol to produce three moles of mono-alkyl esters and one mole of glycerol (Munack, 2006). Since the transesterification reaction is reversible, a catalyst and excess alcohol are added to shifts the equilibrium to the product side, to ensure a high reaction rate for a higher yield percentage of alkyl esters (Fangrui and Milford, 1999). The most commonly used alcohol was methanol due to its lower price and more advantages on physical and chemical properties (polar and shortest chain alcohol) compared to ethanol, propanol and butanol (Duran et al., 2014). As a polar solvent, methanol plays the role of extracting the polar lipid in the raw materials (Wang et al., 2016). After the reaction, the excess methanol can be recovered by vacuum stripping (Cobb et al., 2020).

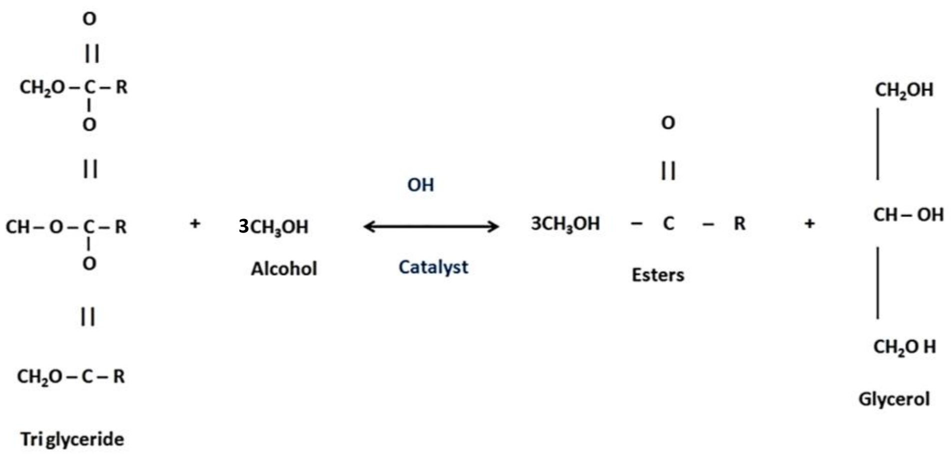

Figure 2. 1 Transesterification reaction for biodiesel production.

There are different types of catalysts used for the transesterification process including homogeneous, heterogeneous, enzymatic, and nanocatalysts (Chozhavendhan et al., 2020). The homogeneous catalyst comprises alkalis and acids. The selection of acid and base catalysts mainly depends on the FFA content of the feedstock oil (Puneet and Sharma, 2016). Commonly used homogeneous catalyst is base catalyst such as sodium hydroxide, sodium methoxide and potassium hydroxide due to its high activity (Gemma et al., 2004). Homogenous catalyst allows the reaction to take place in modest conditions and high yield in a short time with base catalyst (Vlada et al., 2015). However, the major concerns of using a homogeneous catalyst are the occurrence of undesired reaction of saponification that leads to extra separation processes for wastewater produced, the catalyst is not reusable and high sensitivity of catalyst towards high FFA and water content (Abebe et al., 2011). Hence, a heterogeneous catalyst is used because it can be operated in continuous processes, can be reused and regenerate (Masoud et al., 2009). Despite that, heterogenous effectiveness is lower than homogenous catalyst due to a longer reaction time which is up to 24 hours. Heterogeneous catalyst also requires more rigorous reaction condition such as high temperature and pressure (Ji-Yeon et al., 2010).

As for the by-product generated which is the glycerol, the concern will be the type of separation method, the effectiveness of the separation and the handling of the by-product. Some researchers claimed that the best separation method of glycerol after the transesterification process is glycerol washing (Bi et al., 2015, Cobb et al., 2020). Extra glycerol is added to the biodiesel and glycerol mixture to aid the formation of two distinct phase systems for separation. Meanwhile, other researchers were prompted to convert the by-product into value-added products (Janiszewska et al., 2016, Li et al., 2013). To meet the biodiesel standards, any by-products and impurities must be removed thus refining the produced biodiesel. The refining methods mainly include wet washing, dry washing and some membrane technology (Liu et al., 2021). Generally, there are numbers of parameters that influence biodiesel production through transesterification yet five main parameters are FFA content, type of solvent and its molar ratio to oil, type of catalyst and its concentration, reaction temperature and time (Puneet and Sharma, 2016).

2.4 Scum-to-Biodiesel Conversion

As mentioned earlier, scum and sludge are listed as the third generation of biodiesel feedstocks and they are not only high in oil content but also contain many impurities which may be the main concern in biodiesel production (Cobb et al., 2020). The idea of scum-to-biodiesel is mainly to recover the high energy content of scum wasted from WWTP through transesterification technologies. It is also an attempt for considering the prospect of transforming sewage into biorefineries (Frkova et al., 2020). In the last few years, there are three methods related to biodiesel transesterification production: traditional transesterification, in-situ transesterification and two-step esterification/transesterification (Liu et al., 2021). The traditional transesterification method is modified on its procedure but the type of catalyst and solvent are similar.

For the traditional transesterification, the lipid content from scum or sludge is first extracted then followed by the traditional procedures of transesterification hence also known as ex-situ transesterification. The available extraction method is acid hydrolysis, Soxhlet extraction, water bath shocks, and liquid-liquid extraction. Among the methods, the Soxhlet extraction method results in the highest lipid yield (Zhu et al., 2014). Soxhlet extraction used organic extractants such as ethanol, methanol, and hexane to remove lipids at temperatures ranging from 70-80°C. On the other hand, the direct liquid-liquid lipid extraction method exhibit efficient extraction. More than 90% of the lipids in primary sludge (27% of lipid, based on dry sludge) were extracted using this method (Magdalena et al., 2014) and 34.5 wt% lipids were extracted from a dried sludge (Cécile et al., 2018). The main concern for the extraction process would be the type of extractant to be used that falls under the category of polar organic solvent, nonpolar organic solvents, supercritical CO_2, and ionic liquids. Methanol appears to be the most effective polar solvent and hexane for a nonpolar solvent, yet the mixture of polar and nonpolar solvent is more efficient than stand-alone solvent. For instance, extraction of lipid by using a solvent mixture of n-hexane, methanol and acetone yields the highest lipid amount compared to other solvent systems (Dufreche et al., 2007). This system is optimized by manipulating the ratio of each co-solvent in the system and it appears that the highest ratio of n-hexane generated the largest amount of lipid from scum sludge (Wang et al., 2016). However, the problem with using this solvent system is the difficulties of recovery for each co-solvent

(Muhammad and Sohrab, 2011). The potentiality of the extracted lipid from scum and sludge is determined by evaluating its acid value (AV), FFA content, saponification number and fatty acid composition (Cécile et al., 2018).

In-situ transesterification is a process whereby the lipid extraction and esterification/transesterification processes are conducted simultaneously in the same reactor (Ayhan et al., 2017, Siddiquee et al., 2011). Compared to ex-situ transesterification, in-situ transesterification yielded higher overall biodiesel with a 22.7% yield from scum, followed by 9.0% and 1.9% from primary and secondary sludge, respectively (Wang et al., 2016). In another research, in-situ transesterification generated the highest yield of 16.6% biodiesel from sewage sludge with acceptable purity of 94.3% (Zhu et al., 2018). Since both extraction and transesterification processed took place simultaneously, there is essentially no loss in lipid extraction steps and in transferring of extracted lipid from one container to another thus higher yield can be obtained (Liu et al., 2021). Another key that contributed to the higher yield of biodiesel is the capability of this route to extract and react with some inorganic compounds that are difficult to be extracted by extraction processes alone (Ritz and Croudace, 2003, Wang et al., 2013). Nevertheless, challenges still exist as the following: (i) high energy consumption is required for the drying process of raw materials, or else the reaction rate will be inhibited, (ii) the mixture of extraction residues and biodiesel is difficult to be separated as they are all mixed in one vessel, and (iii) with this method, neither homogeneous nor heterogeneous catalyst that is used can be recovered and reused since all products, excess reactants and used catalysts constitute in a mixture (Liu et al., 2021). Given these disadvantages, traditional transesterification is still mainly chosen for biodiesel production and has the potentiality to be applied on an industrial scale.

Two-step esterification/transesterification is developed with the aim of reducing the FFA content in the scum and sludge waste before transesterification as the transesterification process alone is highly sensitive to FFA content and water content. The high FFA content mainly in animal fat and waste oils is due to the hydrolysis of triglycerides into FFA and glycerol as depicted in Figure 2.2 (Babcock et al., 2008). As mentioned earlier, the transesterification process is aided by an alkaline catalyst. However, when the FFA concentration in the lipid is >1%, the performance of the alkaline catalyst is not adequate as the reaction is impaired by the undesirable side reaction of saponification by FFA that produce soap instead of biodiesel as shown in Figure 2.3 and the soap is difficult to be removed (Magdalena et al., 2014, Choi et al., 2014, Ayhan et al.). Hence, it is reasonable to remove FFA or at least reduce its concentration by converting them through an esterification reaction.

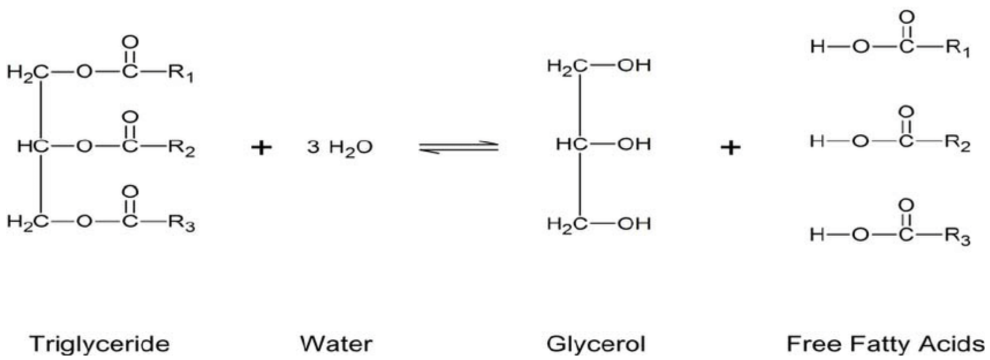

Figure 2. 2 Hydrolysis of triglycerides.

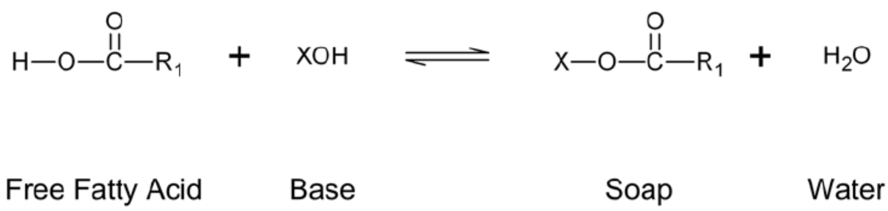

Figure 2. 3 Undesired saponification reaction (X = Na, K, etc.).

Esterification or acid esterification is the reaction of FFA with alcohols with acid as the catalyst such as concentrated sulfuric acid to produce fatty acid methyl ester (FAME) as described in Figure 2.4 (Cobb et al., 2020). The utilization of sulfuric acid converts FFAs to

FAMEs fairly quicker (within an hour) than the traditional transesterification of triglycerides to FAME while the glycerides in the oil will remain unreacted. The water of the reaction is produced and blended in alcohol which will be decanted to remove the wet acidic methanol. The FFA content of the oil can be determined by measuring its acid value which is the milligrams of potassium hydroxide required to neutralize the free fatty acid contained in 1.0g of fat oil. It is a measurement of to what extent to which glycerides in the oil have been hydrolyzed and it is often used as a general characterization of oils (Low and Ng, 1987).

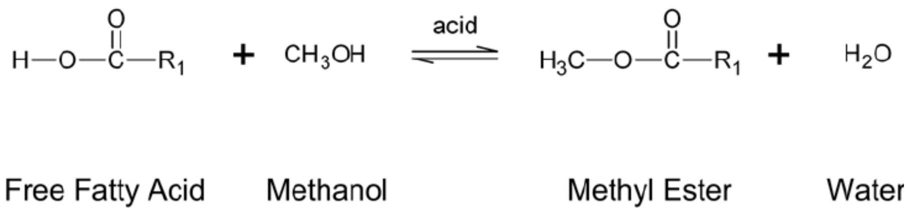

Figure 2. 4 Acid-catalysed esterification reaction.

For waste oils, particularly trap greases and brown greases which generally originated from the household may contain soap and soap-like contaminants. Soap is an undesirable impurity in the production line of biodiesel, and it can be removed through acid washing. The importance of acid washing is to (i) convert any soap in the feedstock to FFA, (ii) increase biodiesel production yield, (iii) break emulsions for improved water/oil separation, and (iv) further remove impurities (Bi et al., 2015). The acidification reaction of soap producing FFA and salt compound which is soluble in the acid solution is depicted in Figure 2.5 (Deb et al., 2017). After the reaction is completed, two layers are formed after the mixture is allowed to be settled by gravitational means and the bottom phase which mainly contain sediment, salt and acid are discharged. The acid washing solution is prepared by dissolving concentrated acid in deionized water. Bi et al found that using a 1.2N acid solution could completely acidify the scum oil while lower normality could not (Bi et al., 2015). Adding acid washing step as pre-