ULTRASONIC ASSISTED OIL EXTRACTION AND BIODIESEL SYNTHESIS OF SPENT COFFEE GROUND

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ULTRASONIC ASSISTED OIL EXTRACTION AND BIODIESEL SYNTHESIS OF SPENT COFFEE GROUND

ABSTRACT

Biodiesel is a potential alternative fuel that can serve as a substitute for petroleum diesel due to its renewability, toxic free, sulphur free and better lubricity. Non-edible oils are studied as a potential biodiesel feedstock with focus on waste products as these can become value added products. Spent coffee ground (SCG) is studied as a potential source of oil for biodiesel production as an alternate waste utilisation instead of being treated as municipal waste. This study evaluates ultrasonic assisted oil extraction from SCG, followed by biodiesel conversion via transesterification. It was found that hexane was the most effective solvent for SCG oil extraction. Soxhlet extraction obtained maximum yield of 12.5% within 3 hours. The highest yield (14.52%) for ultrasonic extraction was obtained using 4mgL^{-1} hexane to SCG ratio, at 30% ultrasonic amplitude for 30 minutes. These improved results were due to the ultrasonic fragmentation of SCG cells, which enhanced interactions between oil and solvents. The infrared absorption spectrum analysis of SCG oil determined suitable functional groups for biodiesel conversion. Then, the SCG oil was successfully converted to biodiesel via ultrasonic assisted transesterification. The optimal fatty acid methyl ester (FAME) yield of 97.11% was achieved with molar ratio of methanol to SCG oil (30:1), 4 wt% potassium hydroxide concentration at 30% ultrasonic amplitude for 3 hours. The catalyst concentration showed the biggest change in terms of FAME. The SCG biodiesel has promising properties which adhere to the American Standards for Testing Materials (ASTM D6751) and European Union Standards for Biodiesel (EN 14214) standards but acidity was beyond the permissible limit. Due to the high acid value, it is recommended that SCG biodiesel be used as a blend with other commercially available biodiesel rather than a pure biodiesel. The high calorific value along with low viscosity, density and corrosion levels make SCG

biodiesel an interesting option for biodiesel blending. In conclusion, ultrasonic assisted oil extraction and transesterification can be a feasible method for SCG biodiesel production. Detailed and in-depth information of the combustion characteristics and long term stability of the biodiesel can be further examined prior to the commercialization of SCG biodiesel.

Keywords: Biofuel; Spent Coffee Ground; Transesterification; Ultrasound; Alternative Fuel

PENGEKSTRAKAN MINYAK DAN SINTESIS BIODIESEL SISA KOPI DENGAN BANTUAN ULTRABUNYI

ABSTRAK

Biodiesel adalah bahan api alternatif yang boleh berfungsi sebagai pengganti diesel petroleum kerana pembaharuan, kebebasan toksik, peleburan bebas sulfur dan pelinciran yang lebih baik. Minyak tidak boleh dimakan dikaji sebagai bahan api biodiesel berpotensi dengan fokus pada produk sisa kerana ini boleh menjadi produk tambah nilai. Sisa kopi (SCG) diteliti sebagai sumber minyak yang berpotensi untuk pengeluaran biodiesel sebagai penggunaan sisa alternatif dan bukannya dianggap sebagai sisa perbandaran. Kajian ini menilai ekstraksi minyak dibantu ultrasonik dari SCG, diikuti oleh penukaran biodiesel melalui transesterifikasi. Heksana didapati sebagai pelarut paling berkesan untuk pengekstrakan minyak SCG. Pengekstrakan Soxhlet memperoleh hasil maksimum 12.5% dalam masa 3 jam. Hasil tertinggi (14.52%) untuk pengekstrakan ultrasonik diperoleh menggunakan 4mgL-1 heksana kepada nisbah SCG, pada 30% amplitud ultrasonik selama 30 minit. Keputusan yang lebih baik ini disebabkan oleh pemecahan ultrasonik sel-sel SCG, yang meningkatkan interaksi antara minyak dan pelarut. Analisis spektrum penyerapan inframerah minyak SCG menentukan kumpulan fungsi yang sesuai untuk penukaran biodiesel. Kemudian, minyak SCG berjaya ditukar kepada biodiesel melalui transesterification dibantu ultrasonik. Kadar metil ester asid lemak (FAME) yang optimum (97.11%) dicapai dengan nisbah molar metanol kepada minyak SCG (30: 1), 4 kali konsentrasi kalium hidroksida 4% pada amplitud ultrasonik 30% selama 3 jam. Kepekatan pemangkin menunjukkan perubahan terbesar dari segi FAME. Biodiesel SCG mempunyai ciri-ciri baik yang mematuhi Piawaian Amerika untuk Bahan Ujian (ASTM D6751) dan Piawaian Kesatuan Eropah untuk Biodiesel (EN 14214) tetapi keasidan berada di luar had yang dibenarkan. Disebabkan nilai asid yang

tinggi, disarankan agar biodiesel SCG digunakan sebagai campuran dengan biodiesel yang tersedia secara komersial dan bukannya biodiesel tulen. Nilai kalori tinggi bersama dengan kelikatan, ketumpatan dan paras kakisan yang rendah menjadikan SCG biodiesel sebagai pilihan yang menarik untuk pengadunan biodiesel. Sebagai kesimpulan, pengekstrakan minyak yang dibantu ultrasonik dan transesterifikasi boleh menjadi kaedah yang boleh dilaksanakan untuk pengeluaran biodiesel SCG. Maklumat terperinci dan mendalam tentang ciri-ciri pembakaran dan kestabilan jangka panjang biodiesel boleh diperiksa selanjutnya sebelum pengkomersialan biodiesel SCG.

Kata kunci: Biofuel; Sisa Kopi; Transesterifikasi; Ultrasonik; Bahan Api Alternatif

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LIST OF SYMBOLS AND ABBREVIATIONS

ASTM D6751	:	American standards for testing materials
A_{EL}	:	Peak area of internal standards
C6	:	Alcohol with 6 carbon chain length
C22	:	Alcohol with 22 carbon chain length
Ca	:	Calcium
CaO	:	Calcium oxide
$CaCO_3$	:	Calcium carbonate
CH_2	:	Methylene
CO_2	:	Carbon dioxide
C=O	:	Carbonyl group
C-O-C	:	Ether group
C-OH	:	Alcohol group
COOH	:	Carboxyl group
COOR	:	Ester group
EN 14214	:	European union standards for biodiesel
FAME	:	Fatty acid methyl ester
FFA	;	Free fatty acid
FTIR	:	Fourier-transform infrared spectroscopy
g	:	Gram
g mol^{-1}	:	Gram per mole of substance
GC	:	Gas chromatography
H	:	Hydrogen
HO_2	:	Hydroperoxyl radical
K	:	Kelvin

kg	:	Kilogram
kHz	:	Kilohertz
KOH	:	Potassium hydroxide
mg	:	Milligram
mg KOH	:	Unit for amount of KOH mass (milligram) required for neutralization
MHz	:	Megahertz
mg L^{-1}	:	Milligram per liter
m_i	:	Initial mass
MJ/kg	:	Megajoule per kilogram
mL	:	Milliliter
MPa	:	Megapascal
N	:	Nitrogen
$NaOCH_3$	:	Sodium methoxide
NaOH	:	Sodium hydroxide
NO_x	:	Nitrogen oxides
O_2	:	Oxygen
OH	:	Hydroxyl
SCG	:	Spent coffee ground
US$	:	United States dollar
VOC	:	Volatile organic compounds
W	:	Watt
W_{EL}	:	Weight (mg) of methyl nonadecanoate
WtE	:	Waste to energy
Wt%	:	Weight percentage
Δm	:	Change in mass
°C	:	Degrees Celcius

%	:	Percent
$\sum A$	:	Sum of area of C8:0 to C24:0 peaks

CHAPTER 1: INTRODUCTION

1.1 Background

Scarcity of fossil fuel resources, increasing price of diesel fuels, global warming and climate change crisis have necessitated the search for fuels from renewable sources. A renewable source of energy is defined as a form energy which produces minimal pollution and does not deplete. Biofuel fits the criteria for renewable energy sources and provide to be a cleaner alternative compared to conventional fossil fuels. Biodiesel is a form of biofuel which consists of a mixture of monoalkyl esters and long chain fatty acids and is non-toxic, biodegradable and can be used in diesel engines with minimal modification (Fonseca et al., 2019).

In 2015, 69% of the global biodiesel output was produced from edible vegetable oils such as soybean oil, rapeseed oil and palm oil (Naylor & Higgins, 2018). Such high percentage of edible sources usage causes a dilemma due to its implications on food security and commodity prices. Despite the fact that oil crops cultivation help boosted rural areas' economies, the large areas needed for fuel's crops cultivation is not sustainable in the long run. Moreover, 70% of the total biodiesel production cost is accountable to the high costs of edible oils, while large planting scales also cause soil degradation (Fonseca et al., 2019).

There is no established way to extract oil from any biodiesel feedstock. Various oil companies utilise mechanical methods to extract oil from oil seeds, but this method may not be suitable for all feedstocks. In terms of biodiesel production, the oil extraction process is essential to prevent any interference with the synthesis of fatty acid methyl esters. Spent coffee ground is neither a conventional biodiesel feedstock nor an oil seed. Therefore, the oil extraction and biodiesel production methods for this feedstock is still in the research phase. The most common method utilised in the oil extraction from spent

coffee ground is pyrolysis, as other researchers emphasize the production of biochar rather than the bio-oil obtained from the feedstock (Kelkar et al., 2015).

Current biodiesel production cost is calculated to be 4.4 times of the price of petroleum derived biodiesel (Fazeli Danesh et al., 2017). This high cost associated with current biodiesel feedstocks have made the progress of biodiesel commercialization to stutter. Previous biodiesel policies have been justified by the high oil prices. However, the energy market have reversed since 2014, where biodiesel production have continued increasing while crude oil prices reduce (Naylor & Higgins, 2017). **Figure 1.1** shows the comparisons between biodiesel production and crude oil prices from 2000 to 2016.

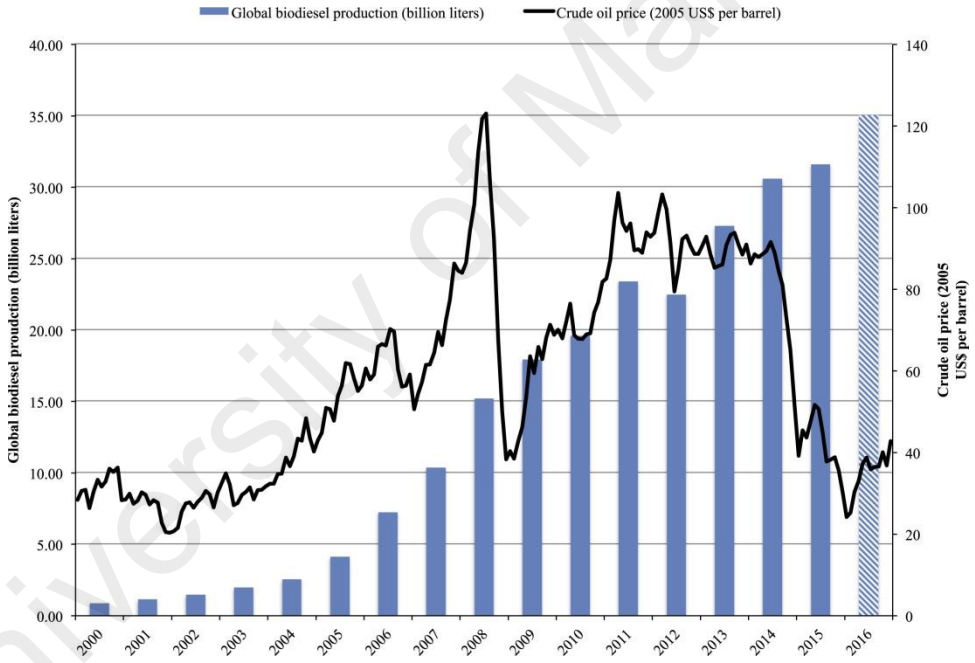


Figure 1.1: Biodiesel production and crude oil prices from 2000 to 2016 (Naylor & Higgins, 2017)

Reduction in equipment taxes, provisional training and learning sessions for farmers and other subsidies are important for the successful industrialization of microalgae biodiesel (Su et al., 2017). Under beneficial energy policies and investments, the development of biodiesel will be encouraged, while production and consumption will also significantly increase (Xu et al., 2016). One such policy is Brazil's "National Program for Biodiesel Production and Uses" policy which introduces tax reductions for biodiesel

production for various feedstock, which may increase people's interest in feedstock growing (dos Santos Alves et al., 2017).

The government is responsible to provide institutional pressures such as legislations and regulations which impact organizations via sanctions or incentives to ensure company adherence to biodiesel commercialization (Barros Ribeiro et al., 2018). Given that the current commercial biodiesel feedstocks are edible oils such as palm and soy, government intervention in the biodiesel market will also complicate the effects on food security. The EU's biodiesel policy signed in Paris in 2015, shows its commitment towards emissions from feedstock production by transitioning to more sustainable feedstocks (Naylor & Higgins, 2018). The policy will directly impact top edible oil producers such as Indonesia (palm) and Argentina (soy). However, this same policy will also transition global biodiesel production to second generation feedstocks such as waste cooking oil and spent coffee ground oil.

In Malaysia, biodiesel has been successfully produced from palm oil and used in commercial diesel blends since 2009. However, the use of palm oil and its residues has come under heavy scrutiny since the Paris biodiesel agreement. The use of spent coffee ground as a biodiesel feedstock promotes biodiesel production from an alternate source, while solving the food waste issue which is prominent globally. The vigorous development of food service establishments in Malaysia, where 9947 new outlets opened from 2006 to 2011, and Malaysian's increasing demand for coffee would also generate a large amount of spent coffee ground waste, making it an abundant source for biodiesel (S. Lee et al., 2017).

1.2 Problem statement

Currently, the dominant energy sources such as crude oil, coal and gas are running low in reserve, prompting the consideration of renewable alternate fuels (Gebremariam & Marchetti, 2018). The combustion of fossil fuels also produce carbon dioxide and methane gas emissions which are harmful to the environment and contributes to global warming. Therefore, it is essential to find a suitable alternate source of energy that is environmentally friendly and sustainable. One of the suggested alternatives is using non-edible oils as biodiesel feedstock.

Although crude vegetable oils are a promising alternative energy source for diesel engines, it has clear disadvantages such as lower volatility, higher viscosity and poor cold condition efficiency (Ambat et al., 2018). Therefore, vegetable oil derivatives such as biodiesel are studied as it demonstrates similar properties to petroleum diesel but reduced output of pollutants and greenhouse emissions. Among the wide variety of feedstock capable of being converted into biodiesel, palm oil, an edible oil, is known to produce the highest amount of oil per area at 5000kg oil per hectare, amounting to 5.3 wt% of fatty acids (Moazeni et al., 2019b). Besides that, most commercial biodiesel being produced in the world today is made from edible oils, resulting in competition between alternative energy and food production. This scenario, known as the food vs fuel debate, questions the use of edible oils for energy use rather than food production. The demand of edible oil as a food source would drive the feedstock price up, making the utilization of non-edible oils and waste materials an interesting option due to the lower feedstock price and reduction of competition with the food industry (Ambat et al., 2018). Although spent coffee ground does not provide direct competition with the food industry, the production of it is directly from consumer consumption, which may be an issue due to the availability of the feedstock for commercialization purposes.

Vegetable oils and animal fats tend to have higher viscosity due to the long carbon chains at the triglyceride molecules which tangle up. The transesterification process converts these oils to biodiesel while reducing the viscosity and making it usable in a diesel engine (Knothe & Steidley, 2005). However, the process relies on the immiscibility of the alcohol and oil, where the mass transfer resistance will reduce reaction rate, requiring further agitation to save time and reduce energy loss (Sánchez-Cantú et al., 2019). Biodiesel is a highly oxygenated fuel that has improved combustion efficiency and emits less unburnt hydrocarbons, carbon monoxide, carbon dioxide and sulphur dioxide (Y.-C. Lin et al., 2006). The density of biodiesel is generally higher than diesel fuel and is dependent of fatty acid composition and purity (Barabás & Todoruţ, 2011). Biodiesel from all sources also have lower mass energy content, about 10%, than petroleum diesel (Hoekman et al., 2012). The various parameters such as methanol volume, catalyst concentration, reaction time and ultrasonic irradiation can have significant influence on the final conversion, in particular in the yield of product (Suresh et al., 2018). In terms of spent coffee ground biodiesel, the lack of studies regarding the feedstock make a direct comparison with other techniques difficult.

In this research, biodiesel is produced from spent coffee ground oil using ultrasonic assistance. Initially, the effect of extraction solvent, solvent to spent coffee ground ratio, ultrasonic power and ultrasonic period were studied to optimize oil extraction from spent coffee ground. Ultrasonic assisted transesterification was conducted on the oil to analyze the effect of different reaction parameters to fatty acid methyl ester yield. Optimum methanol to oil molar ratio, catalyst concentration ultrasonic power and reaction time were determined to obtain highest ester yield, and the physiochemical properties of the biodiesel were tested and compared with ASTM D6751 and EN 14214 biodiesel standards.

1.3 Research objectives

The aim of this research is to investigate biodiesel production from spent coffee grounds using ultrasonic assistance in the oil extraction and transesterification process. The spent coffee ground was subjected to ultrasonic assisted oil extraction and compared with conventional Soxhlet oil extraction techniques prior to ultrasonic assisted transesterification to produce spent coffee ground biodiesel. Thus, the objectives of this research are as follows:

1. To investigate the oil extraction from spent coffee grounds based on type of extraction solvent, solvent to spent coffee ground ratio, ultrasonic power and ultrasonic period.
2. To investigate the effect of methanol to oil molar ratio, catalyst concentration ultrasonic power and reaction time on biodiesel production to improve fatty acid methyl ester yield.
3. To analyse the physiochemical properties of the produced biodiesel in comparison with the ASTM D6751 and EN 14214 standards.

1.4 Scope of study

This research encompasses three main scopes which include the oil extraction from spent coffee ground, followed by the transesterification of the oil to produce spent coffee ground biodiesel and further physiochemical property testing of the biodiesel.

In the first scope, the oil extraction was conducted on a dried spent coffee ground. Although it was found that presence of moisture does not significantly affect the oil yields, the drying process was conducted to avoid the growth of mould which may affect the spent coffee ground oil quality. The various parameters tested in this scope included the type of solvent, solvent to spent coffee ground ratio, ultrasonic amplitude and extraction period. The use of ultrasonic assistance was also compared to conventional

Soxhlet extraction methods to show the difference in terms of oil yield, amount of solvent used and extraction time.

Prior to the second scope, the spent coffee ground oil was also subjected to various property tests. The acid value was essential to determine the type of catalyst which should be used for the biodiesel production. In the second scope, the various parameters affecting transesterification efficiency is tested. These parameters include the molar ratio of methanol to spent coffee ground oil, ultrasonic amplitude, ultrasonic period and catalyst concentration. It is worth noting that while some research has quantified reaction temperature as a parameter affecting transesterification efficiency, it was disregarded in this study as it is difficult to stabilise the reaction temperature throughout when a sample is subjected to the oscillations of an ultrasonic probe. The reaction temperature is also a kinetically controlled parameter, similar to the ultrasonic period which is simpler to quantify. The efficiency of the reaction is determined by measuring the fatty acid methyl ester yield of the product, which is the main product of the transesterification reaction along with a glycerol by-product.

After obtaining the maximum yield for fatty acid methyl ester, the research moved on to the final scope. In the third scope, the spent coffee ground biodiesel physiochemical properties were measured and compared with the ASTM D 6751 and EN 14214 standards. The various properties tested in this scope included the acid value, kinematic viscosity at 40 °C, density at 15 °C, calorific value, oxidation stability at 110 °C and copper corrosion level. Furthermore, the fourier transform infrared spectrum for both the spent coffee ground oil and biodiesel were compared to show the new functional groups after the transesterification reaction.

1.5 Significance of study

Although the field of biodiesel production have been saturated with research on various alternative feedstocks, emerging technologies and cost effective techniques, there is still some significant findings discovered during this research. The use of spent coffee ground as a biodiesel feedstock is still rarely studied due to the relatively low oil yields compared to other biodiesel feedstocks. However, this study determined that the use of ultrasonic assistance is able to extract a higher percentage of oil from the spent coffee ground with a significantly lower amount of solvent use and shorter time. Besides that, the transesterification reaction of spent coffee ground oil using ultrasonic assistance also significantly lowered the reaction time. By combining an emerging technology with a rarely studied feedstock, this study is able to improve the viability of spent coffee ground as a biodiesel feedstock. The latter stages of the research also determined that spent coffee ground biodiesel is suitable to be used as a biodiesel blend rather than in the form of pure biodiesel. Although the objectives of this study has been achieved, there is still space for further research in terms of optimisation of the production process, combustion characteristics study and economic analysis of the spent coffee ground biodiesel commercialisation. Therefore, the results obtained in this study will be important information for these future research.

1.6 Thesis outline

Chapter 1 will introduce background information regarding biodiesel and its current status. Problem statements and objectives of this research will also be defined.

Chapter 2 is the literature review regarding the different methods of oil extraction and biodiesel production, various parameters affecting the oil extraction mechanism and transesterification mechanism, as well as the important physiochemical properties of biodiesel.

Chapter 3 explains the materials and detailed methodology of the research.

Chapter 4 describes the results obtained from the research and provides an analysis, discussion and compared with results from previous studies.

Chapter 5 concludes the results of this research, presents key findings and suggests future recommendations.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This section of the research will explain the value of spent coffee ground as a biodiesel feedstock and evaluate other similar works that have been published. Section 2.3 will focus on the oil extraction techniques and influencing factors, with emphasis on the ultrasonic effect on extraction yield. Besides that, the biodiesel production parameters such as type of catalyst, amount of alcohol used and agitation method will be discussed along with its effects on the fatty acid methyl ester (FAME) yield in section 2.4. FAME composition, chain length and degree of unsaturation will also be discussed with its effect on the biodiesel property. Section 2.6 will discuss the various physiochemical properties of biodiesel and the corresponding effects. Finally, a brief summary and research gaps that are present in this field of study will be mentioned.

2.2 Spent coffee ground

Food waste is a major problem affecting current global environmental, social and economic issues. Despite the variation in terms of waste composition and geographical distribution, food waste is an urgent issue in developed and emerging economies, underlining the political importance and urgency of the mitigation process (Filimonau et al., 2019). Unsustainable food consumption and production patterns will lead to depletion of resources, pollution, climate change, losses in biodiversity and soil fertility (Zabaniotou & Kamaterou, 2019). The waste to energy (WtE) concept is an interesting thermo-chemical pathway which is suitable for mass production and compatible with the current infrastructure of the energy and chemical industry (Cho et al., 2015).

Coffee is the world's second largest traded commodity, after oil, with approximately 8 million tons of coffee produced each year (Döhlert et al., 2016). In 2016 alone, the worldwide coffee bean generated a revenue of around US$25 billion (Massaro

Sousa & Ferreira, 2019). A large amount of heat energy is used to convert green coffee beans into brown roasted beans for the brewing process, generating large amounts of volatile organic compounds (VOCs) (Allesina et al., 2017). The great demand for this beverage also produces a large amount of residual waste after brewing. Every 1 ton of coffee beans produces 650kg of coffee residue after brewing, known as spent coffee ground (SCG) (Murthy & Madhava Naidu, 2012). The global coffee industry produced an estimate of 9.34 million tons of waste in 2017, which were either incinerated, dumped in landfills or composted (Zabaniotou & Kamaterou, 2019). Therefore, a combined solution of SCG recollection and reuse of SCG for alternate energy production would be beneficial to the coffee industry. **Figure 2.1** shows the spent coffee ground and coffee beans before the brewing process.

Figure 2.1: Spent coffee ground and coffee beans before the brewing process

Production of oil from non-edible sources such as SCG can also help overcome the food versus fuel dispute (Palconite et al., 2018). First generation biodiesels utilise food crops as the source of oil, which results in direct competition between the food and fuel sectors. Similar to other second generation feedstocks such as non-edible oils and waste cooking oils, SCG oil also overcome the problems that the first generation feedstock face such as the food vs fuel debate, environment and energy issues (Y. Singh et al., 2017). The abundance of SCG oil would also make it a readily available feedstock with a lower production cost than edible oils (Gui et al., 2008). SCG after oil extraction has also been identified as a suitable material for production of garden fertilizer, feedstock

for ethanol production, biogas production and fuel pellets (Atabani et al., 2019). However, the use of SCG oil for biodiesel production is still relatively new and require further research prior to commercialisation.

SCG is known to contain various compounds such as oils, carbohydrates, non-protein nitrogen and other carbon containing materials where the composition varies with type of plant, geographical location, age, climate and soil conditions (Karmee, 2018). SCG is an important source of polysaccharides, where 45.3% are sugars polymerized into cellulose and hemicellulose structures. The phenolic compounds in SCG are also known for having antioxidant, anti-bacterial, antiviral, anti-inflammatory and anti-carcinogenic properties for human health (Zabaniotou & Kamaterou, 2019). The chemical composition of SCG can be seen in **Figure 2.2**.

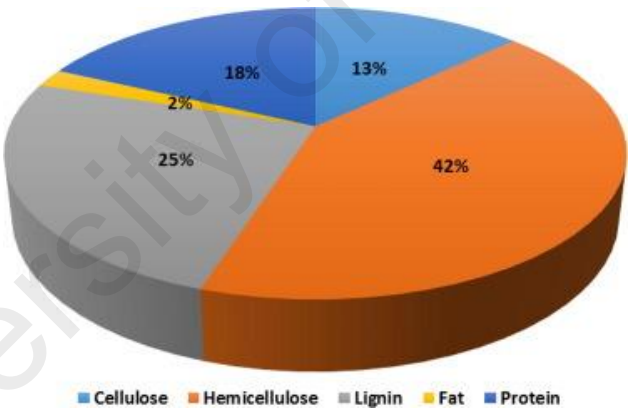


Figure 2.2: Chemical composition of SCG (Zabaniotou & Kamaterou, 2019)

Although some SCG is used as compost or animal feed, most is often burnt as waste and retained as landfill (Kelkar et al., 2015). SCG is often disposed in undifferentiated garbage or municipal waste, partly decomposing into methane which contributes to climate change (Allesina et al., 2017; Somnuk et al., 2017). The disposal of SCG is troublesome as it releases contaminants such as caffeine, tannin, polyphenol and consumes high amounts of O_2 during decomposition (Chun et al., 2019). SCG is seen as one of the prominent solid biomass resource which can replace fossil fuels (Kang et

al., 2017). Charcoal produced from SCG can also be used as an adsorbent for removing pollutants such as phenols and harmful dyes from aqueous streams (Kelkar et al., 2015). However, critical issues during biomass handling such as blockage of pipes, silo outlets and feeding devices result in non-uniform flow into furnace and reactors, disrupting operation efficiency (Massaro Sousa & Ferreira, 2019).

Besides being used as solid fuel, oil extracted from SCG can also be used as potential feedstock for biodiesel. Coffee oil as biodiesel feedstock is inexpensive, has high stability due to high antioxidant content, and has a good aroma (Al-Hamamre et al., 2012). SCG contains 10-20 wt% oil, where 80-90 wt% of the oil is glycerides which include free fatty acids (FFA) (Park et al., 2016). Assuming 16wt% of oil in SCG, the use of SCG oil as biodiesel feedstock would be able to produce 0.9 million tons of biodiesel, which is the equivalent of 3.5% of the world fuel supply in 2014 (26 million tons) (Phimsen et al., 2016). De-oiled SCG is known to be a high energy content solid fuel, which can be used for heat and steam generation (Tuntiwiwattanapun et al., 2017). Although the oil percentage of SCG is relatively low compared to other commercial biodiesel feedstocks, the utilisation of a waste product as a source of oil is beneficial as a waste to energy concept.

Naturally, oil extracted from coffee has high amounts of antioxidants and little saponified matter, meaning the oil is viscous and does not congeal easily (Al-Hamamre et al., 2012). Crude oil contains triacylglycerols and minor fractions of free fatty acids, monoacylglycerols, diacylglycerols, phospholipids, glycolipids and unsaponifiable fractions such as sterols, hydrocarbons and tocopherols (Perrier et al., 2017). Caporaso et al. (Caporaso et al., 2018) found that coffee oil is constituted by 75% triacylglycerols, 20% diterpene esters, 2-3% sterols, 1% FFA and 0.05% tocopherols.

2.3 Oil extraction

There is currently no commercially established way to extract oil from biodiesel feedstock. However, much research has been done to reduce solvent consumption, to enhance extraction yield, to reduce extraction time, to improve end product properties, among others (Neto et al., 2013). A few factors have been identified as crucial for large scale oil extraction, they are extraction efficiency, process duration, reactivity with oil, capital and operational cost, process safety and waste generated (Islam et al., 2014). Typically, biodiesel production involves oil extraction to prevent any interference with the synthesis of fatty acid methyl esters.

Simple mechanical methods use equipment such as screw press, bead milling, piston, extruder or pulverization in mortar to separate biomass cake from the oil component. Abbassi (Abbassi et al., 2014) has reported that the utilization of hydraulic pressing alone for *N. oculata* microalgae can only achieved 51.05 ± 3.23% disruption fraction for lipids, whereas the addition of liquid N increased the disruption fraction to 94.77 ± 0.72%. This significant increase is due to the sudden freezing of microalgae cells, rendering the cell wall brittle, thus aiding the release of intracellular lipid. On the other hand, Meullemiestre (Meullemiestre et al., 2016) found that bead milling showed better extracted lipid quality as compared to ultrasonic and microwave methods.

Generally, mechanical methods result in high biomass losses and low selectivity towards the oils (Peralta-Ruiz et al., 2013). However, certain mechanical processes reduce harmful solvent utilization as well as decrease processing duration (X. Zhang et al., 2014). Moreover, there is also demand for vegetable oils which have not been in contact with chemical solvents, particularly in the food and cosmetics industry (Uitterhaegen & Evon,

2017). There are various equipment available in mechanical extractions but most are not feasible due to high losses (Rawat et al., 2013).

Sudden depressurization technique is also a common oil extraction method, able to obtain intracellular compounds as well. During static compression, a diffusible gas such as supercritical carbon dioxide is allowed to penetrate the cell wall until saturation is achieved before a sudden depressurization is initiated. A sharp pressure gradient is formed along the cell wall where the gas expanded that result in high disruption efficiency (Uquiche et al., 2016). The main advantage of sudden depressurization is that the process is free from toxic solvents (Hernández et al., 2014). When the decompression rate is increased, the efficiency of disruption will also increase, since it induces a higher pressure drop along the cell wall (Gaspar et al., 2003). Halim et al. (Halim et al., 2011) found that the use of supercritical carbon dioxide was able to shorten the *Chlorococcum* sp. lipid extraction time by 5.6 times in comparison to conventional Soxhlet extraction.

Electric pulse treatment produces pulsed electric fields to affect the membrane properties of a biological cell. Under application of an electric field, the external cell membranes will receive an increase of transmembrane voltage that increases the membrane's permeability and conductivity (Silve et al., 2018). Electric pulse treatment is also known as electroporation. Electroporation is highly selective and allows release of intracellular matter, while the extraction of lipid will require use of solvent (Parniakov et al., 2015). Jaeschke (Jaeschke et al., 2016) achieved 83% lipid yield from *Heterochlorella luteoviridis* under moderate electric field and ethanol pre-treatment. Meanwhile, Garoma & Janda (Garoma & Janda, 2016) reported that lipid extraction for *Chlorella vulgaris* using electroporation exhibited low lipid yields (5.3%). However, this method obtained the highest energy gain per energy input compared to microwave and ultrasonic methods with n-hexane/methanol/water solvent solution.

Pyrolysis, thermally degrades biomass by heating it in the absence of oxygen, resulting in bio-oils, biochar and other gaseous products (Yang et al., 2019). The pyrolysis process can also be conducted with the presence of a catalyst to improve the yield of a selected product or reduce the intensity of the reaction conditions. For maximum oil extraction, fast pyrolysis is often used. Long pyrolysis periods impact oil yields as it promotes the cracking into gaseous products as well as re-polymerization into biochar (Kelkar et al., 2015). Pyrolysis temperature can also affect the calorific value of the bio-oil, making it advantageous in the use for combustion equipment such as burner, gas turbine and diesel engines (Bok et al., 2012). However, given the high temperature the process is conducted in, pyrolysis is usually energy intensive, compromising the economic viability of its industrial application (Mutsengerere et al., 2019).

Besides mechanical methods of lipid extraction, other methods of lipid extraction include the use of chemicals or enzymes to disrupt the cell wall. Chemical substances interact with the cell membranes to allow direct passage of intercellular components to the surrounding (T. Dong et al., 2016). Solvent extraction methods are also known as leaching. The Soxhlet technique is widely considered as the conventional solvent extraction method. The technique is said to be efficient in oil extraction since sample remains in contact with solvent and allows the transfer of oil to the solvent matrix without any chemical reaction (Fornasari et al., 2017). The Soxhlet technique is also not viable for large scale production due to the long extraction time which risks the degradation of oil compounds (Zhong et al., 2018).

A standard Soxhlet apparatus will include the bottom, heating element with a distillation flask containing organic solvent, above which is the Soxhlet chamber containing porous thimble and the target sample (Jain et al., 2018). The process effectively recycles a solvent which dissolves a larger amount of the desired compound

by suspending the solid matrix in the reflux solvent (Karmakar & Halder, 2019). The setup of the Soxhlet technique can be seen in **Figure 2.3**.

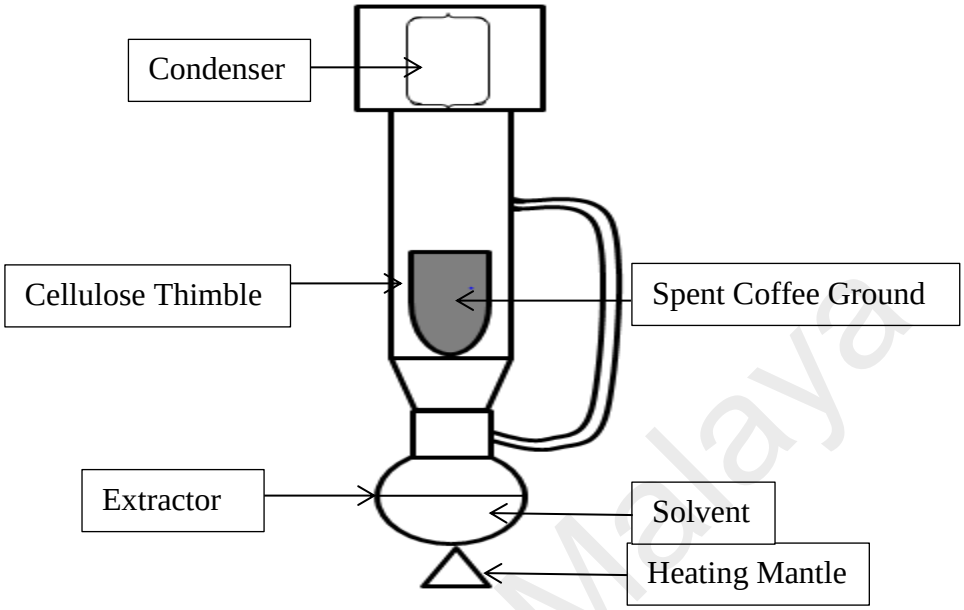


Figure 2.3: Setup of Soxhlet extraction method

The efficiency of the Soxhlet process often depends on the use of non-polar and polar solvents (Abomohra et al., 2016). For example, polar solvents are paired with non-polar solvents to ensure total extraction of all neutral oils, which include free-standing globules and membrane associated complexes (Halim et al., 2012). However, the process is not suitable for industrial use due to its long extraction time which may risk degradation of the oil compounds (Zhong et al., 2018). The Soxhlet method is also known to have other disadvantages such as low efficiency and high cost (L. Zhang et al., 2017).

Ultrasonic assistance is a promising technique as it facilitates the mixing of solutions and does not require high temperatures to disrupt cell walls (Gerde et al., 2012). This technique utilizes sound waves to propagate pressure fluctuations that induces cavitation (Mubarak et al., 2015). It has been reported that ultrasonic assistance reduces extraction time, solvent/sample ratio and lowers extraction temperature, which minimizes thermal damage to the extracts (Pereira et al., 2017). However, ultrasonic treatment also generates

a metallic and rancid odor while inducing physical and chemical changes to the oil components (L. Zhang et al., 2017).

Oil extraction using solvents can be done on either dry or wet biomass. However, extraction of oil from dry biomass is usually more efficient (T. Dong et al., 2016). The drying process is energy and cost intensive but wet extraction usually resulted in lower yield due to the tendency of cells to remain in the water phase and not interact with the organic solvents (Steriti et al., 2014). Considering the scale up difficulty faced by mechanical modes of oil extraction, the solvent method on dry biomass is usually more suitable for commercial use as it is less energy intensive and has shown to produce higher yields of oil extraction (Steriti et al., 2014).

2.3.1 Solvent extraction mechanism

Extraction of oils is a mass transfer operation dependent on the nature of solute and solvent, selectivity of solvent and level of convection of medium (Araujo et al., 2013). Oils are highly soluble in organic solvents such as hexane, benzene, cyclohexane, acetone and chloroform (Adeoti & Hawboldt, 2014). Due to greater contact area between solvent and liquid, small particle sizes are preferable during the solvent extraction process (Bhuiya et al., 2016). The kinetic mechanism of solvent-based oil extraction generally involves two steps. Initially, solvent washing will extract free oil from particle surface and cracks followed by solvent diffusion where the solvent will penetrate into solid particles to recover entrapped oils. The extraction process will cease when there is a formation of stagnant layer or diffusion barrier surrounding the sample (Tan et al., 2019). The oil extraction are often affected by several factors such as solvent type and volume, particle size, convection surrounding solvent-oil mixture and temperature (Abdullah & Bulent Koc, 2013). The solvent should have low viscosity, set at a high temperature to improve solubility while being agitated to increase the diffusion rate across the particle

surface (Karmakar & Halder, 2019). Although solvent extraction has the advantage of high oil yields, the quality of oil may be affected (Kemerli-Kalbaran & Ozdemir, 2019). Oil extraction yield will become constant after a certain extraction period. This may be due to the extraction system reaching a basic osmotic pressure dynamic balance (P. Liu et al., 2017). However, Samaram et al. (Samaram et al., 2014) reported that prolonged extraction period at an elevated temperature would also induce a chemically unstable oil.

2.3.2 Extraction solvent

Oil solubility is dependent on the relative strength of interactions between solvent and the hydrophilic or hydrophobic constituents of the oil molecules (Adeoti & Hawboldt, 2014). It is essential that the solvent make physical contact with the oil particles. The solvent used during extraction should also be chosen based on the intrinsic physical and chemical characteristics of the sample matrix (Fornasari et al., 2017). Efficient oil extraction can be achieved via total solvent penetration into oil storage and matching polarity of targeted compounds (Adeoti & Hawboldt, 2014). The solvents can also be emitted during the extraction process, making the recovery process a necessary step to avoid toxic air pollutants (Baümler et al., 2016).

Generally, oil extraction from biomass has used hexane as the commercial solvent since it is cheapest compared to other solvents (Veeranan et al., 2017). Hexane has high solubility with oils, which allows the solvent to target oils in condensed vapors (Jain et al., 2018). Hexane also has good affinity with triglycerides of oils, which is the targeted component for biodiesel production (Perrier et al., 2017). It should be noted that individuals who handle with hexane in the long term have experienced nervous system injuries as well as irritation to the eyes and respiratory tract (Dagostin et al., 2015).

The original oil extraction method developed by Folch used chloroform and methanol is known to be fast and quantitative (Halim et al., 2012). This method is effective as it utilizes a polar (methanol) and non-polar (chloroform) solvent. Polar solvents surround the oil components and forms hydrogen bonds which are strong enough to displace the oil-protein association, while non-polar solvents form van der Waals associations with neutral oils (Halim et al., 2012). Methanol seems to be a promising alternative since it is less toxic but are also prone to extracting non-oil components due to their high polarity (Perrier et al., 2017). Polar solvents are also effective for the

extraction of polar components such as resin (Amalia Kartika et al., 2018). This means that using methanol as an extraction solvent may risk the extraction of other unwanted foreign substances.

Similar to hexane, chloroform is a popular non-polar solvent for oil extraction. However, the high flammability and toxicity of chloroform make it a risk for commercial use. Chloroform extraction without stabilization (addition of alcohol) may form phosgene, which is an extremely toxic (Fuhrmann et al., 2009). Although oil extraction techniques are cheap and easy to execute, the main drawbacks include the use of these toxic solvents and long extraction time (Mubarak et al., 2015). Therefore, an accelerated method of oil extraction should be introduced to reduce the effect of these drawbacks.

Nanoparticles can easily penetrate and interact with biomolecules due to their size. Abdul Razack (Abdul Razack et al., 2016) found that silver nanoparticles cause cell wall damage to *Chlorella vulgaris* and are suitable for lipid extraction. Zinc oxide nanoparticles are also able to increase the permeability of cellular membranes and depolarise cells (C.-H. Tang et al., 2017). W.-C. Huang & Kim (W.-C. Huang & Kim, 2016) studied the use of nickel oxide nanoparticles for *Chlorella vulgaris* lipid extraction and found a 208% increase in extraction efficiency. However, the synthesis cost, environmental concerns and reusability of nanoparticles have yet to be fully addressed for commercial applications of these technologies (S. Y. Lee et al., 2017).

Supercritical fluids have emerged as an interesting alternative to conventional solvents due to their low viscosity, high diffusivity, easy separation, high dissolving power and low surface tension (Patil et al., 2018). Supercritical CO_2 is the most widely used supercritical fluid for extraction of bio-compounds and is recyclable (Goto et al., 2015). S. Tang (S. Tang et al., 2011) achieved 33.9% lipid yield from *Schizochytrium limacinum* powder with ethanol (95%) and supercritical CO_2 (5%) as extraction solvents. Millao &

Uquiche (Millao & Uquiche, 2016) studied the effects of supercritical CO_2 on *Nannochloropsis gaditana* lipid extraction and found that temperature and CO_2 density increase lead to higher lipid and carotenoid yields. In order to make supercritical CO_2 lipid extraction process more economical, simultaneous lipid and carotenoid extraction have been explored.

Ionic liquids are green organic solvents that are non-volatile and possess good thermal stability (Kim et al., 2012). Ionic liquid has been applied to not only extract lipid, but also to recover other valuable compounds such as proteins and polysaccharides from wet biomass (Olkiewicz et al., 2015). Choi (Choi et al., 2014) compared the lipid yields of *Chlorella vulgaris* with organic solvents and ionic liquids, and found that 1-ethyl-3-methyl imidazolium acetate, 1-ethyl-3-methyl imidazolium diethylphosphate, 1-ethyl-3-methyl imidazolium tetrafluoroborate, and 1-ethyl-3-methyl imidazolium chloride showed high lipid yields of more than 200 mg g^{-1} cell compared to 185.4mg/g cell achieved by the conventional hexane-methanol solvent. However, there are cases where certain ionic liquids resulted in lower lipid yield than conventional organic solvents. In addition, Olkiewicz (Olkiewicz et al., 2015) found that ionic liquids showed better extraction yields from raw sludge than dried sludge, which would eliminate the need for costly drying process.

Enzyme can facilitates the recovery of lipid by selective degradation of cell wall and membrane while preserving most labile compounds (Zuorro, Miglietta, et al., 2016). Published studies have concluded that proper enzyme selection and optimal process conditions determination are essential for effective enzymatic treatment (Zuorro, Maffei, et al., 2016). Sierra (Sierra et al., 2017) found that lipid yield of *Chlamydomonas reinhardtii* incubated with autolysin was found to be 30% higher than without biomass treatment. High lipid extraction (88.3%) was achieved from slurry of *Nannochloropsis*

oceanica with the use of thermal lysin, *Aspergillus niger* cellulose and surfactants (Chen et al., 2016). The combination of several cell disruption methods may help increase lipid yields from microalgae. However, it should be noted that enzymes should not be exposed to mechanical, thermal or chemical stress to ensure reusability.

2.3.3 Ultrasonic effect on extraction process

The oil extraction process can be further improved by using energy intensive techniques such as ultrasonic waves in the presence of a suitable solvent. In recent years, ultrasonic assistance extraction has gained much attention because it is inexpensive, efficient, disrupts cell walls, reduces particle size and enhances the mass transfer across cell membranes (Khoei & Chekin, 2016). Ultrasonic waves are vibrations created by a ultrasonic source comprised of sounds waves within the range of 18 kHz to 100 MHz (Karmakar & Halder, 2019). Ultrasonic waves produce localized high pressure and temperature points due to oscillation of cavitation bubbles and shock waves created by the collapse of those bubbles (L. Zhang et al., 2017). The process can also be conducted in lower temperatures, which minimize the risk of thermal damage to the extracted components (Mohammadpour et al., 2019).

Ultrasonic waves have been known to improve oil recovery, oil mobility and oil percolation paths (Rezaei Dehshibi et al., 2019). When a sample is irradiated with ultrasonic waves, an extra acoustic pressure adds up to the already present hydrostatic pressure, creating high pressures in the cavitation bubbles which enhances the formation of radicals and chemical reaction enhancing shockwaves as a result of the collapse of those bubbles (Karmakar & Halder, 2019). However, the use of ultrasonic assistance during oil extraction of spent coffee ground has been rarely studied.

The ultrasonic waves can be transmitted to the medium via an ultrasonic probe or ultrasonic bath. It is known that an ultrasonic probe is more efficient than an ultrasonic bath. The ultrasonic power density of an ultrasonic probe is almost 100 times greater than supplied by an ultrasonic bath (Bhangu et al., 2017). This can be due to the direct cavitation towards the oil bearing medium when using an ultrasonic probe, rather than when the cavitation is subjected to two different mediums when using an ultrasonic bath.

However, there are various factors which influence the ultrasonic probe reactor design such as probe to reactor diameter ratio, reactor height, immersion depth and chamber characteristics (material and shape) (Mostafaei et al., 2015).

The phenomenon of ultrasonic cavitation is basically the expansion and contraction of transfer media bubbles. The several mechanical mechanisms where ultrasound improve the effective mixing of solutions are (Juliano et al., 2017):

i. Standing wave oil droplet trapping effect (radiation forces which promote the formation of standing wave sound field)
ii. Semi-stable or stable cavitation bubbles (creating rubbing effect in oil bearing matter which releases the oil particles)
iii. Acoustic steaming (permitted by a gradient in the velocity field due to spatial attenuation of sound wave in the medium, friction between vibrating element and surrounding medium as well as scattering of sound waves)
iv. Internal heating (energy release by violent cavitation bubble collapse resulting in rise in temperature)

Besides the mechanical effects of ultrasonic assistance on the reaction, there are also chemical effects which affect the reaction mechanism. Ultrasound is known to induce radicals such as H, OH, HO_2 in aqueous solutions which improve reaction kinetics (Mostafaei et al., 2015). One consideration for ultrasonic treatment is that it provokes oxidative degradation in edible oils, since temperature rise occurs in a short time period (Pingret et al., 2013). The frequency of ultrasonic cavitation is found to be the influencing factor which affects quality of oils, especially the oxidation stability (L. Zhang et al., 2017).

X. Zhang (X. Zhang et al., 2016) studied the use of ultrasonic assistance for biodiesel production of *Trichosporon oleaginosus* sludge, and found that the duration was shortened by 23 hours with a yield of 95%. Gerde (Gerde et al., 2012) found that by increasing the sonication power, the extraction of intracellular products also increases, but may also led to poorer quality of oil because of oil oxidation. Therefore, while increasing the oil yields via ultrasonic assistance is beneficial, it is essential to analyze the physiochemical properties of the oil prior to the transesterification process.

2.3.3.1 Ultrasonic Amplitude

Ultrasonic waves improve rate of extraction since it breaks the cells and releases their contents into the extraction environment (Hernández-Santos et al., 2016). The ultrasonic power produced by a transducer can be indicated by the amplitude of the ultrasonic cavitation (Tiwari, 2015). Metherel (Metherel et al., 2009) observed enhanced oil extraction yields from flaxseed and attributed it to longer extraction times and higher ultrasonic amplitudes. However, it should be noted that an increase in ultrasonic amplitude will directly correlate to the economic value of the proposed process (Koubaa et al., 2016). This is especially important for a commercial scale operation, where the amount of energy consumed per weight of treated sample should be measured for economic feasibility. Moreover, amplitudes beyond the optimum levels result in undesirable degradation of oil compounds and probe erosion which leaves residues in the extracted compounds (Tiwari, 2015).

2.3.3.2 Ultrasonic Pulse

When utilizing ultrasonication, it can be applied in a pulse or continuous mode. In the case of continuous ultrasonication, ultrasonic waves are delivered without pause to the medium, resulting in no relaxation phase for the liquid phase, thus increasing the thermal energy to unfavorable conditions (Tan et al., 2019). In the case of pulse mode, the ratio of working time and idle time can be increased to improve conversion efficiency. Xie (Xie et al., 2015) found that pulsed ultrasonic waves provided a more enhanced separation because it implements coalescence of small degassing bubbles more effectively and promotes a higher amplitude of sound propagation. Furthermore, pulsed mode extraction is found to save 50% of energy compared to the continuous mode (Tiwari, 2015).

2.4 Biodiesel production process

Biodiesel is commonly produced via the transesterification reaction of oil with methanol and a base catalyst which results in a fuel containing a mixture of FAME ranging from C6 to C22 (Hupp et al., 2018). The reaction is a reversible reaction; therefore excess alcohol is added to shift equilibrium to the side of the products. There are several factors which affect the production yield of biodiesel, including methanol to oil ratio, catalyst concentration and reaction time. However, the optimum conditions for various biodiesels have been largely inconsistent. This is because the conditions are strongly dependent on the properties of the feedstock (Dorado et al., 2004). The process selection for the biodiesel production process can be seen in **Figure 2.4**.

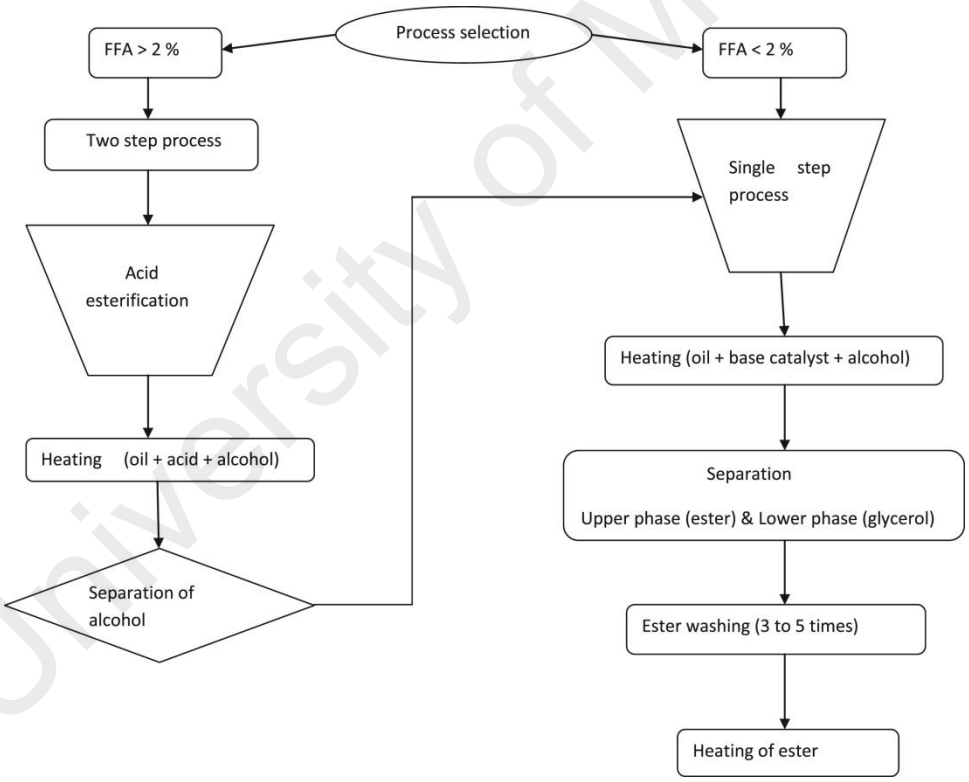


Figure 2.4: Biodiesel production flowchart

The reaction mechanism for the transesterification process is dependent on type of catalyst used. For a base catalyzed process, methoxide is produced from methanol and

base catalyst. The nucleophilic attack of methoxide on carbonyl groups of the triglycerides forms a tetrahedral intermediate, which breaks down and regenerates the catalyst (Farobie & Matsumura, 2017). **Figure 2.5** shows the reaction mechanism between triglycerides and base catalyst.

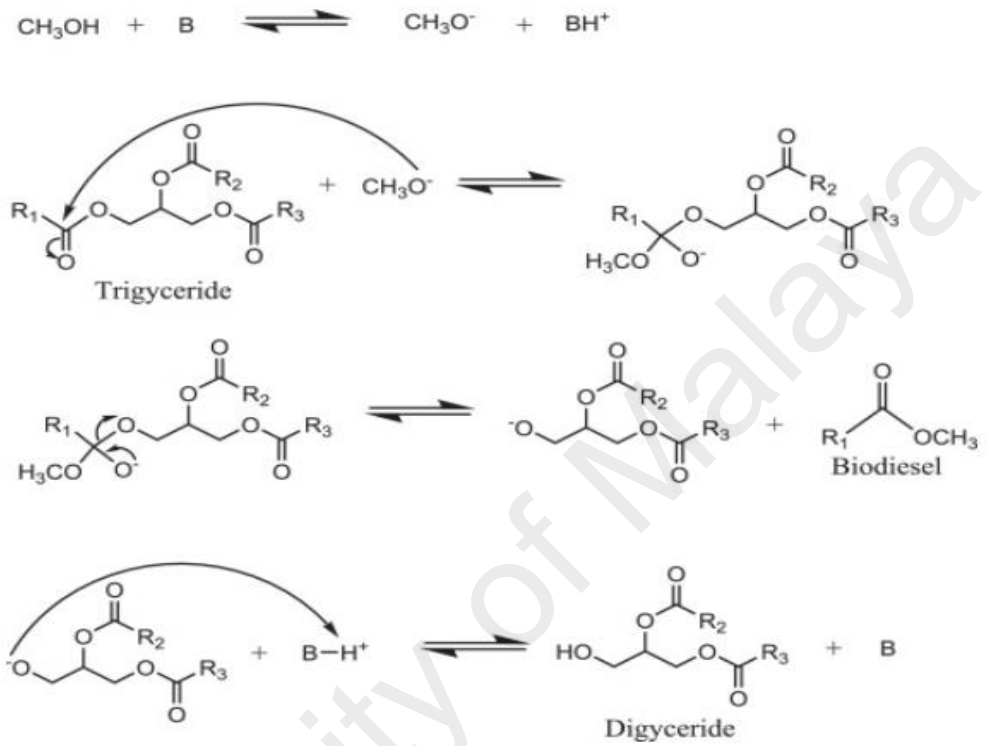


Figure 2.5: Reaction mechanism for homogenous base catalyzed transesterification (Farobie & Matsumura, 2017)

This process repeats itself twice, beginning from a triglyceride to diglyceride and finally monoglyceride, to produce fatty acid methyl esters and glycerol. The fatty acid methyl esters are a product of the reaction between triglycerides from the oil and base catalyst. **Figure 2.6** shows the stepwise reactions from triglycerides to fatty acid methyl esters.

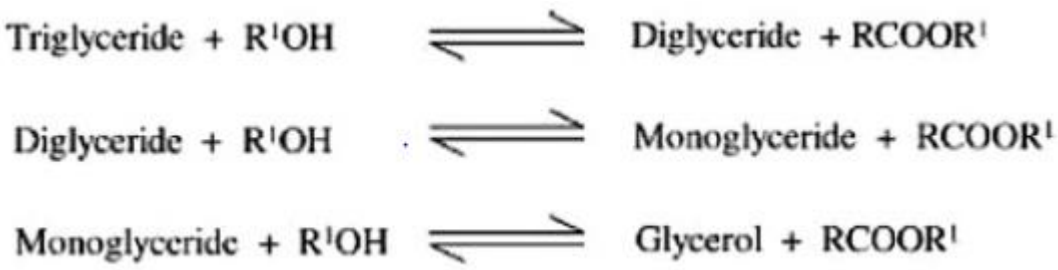


Figure 2.6: Stepwise production of alkyl esters from triglycerides in transesterification

However, there are several technical challenges for the transesterification process. One major issue is the cost of biodiesel feedstock. There are more than 350 types of oil feedstock that are available for biodiesel production in the world today (kumar & Sharma, 2016). Feedstock for biodiesel may come from animal fats, non-edible vegetable oil or edible vegetable oil. Currently, more than 95% of the world biodiesel is made from edible vegetable oil (Gui et al., 2008). Due to overwhelming increase in global food demand, the use of edible vegetable oil for biodiesel commercial production has been unsuccessful due to the fluctuating price. Thus, there is a need to branch into non-edible vegetable oils as source of feedstock for biodiesel. In the last two decades, different generations of biodiesels are being developed (Brennan & Owende, 2010; Naik et al., 2010). As shown in **Table 2.1**, the generations differ by type of feedstock and processing technology.

Table 2.1: Differences between Generations of Biodiesel

Biodiesel	Feedstock	Processing Technology	References
First Generation	Edible Vegetable Oils	Esterification and Transesterification of oils	(Sakthivel et al., 2017),(Mancaruso et al., 2011)
Second Generation	Non-edible vegetable oils, waste cooking oil, lignocellulosic feedstock materials, Animal Fats	Esterification and transesterification of oils/ seeds (utilizes organic catalyst/additives)	(Bhuiya et al., 2014), (Bhuiya et al., 2016)
Third Generation	Aquatic cultivated feedstock (microalgae)	Algae cultivation, harvesting, oil extraction, transesterification	(Saladini et al., 2016), (Alaswad et al., 2015)

There are many criteria which vindicate the merit of a biodiesel feedstock. Besides being cost effective, the feedstock should have high oil content, able to react at moderate conditions and the corresponding biodiesel should have suitable properties. In spite the fact that second generation feedstocks do not provide direct competition with agricultural crops, the feedstock still requires agricultural routines such as fertilizers, irrigation and harvesting to maximize productivity. Energy crops cultivation could release 17-420 times more CO_2 emissions than the annual reductions that the corresponding biofuel would achieve. (Hajjari et al., 2017). Therefore, waste products such as SCG are an interesting concept for biodiesel production as they are an inevitable product of human consumption and do not require any additional agricultural process. Using waste feedstock for biodiesel production have also been reported to have similar or lower NO_x emissions than first generation biodiesels (Adewale et al., 2015). Besides that, the free fatty acid content of the feedstock is also an important criteria as it dictates the type of catalyst that should be used (Manaf et al., 2019).

Previous studies have found SCG to be capable to produce biodiesel via oil extraction followed by transesterification or in-situ transesterification. Son et al. (Son et al., 2018) obtained 86.33% of FAME using supercritical methanol in biodiesel conversion from SCG. Park et al. (Park et al., 2016) achieved a maximum yield of 16.75 wt% (based on dry weight) FAME from in-situ transesterification of wet SCG. A maximum FAME yield of 11.8% was achieved by Park et al. (Park et al., 2018) when the solvo-thermal effect of 1,2-dichloroethane was integrated with transesterification of SCG at 160°C. Oliveira et al. (Oliveira et al., 2008) achieved a higher FAME yield from defective coffee beans than healthy coffee beans which was attributed to the higher amount of free fatty acids available.

The scaling up production would also have other adverse effects such as increasing food prices, water scarcity and land reclamation (J. Sun et al., 2019). One way to improve the scaling up production is to introduce the biorefinery process. Biorefinery is an industrial scale facility where biomass and its intermediates are converted to valuable products such as chemicals, materials and energy products (Zhu, 2015). While biofuel production is the one of the main objective of waste coffee ground recycling companies, the production of other high value products is crucial for companies to remain profitable in the short term (Su et al., 2017). There have been novel researches regarding the uses of SCG as a biocatalyst for biodiesel production, substrate for carotenoids production and solid fuel (Kang et al., 2017; Moreira et al., 2018; Sarno & Iuliano, 2018). A SCG biodiesel market would also generate interests in the commercialization of these bio-products. The introduction of waste coffee ground biodiesel market may also affect conventional coffee product markets.

2.4.1 Catalyst type

The transesterification reaction is commonly catalyzed by base catalysts such as sodium hydroxide and potassium hydroxide to improve reaction rates and yield of biodiesel (Samani et al., 2016). A base catalyzed reaction occurs by creating a nucleophilic alkoxide from the alcohol which attacks the carbonyl group of triglycerides, whereas in an acid catalyzed reaction, the carbonyl group of triglycerides is protonated and the alcohol will attack the protonated carbon to create a tetrahedral intermediate (Endalew et al., 2011). The drawback of acid catalyzed transesterification is the low yield compared to conventional base catalyzed (Sivaramakrishnan & Incharoensakdi, 2017). Moreover, acid catalyzed reactions are sensitive to moisture, require higher temperatures and have slower reactions (Fonseca et al., 2019).

Base catalyst demonstrates faster reaction kinetics than acid catalyzed but can only be used for transesterification of oils with less than 2% FFA to avoid saponification and difficulty of ester separation (Ho et al., 2016). Saponification also hinders separation of glycerol and ester as it increases the viscosity and forms a gel layer (Berchmans & Hirata, 2008). Under comparable conditions, a homogenous base catalyzed transesterification reaction rate is 4000 times faster than that of an acid catalyzed transesterification reaction (Fukuda et al., 2001). This suggests that acid catalysts should only be used in the transesterification process when necessary.

Recent novel studies have proposed the use of heterogeneous catalyst. The use of calcium oxide (CaO) catalyst, which can be synthesized from egg shells, mollusc shells, chicken bone, oyster and mud crab shell is gaining much attention for biodiesel production (Kings et al., 2017). CaO catalyst recycles shell waste from being disposed and its usage also increases the commercial value of seafood production (Mazaheri et al., 2018). The catalytic capacity of CaO in transesterification is dependent on the existence

of basic sites and their spatial dispersion (Marinković et al., 2016). Nevertheless, CaO is a basic catalyst and can only be used for transesterification of microalgae with low free fatty acid content. Research has found that lipases work at lower temperature (25-50 °C) and the subsequent separation of biodiesel and glycerol is relatively easier (Navarro López et al., 2016). The catalytic activity of this type of catalyst depends on the calcium content as well as surface area. However, it should be noted that the preparation of these catalyst involve a process known as calcination, where the shells which consists mainly of $CaCO_3$, will be heated at 600-1000°C to obtain the catalytic CaO (Shan et al., 2018).

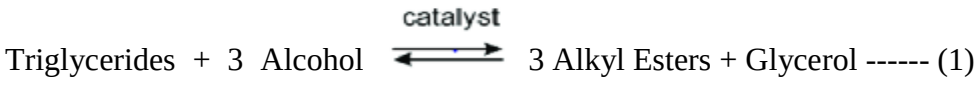
There is also a favorable trend of using lipase in biodiesel production due to its high production rate and low cost (Amini et al., 2017). Guldhe (Guldhe et al., 2016) optimized the transesterification of oil from *Scenedesmus obliquus* using immobilized *Aspergillus niger* as catalyst and obtained a 90.82% conversion yield. However, the use of extracellular lipases requires an immobilization process, and the subsequent recovery and purification are also costly and difficult (Navarro López et al., 2016). Lipases are also relatively costly and have a gradual decrease in their catalytic activity (Karmakar & Halder, 2019). The use of heterogeneous catalyst allows for easy catalyst recovery as alcohols do not mix with the solid catalyst (Chouhan & Sarma, 2011).

On the industrial scale, homogenous base catalyst is often utilized due to lower reaction time, higher conversion yield and relatively small amount of catalyst used (Fonseca et al., 2019). Unfortunately, these base catalysts are hard to recycle and corrosive to the reactors (Shan et al., 2018). It is also worth noting that the efficiency of base catalyst is dependent on the amount of impurities within the feedstock (Fonseca et al., 2019). On the other hand, for heterogeneous catalyst, there tends to have three phases with oil and alcohol which reduces the rate of reaction due to mass transfer limitations (Baskar & Aiswarya, 2016).

Common types of homogenous base catalyst being used are sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide ($NaOCH_3$). Sodium methoxide acts as a better catalyst because it does not form water as a by-product. This significantly reduces acid value of reaction product (Dalai et al., 2012). However, due to their toxicity, expensive price and difficulty of disposal, $NaOCH_3$ is not a viable option for commercial use. NaOH is preferred due to its low molecular weight, whereas KOH is also suitable because it can react with phosphoric acid during the neutralization phase to produce potassium phosphate, a commercial fertilizer (Manaf et al., 2019).

2.4.2 Alcohol

The transesterification reaction is a reversible reaction with the stoichiometric molar ratio of one triglyceride to three alcohols. The alcohols act as an acyl acceptor for the transesterification reaction (Aguieiras et al., 2015). The single step reaction is shown in Equation 1.



Although the stoichiometric molar ratio of alcohol to oil is three to one, excess alcohol is required to push the forward reaction and break the glycerin-fatty acid linkages during the transesterification of triglycerides (Musa, 2016). Low alcohol to oil ratios will reduce the conversion efficiency of triglycerides to methyl esters, whereas excessively high ratios will also reduce the yield (Verma & Sharma, 2016). Biodiesel can be produced by a variety of alcohols, with the requirement that the produced biodiesel meets the technical standards. However, long chain alcohols tend to be avoided due to the steric hindrance effect (Musa, 2016).

The optimum alcohol-oil ratio depends on various factors such as the type of oil, alcohol and catalyst (Dalai et al., 2012). The synthesis of biodiesel is often limited by mass transfer limitations and necessity of high molar ratios of alcohol to oil, which results in high production cost and energy usage (Salamatinia et al., 2013). However, excessive amounts of methanol will also have a detrimental effect on the biodiesel yield. The excess methanol will interfere with glycerol separation due to the increasing solubility of glycerol in ester phase, provoking the reverse reaction which decreases the biodiesel yield (Thoai et al., 2019).

Commonly, methanol and ethanol are used in the biodiesel production process, each with their own pros and cons. These alcohols are often utilized at temperatures below

their boiling point. However, these alcohols are not miscible with triglycerides at room temperature, requiring an external excitation mechanism such as stirring, ultrasonic or microwave assistance to enhance the mass transfer (Li et al., 2013). Majority of the transesterification processes utilize methanol due to its suitable physiochemical properties, low cost, mild reaction conditions, good reactivity and ease of separation (Thoai et al., 2019). However, the disadvantage of using methanol is that it is toxic and non-renewable.

Longer chain alcohols such as ethanol, isopropanol and butanol are introduced as potential alcohol replacements. The use of longer chain alcohols also improves the cold flow properties and oxidation stability of the produced biodiesel (R. Huang et al., 2015). However, alcohols with chain length of more than 5 are avoided to increase the reaction rate and reduce viscosity of the produced biodiesel (Gao et al., 2019). Reddy et al. (Reddy et al., 2014) reported that fatty acid ethyl esters have better cetane number, oxidation stability and cold flow properties than fatty acid methyl esters. However, the separation of ethyl esters is complicated due to formation of unexpected emulsion within the product mixture (Thoai et al., 2019). Higher conversion rates under similar reaction conditions have also been achieved with methanol than with ethanol (Veljković et al., 2018).

2.4.3 Ultrasonic effect on transesterification process

The transesterification process may be a well established method, but the mass transfer restrictions and low energy utilization prove to be the downfall of the process (J.-J. Lin & Chen, 2017; Veljković et al., 2012). The immiscibility of oil and alcohol leads to formation of two phases, reducing mass transfer rate and requiring a longer reaction time (Gholami et al., 2018). Therefore, the use of microwave or ultrasonic assistance during transesterification is beneficial as it improves biodiesel synthesis efficiency. The respective advantages of conventional stirring, ultrasonic and microwave assisted methods can be seen in **Table 2.2**.

Table 2.2: Advantages of conventional stirring, ultrasonic and microwave assisted methods

Conventional stirring	Ultrasonic Assistance	Microwave Assistance
Traditionally done in a batch stirred vessel with a shaft and impeller, but is time, energy and cost consuming since the mixing only occurs at a macro level (Sajjadi et al., 2017).	High temperature and pressure conditions create free radicals which cause reaction to occur instantly (G. Kumar, 2017)	Short chain alcohols (Methanol or ethanol) have strong polarity and are active microwave absorption media (Yu et al., 2017).
Increasing stirring speed can increase the effective collisions between oil and alcohol molecules (Peiter et al., 2018).	High temperature, high pressure, acoustic microstreaming, turbulence and high shear forces generate finer emulsions between immiscible fluids which enhance mass transfer and transesterification reaction rates (Gupta et al., 2017).	Microwave technology allows rapid, safe and cost effective high purity biodiesel production without the need of drying (Virot et al., 2008; Wahidin et al., 2014)
Methyl esters are not as soluble in the catalytic system during stirring, which makes the separation process easier (Masri et al., 2018).	Ultrasonic can also help in the extraction of valuable components such as pigments and carotenoids (Sivaramakrishnan & Incharoensakdi, 2017).	Microwaves create electromagnetic fields which align polar molecules and create heat due to friction from slower orientation of molecules and time rate change of the

		fields (Jermolovicius et al., 2017).
A clearer phase change formation can be obtained at high stirring speeds, but excessive agitations may cause reduced biodiesel yield due to hydrolysis of biodiesel (Fadhil et al., 2017).	Approximately 5000K and 100MPa produced during collapse of ultrasonic bubbles (Jookjantra & Wongwuttanasatian, 2017).	Microwave technology has been upraised to work on a continuous flow pattern in an energy efficient manner (Panadare & Rathod, 2016).

Similar to oil extraction methods, sonication encourages better oil solubilisation. The pressure variations which occur in the mixture due to ultrasonic irradiation induces a large amount of microbubbles which collapses and increases the interfacial area of the reactant boundary (Choedkiatsakul et al., 2014). Martinez (Martínez et al., 2017) found that ultrasonic assistance improved yield of biodiesel from transesterification of *Spirulina* sp. and a higher oil recovery. Conventional biodiesel synthesis time of 24 hours was reduced to 30 minutes via ultrasonic assistance when applied on Neem oil with lipase catalyst (Gupta et al., 2017). Maghami (Maghami et al., 2015) reported a higher biodiesel yield from fishmeal plant waste oil using ultrasonic methods than conventional methods under similar conditions. However, Teixeira (Teixeira et al., 2009) reported similar conversion yield but reduced reaction time for the transesterification of beef tallow. A combined ultrasonic and mechanical stirring reactor was also explored on transesterification of palm oil and showed better reaction rates than both the standalone reactors (Choedkiatsakul et al., 2014).

On the other hand, microwave allows selective heating, faster energy transfer and thus more efficient heating (Wahidin et al., 2014). The microwaves affect molecule movements via ionic migration or dipole rotation while providing thermal energy to the solvents through convection, conduction and radiation from the reactor surface (Hong et

al., 2016). Cheng (J. Cheng et al., 2013) found that the kinetic rate of direct biodiesel synthesis with microwave assistance was 6 times faster than the conventional extraction-transesterification of *Chlorella pyrenoidosa* oil. Sharma (Sharma et al., 2016) optimized biodiesel production from *Chlorella vulgaris* under microwave irradiation and achieved an 84.01% yield. Teo (Teo & Idris, 2014) reported that biodiesel produced with microwave assistance showed higher lubricating property, good cetane number and shorter carbon chain FAME compared to biodiesel produced using the conventional method.

2.5 Fatty acid methyl ester composition

According to the ASTM D6751, biodiesel is made up of mono-alkyl esters of long chain fatty acid fuel (Santana et al., 2019). Fatty acid composition is important as it determines the fuel properties of the biodiesel produced (Issariyakul & Dalai, 2014). Fatty acid composition of the biodiesel and feedstock oil do not alter and remain the same (Kumar & Sharma, 2015). It should be noted that the use of ultrasound will also not affect the fatty acid composition of oil (Perrier et al., 2017). However, there is only a standard for FAME (EN 14 214) but no similar standard for fatty acid ethyl esters (Bolonio et al., 2019).

Ideally, biodiesel should consists of 100% FAME, but low conversion, side reactions and difficulty in separation result in impurities such as glycerol, monoglycerides and diglycerides which remain in the biodiesel (Bouaid et al., 2016). The quality of the produced biodiesel can be quantified by analyzing the fatty acid methyl ester content. Typically, there are 5 major fatty acids which dominate the composition of biodiesel produced from vegetable oils, which are palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) (Seffati et al., 2019). The gas chromatography equipment can be used to accurately measure major and minor compounds and provide the corresponding area for each component (Ambat et al., 2018). The fatty acid composition will determined via gas chromatography which will be described in the methodology.

The fatty acid composition can also be used to predict the biodiesel properties using artificial neural networking (Mostafaei et al., 2015). It should be noted that accurate fuel properties of a biodiesel are influenced by various factors such as the components, chain size and degree of unsaturation. Polyunsaturated esters often affect the oxidation stability of the fuel, whereas saturated fatty acid esters will affect the cold flow properties (Ambat

et al., 2018). Besides the unsaturation levels, the fuel quality is also affected by oxidation stability, ignition quality and cold flow properties (Kumar & Sharma, 2015).

The chemical weight of biodiesel can be distributed as such: carbon (76-77%), hydrogen (11-12%), and oxygen (10-12%) (Ruhul et al., 2016). The carbon and hydrogen ratio is affected by the fatty acid content, which influences the fuel injection, performance and emission of the diesel engine. Properties which are difficult and expensive to test can also be predicted by the fatty acid composition. For example, cetane number characterization requires the mixing of reference fuels (n-cetane and hepta-methylnonane) in various volumes under standard test conditions (Baghban et al., 2018). The FAME composition can also be altered (chain length and degree of unsaturation) to significantly reduce the cloud point of biodiesel (Senra et al., 2019).

2.6 Biodiesel physiochemical properties

Raw oil has been directly tested for engine use, but has encountered various problems. The low volatility and coagulation at low temperatures induce deflagration, causing the fuel injector to make noise and oil ring to fail. Besides that, carbon deposits are present due to the presence of unsaturated fatty acids, resulting in other engine problems (Hong et al., 2014). Therefore, the synthesis of biodiesel from raw oils solves these issues as biodiesel can be directly used in a diesel engine without requiring modification.

Compared to petroleum diesel, biodiesel has higher density, viscosity, cetane number, flash point and absence of aromatic compounds and sulphur links (Ruhul et al., 2016). Biodiesel may be the more environmentally friendly alternative, but it comes at the cost of performance. This has led to many consumers to be skeptical towards the use of biodiesel. Certain properties are related to the chemical composition of FAME, such as the viscosity, cetane number, cloud point, distillation and iodine value, whereas others depends on the production and storage process, such as the flash point, methanol content, metal content, sulphur number, acid value and cold soak filterability (Hoekman et al., 2012).

Currently, there are several standards that are being employed throughout the world for biodiesel specifications. These standards are essential as they serve as a minimum requirement for biodiesel properties prior to its commercialization. The United States of America (US) and European Union (EU) both have standards of their own, and are often used as reference for other countries' biodiesel standards. The US employs the ASTM D6751 which place emphasis on biodiesel blending. In Europe, the standards used for biodiesel property determination are from the EN 14214. Both standards consists of various biodiesel properties such as acid value, kinematic viscosity, density, oxidation stability and copper corrosion levels.

2.6.1 Acid value

Acid value is also known of the neutralisation number. It is defined as the mass of KOH in milligrams required to completely neutralise the acid value in one gram of substance (Leung et al., 2006). Acid value of biodiesel indicates the content of free fatty acids, corrosiveness of fuel and presence of water. A higher acid value would result in saponification of base catalyst, which will reduce efficiency of the transesterification process (Olutoye et al., 2016). Acid value is known to increase gradually with oxidation, due to the hygroscopic nature of biodiesel to hydrolyze the ester bonds (Liu et al., 2018). Oxidative reaction of double bonds form peroxides which further disintegrate to aldehydes and finally acids (Tomić et al., 2019). Both the EN 14214 and ASTM D6751 has suggested that biodiesel acid value should be lesser than 0.50 mg KOH, while the ASTM D7467 has suggested that for biodiesel blends of 6-20%, the acid value should be lesser than 0.30 mg KOH (Lawan et al., 2019).

2.6.2 Kinematic Viscosity

Viscosity of a fluid can be defined as the fluid's resistance against gradual change by shear stress or tensile stress. Viscosity is one of the important properties of a biodiesel due to the effects it has on fuel atomization and fuel penetration in the combustion chamber (Hosseini et al., 2019). Initially, when raw oils were tested in diesel engines, the viscosity was the main obstacle. Transesterification is known to reduce the viscosity to an acceptable range for proper usage (Kumar & Sharma, 2015). In an identical carbon chain, the viscosity is affected by the functional groups. The influence of the functional groups go from COOH > C-OH > COOR > C=O > C-O-C (Bolonio et al., 2019). Besides that, viscosity is also known to increase with fatty acid chain length (Hoekman et al.,

2012). Viscosity is also temperature dependent, meaning that its properties vary with change in temperature. High viscosity fuels reduce the aerodynamic disturbance on the surface of the liquid jet injected through the nozzle and delays the breakup, demanding more energy from the fuel pump and reduces the net power output (Das et al., 2018). High viscosity biodiesels also result in increased smoke and greenhouse gas emissions due to the poor combustion and fuel atomization (Seffati et al., 2019).

2.6.3 Density

Density or specific gravity of a fuel is defined as the mass of the fuel per unit volume, being measured at vacuum conditions. Density directly affects a fuel's engine performance, as cetane number, heating value and viscosity is related to density. Changes in density will also influence energy output from engine due to the difference in injected fuel mass (Constantino et al., 2019). Since the diesel engine meters fuel based on volume, a difference in fuel density will directly cause fuel mass that reaches the combustion chamber to reduce, thus affecting energy produced by that fuel dosage (Tomić et al., 2019). The main factor affecting the density of a biodiesel is the degree of unsaturation, where higher unsaturation leads to increased density (Hoekman et al., 2012). The density of biodiesel is generally higher than petroleum diesel and is dependent of fatty acid composition and purity (Barabás & Todoruţ, 2011). This means that a higher mass flow rate of biodiesel is consumed than petroleum diesel (Gao et al., 2019).

2.6.4 Calorific Value

Biodiesel from all sources also have lower mass energy content, about 10%, than petroleum diesel (Hoekman et al., 2012). The percentage of calorific value decrease

between biodiesel and petroleum diesel is approximately 4-5% (McCarthy et al., 2011). This is due to the high oxygen content of biodiesels, which is affected by the fatty acid carbon chain (Hoekman et al., 2012). Longer carbon chains have higher unsaturation levels, lower mass fraction of oxygen, resulting in higher calorific values. Common biodiesels made from known feedstocks such as Jatropha oil and cotton seed oil have calorific values with the ranges of 37-41 MJ/kg (Thapa et al., 2018). An important note is that calorific value is often measured on a mass basis, while fuel is consumed on a volumetric basis. Therefore, biodiesels with higher calorific values are preferred.

2.6.5 Oxidation Stability

The oxidation of biodiesel is affected by various factors. The primary factor can be explained by the ester composition of the biodiesel. Polyunsaturated fatty acid methyl esters, esters with more than two double bonds, are susceptible to oxidation due to the bis-allylic CH_2 positions (Knothe & Steidley, 2018). Initially, biodiesel oxidation results in production of peroxides and hydroperoxides, which degrade to aldehydes, ketones, alcohols and low molecular weight acids, resulting in insoluble deposits and changes in the biodiesel acid value, peroxide value, kinematic viscosity, density and iodine value (Liu et al., 2018). Oils with short induction periods are also susceptible to accelerated oxidation by presence of metal ions, light, temperature, forming peroxides and other oxidative products and lead to reduced storage periods (Gregório et al., 2018). While the standard Rancimat testing method can give reliable oxidation stability results for biodiesels under accelerated conditions, further studies should be done on more realistic conditions (Kovács et al., 2015). Recent research have investigated the use of additives such as antioxidants, phytohormone and oxygen vector to reduce oxidative damage (X.-M. Sun et al., 2017). Although any antioxidant is suitable to be used in biodiesel from

any feedstock, certain antioxidants show better improvements in oxidation stability than others (Mittelbach & Schober, 2003). Therefore, the compatibility of antioxidants to biodiesel should be investigated along with its effects on other properties prior to commercialization.

2.6.6 Corrosion level

Degraded products of biodiesel such as insoluble gums, organic acids, aldehydes and presence of moisture are the main reason behind biodiesel container corrosion (Deyab & Keera, 2016). Biodiesels also tend to corrode more than petroleum diesels due to their hygroscopic nature, which promotes water adsorption and hydrolysis and resulting in acidification and microscopic level corrosion (Ching et al., 2016). Acidic content which generate during biodiesel oxidation also causes corrosion wear on the fuel supply system and fuel storage facilities (Tomić et al., 2019). Although engine parts are also made of other metals, alloys and elastomers, copper is chosen as the test material due to it being more prone to corrosion than other alloy metals (B. Singh et al., 2012). However, it is suggested to assess the compatibility of biodiesel with different materials by exposing the biodiesel to various metal types, duration and temperatures (Fazal et al., 2018). Corrosion inhibitors have also been suggested to reduce the corrosion rate in fuel tanks (Deyab et al., 2019).

2.7 Summary and Research Gaps

Based on the literature discussed in the work, SCG is a promising feedstock for biodiesel production. However, the oil extraction and transesterification process is hardly studied. Furthermore, majority of studies performed on SCG biodiesel production utilize

conventional stirring as the reaction mechanism. The use of ultrasonic assistance is also able to further improve oil and biodiesel yields. The optimum parameters for oil extraction and transesterification processes with ultrasonic assistance may be different than that of conventional techniques. While SCG is a valuable asset in biochar production, there are still limited studies done on the biodiesel production from this feedstock. Further research could be directed on the cost effectiveness of the SCG biodiesel production process as well as a SCG biorefinery process to further increase cost effectiveness. Besides that, SCG after oil extraction could also be further used as a feedstock for biochar production, which would become a value added product. An integrated biorefinery process to extract oil for biodiesel conversion and to convert the cellulosic material within SCG into bioethanol could also be investigated. In this study, SCG was utilized as the feedstock for biodiesel synthesis with ultrasonic assistance.

CHAPTER 3: MATERIALS AND METHODS

3.1 Introduction

The research can be separated into three main sections, similar to the objectives, where the oil is first extracted from SCG, followed by transesterification to produce SCG biodiesel, and finally the physiochemical property testing of SCG biodiesel in comparison with ASTM D6751 and EN 14214 biodiesel standards. Initially, the SCG will be dried prior to extraction. Once completely dried, the mass change of SCG before and after the drying process will be used to determine moisture content. The optimum extraction conditions will then be conducted on wet SCG as a comparison. The transesterification parameters which will be tested will be described in this section. The methodology for analyzing the physiochemical properties of the SCG oil and biodiesel will also be mentioned. The methodology flowchart can be seen in **Figure 3.1**.

3.2 Materials

SCG (*Coffea arabica*) was obtained from a local cafe in Petaling Jaya, Malaysia. The SCG was subjected only one brewing stage before its collection. The SCG was oven dried at 60°C. Other chemicals and solvents such as 2-proponal (99.7%), hexane (99%), chloroform (99%), methanol (99.8%), and potassium hydroxide (KOH) were purchased from Merck Sdn. Bhd. The equipment used includes the Anton Paar SVM 3000 viscometer, Q500-20 ultrasonic probe equipped with 1 inch diameter tip (500 W power rating, 20 kHz frequency), Perkin-Elmer Spectrum 400 FTIR spectrometer, Agilent 7890A Gas Chromatography, Metrohm 873 Biodiesel Rancimat and Paar 6100 bomb calorimeter. All chemicals and reagants used in this study were analytical grade.

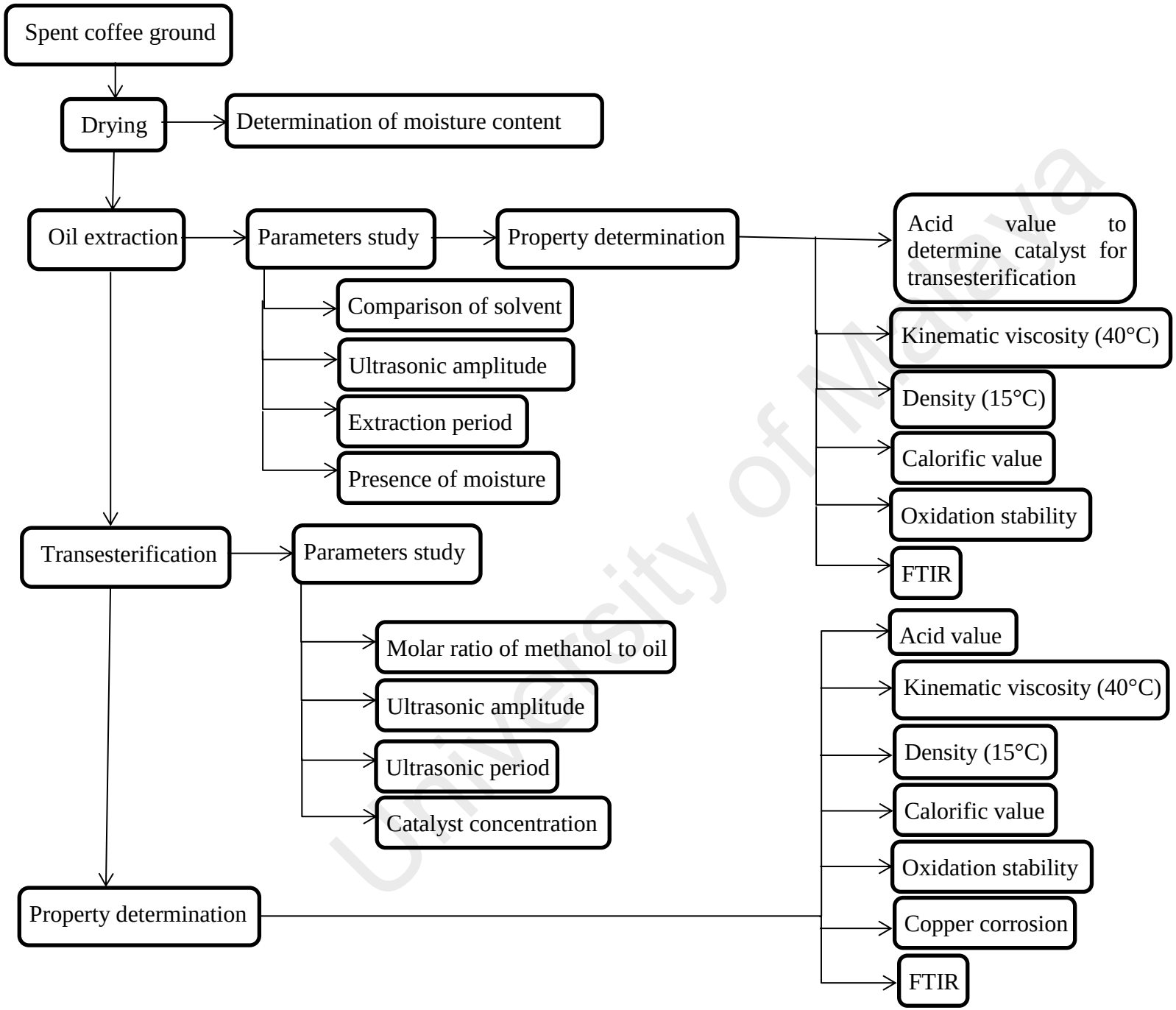


Figure 3.1: Methodology flowchart

3.3 Oil extraction

3.3.1 Coffee ground drying

The moisture content of SCG was measured immediately after collection by measuring mass before and after drying. Drying was conducted by spreading SCG across metal pan and dried at 60 °C for 36 hours. This temperature was chosen as oil content in raw materials is known to decrease at high drying temperatures (>60 °C) due to the oxidation of fatty acids (Skorupskaite et al., 2016). SCG had to be dried to avoid growth of mold during storage period. Mass of SCG was weighed before drying and at intervals of 12 hours. It was found that mass did not change after 36 hours which suggested most of the sample has been dried. The moisture content of SCG was calculated using Equation 2.

$$\text{Moisture content (\%)} = \frac{\Delta m}{m_i} \times 100\% \qquad \text{------ (2)}$$

where Δm (g) is the difference between final and initial mass of dried SCG, m_i (g) is the initial mass of SCG.

Moisture content of SCG was found to be 20%. For more accurate oil yields, mass of SCG will only be weighed after drying process. **Table 3.1** shows the change of mass of SCG as drying time increases. Mass of SCG remained constant after the 36 hours mark.

Table 3.1: Mass change of SCG against time

Drying time (hours)	Mass (g)
0	155.5
12	129.7
24	124.6
36	124.6
48	124.6

3.3.2 Soxhlet Extraction

20g of SCG was weighed in a cellulose thimble before being placed in a Soxhlet extractor and heated under reflux. Solvents used for this extraction method included hexane, chloroform and methanol. 250ml of chosen solvent was poured into extractor before heating process began. Time between first drops of oil until reflux solution became colorless was recorded. Average cycle time was 15 minutes, where temperature is adjusted based on solvent to maintain this constant cycle frequency. Solvent mix with extracted oil was evaporated at 60°C using a rotary evaporator to obtain extracted oil weight. The extraction was conducted in sets of three for each solvent and the mean value of extraction yield was calculated based on dried mass of SCG.

3.3.3 Ultrasonic Extraction

16g of SCG is measured and placed into a reactor. The selected solvent is added based on volume: SCG mass ratios of 3, 3.5, 4, 4.5 mgL^{-1} and placed into ultrasonicator. Ultrasonic probe is immersed into sample such that tip is entirely submerged within the solvent mixture. The ultrasonic waves were set at 5 seconds ultra-sonication with 2 seconds intervals. Other parameters being optimized included extraction time (15, 20, 25, 30 minutes) and ultrasonic amplitude (20, 25, 30, 35%). Due to the continuous compression and rarefaction ultrasonic cavitation cycle, temperature is disregarded as an optimization parameter. After the extraction process, the solvent mix with SCG oil will be separated from SCG via gravitational filtration using filter paper. The sample will be evaporated at 60°C using a rotary evaporator. Then, yield of oil is calculated from Equation 3.

$$\text{Oil yield percentage} = \frac{\text{mass of flask after exaporation} - \text{mass of empty flask}}{\text{mass of dried SCG}} \times 100\% \text{ ------ (3)}$$

3.4 Biodiesel production

20g of SCG oil is measured and placed into a reactor. The molar mass of SCG oil is known to be 862.8 $gmol^{-1}$ (Rocha et al., 2014). Previous studies have found methanol to be more suitable for transesterification of coffee oil due to ease of phase separation when compared to ethanol (Oliveira et al., 2008). Methanol and oil molar ratio was calculated and added with measured catalyst weight into a beaker for mixing. Methanol and KOH catalyst were heated and stirred until catalyst is fully dissolved before being poured into reactor. Ultrasonic probe is immersed into sample such that tip is entirely submerged within the solvent mixture. The ultrasonic waves were set at 5 seconds ultra-sonication with 2 seconds intervals. The parameters which will be optimized include molar ratio of methanol to SCG oil (10, 20, 30, 40, 50, 60), catalyst concentration (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 wt%), ultrasonic period (0.5, 1, 15, 2, 2.5, 3, 3.5, 4, 4. 5, 5 hours), ultrasonic amplitude (20, 25, 30, 35, 40%) to achieve maximum FAME content. Similar to ultrasonic extraction, temperature is disregarded as an optimization parameter due to the continuous cavitation cycle. After transesterification, the mixture is allowed to settle before separated. The bottom layer (glycerol layer) will be removed before washing is conducted on the top layer. Washing is done with warm water (60 °C) several times until no impurities can be seen in the water. The biodiesel will then be placed in a rotary evaporator to remove any remaining moisture. The top layer, which is the biodiesel layer, will be tested for FAME content. FAME content was tested using the Agilent 7890A Gas Chromatography. **Figure 3.2** shows the phase separation after transesterification.

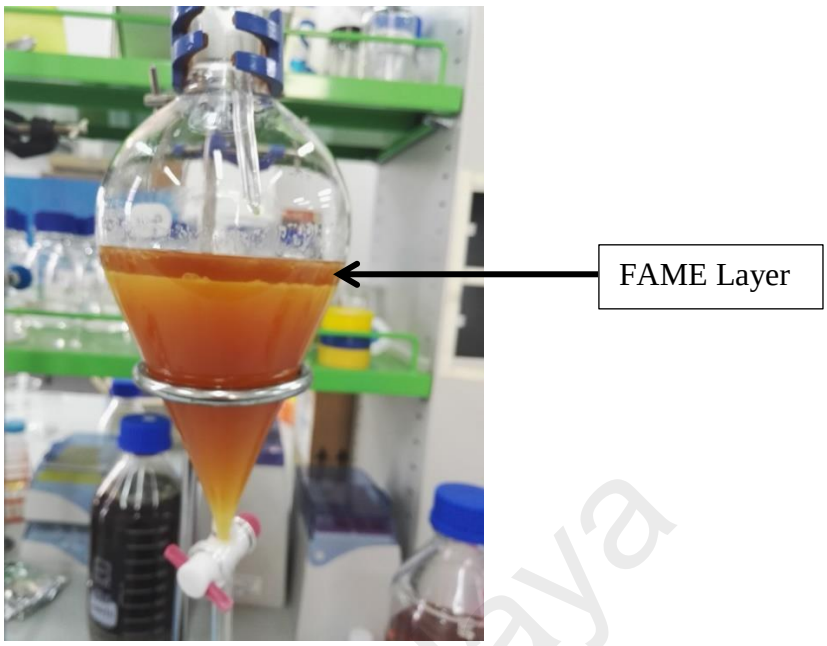


Figure 3.2: Phase separation after transesterification

3.4.1 Ultrasonic probe

The ultrasonic probe or horn used in this thesis is the Q500-20 ultrasonic probe equipped with 1 inch diameter tip with a 500 W power rating and up to 20 kHz frequency. The sample will be placed into the reactor, where the tip of the probe will be fully immersed in the solvent and sample mixture. The probe will be in the centre of the reactor to ensure even ultrasonication to the entire sample. One important precaution is to ensure that the probe tip is fully immersed to ensure direct sonication to the sample. The probe is also cleaned by wiping with washing methanol followed by sonication in distilled water for 5 minutes. **Figure 3.3** shows the schematic of the ultrasonic assisted setup.

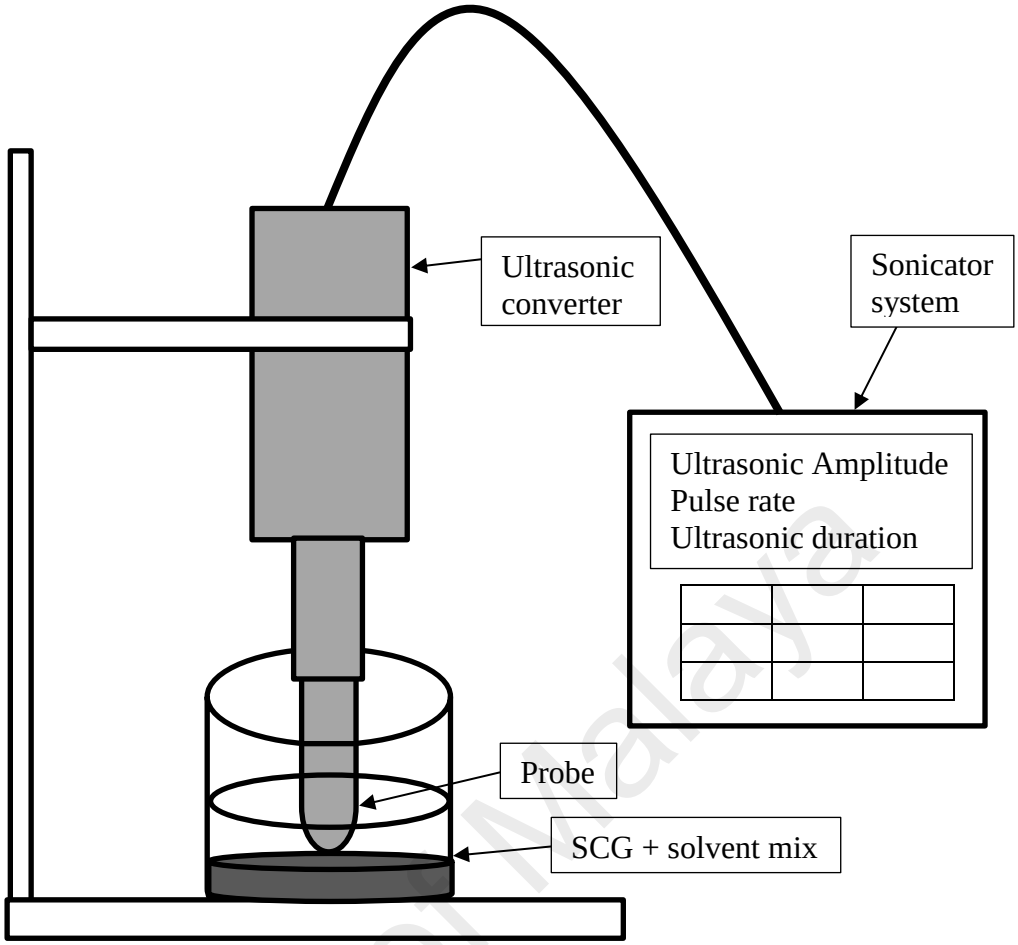


Figure 3.3: Schematic of ultrasonic assisted setup

The ultrasonication time, amplitude and frequency of ultrasonic waves can be changed using the sonicator system. However, the system should be set at a moderate level to avoid energy wastage, deteriorating the sample and risk of breaking the equipment. The ultrasonication can also also be set for continuous or pulsed modes. However, to increase the efficiency of the system, a pulsed mode is selected.

3.5 Gas chromatography analysis

Gas chromatograph fitted with a flame ionization detector was used to determine the FAME content and linolenic acid methyl ester content of the biodiesel according to the EN 14103:2011 standard test method. Carbon chains (C8-C24) present in the FAME layer were also determined using Agilent 7890A Gas Chromatography. The characterization of FAME was conducted using EN141023:2011 standard with methyl nonadecanoate as the

internal standard. This method is suitable for use with the gas chromatograph equipped with HP-INNOWax high-polarity column (length × inner diameter × film thickness: 30 m × 0.25 mm × 0.25 μm, stationary phase: polyethylene glycol). The oven temperature protocol was 60 °C held for 2 minutes, heated to 200°C at 10 °C/min and then to 240 °C at 5 °C/min. The temperature was then held at 240 °C for 7 minutes. Helium gas was used as the carrier gas. Flow rate for helium 1.5 ml/min. FAME yield was obtained by comparing area of methyl ester peaks with peaks of internal standard using the Equation 3.

$$E = \frac{(\sum A) - A_{El}}{A_{El}} \times \frac{W_{El}}{m} \times 100\% \text{ ------ (3)}$$

Where E represents the FAME content (%), $\sum A$ the sum of area of C8:0 to C24:0 peaks, A_{El} the peak area of internal standards, W_{El} the weight (mg) of methyl nonadecanoate while m is the weight (mg) of the sample.

3.6 Fourier transform infrared (FTIR)

All organic compounds absorb light in the visible and ultraviolet region, making it possible to analyze the various aromatic compounds within the fuel (Atabani et al., 2019). Structural information of the oil can be determined using Perkin-Elmer Spectrum 400 FTIR spectrometer. FTIR can be performed to identify the dominant chemical bonds and functional groups such as oxygen containing groups, carbonyl, hydroxyl and carboxylic groups. Strong absorbing peaks are determined with their wavelength corresponding to the functional groups present within the sample. In addition to the wavelength position of the peak, peak shape and intensity are also unique to each bond. These data will then be correlated to previous works to determine functional groups present within the sample. The difference in both oil and biodiesel peaks can also show that the transesterification reaction was successfully completed.

3.7 Physiochemical property analysis

The SCG biodiesel physiochemical properties were determined via methods described in the standards EN 14214 and ASTM D6751. The methods and equipment used are described in **Table 3.2**.

Table 3.2: Biodiesel physiochemical property testing methods and equipment

Properties	Equipment	Test method
Acid value	Manual titration	ASTM D664
Viscosity @ 40 °C	Anton Paar viscometer SVM 3000	ASTM D445
Density @ 15 °C	Anton Paar viscometer SVM 3000	ASTM D127
Calorific value	Paar 6100 bomb calorimeter	ASTM D240
Oxidation stability	Metrohm 873 biodiesel rancimat	EN 14112
Copper strip corrosion	Copper corrosion bath	EN ISO 2164

Biodiesels which are produced via single step base catalysed processes can only be done on oils with low acid values to avoid saponification (Wang et al., 2017). The acid value of the SCG oil and biodiesel was measured using the titration process. A standard solution of 0.1 M KOH was prepared as titrant. 5g of sample was accurately weighed before mixed with 25 mL of 2-propanol in a conical flask. The mixture was allowed to mix and heated before 10 drops of a selected indicator was added in. Phenolphthalein was used as indicator in this titration. The sample is assumed to be neutralized when the colour of the mixture changed to pink and lasted for 30 seconds. The acid value of the SCG oil should be less than 4mg KOH for direct base catalysed transesterification. After transesterification, the acid value of the biodiesel should be less than 0.5 mg KOH as stated in both EN 14214 and ASTM D6751 standards. The acid value is calculated using Equation 4.

$$\text{Acid Value} = \frac{(A-B)\times M \times Molecular\ weight\ of\ KOH}{m} \quad \text{------ (4)}$$

Where

A = Volume of KOH solution used in the titration of the sample (mL)

B = Volume of KOH solution used in the titration of the blank (mL)

M = Molarity of KOH solution (mol/L)

M = mass of sample (g)

Biodiesels tend to have high viscosities which result in larger droplet sizes, more complication combustion and poor fuel atomisation (Aminian & ZareNezhad, 2018). Viscosity is tested using the Anton Paar SVM 3000 viscometer. The apparatus is also capable of measuring the density of the oil. Before testing, ensure that the temperature is set at 40°C, as set by the ASTM D445 for viscosity testing. The system was cleansed using toluene before the sample was injected into the equipment for testing. An outer cylinder (tube) is driven by a motor at a constant speed and is filled with the sample. A low-density inner cylinder (rotor) is held in the centre of the higher-density sample by buoyancy forces. Consequently, a measuring gap is formed between the tube and the rotor. The rotor is forced to rotate by shear stress in the liquid and is guided axially by a magnet and a soft iron ring. A permanent magnet in the inner cylinder induces eddy currents in the surrounding copper casing. The sample's shear forces drive the rotor while magnetic effects retard its rotation. Shortly after the start of the measurement, the rotor reaches a stable speed. This is determined by the equilibrium between the effect of the eddy current brake and the shear forces at work in the sample. The measurements of rotor speed can calculate the viscosity and density simultaneously. After first results were out, the tests were repeated twice using the same sample to verify the accuracy of the results. While viscosity was tested at 40°C, the density was tested at 15°C.

The calorific value or heating value shows the biodiesel heat of combustion, and are usually lower than diesel fuels due to the higher oxygen content (Giakoumis & Sarakatsanis, 2018). Calorific value of the SCG oil is tested using Paar 6100 bomb calorimeter. The system ignites a thread which combusts the biodiesel sample, where the system will measure total energy produced per unit mass of sample. The sample was weighed in metal cap before being placed in the bomb. The bomb was then filled with O_2 gas before being placed into the chamber. Once full ignition was completed, the equipment will generate the mass energy content.

Biodiesels tend to oxidise over time due to several factors such as sunlight and microbial contamination which result in changes to the chemical composition of the fuel (Liu et al., 2019). The oil and biodiesel oxidation stability will be tested using Metrohm 873 Biodiesel Rancimat equipment at 110°C to determine their minimum induction period. The oxidative stability test measures the rate at which biodiesel fuel decomposes when subjected to heightened temperatures and intense aeration. These conditions accelerate the oxidation of biodiesel and allow for a rapid measure of fuel stability which can correlate to the slower oxidative process under normal storage conditions. During oxidation stability test, 7.5 g of biodiesel was heated to 110°C by a heating block with an air flow of 10 L/h passing through the biodiesel. When biodiesel was exposed to air, acids began to form, which were transferred to a measuring vessel containing 60 mL of distilled water and fitted with an electrode for measuring the conductivity. In the measuring vessel, the change in the conductivity of distilled water caused by the formation of volatile short-chain carboxylic acids (mainly formic and acetic) in the biodiesel was recorded by a computer continuously. Once the acid concentration in the water was high enough, the conductivity underwent a rapid increase that was called an induction period.

The level of corrosion of biodiesel is tested via the copper strip corrosion test method. Copper is chosen as the selected metal as it is used in various engine parts such as the fuel

tank gasket, washer and bushing (Rocabruno-Valdés et al., 2019). The copper strip will be immersed in our sample and placed in a container. The container will then be immersed in 50 °C warm water for three hours. After the immersion period, the strip will then be wiped gently and compared with the ASTM standard strip to determine corrosion intensity. **Figure 3.4** shows the copper strip corrosion ASTM standard.

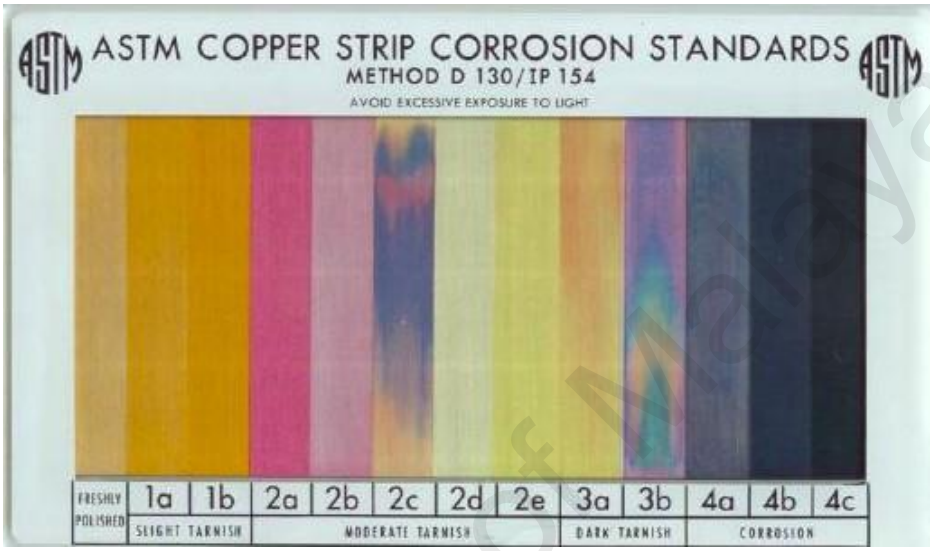


Figure 3.4: Copper strip corrosion ASTM standard.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This section of the work discusses the results obtained from the study and the feasibility of using SCG as a biodiesel feedstock. Initially, conventional Soxhlet extraction with different solvents is tested to be used as a comparison. This is followed by testing of parameters for ultrasonic extraction. An infrared absorption spectrum of the SCG oil will be tested to determine if the functional groups of oil is present. Once the best parameters were determined, the properties of the oil were measured to determine if a two-step transesterification process is required. The FAME yield was used as the selected measurement for biodiesel production as this can be seen as the effectiveness of the conversion of triglycerides in the oil into FAME (Ong et al., 2019). An infrared absorption spectrum of the SCG biodiesel will also be tested to check for the biodiesel functional groups. Once the conditions for the highest FAME yield was obtained, the properties of the produced biodiesel will be tested and compared with the ASTM D6751 and EN 14214 standards.

4.2 Comparison of oil extraction by different solvents

After preparing the Soxhlet extraction setup as stated earlier, the solvent to SCG ratio was found to be 12.5 mL: 1 g. The different oil yield by each solvent is also shown in **Table 4.1**.

Table 4.1: Oil yields of SCG using various solvents under Soxhlet extraction

Solvent Used	Oil yield (%)	Extraction Time (hours)
Hexane	12.5 ± 0.3	3
Chloroform	12.3 ± 0.8	7
Methanol	11.9 ± 0.2	12

Results showed that the highest yield was 12.5% (2.5 g Oil/20 g SCG) using hexane for 3 hours. Chloroform required longer timing (7 hours) to achieve similar oil yields whereas oil extraction using methanol resulted in a more viscous extraction product. The viscous product may be the result of contaminants being extracted together with the oil components. The superior performance of hexane solvent for oil extraction was also reported by Reshad (Reshad et al., 2015) on the oil extraction from rubber seed. (Al-Hamamre et al., 2012) also obtained a higher oil yield (15.3%) when using the Soxhlet technique and hexane solvent. Although the oil yield is higher than that reported in this study, this may be due to source in which the SCG was obtained. Methanol may have extracted other non-oil components due to its polarity as suggested by Perrier (Perrier et al., 2017). Methanol would not be a suitable extraction solvent as a key requirement for oil release is that there is no significant contamination by other cellular components (Araujo et al., 2013). From results in the Table 2, this may suggest that SCG contains lesser polar oils, which explains the lower extractability of methanol compared to hexane. Due to the alcohol's low selectivity towards triglycerides, the extraction is expected to involve other compounds such as phosphatides, polyphenols, pigments and soluble sugars (Baümler et al., 2016). An ethanol and chloroform solvent mix was found to produce the highest oil yield for microalgae Chlorella sp. (Ramluckan et al., 2014). This suggests that selection of solvent for oil extraction is also dependent on feedstock used. Effective oil extraction requires total solvent penetration into oil storage and matching polarity of the targeted compounds (Adeoti & Hawboldt, 2014).

4.3 Ultrasonic oil extraction parameters

Oil extraction was also conducted using ultrasonic assistance. Ultrasonic assistance is known to reduce extraction period and solvent use while producing higher extraction

yields than conventional techniques (Palconite et al., 2018). The extraction conditions which were optimized included type of solvent, solvent to mass ratio, extraction time and ultrasonic amplitude. Initially, the extraction was conducted at 20% amplitude for 30 minutes at alternating solvent to mass ratios for each solvent.

4.3.1 Comparison of solvent

The organic solvents extract oil by rupturing cell walls and disrupting the interaction forces between oil and tissue matrix (Adeoti & Hawboldt, 2014). The driving force of the oil extraction process is the concentration gradient between solvent and oil compound, where a higher volume of solvent will increase the concentration gradient and stimulate mass transfer (Mueanmas et al., 2019). Proper solvent usage will significantly reduce the required extraction time and avoid wastage. **Figure 4.1** shows the comparison of extracted oil against solvent to SCG ratio for all three solvents.

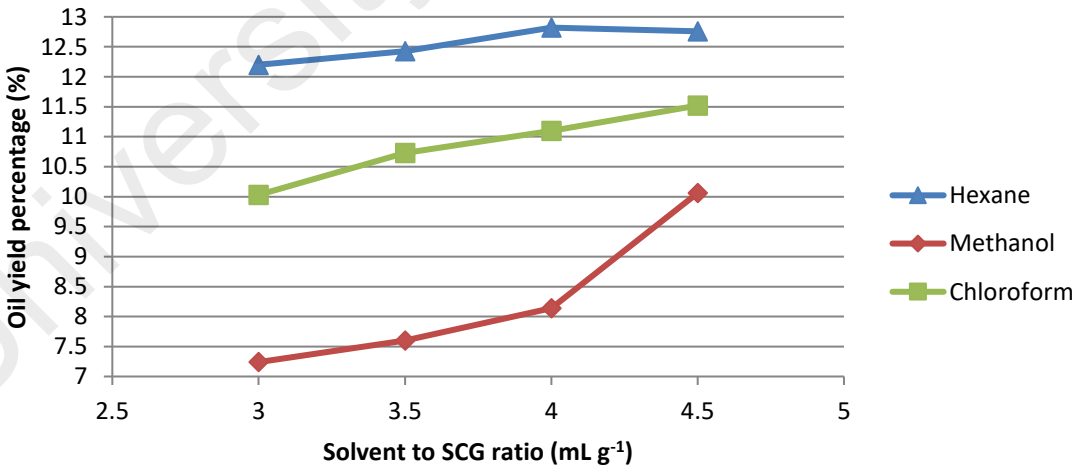


Figure 4.1: Ultrasonic oil extraction using various solvents and solvent to SCG ratio

Similar to the Soxhlet extraction results, hexane showed the highest extractability compared to chloroform and methanol. At solvent to SCG ratio (4.0 mL g^{-1}), hexane showed highest extraction yield of 12.82%. Both chloroform and methanol still showed

increasing extraction yields at solvent to SCG ratio (4.0 mL g^{-1}), which suggests that more solvent is required for maximum oil extraction efficiency. The ultrasonic extraction using hexane was significantly lower than the amount of solvent required for Soxhlet extraction, which was conducted at a ratio 12.5:1.

The shear forces generated by the ultrasound near the oil glands of SCG induce its rupture and results in erosion, microfractures and cell wall breakdown which induces larger area of contact between solvent and materials and intensified oil extraction (Hashemi et al., 2018; Tavares et al., 2017). However, Cheng et al. (W.-Y. Cheng et al., 2016) reported that Soxhlet oil extraction gave a higher yield compared to ultrasonic-assisted and explained heat treatment was more suitable for oil extraction from kenaf seeds. Given that ultrasonic oil extraction from SCG yielded higher yields than conventional Soxhlet extraction at lower solvent usage and shorter extraction time, it can be said that ultrasonic extraction is a more suitable mode of oil extraction from SCG. The remaining tests were conducted using hexane as the selected solvent as it showed the best performance among all three solvents.

4.3.2 Ultrasonic amplitude

With an increase in ultrasonic amplitude, bubble collapse becomes more violent which leads to greater extraction yields. However, if the ultrasonic amplitude is too high, it leads to energy wastage. The trend of oil extracted against ultrasonic amplitude is shown in **Figure 4.2**.

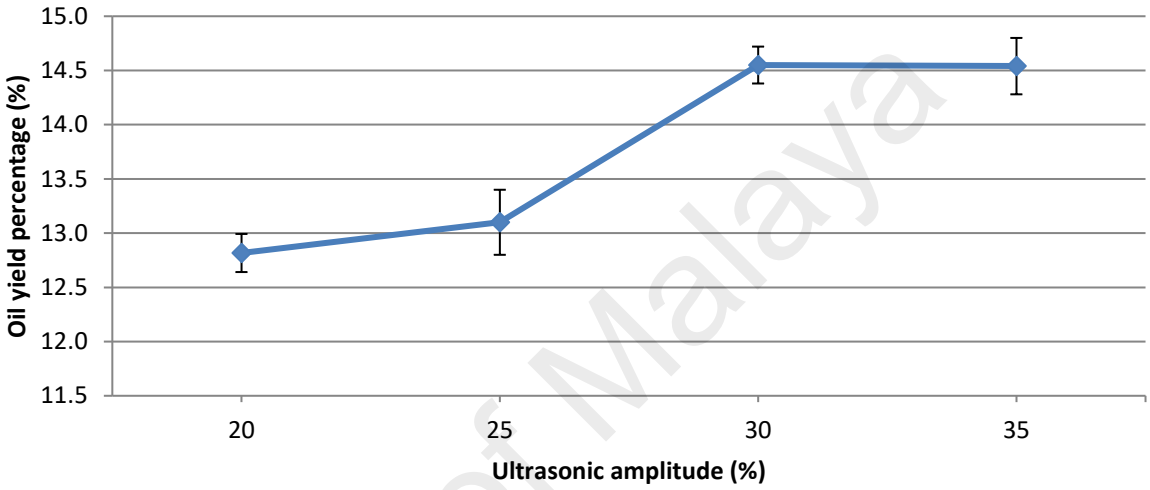


Figure 4.2: Oil extracted using ultrasonic assistance against ultrasonic amplitude

It was noticed that between amplitudes of 25% to 30%, there was a significant increase in oil extraction using hexane. This increase is expected as increased ultrasonic power can enhance the molecular diffusion of oil particles into the hexane phase, increasing the amount of oil exudation from SCG. The extraction yield remained constant after this amplitude. The optimum conditions found that oil extracted from SCG can be up to 14.55% using ultrasonic assistance, which is significantly higher than using Soxhlet extraction methods.

Sicaire et al. (Sicaire et al., 2016) found that solvent to solid ratio and ultrasonic intensity were the main influences of oil extraction from rapeseed. Similar to previous studies, it was found that there was a slight decrease in extraction yield when ultrasonic power exceeded optimum values (>30%). Liu et al. (P. Liu et al., 2017) found that oil

extraction yield would decrease after a certain ultrasonic power threshold due to intense heating which causes decomposition and volatility of the oil.

4.3.3 Extraction period

Optimum period during extraction avoids excessive use of power and reduces the risk of destruction of oil. **Figure 4.3** shows the trend of oil extracted against extraction period.

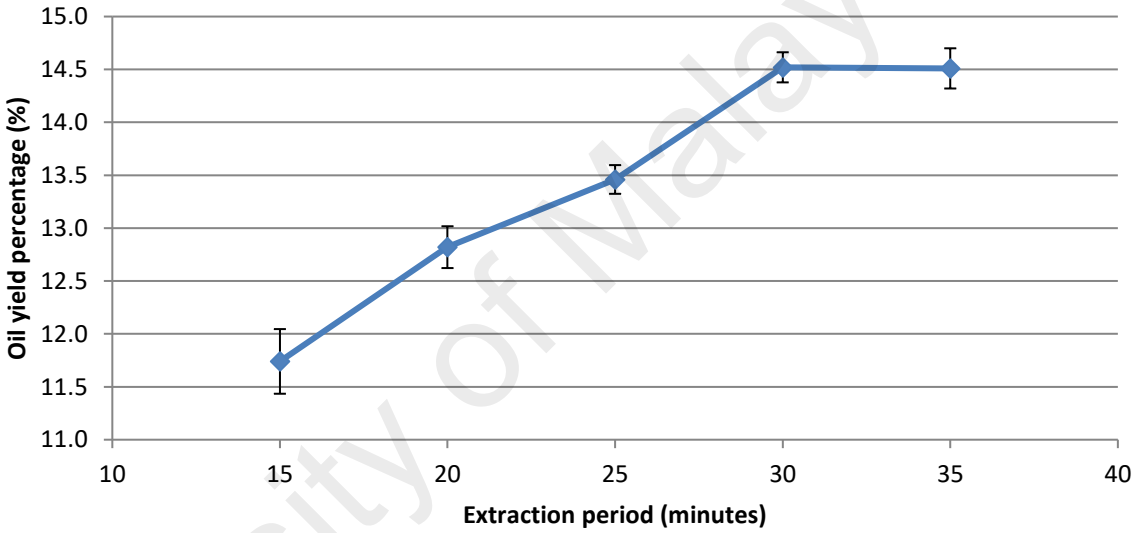


Figure 4.3: Oil extracted using ultrasonic assistance against extraction period

A sufficient extraction time is required to break cell walls, extract the lipids and achieve an equilibrium (Son et al., 2018). From the results, the optimum period for SCG ultrasonic oil extraction using hexane is 30 minutes, significantly lower than the 3 hours required by Soxhlet extraction for the same solvent. This is significant as the oil is not subjected to intense heating for long periods, reducing the risk of degradation. High extraction rates require longer extraction period, but extended periods of extraction increase energy consumption and risk the degradation of target compounds (X. Chen et al., 2014).

The optimum extraction period for ultrasonic oil extraction from SCG was 30 minutes, similar to that found by Zhang et al. (Z.-S. Zhang et al., 2008) for flaxseed oil. The initial rapid rate of oil extraction can be explained by the penetration of solvent into cellular structure, followed by a slower extraction rate due to external diffusion of oil constituents through the porous residual solids (Goula, 2013). A significant amount of solvent would also be lost due to evaporation and reduce the extraction efficiency. As the SCG cell walls rupture, impurities would suspend within the extract, reducing the solvent's permeability into cell structures (Tian et al., 2013). Additionally, the unnecessary extended periods of ultrasonication cause target components (SCG oil) to re-adsorb into ruptured tissue particles due to the larger specific surface area (J. Dong et al., 2010).

4.4 Physiochemical properties of oil

The acid value was tested to determine whether pre-treatment is required prior to transesterification. The cavitation effect generated within the SCG and solvent mix produces a harsh environment with high temperature and pressure which accelerates the oxidation of SCG oil and increase acid value to a certain degree (L. Zhang et al., 2017). The acid value of ultrasonic extracted SCG oil was measured to be 4.00 mg KOH g^{-1}, which was lesser than 2% of the free fatty acid content. Although this acid value may be considered high for a base catalysed transesterification, an acid catalysed esterification reaction yielded a solid sludge which could not be washed. On the other hand, when subjected to a base catalysed transesterification reaction, there was a clear separation of glycerol and biodiesel phase, suggesting that the base catalysed reaction is applicable. Therefore, the SCG oil was then subjected to base catalysed transesterification for further testing. The crude SCG oil was observed to have a dark brown colour, highly viscous and

had a sweet aroma. The viscosity of the oil was determined to be quite high at 46.8 ± 0.2 mm^2/s which may cause poor fuel atomization and low volatility, and in turn lead to incomplete combustion and severe engine deposits (Kanaveli et al., 2017). Density of the SCG oil was measured to be 919.6 kg/m^3. The SCG oil calorific value was 40.04 ± 0.2 MJ/kg, exceeding other biodiesel feedstocks such as waste cooking oil (Madheshiya & Vedrtnam, 2018), cotton seed oil (Shankar et al., 2017) and rice bran oil (Mazaheri et al., 2018). The high calorific value may be due to the high carbon to oxygen ratios (Kelkar et al., 2015). It was found that the induction time for conventionally extracted oil was 23 hours, whereas the ultrasonic extracted oil had an induction time of 7 hours.

4.5 Biodiesel production parameters

4.5.1 Molar ratio of methanol to SCG oil

Excess alcohol is required to enhance alcoholysis and ensure complete conversion of oils into esters (Tan et al., 2019). **Figure 4.4** shows the FAME yield at varying methanol to SCG oil molar ratios (10-60).

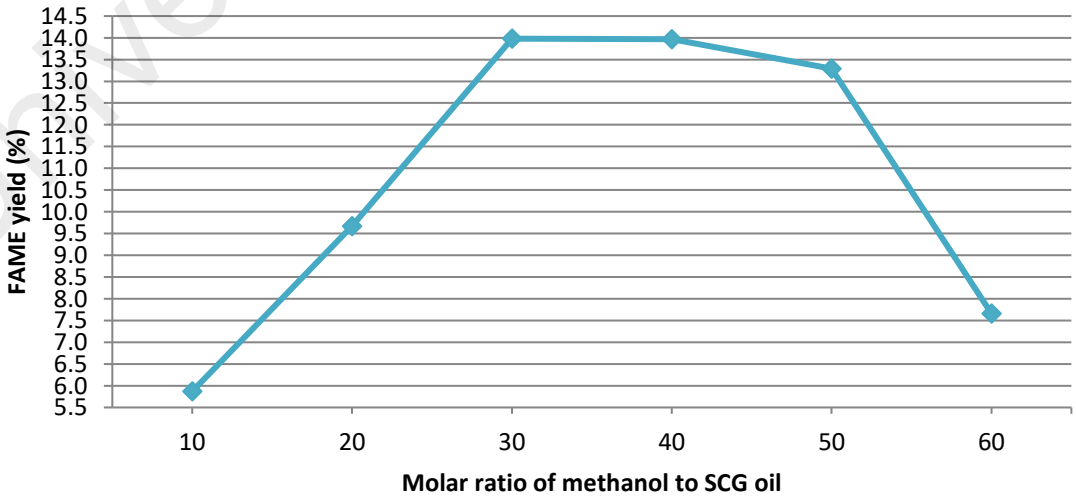


Figure 4.4: FAME yield against molar ratio of methanol to SCG oil

It can be seen that lower molar ratios have poorer FAME conversion rates. The FAME yield peaks at 13.98% when molar ratio of methanol to SCG oil was at 30. This is considerably high when compared to other feedstocks such as soybean oil, castor oil and waste cooking oil which generally use 6:1 as the optimised molar ratio in the ultrasonic transesterification process (Ho et al., 2016). However, the volume of methanol used for molar ratio 30 is calculated to be 1.4ml g^{-1} of SCG oil, much lower than that optimised in the in-situ transesterification of SCG (8.33ml g^{-1}) (Park et al., 2016).

The stoichiometric molar ratio of methanol to oil for transesterification, a reversible reaction, should be 3:1 (Tan et al., 2019). In reality, excess methanol is required to push the equilibrium towards formation of methyl esters (Dhawane et al., 2018). This forward reaction push would also ensure that majority of the methanol and catalyst is utilised in the reaction. The mass transfer between phases directly influence the beginning rate of reaction, because the methanol has low miscibility with oils and low Reynolds number due to the poor agitation during the initial stages (Pisarello et al., 2018). Thus, higher molar ratios enhance the miscibility and increase the surface contact area between alcohol molecule and FFA (Mueanmas et al., 2019). An increase in methanol concentration will contribute to an increase in FAME yield due to the triglycerides and intermediates instantly being converted to esters in the presence of excess methanol (Badday et al., 2012). Beyond the optimum ratio, excess methanol inhibits the interaction between oil and methanol (Thiruvenkadam et al., 2019). This results in poorer conversion yields of FAME. The polar hydroxyl group in methanol also aids the recombination of glycerol and esters (Verma & Sharma, 2016).

4.5.2 Ultrasonic amplitude

Optimisation of ultrasonic amplitude will reduce the total energy required for oil extraction. **Figure 4.5** depicts the FAME yield of SCG biodiesel at different ultrasonic amplitudes.

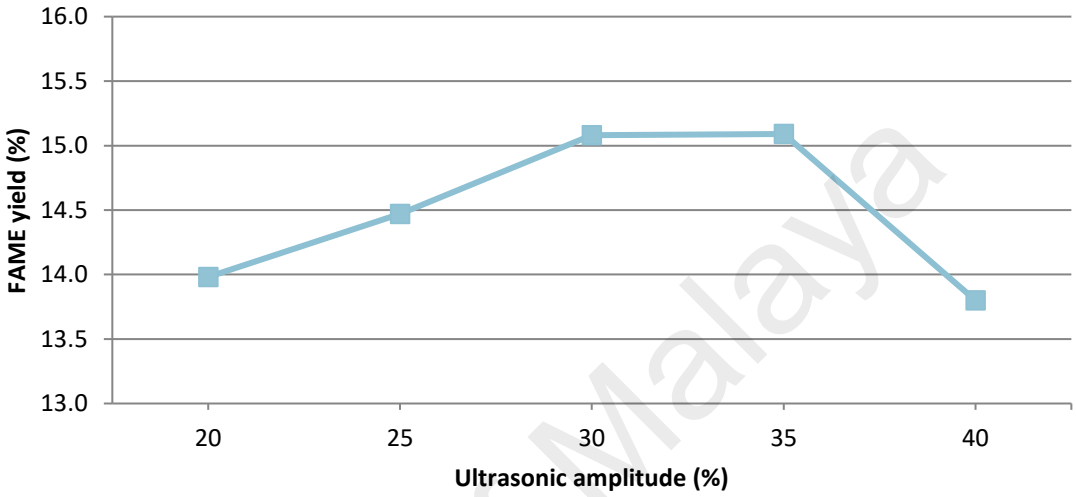


Figure 4.5: FAME yield against ultrasonic amplitude

It can be seen that the rate of change of FAME yield is low (<2%) when compared to other parameters. However, there was a clear increase in FAME yield as ultrasonic amplitude increase until the peak (30%) before a sharp drop off beyond that amplitude. This can be due to the enhanced ultrasonic power which generates a greater number of cavitation bubbles that could act as a barrier against energy transfer throughout the liquid (G. Chen et al., 2014). Despite the 30% and 35% amplitude contributing to similar FAME yields, the 30% amplitude is chosen as the optimum amplitude due to milder reaction conditions allowing better process economy (Badday et al., 2012).

High amplitude ultrasonic reactions will allow lower catalyst usage, shorter reaction time and better product yield by dissipating more energy into the system that enhances the rate of mass transfer due to asymmetric cavity collapse (Badday et al., 2012). A system utilising more energy efficient technologies can also significantly reduce the

production costs. This improved mass transfer rate also allows better mixing of oils and alcohol, which in turn increase the FAME yields. However, it should be noted that excessively high amplitudes will lead to rapid deterioration of probe, resulting in liquid agitation instead of cavitation and poor transmission of ultrasound through the medium (Chemat et al., 2017). Rocha et al. (Rocha et al., 2014) obtained lower oil yields from SCG when conducted in ultrasonic bath, which suggests that direct ultrasonication using an ultrasonic probe is more efficient.

4.5.3 Ultrasonic period

Similar to extraction period, optimisation of transesterification period is important to reduce excessive power usage. The FAME yield against ultrasonic period is presented in **Figure 4.6**.

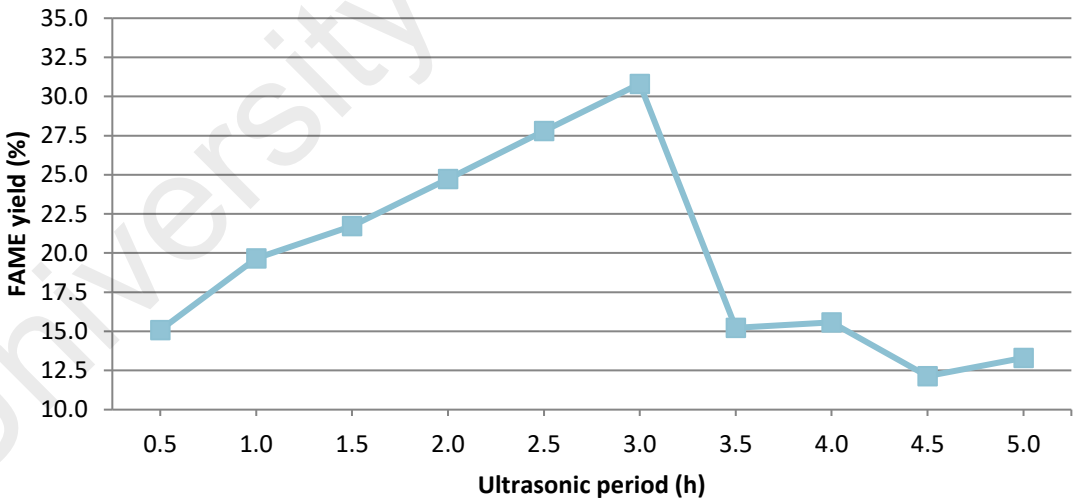


Figure 4.6: FAME yield against ultrasonic period

A steady increase in FAME yield can be seen as the period increased until the 3 hour mark. After 3 hours, the FAME yield sharply decreased. Ultrasonic assistance is known to be able to shorten reaction time for biodiesel conversion. The 3 hours required using

ultrasonic assistance is a direct improvement from conventional solvent transesterification of SCG which required 12 hours for optimum conversion (P. Liu et al., 2017).

Since the transesterification reaction is kinetically controlled, it is often affected by temperature and time. Temperature changes during long sonication periods have been known to destroy the oil (Bahmani et al., 2018). It is also difficult to maintain the temperature throughout the ultrasonication process due to the constant compression and rarefactions, resulting in a temperature which will constantly fluctuate. By controlling the reaction period, the total amount of energy introduced into the system can be easily quantified. Furthermore, given the large heat capacities of certain oils, the effect temperature has during the transesterification reaction is small when compared to the time (Lee et al., 2011). Extended reaction times would decrease FAME yields due to degradation and polymerization of oil products (Thiruvenkadam et al., 2019).

4.5.4 Catalyst concentration

Since the purpose of a catalyst is to enhance reaction rate by reducing activation energy, increased amounts of catalyst is likely to push the reaction at a faster rate (Mardhiah et al., 2017). **Figure 4.7** presents the FAME yield against catalyst concentration.

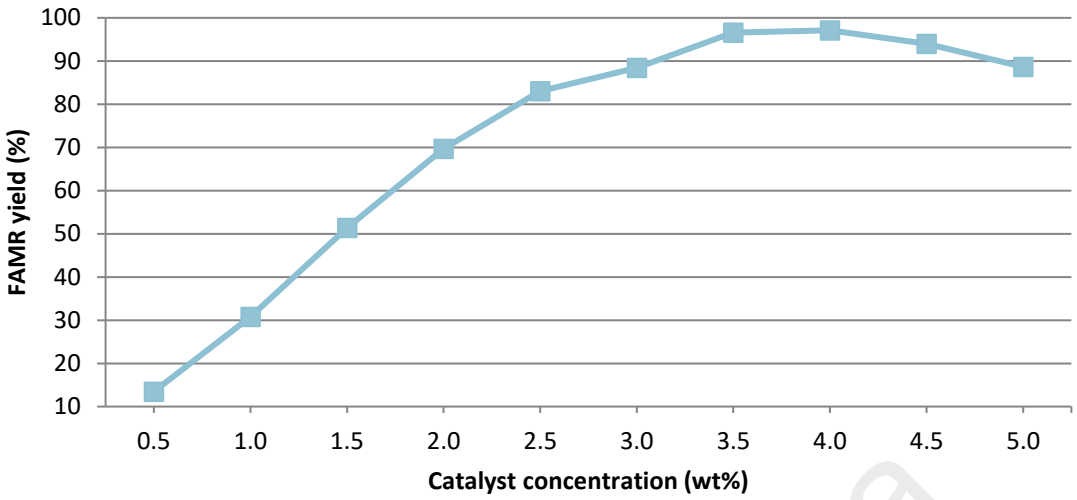


Figure 4.7: FAME yield against catalyst concentration

This parameter shows the highest change in terms of FAME yield when compared to other parameters. The FAME yield achieves a maximum of 97.11% at the 4 wt% catalyst concentration. Excessive use of catalyst showed a decreasing trend due to the emulsions formed which made biodiesel recovery difficult (Verma & Sharma, 2016). Application of base catalyst is said to be able to provide a faster reaction rate when compared to acid catalyst (Atadashi et al., 2013). This can be seen from the time taken for biodiesel conversion in this study compared to the acidic catalyst utilised by Liu et al. (Y. Liu et al., 2017). However, the amount of catalyst used in transesterification of SCG oil is higher than the commercial biodiesel preparation amount (1%) (Baskar & Aiswarya, 2016).

Catalyst concentration has been found to be the most significant factor in biodiesel production as an increase in catalyst loading results in increase in methoxide, which is the complex between methanol and catalyst (Badday et al., 2012). This can explain the biggest deviation in terms of FAME yield when compared with other parameters. Besides that, the significantly lower FAME yields during the previous parameter testing can also be explained by the lack of catalyst available to push the forward reaction. However,

excessive catalyst loading is known to cause emulsification, which increases viscosity and makes the separation process more difficult (Verma & Sharma, 2016).

4.6 Biodiesel properties

After obtaining the best parameters for highest FAME yield, the biodiesel was then subjected to FAME profiling, FTIR analysis and various physiochemical property testing. The FAME profiling can determine the prominent esters present within the biodiesel, while FTIR analysis can show the various functional groups present within our SCG oil and biodiesel. Finally, the properties testing will be conducted and compared with ASTM D 6751 and EN 14214 standards.

4.6.1 Biodiesel fatty acid methyl ester profile

The fatty acid composition was determined via gas chromatography as described in the methodology. SCG biodiesel is known to have similar fatty acid compositions to corn and soybean biodiesel (Efthymiopoulos et al., 2019). The fatty acid methyl ester profile for the optimized biodiesel is reported in Table 3.

Name of Fatty Acid Methyl Ester	Formula	Area	Percentages (%)
Methyl Hexanoate	$C_5H_{11}COOCH_3$	-	-
Methyl Octanoate	$C_7H_{15}COOCH_3$	-	-
Methyl Decanoate	$C_9H_{19}COOCH_3$	-	-
Methyl Laurate	$C_{11}H_{23}COOCH_3$	-	-
Methyl Tetradecanoate	$C_{13}H_{27}COOCH_3$	-	-
Methyl Palmitate	$C_{15}H_{31}COOCH_3$	1286.3	32.8
Methyl Palmitoleate	$C_{15}H_{29}COOCH_3$	-	-
Methyl heptadecanoate	$C_{16}H_{33}COOCH_3$	-	-
Methyl Octadecanoate (stearic acid)	$C_{17}H_{35}COOCH_3$	277.7	7.1
Methyl cis - 9 - octadecenoate (methyl oleate;cis - 9-oleic methyl ester	$C_{17}H_{33}COOCH_3$	359.8	9.2
Methyl Linoleate	$C_{17}H_{31}COOCH_3$	1731.1	44.1
Methyl Linolenate	$C_{17}H_{29}COOCH_3$	99.7	2.5
Methyl Arachidate (Eicosanoic acid)	$C_{19}H_{39}COOCH_3$	55.5	1.4
Eicosenoic methyl ester	$C_{19}H_{37}COOCH_3$	-	-
Methyl Docosanoate	$C_{21}H_{43}COOCH_3$	-	-
Methyl Erucate	$C_{21}H_{41}COOCH_3$	-	-
Methyl Lignocerate	$C_{23}H_{47}COOCH_3$	-	-
Total		3810.1	97.1

The methyl esters formed are also dependent on fatty acids available within SCG oil. There are two main fatty acid methyl esters found, namely methyl linoleate (44.1%) and methyl palmitate (32.8%). This is expected as the two main fatty acids found in roasted coffee oil are palmitic acid (46.1%) and linoleic acid (32.9%) (Hurtado-Benavides et al., 2016). Linoleic acid is a polyunsaturated fatty acid and stimulates the formation of odor compounds but is susceptible to breakdown of double bonds and oxidation (N. Kumar, 2017). On the other hand, palmitic acid is a saturated fatty acid which promotes oxidation stability (Hurtado-Benavides et al., 2016).

The remaining methyl esters found in SCG biodiesel are a mixture of saturated methyl cis-9-octadecenoate (9.2%), methyl octadecanoate (7.1%), methyl arachidate (1.4%) and unsaturated methyl linolenate (2.5%). The higher content of saturated methyl esters also explains the high oxidation stability of SCG biodiesel since the rate of oxidation of saturated methyl esters are much slower than unsaturated ones (Tomić et al., 2019).

4.6.2 Comparison between FTIR of SCG oil and SCG biodiesel

Infrared absorption spectrum of SCG oil can be seen in **Figure 4.8**. Peaks between 722 cm^{-1} and 1466 cm^{-1} are associated to various CH groups. There is bending of cis C=C observed at peak 722 cm^{-1}, vibration of –C-O ester groups which corresponds to the large area at peak 1158 cm^{-1} and –C-H bending of methylene (CH_2) at the 1466 cm^{-1} (Sodeifian et al., 2018). The sharp peak at 1746 cm^{-1} corresponds to stretching of carbonyl group C=O (1700-1800cm^{-1}) (Sander et al., 2018). The two intense bands at 2852 cm^{-1} and 2924 cm^{-1} are due to CH_2 asymmetric and symmetric stretching vibrations (Purandaradas et al., 2018). The peaks at 1158 cm^{-1} and 1746 cm^{-1} signify important functional groups that are found in other biodiesel feedstocks which proves that SCG oil is suitable for biodiesel conversion.

The infrared spectrum of SCG biodiesel, shown in **Figure 4.9**, has similar peaks to that of SCG oil with slight differences noticed in the 1000-2000 cm^{-1} wavelength range. These differences distinguish the presence of methyl ester from crude oils. The large area peak at 1175 cm^{-1} corresponds to –C-O ester group (Sodeifian et al., 2018). Another notable difference is the two absorption peaks at 1438 cm^{-1} and 1463 cm^{-1} which specifies the $–CH_2$- scissors vibration (Kuepethkaew et al., 2017). The peak at 1740cm^{-1} is also more intense than the peak obtained from SCG oil (1746 cm^{-1}) and can be attributed to strong stretching of CO double bonds (Milano et al., 2018). The presence of these additional peaks in the infrared spectrum of the SCG biodiesel signify that the transesterification reaction has occurred, producing the functional groups that are coherent with these wavelengths.

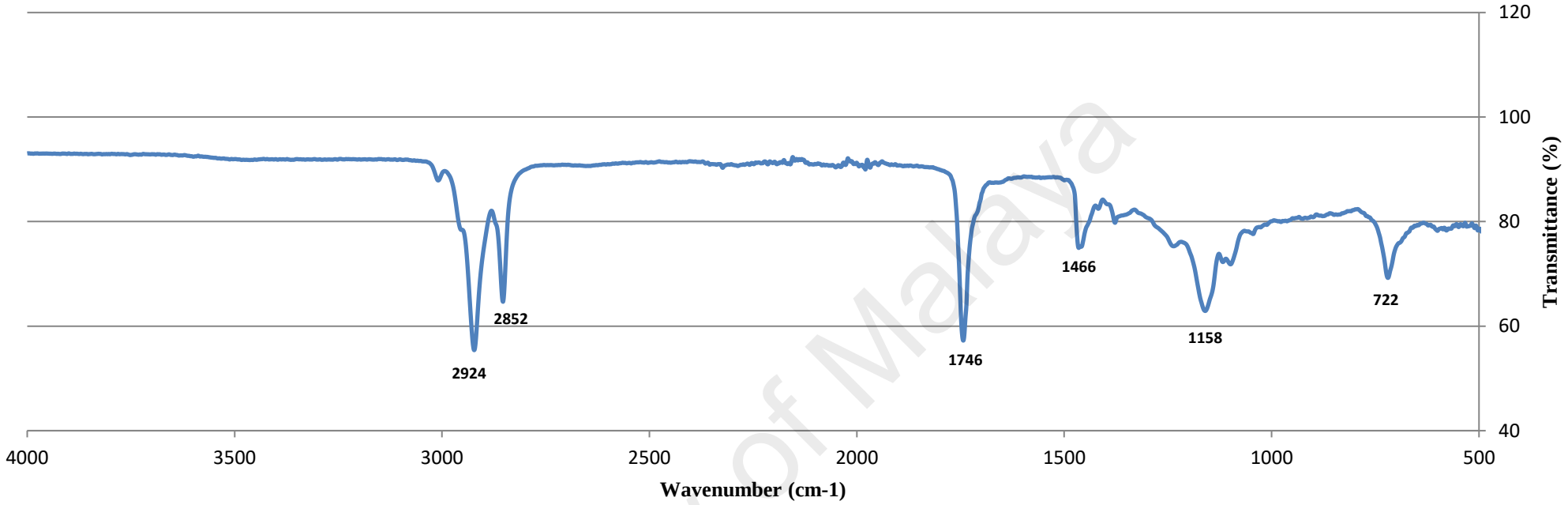


Figure 4.8: FTIR of extracted SCG oil

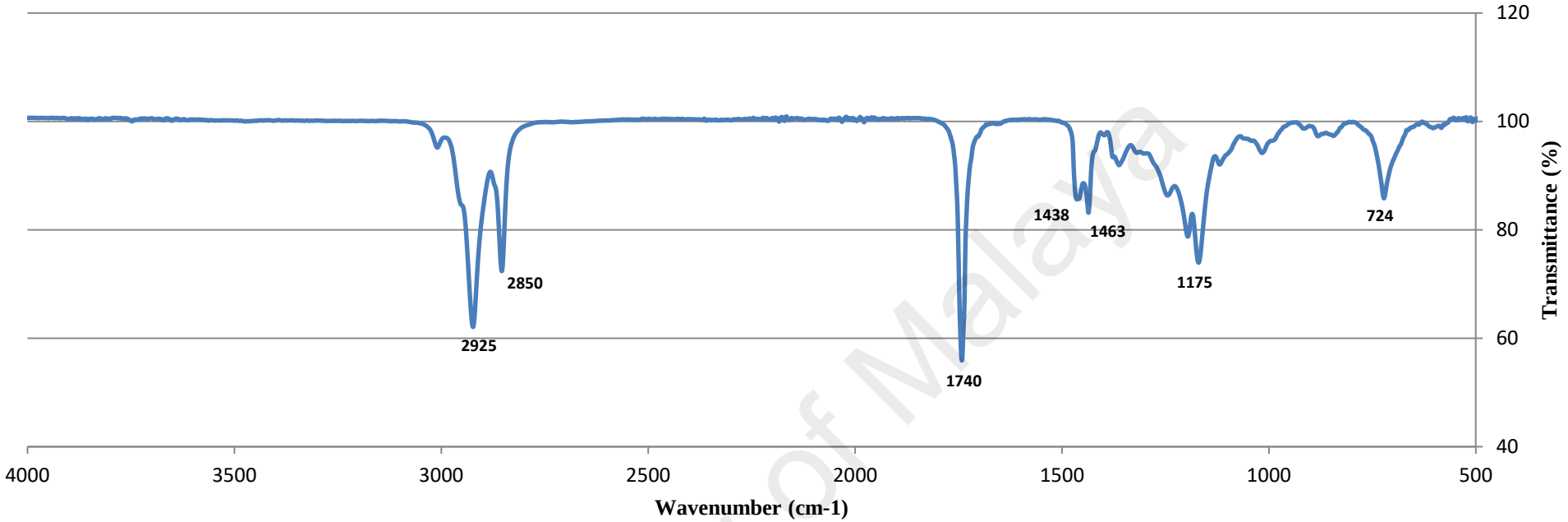


Figure 4.9: FTIR of extracted SCG biodiesel

4.6.3 Physiochemical properties of biodiesel

The physiochemical properties of the SCG biodiesel is tested according to ASTM D6751 and EN 14214 standards and shown in **Table 4.2**.

Table 4.2: Physiochemical Properties of SCG Oil and SCG Biodiesel

Property	Unit	SCG Oil	SCG Biodiesel	ASTM D6751	EN 14214
Ester Content	%	-	97.11	-	Minimum 96.5
Acid value	mg KOH g^{-1}	4.00 ± 0.2	1.10 ± 0.3	Maximum 0.5	Maximum 0.5
Kinematic Viscosity @ 40 °C	mm^2/s	46.8 ± 0.2	4.16 ± 0.2	1.9 to 6.0	3.5 to 5.0
Density @ 15 °C	Kg/m^3	919.6 ± 2.3	886.2 ± 2.2	880	860 to 900
Calorific Value	MJ/kg	40.04 ± 0.2	39.8 ± 0.2	Minimum 35	-
Oxidation Stability @ 110°C	Hours	23 ± 1.3 (Conventional Soxhlet Extraction) 7 ± 2.2 (Ultrasonic Extraction)	5 ± 0.6	Minimum 3	Minimum 6
Copper corrosion strip test	-	-	1a	3	1a

Unfortunately, the acid value of biodiesel produced was found to be 1.10 mg KOH, exceeding the maximum limit for both ASTM D6751 and EN 14214 standards. However, despite this high acid value, the copper strip corrosion test found that corrosion levels due to the biodiesel was 1a, slight tarnished. This low level of corrosion may be due to the presence of natural antioxidants in the biodiesel which are known to retard the corrosiveness of the copper release (B. Singh et al., 2012). SCG biodiesel also contains higher concentration of saturated esters, which do not easily oxidise in the presence of metals (Fazal et al., 2018). However, the viscosity was lowered to 4.16±0.2 mm^2/s after transesterification as a result of glycerol being removed (Issariyakul & Dalai, 2014). The density of the biodiesel decreased to 886.2 kg/m^3, within the permissible limits of the standard. Both viscosity and density of SCG biodiesel was found to be similar to coffee bean biodiesel (Oliveira et al., 2008). The calorific value did not show much change after transesterification but it still lower than the calorific value of diesel fuel (44.8 MJ/kg) (Asokan et al., 2018). As expected, the ultrasonic treatment caused a reduction in oxidation stability of the oil. Presence of solvent may have reduced the cavitation effect on the oil, reducing the oxidant effect, thus limiting oil oxidation (Perrier et al., 2017). Since SCG biodiesel was subjected to two ultrasonic treatments (extraction and transesterification), oxidation stability was expected to be low. The oxidation stability of SCG biodiesel was found to be 5 hours, beyond the minimum requirement for ASTM D6751 (3 hours) standards but less than that set by EN 14214 (6 hours) (Cremonez et al., 2016).

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Spent coffee ground as a biodiesel feedstock is advantageous as it is abundant, utilizes a food waste and avoids the side effects it has as a result of being disposed. Oil was successfully extracted from spent coffee ground using ultrasonic assistance and converted into biodiesel. The best conditions for ultrasonic oil extraction from spent coffee ground is using hexane solvent at $4mlg^{-1}$ ratio to spent coffee ground, 30% ultrasonic amplitude for 30 minutes regardless of moisture content within spent coffee ground and achieved 14.52%. Ultrasonic greatly reduced the amount of solvent required, shortened extraction time and had higher extractability than conventional Soxhlet extraction methods.

After extraction, the parameters for transesterification of SCG oil were optimised. Maximum FAME content was found to be 97.11% at molar ratio of methanol to SCG oil 30, 4 wt% catalyst concentration ultrasonicated with 30% ultrasonic amplitude for 3 hours. Catalyst concentration shows the biggest change in terms of FAME yield during the transesterification process. The infrared absorption spectrum of our result also show the peaks which correspond to the functional groups present within a biodiesel. Majority of the FAME was found to be methyl linoleate (44.12%) and methyl palmitate (32.79%). These esters were the major constituents which creates the aromatic smell of SCG biodiesel along with its antioxidant properties.

Besides acid value, the other properties of SCG biodiesel are coherent with the biodiesel standards. This suggests that using SCG oil as a blend to produce biodiesel is an economical and environmentally friendly alternative to improve the overall biodiesel production cost and reduce the production of municipal waste. Conversely, the high calorific value and low viscosity of SCG biodiesel enhances the power performance and reduces fuel consumption. Therefore, further studies on suitable feedstock blends with

SCG and its corresponding engine performance should be carried out to assure optimisation in engine operation. It is aspired that the results obtained from this study can help the government in contributing towards an environmental friendly biodiesel production globally.

5.2 Recommendations

There are various implications which must be considered before SCG biodiesel can be technically and economically sustainable. These include the availability of feedstock, economic and environmental effects of the production process and the organisational regulations and provisional measures for large scale production. Understanding and facilitating these implications will ensure efficient commercialisation of our biodiesel. The EU's biodiesel policy signed in Paris in 2015, shows its commitment towards emissions from feedstock production by transitioning to more sustainable feedstocks (Naylor & Higgins, 2018). The policy will directly impact top edible oil producers such as Indonesia (palm) and Argentina (soy). However, this same policy will also transition global biodiesel production to second generation feedstocks such as waste cooking oil and Jatropha oil.

Although unmodified diesel engines are able to utilize pure biodiesel (Szulczyk & Atiqur Rahman Khan, 2018), biodiesel has not been used commercially due to issues with storage stability and availability of feedstock. The concept of biodiesel blending resolves such issues by enhancing biodiesel properties while ensuring that the source does not heavily rely on a single source. Biodiesel production is also too expensive to compete with petroleum diesel, where majority of the cost coming from costs of feedstock (Moazeni et al., 2019a). The use of multiple sources for biodiesel rather than a singular source promotes economic sustainability while avoiding monopolization of the biodiesel

market. Emerging transesterification techniques such as non-catalytic supercritical methods, microwave assistance and reactive distillation should also be considered as alternative techniques to enhance overall biodiesel production energy and cost efficiency (Tan et al., 2019). The economics of biodiesel production can also be improved by recovering excess alcohol, high quality glycerol and using a recyclable catalyst (Gebremariam & Marchetti, 2018).

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

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2. Goh, B. H. H., Ong, H. C., Chong, C.T., & Leong, K. Y. (2019). Ultrasonic assisted oil extraction and biodiesel synthesis of spent coffee ground. *Fuel (under review)*