DURBAN UNIVERSITY OF TECHNOLOGY

Green synthesis of fuel grade hydrocarbons from spent coffee grounds

Submitted in fulfilment of the requirements for the degree of Master of Engineering: Chemical Engineering in the Faculty of Engineering and The Built Environment at the Durban University of Technology

by

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2021

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ABSTRACT

Spent coffee grounds (SCGs) are the main residue that remains after a coffee beverage has been brewed from coffee beans. They are a potential source of oil that can be used as a sustainable and environmentally friendly feedstock to produce fuel-grade hydrocarbons. However, the use of fossil fuel-based solvents such as hexane for oil extraction and non-reusable catalyst like sodium hydroxide (NaOH) for converting the oil to fuel-grade hydrocarbons render the valorisation of SCGs uneconomical and pose a threat to the environment. Considering these issues, green solvents and green catalysts need to be developed, to improve the process overall efficiency. SCGs high moisture content can have negative impact of the quantity of oil extracted. The high free fatty acid content on the oil extracted from SCGs oil can negatively affect the quality of the fuel-grade hydrocarbons produced from the oil extracted from the SCGs. This reduces the environmental benefit of using the coffee waste for fuel production. Therefore, a better understanding of the nature of the SCGs as a feedstock and processing route is required, to improve the overall process efficiency. The present study was divided into three major sections namely: characterisation of SCGs in terms of moisture content, particles size, and oil content; extraction of lipids from SCGs which includes the use of hexane as a datum solvent, and 2-methyltetrahydrofuran (2-MeTHF) as an understudy green solvent. The oil extraction experiments investigated the effect of the solids-to-solvent ratio and the effect of extraction time on the yield of lipids for both solvents. The final part of the experimental work involved synthesising lithium doped calcium oxide (Li-$CaO_{(s)}$) as a renewable catalyst for the transesterification of the SCGs oil. Calcium oxide was derived by the calcination of chicken eggshells in a kiln for 7 h at 600 °C and doped with lithium for 4 h at 900 °C. The effect of catalyst loading and reaction period on FAME yield was investigated. Three SCGs samples from three retailers were used. The samples were found to have an average moisture content of 67.89 wt% of the initial SCGs used on a dry basis, a particle size of 500 µm on average and 27.76 wt% oil of the initial SCGs used. It was observed that 2-MeTHF provided a higher oil yield of 27.76 wt% relative to19.03 wt% which was achieved by hexane, using a Soxhlet apparatus. The optimum oil extraction conditions were observed to be 4.50 h extraction time at 1:18 solvent-to-solid ratio for 2-MeTHF. One-step transesterification reaction was used for production of FAME. The optimum reactor conditions were observed to be 65 °C reactor temperature, a catalyst loading of 4 wt% of the oil used, a 2 h reaction time and a methanol-to-oil molar ratio of 12:1. These reactor conditions achieved a maximum oil conversion of 97.81 wt%.

DECLARATION

I, Bhekuyise Mkhonto, declare that:

i. The research reported in this thesis, except where otherwise indicated, is my original work.
ii. This thesis has not been submitted for any degree or examination at any other university.
iii. This thesis does not contain other persons' data, pictures, graphs or other information unless specifically acknowledged as being sourced from other persons.
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Signed: B. Mkhonto Date: December 2021

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NOMENCLATURE

ASTM D 6751	American Society for Testing and Materials
AV	Acid value
CaO	Calcium oxide
CH_3ONa	Sodium methoxide
DUT	Durban University of Technology
DMC	dimethyl carbonate
DoE	Design of experiments
SA	South Africa
SCGs	Spent coffee grounds
FAME	Fatty acid methyl esters
FFA	Free fatty acids
FA	Fatty acids
GHG	Greenhouse gas emissions
h	hour
SFE	Supercritical fluid extraction
UAE	Ultrasound assisted extraction
MAE	Microwave assisted extraction
2-MeTHF	2-methyl tetrahydrofuran
IPA	Isopropyl alcohol
IUPAC	International Union of Pure and Applied Chemistry

NaOH	Sodium hydroxide
KOH	Potassium hydroxide
KV	Kinematic viscosity
HHV	Enegry content
Li	lithium
ER	Site Eley-Rideal model
M	Moisture content
HCl	Hydrochloric acid
SV	Saponification value
Li-CaO	Lithium doped calcium oxide
RMS	Response surface methodology
Y	Mass percentage yield

PREFACE

Publications:

Mkhonto, B and Chetty, M. (2021) 2-methyltetrahydrofuran as a potential green solvent for lipid extraction from spent coffee grounds for fuel grade hydrocarbons. *Chemical Engineering Transactions*, Vol. 89. No. 20. **ISBN** 978-88-95608-87-7; **ISSN** 2283-9216. DOI: 10.3303/CET2189069. (H-index:32).

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Conferences:

Mkhonto B and Chetty M 2021. 2-Methyltetrahydrofun as a potential green solvent for extraction of lipids from spent coffee grounds for the production of fuel-grade hydrocarbons. *Proceedings of the 7th International Conference on Low Carbon Asia and Beyond,18th - 19th October 2021, Malaysia*

Mkhonto B and Chetty M 2022. Green Synthesis of Fuel Grade Hydrocarbons from Spent Coffee Grounds in South Africa. *International Conference on "Chemical, Biological and Environmental Engineering JCBEE on March 17-18, 2022 in Johannesburg, South Africa*

CHAPTER 1

1.0 Background

The global energy demand has soared in recent years, which has resulted in an increased use and reliance on fossil fuels. The extraction and processing of fossil fuels to meet the demand has a detrimental effect on the environment due to land pollution, emission of greenhouse gases which lead to climate change and global warming (Tarigan *et al*., 2019). In addition, petro-diesel powered vehicles are major contributors to the total carbon dioxide footprint in urban areas (Tshifularo *et al*., 2018). The continued use of fossil fuels is not sustainable in the long term as they are finite, therefore the reserves are dwindling rapidly with extraction. The energy security and economic growth for countries which imports most of its liquid fuels are greatly threatened since the external supply of fossil fuels has become unsteady and expensive thus hindering economic growth (Tshifularo *et al*., 2018).

Taking into consideration the global environmental protection and long-term supply of petrochemical-based fuels, it has become necessary to develop non-petrochemical-based fuels which are comparable to petrochemical-based fuels. The alternative fuels should not only be sustainable but also be environmentally friendly and produced from locally produced substrates (Raley, 2018). The most notable renewable energy sources which can complement fossil fuels among others include wind, hydro, nuclear, solar energy, and biofuels. According to Martin *et al*. (2010), biofuels such as bioethanol, biobutanol, and FAME have the potential of replacing petroleum-based fuels. For any fuel to be considered renewable, all the raw materials used in its production must be derived from renewable resources (Chemat *et al*., 2019).

Currently, edible vegetable oils and animal fats account for 95 % of FAME production. (Duncan, 2016; Ifeanyichukwu, 2020). However, producing alternative fuels from vegetable oils grown for human consumption has hampered biofuel production in most parts of the world. Bioethanol and biobutanol, which are currently produced from corn and sugarcane as well as biodiesel produced from canola, palm, coconut, and soybean oil have gained much attention in recent years. However, major challenges associated with growing these food plants for fuels are that it can cause deforestation and compete with agriculture (food base) for land and water (Blinová *et al*., 2017). The high cost of feedstock for FAME production which accounts for 85 % of the total cost of production, has made FAME unattractive amongst developing countries (Blinová *et al*., 2017).

The primary requirements for biofuels are that they must be produced from renewable nonedible materials, they must be cheap to produce and environmentally friendly. Biofuels are primarily classified into three brackets i.e., primary biofuels and secondary biofuels (Binyam *et al*., 2018). Primary biofuels are those where the organic material is used fundamentally in its indigenous form (as gleaned). These fuels are directly burned, to provide cooking energy and home heating. In some cases, they are used to generate electricity in both small and large industrial scales. Secondary biofuels such as ethanol, FAME and biobutanol are synthesised by refining non-edible biomass and wood waste. These second-generation liquid fuels can be used to generate electric power. However, they are mostly produced for the transportation sector (Binyam *et al*., 2018). To address the issues associated with the utilisation of food sources for biofuel production, non-edible sources such as sugar cane bagasse for biobutanol production, jatropha, and spent coffee grounds (SCGs) for FAME production are gaining a lot of attention from researchers.

1.1 Problem statement

The ever-increasing global population has subjected the worlds energy supply chain under immense pressure, resulting in an accelerated depletion of crude oil reserves. The negative effects of using crude oil derived fuels, on the environment are well documented. This has prompted the need to source alternative and renewable energy feed stocks. This feedstock must be environmentally friendly, and it must be economically feasible. Oil containing solids are dumped in landfills daily. Dumping of these solids in the landfills can have a detrimental effect on the environment. These effects include as serving as breathing ground for diseases carrying pests, compromising both surface and groundwater quality. Unless these solids are converted to valuable products, they will remain an environmental hazard. One of the most common, oil (10 – 20 wt%) containing waste solids are SCGs (Blinová *et al*., 2017; Binyam *et al*., 2018). It is estimated that 6 billion tons per year of SCGs are produced globally from the treatment of roasted coffee beans with hot or boiling water to prepare instant coffee beverage (Blinová *et al*., 2017). Approximately 2 kg of wet SCGs are generated for every 1 kg of instant coffee brewed (Murthy and Naidu, 2012; Cameron and O’Malley, 2016). With some authors suggesting that for every 1000 kg of roasted coffee beans processed 910 kg of SCGs are generated (Cameron and O’Malley, 2016). Moreover, it is estimated that for every

1000 kg of SCGs decomposing in the landfills, 682 kg of carbon dioxide is produced annually (Cameron and O'Malley, 2016). SCGs also contribute to the enormous financial cost to taxpayers who pay for the maintenance and running of the landfills. (Giller *et al.*, 2017). Therefore, the critical issues associated with the use of conventional fossil fuels and the disposal of SCGs have driven researchers and engineers to investigate and develop novel methods of converting coffee waste into fuel-grade hydrocarbons.

The challenge with popular methods of extracting and converting oil from SCGs is that they rely on fossil-based solvents for oil extraction. The use of non-reusable catalysts for the transesterification reaction negatively impacts the financial feasibility of FAME production (Duncan, 2016).

1.2 Aim and objectives of the study

This study aims to investigate the possible use of SCGs as a potential source of oil, which can be used as a feedstock for fuel-grade hydrocarbons production, in the presence of a renewable catalyst. The experimental work will enable the determination of oil extraction efficiency from SCGs using green solvents as well as the conversion of the SCGs oil into fuel-grade hydrocarbons in the presence of a renewable catalyst. In addition, the fuel and liquid properties of oil and fuel-grade hydrocarbons produced will be analysed to ascertain their quality.

The objectives of this research include investigating the following parameters:

i. Characterisation of various types of SCGs.
ii. Green solvent selection for oil extraction from SCGs.
iii. To investigate the yield of fuel-grade hydrocarbons from SCGs oil using a renewable catalyst.
iv. Develop a model for the oil extraction and fuel-grade hydrocarbons production using DoE.

1.3 Research scope

This research study will provide novel knowledge on the recovery of oil from the SCGs employing a polar green solvent (2-MeTHF). The scope of this study will be limited to:

- **Extraction of oil from SCGs:** Extraction of oil from SCGs utilising a Soxhlet apparatus, two different solvents (2-MeTHF and hexane), while studying the impact of extraction period and solids-to-solvent ratio on the oil extraction yield for each solvent. The Design of Experiment software will be used to develop a model for the oil extraction using 2-MeTHF.
- **Investigation of the quality of the oil:** The oil obtained will be tested for kinematic viscosity, density, acid value and saponification value. This will provide an insight into the appropriate transesterification route for the extracted from SCGs oil.
- **Synthesis of calcium oxide from eggshells:** Crushing and calcining of eggshells will be carried out to produce calcium oxide which will be doped with lithium to improve the catalyst reaction sites.
- **Transesterification:** The selection of a suitable transesterification route will depend on the quality of the SCGs oil. Transesterification will be carried out with wood alcohol (methanol) in the presence of the eggshell-derived calcium oxide to produce fuel-grade hydrocarbons. The impact of reaction period and catalyst quantity on the degree of the oil conversion will be studied. The transesterification data obtained will be used to develop a model.
- **Investigation of the quality of the FAME**: The fuel-grade hydrocarbons produced will be subjected to density, kinematic viscosity, and acid value tests. The results obtained will indicate whether the FAME produced satisfies the requirements stipulated by EN 14214 standards.

1.4 Thesis outline

Chapter 1: This section describes the context and motivation for conducting this research. In addition, it sets out the purpose and objectives of this study.

Chapter 2: This chapter introduces the literature from previous studies, concerning the extraction of oil from SCGs and other oil-bearing seeds. It describes different methods that can be used to extract and convert the oil to fuel-grade hydrocarbons. It also describes the factors that affect both the oil extraction and the transesterification of the oil to FAME.

Chapter 3: This section outlines the experimental apparatus and methods employed in this study. It also describes the parameters employed for data analysis.

Chapter 4: This section will introduce and discuss the results obtained. The main trends observed from the experimental results are underlined and contrasted with those found in literature.

Chapter 5: The limitations of the current study and a possible future research proposal on this topic are presented.

Chapter Two

2.0 Introduction

This section investigates the global coffee consumption trends (2.1), there after evaluate the generation of SCGs (2.2). Sub-section 2.3 and 2.4 investigates the potential use of SCGs as source of oil and other valuable chemical compounds. Sub-sections 2.5 to 2.7 investigate creative methods of extracting oil from SCGs as well as the process factors influencing oil extraction from SCGs. The potential use of green solvent from SCGs is also evaluated. Su-sections 2.8 to 2.10 evaluates the use of SCGs oil as substrate for FAME production, possible process routes are investigated. Possible types of catalyst that can be used during the transesterification of SCGs oil are also investigated (2.11) and the factors affecting the transesterification reaction are also investigated (2.12). Sub-section 2.13 concludes this section and evaluate potential areas of study regarding the valorisation of SCGs.

2.1 Literature Review

Coffee is a crop grown in more than 80 countries, with Brazil and Vietnam contributing about 40 % and 20 % of the world's coffee production in 2018. (Shahbandeh, 2020). Coffee is the second largest trade product after crude oil products (Blinová *et al.*, 2017; Efthymiopoulos *et al.*, 2019). According to the International Coffee Association (2021), 10.16 billion tons of roasted coffee were produced in the 2020/21 season, a decrease of 2.2% from 2019/20 season (International Organization of Coffee, 2021). Figure 2.1 shows the percentage of each country's contribution to global coffee production in 2020/21.

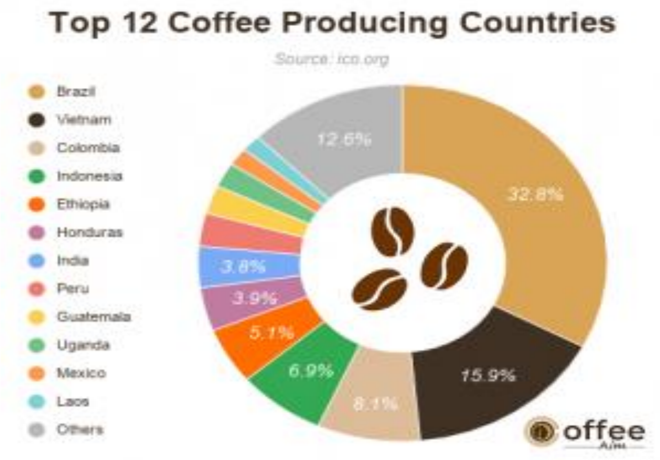


Figure 2.1: Global production of coffee in 2020/21 per country (Khan, 2021).

From Figure 2.1 it is evident that Brazil is the undisputed leader in global coffee production, accounting for 32.80 % of the total world production followed by Vietnam at 15.90 %. These numbers change from season to season; however these two countries always outshine the other producers (Khan, 2021).

It is estimated that there are about 80 species of coffee (Murthy and Naidu, 2012). However, there are only two types of coffee beans that are cultivated in large quantities for commercial purposes: *Coffee Arabica* and *Coffeeacanephora*. *Coffea Arabica* is ranked as the most produced of the two coffee species, due to its flavourful taste prompted by the roasting of the coffee bean (Efthymiopoulos *et al*., 2019) and occupies 70 to 75 % of the global production (Jenkins *et al*., 2014). *Coffea canephora* is said to contain twice the amount of caffeine relative to *Coffea arabica* (Jenkins *et al*., 2014). The caffeine content of *Coffea canephora* is approximately 2.50 wt% on a dry basis, while that of *Coffea arabica* is said to be approximately 1.50 wt% on a dry basis (Efthymiopoulos *et al*., 2019) and are mostly used in brewing of coffee beverages like instant coffee.

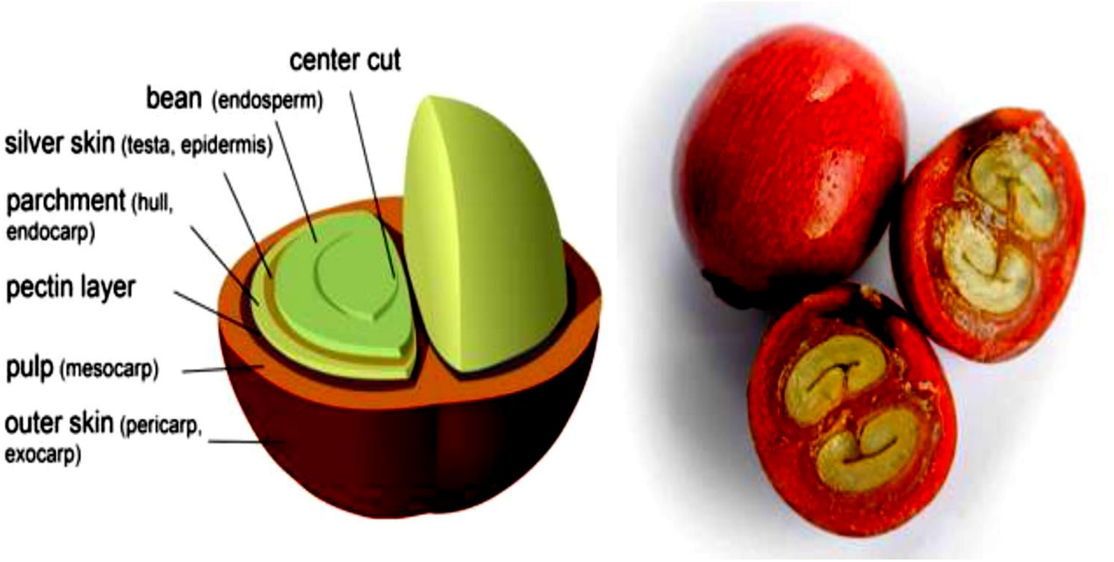


Figure 2.3: Centre cut of a coffee cherry right: ripe coffee cherry (Verhagen, 2018).

Figure 2.2 depicts a coffee bean seed of a coffee cherry that grows on the coffee plant, each coffee cherry contains two coffee beans. The cherries are harvested when they are ripe and sorted to remove the outer layer along with the defective beans and debris. The coffee beans are then fermented and dried to reduce the moisture content from 65 wt% to 11 – 13 wt% in the sun or air dryers to prevent spoiling. The dried green coffee beans are then stored in a moisture-free environment (Verhagen, 2018). The primary objective of raw coffee (berries) processing is to remove all the layers wrapping the beans and to reduce the moisture content of the coffee beans (Cruz *et al.*, 2012).

Concerning South Africa (SA), the average annual coffee consumption is estimated to be 42.79 million kg for the past decade (Index Mundi, 2020). The country produces a small amount of coffee annually, which is about 120 000 kg grown locally (SA Department of Agriculture, 2017). SA coffee consumption only accounts for 0.42 % of the global consumption. Figure 2.3 depicts the yearly coffee consumption in SA. for the last decade.

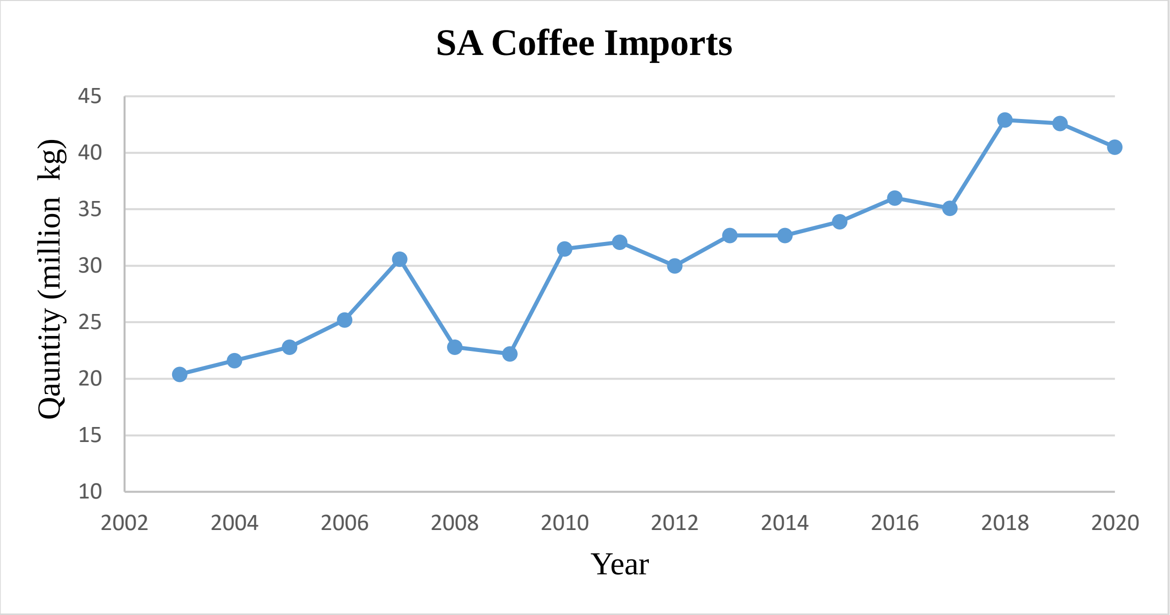


Figure 2.4: South African coffee annual import for the last decade (Index Mundi, 2020).

2.1.1 Processing of coffee beans

Immediately after harvesting the coffee cherries, the cherry processing process starts. Traditionally there are three distinct processing techniques employed for pulp (mesocarp-Figure 2.2) removal to produce raw (green) coffee beans namely, dry, wet, and semi-dry processing. The method used is dependent on the coffee breed and the region of production. (Farah, 2012).

The dry processing technique, is used for all the *Coffee Arabica* and *Coffeeacanephora* globally and about 80 % of Brazilian and Ethiopian Arabicas (Farah, 2012). In this method the coffee berries are either left to dry in the sun or subjected to hot air drying after the parchment and pulp (Figure 2.2) are mechanically removed (Farah, 2012). Figure 2.4 depicts the schematic diagram of the three major methods used during the processing of the freshly harvested coffee berries to produce green coffee beans, along with the by-products that are generated.

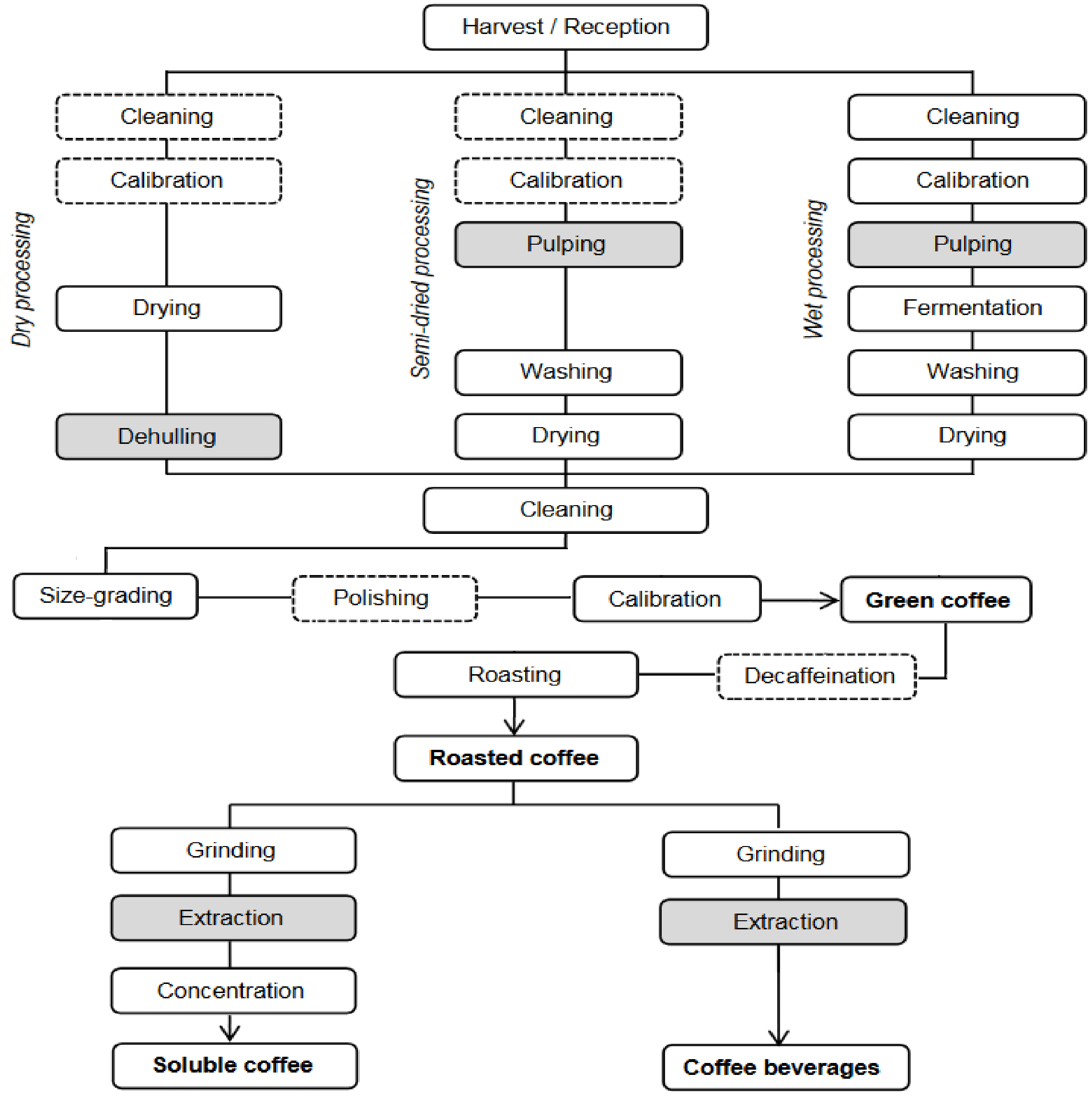


Figure 2. 4: Flow diagram depicting the main coffee processing methods (Blinová *et al*., 2017).

The wet processing method is used in some producing countries to process small amounts of *Robusta* and *Arabicas* (Farah, 2012; Murthy and Naidu, 2012). In this method, the pulp is mechanically cleaned and the sticky mucilage (part of the mesocarp) which adheres to the parchment is separated by fermentation before washing. Followed by polishing, drying (by the sun or air drying), and peeling of the parchment to produce green coffee beans (Farah, 2012; Murthy and Naidu, 2012).

The semi-dry process is the most recent processing method and is mostly used in Brazil (Murthy and Naidu, 2012). It combines both the wet and dry processing techniques where the pulp is removed without removing the mucilage before drying. The green coffee beans are obtained by peeling the dry parchment and the sticky mucilage (Farah, 2012). After processing the resulting green coffee beans are sorted based on colour, size, and shape. Defected coffee beans which account for almost 20 % of the total crop are removed before commercialisation in the international market (Efthymiopoulos *et al.*, 2019). The remaining green coffee beans are sent to storage. Processing involves roasting and steam treatment or decaffeination (Farah, 2012). The defective coffee beans are sold in the local market of the producing country (Fuller and Rao, 2017).

After processing the resulting green coffee beans are roasted to activate the pleasant coffee aroma and flavor for beverage preparation (Farah, 2012; Murthy and Naidu, 2012;Fuller and Rao, 2017). A small percentage of the green coffee beans are subjected to decaffeination before roasting (Jenkins *et al.*, 2014; Fuller and Rao, 2017; Blinova *et al.*, 2017). Roasting is carried out in three steps: (1) Drying, where water is evaporated and the volatile aromatic compounds are gradually released. (2) Pyrolysis, which is carried out in temperatures ranging between 210 – 240 °C depending on the degree of roasting required. (3) Air or water cooling (Farah, 2012).

The roasted coffee beans are ground for particle size reduction (surface area increase) to improve the extraction of essentials aromatic oils during the brewing process. There are numerous different brewing techniques, such as percolation espresso, boiling, and drip-filtering to name a few. All these methods utilise hot water 90 – 95 °C or boiling water to extract the essential aromatic oils from the coffee beans (Farah, 2012; Fuller and Rao, 2017). This results in approximately 9 wt% of the coffee mass being dissolved in the water (Tarigan *et al.*, 2019). However as high as 30 wt% coffee solubility in water have been reported (Jenkins *et al.*, 2014).

2.2 Spent coffee grounds (SCGs)

After extraction of essential aromatic oils (brewing), a solid residue (biomass) called spent coffee grounds (SCGs) remains. SCGs can be grouped into two classes, those that are generated during the production of instant coffee and those that are generated during coffee brewing (Cruz *et al.*, 2012). Restaurants and coffee shops generate a considerable amount of SCG through the direct brewing of roasted coffee beans through espresso machines and drip-filtering. Approximately 50 % of the global roasted coffee beans are used in this manner (Cruz *et al.*, 2012).

SCG obtained after the brewing process contains about 75 – 85 wt% moisture, with particle size ranging between 75 – 430.50 µm after drying with a pH value ranging between 4.20 to 5.70, (Cruz *et al*., 2012; Go *et al*., 2016). SCGs are technically a waste that must be disposed of, however poses a serious environmental problem due to the high oxygen demand for decomposition of its organic materials and the toxic nature of the organic compounds present in the SCGs such as caffeine, tannins, and polyphenols (Efthymiopoulos *et al*., 2019). SCGs also contributes towards the huge financial cost on taxpayers of running and maintaining landfills.

i. *Chemical Composition of SCGs:*

Spent coffee grounds contain large amounts of organic compounds (i.e., fatty acids; lignin, cellulose, hemicellulose, and other polysaccharides) that can be exploited as a source of value-added products (Fadli, 2017). The chemical characterisation includes elemental analysis, mineral composition, and ash content (Binyam *et al*., 2018), as depicted in Table 2.1.

Table 2.1: Characterization of SCGs (Efthymiopoulos, 2018).

References	Elemental composition (%)						Lipids (%)	Crude protein (%)	Carbohydrates (%)	Lignin (%)	Sugar (%)	Ash (%)
	C	H	N	O	S	P						
Somnuk et al. (2017)	52.95	6.76	2.10	38.07	0.12	-	14.7	14.39	21.43	-	14.09	1.59
Vardon et al. (2013)	56.1	7.2	2.4	34.0	0.14	0.18	16.2	15.4	-	-	-	1.8
Todaka et al. (2016)	55.86	7.02	2.33	34.79	-	-	21.27		-	-	-	2.17
Go et al. (2016)	-	-	-	-	-	-	13.78-16.51	10.95-11.03	25.36-34.14		-	1.63-1.73
Pujol et al. (2013)	57.16-59.77	7.17-7.57	1.18-1.32	-	-	-	19.67-25.41	-	-	19.84-26.51	22.00-24.13	-
Acevedo et al. (2013)	-	-	-	-	-	-	26.4	10.32	36.87	-	-	0.47
Caetano et al. (2014)	67.3	-	2.2	-	-	-	6.0	13.7	-	33.6	-	2.2
Tsai et al. (2012)	52.54	6.95	3.46	34.82	0.10	-	-	-	-	39.4	-	0.73

It can be observed in Table 2.1 that dry SCGs have a high carbon and oxygen content, but nitrogen, phosphorus, ash, and sulphur are present in low quantities. Lignin and carbohydrates are present in identical proportions, ranging from 19.80 – 39.40 wt% and

21.40 – 36.80 wt% respectively. Proteins and sugars constitute a small amount of the total composition of the SCGs mass, ranging from 10.32 – 15.40 wt% and 14.09 – 24.13 wt% respectively. With oil constituting about 6 – 26.40 wt% of the SCGs total mass. In addition, SCGs have been reported to contain extractives 51 – 55 wt% such as ethanol, tannins 0.02 – 4 wt%, sterols 0.50 – 3.10 wt%, caffeine 0.02 wt%, polyphenols 1.50 – 6 wt% and chlorogenic acid 2.30 wt%, (Murthy and Naidu, 2012). There is a noticeable variation in SCGs composition, which could be attributed to several factors such, as the type of coffee beans used, roasting temperature and duration, origin of the coffee beans, method of brewing, and methods used for the analyses (Go *et al*., 2016).

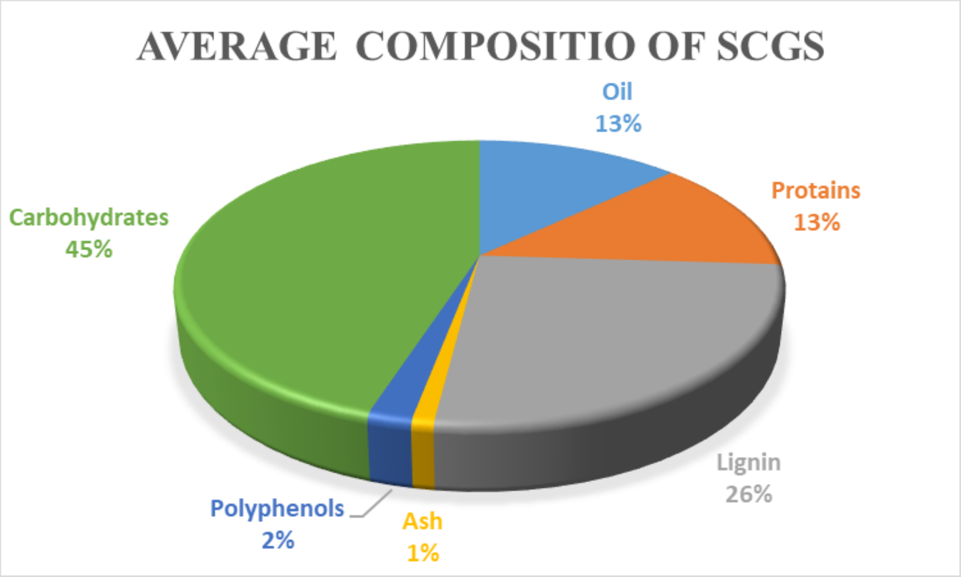


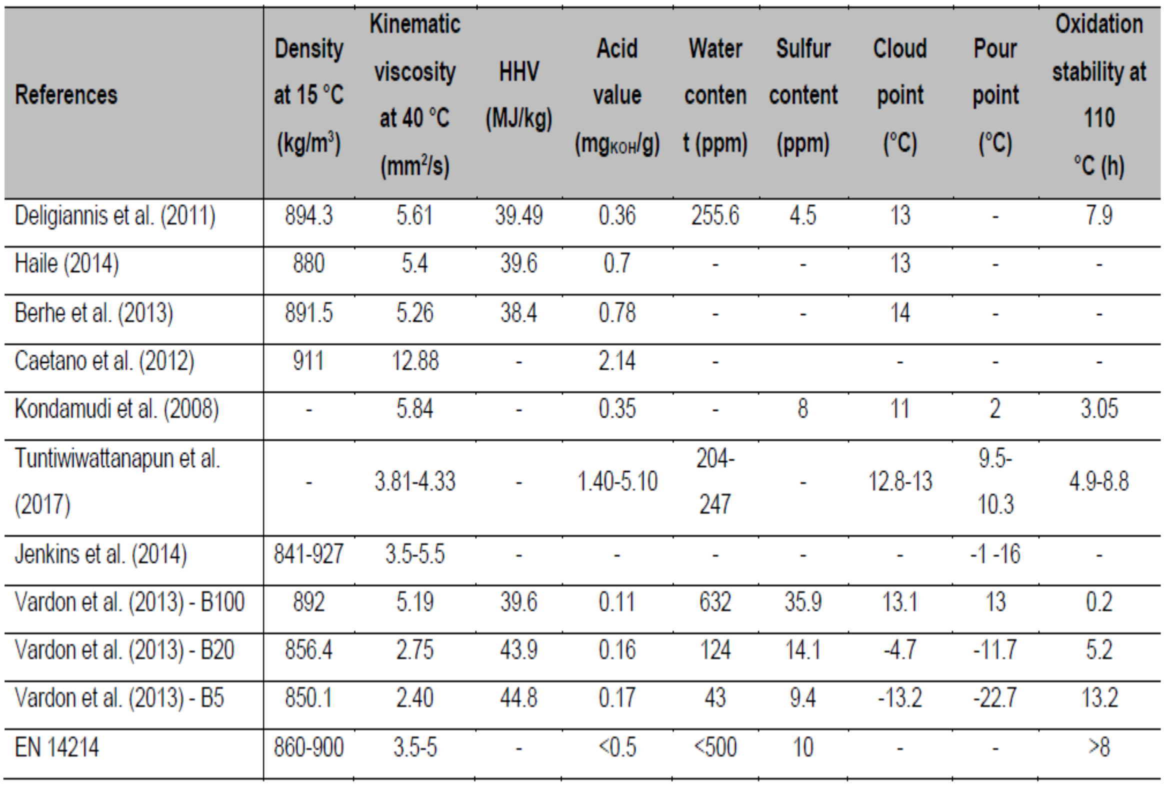
Figure 2.5: Average composition of spent coffee grounds (Binyam *et al*., 2018).

Figure 2.5. depicts the average chemical composition of dry SCGs, therefore it can be concluded that SCGs are a unique and special biomass and can be used as a source of different valuable chemical compounds.

ii. *SCGs derived fuel Grade hydrocarbons characterisation:*

Table 2.2 depicts a summary of some important results of the fuel properties of fuel-grade hydrocarbons produced from SCGs oil. These properties include kinematic viscosity, density, sulphur content, cloud point, oxidation stability, acid value, water content, pour point, and energy density.

Table 2.2: Properties of FAME derived from SCGs oil (Efthymiopoulos, 2018)



References	Density at 15 °C (kg/m^3)	Kinematic viscosity at 40 °C (mm^2/s)	HHV (MJ/kg)	Acid value (mg$_{KOH}$/g)	Water content (ppm)	Sulfur content (ppm)	Cloud point (°C)	Pour point (°C)	Oxidation stability at 110 °C (h)
Deligiannis et al. (2011)	894.3	5.61	39.49	0.36	255.6	4.5	13	-	7.9
Haile (2014)	880	5.4	39.6	0.7	-	-	13	-	-
Berhe et al. (2013)	891.5	5.26	38.4	0.78	-	-	14	-	-
Caetano et al. (2012)	911	12.88	-	2.14	-		-	-	-
Kondamudi et al. (2008)	-	5.84	-	0.35	-	8	11	2	3.05
Tuntiwiwattanapun et al. (2017)	-	3.81-4.33	-	1.40-5.10	204-247	-	12.8-13	9.5-10.3	4.9-8.8
Jenkins et al. (2014)	841-927	3.5-5.5	-	-	-	-	-	-1 -16	-
Vardon et al. (2013) - B100	892	5.19	39.6	0.11	632	35.9	13.1	13	0.2
Vardon et al. (2013) - B20	856.4	2.75	43.9	0.16	124	14.1	-4.7	-11.7	5.2
Vardon et al. (2013) - B5	850.1	2.40	44.8	0.17	43	9.4	-13.2	-22.7	13.2
EN 14214	860-900	3.5-5	-	<0.5	<500	10	-	-	>8

The liquid properties of the fuel-grade hydrocarbons derived from SCGs oil must be the same as those of petroleum diesel (Blinová *et al*., 2017). The density of petroleum diesel ranges between 830 – 850 kg/m^3 (Binyam *et al*., 2018), in Table 2.2 the value of SCGs fuel-grade hydrocarbons ranges from 850.10 – 927 kg/m^3 which is within range of the petroleum dieselise, i.e., 860 – 900 kg/m^3, although it is mostly on the upper limits. Density is a vital fuel parameter for diesel injection fuel systems since they operate on a volume measuring system (Jenkins *et al*., 2014). Variations in SCGs FAME density may be attributed to numerous factors, such as incomplete transesterification reaction, the origin of the coffee beans, and the bean type (Caetano *et al*., 2013). According to Jenkins *et al*. (2014), properties such as density and viscosity are also affected by oil-insoluble chemical compounds present in SCGs FAME.

Kinematic viscosity is a vital liquid property of fuel, which affects the flow of the fuel through the fuel supply system and automisation during the fuel injection process (Jenkins *et al*., 2014). The kinematic viscosity of petroleum diesel ranges between 3.50 – 3.59 mm^2/s, (Binyam *et al*., 2018), in Table 2.2. The kinematic viscosity of pure SCGs FAME from previous studies ranges between 2.40 – 12.88 mm^2/s, most studies showed that the viscosity of SCGs FAME is higher than the specification limit of 5 mm^2/s (Efthymiopoulos, 2018), which might be attributed to incomplete transesterification reaction and the presence of glycerol which remained after the purification stage (Deligiannis *et al.*, 2011). Some authors have reported that the viscosity of fuel-grade hydrocarbons derived from SCGs oil varies between 3.50 − 5.50 mm^2/s depending on the brewing method and the origin of the coffee beans (Jenkins *et al.*, 2014). Jenkins *et al.* (2014) suggested that the brewing method used plays a crucial role in the viscosity of resulting FAME. By removing different chemical compounds before oil extraction and transesterification. It is suggested that refining the oil before transesterification and mixing the FAME with petroleum diesel would reduce the viscosity of the resulting fuel grade hydrocarbons (Vardon *et al.*, 2013).

The energy content (HHV) of SCGs fuel-grade hydrocarbons (Table 2.2) was found to be slightly lower, i.e., 38.80 − 44.80 MJ/kg than that of petroleum diesel which is about 45.50 MJ/kg (Binyam *et al.*, 2018). But comparable to FAME derived from soybean oil, 39.90 MJ/kg and FAME derived from other plant-based oil (Vardon *et al.*, 2013). The variation in FAME energy content noticed in Table 2.2, can be attributed to different FA profiles of different samples. Since the quantity of energy present in the sample depends on chain length and the number of unsaturated FA present in a sample (Efthymiopoulos *et al.*, 2019). The increase in unsaturated FA lowers the energy content of FAME due to lower energy released during the breaking down of single bonds compared to double bonds (Vardon *et al.*, 2013).

Acid value (AV) is one of the most important fuel properties of oil-based fuels, in Table 2.2 the value of SCGs derived FAME ranges between 0.36 − 5.10 mg_{KOH}/g, with some values significantly higher than the standard limit of 0.50 mg_{KOH}/g (Efthymiopoulos *et al.*, 2019). High fuel AV can have a detrimental effect on the life span of an engine, by corroding the fuel supply system and fuel sediment thus plugging the fuel filter (Tuntiwiwattanapun *et al.*, 2017). Esterification of FFA before transesterification reaction was found to reduce the AV of the resulting FAME by Caetano *et al.* (2014).

Previous studies (Table 2.2) show that the water content of SCGs FAME is higher than the accepted limit of 348 ppm (Fregolente et al., 2015). The high-water content, i.e., 632 ppm in a study conducted by Vardon *et al.* (2013) can be attributed to poor drying after the FAME washing stage. High water content in fuel can cause corrosion of the fuel supply system and can also promote FAME degradation during storage (Tuntiwiwattanapun *et al.*, 2017), hence it is important to keep water content as low as possible.

The sulphur content of SCGs FAME is low (Table 2.2) with most previous studies reporting values less than 10 ppm. According to Martins *et al*. (2010), low sulphur content can result in low sulfur oxide production during combustion and produce low particulate matter compared to petroleum diesel. The high sulphur content obtained by Vardon *et al*. (2013) can be attributed to traces of sulphuric acid or magnesium sulphate in the FAME as they were used in the SCGs pre-treatment catalyst and FAME drying agent respectively.

The cloud and pour points of SCGs fuel-grade hydrocarbons are fuel properties that indicate the temperature at which FAME becomes cloudy. This cloudy appearance is caused by the formation of solids. When the fuel is cooled to temperatures below room temperature (Efthymiopoulos *et al*., 2019). While the pourpoint is defined as the temperature at which the fuel stops flowing (Efthymiopoulos *et al*., 2019). Both of these fuel properties are strongly dependent on the degree of saturation of the FAME, with a high degree of unsaturated esters leading to low pour and cloud points (Efthymiopoulos, 2018). Generally, the SCGs fuel-grade hydrocarbons have a relatively high cloud point, with most studies reporting a value of 13 °C (Table 2.2). This high compared to mineral diesel with a cloud point of -18°C. Which makes the SCGs fuel-grade hydrocarbons unsuitable for use in cold climates (Tuntiwiwattanapun *et al*., 2017).

Oxidation stability is the fuel property that indicates the resistance of FAME to oxidation during storage (Bhuiya *et al*., 2016; Tuntiwiwattanapun *et al*., 2017). FAME is prone to oxidation compared to petroleum diesel (Martín *et al*., 2001; Deligiannis *et al*., 2011). FAME derived from SCGs oil generally has good oxidation stability compared to FAME produced from oil extracted from other sources. This is due to antioxidants present in the SCGs oil (Deligiannis *et al*., 2011; Al-Hamamre *et al*., 2012). These natural antioxidants can be lost during the transesterification reaction hence producing poor oxidative stability FAME (Vardon *et al*., 2013). The oxidation rate of FAME is mainly linked to FA composition, with monounsaturated FA, such as oleic acid which can be found in high fractions in SCGs derived FAME.

The other crucial FAME fuel property not presented in Table 2.2 is the cetane number which is an indicator of the fuel's ignition quality in diesel engines, and it liked to the ignition delay time (Martín *et al.,* 2001), with shorter ignition delay time signifying higher cetane number. The cetane number of FAME has been reported to range between $50 - 65$ which is comparable to that of petroleum diesel with cetane number which ranges between $40 - 55$, (Binyam *et al*., 2018). The cetane number of SCGs fuel-grade hydrocarbons was determined by Vardon *et al*. (2013) who found it to be 61.10 for pure SCGs fuel-grade hydrocarbons, with blended samples of B20 and B5 attaining cetane numbers of 51.90 and 50.50 respectively, which are within the specification limit of 51 (BSI Standard, 2014).

2.3 Valorisation of SCGs

Currently, a small portion of the SCGs is used as low-cost compost because of their high nutrition content. Compost derived from SCGs can be used to enhance soil nutrition and improve resistance against pathogens. Studies have shown that SCGs can be used as a medium for mushroom cultivation with a high yield (Cameron and O'Malley, 2016). Several studies have been conducted to valorise and exploit, the high-value chemical compounds present in the SCGs (Martín *et al*., 2001; Abdullah and Bulent Koc, 2013; Acevedo *et al*., 2013; Akgün *et al*., 2014; Boualdab, 2016; Blinová *et al*., 2017; Liu *et al*., 2017; Binyam *et al*., 2018; Efthymiopoulos *et al*., 2019). These include the utilisation of SCGs as a source for oil, antioxidants activated carbon production, and as a source for terpenes (Campos-Vega *et al*., 2015).

In some studies, SCGs have been considered as a source of sugars and polysaccharides (Pujol *et al*., 2013). The utilisation of SCGs as an absorbent for the removal of dyes in wastewater (Franca *et al*., 2009) or the removal of metal ions from wastewater has been explored (Fiol *et al*., 2008). However, these strategies have not been implemented at an industrial scale (Mebrahtu, 2014). The oil content of SCGs have spiked a lot of interest from researchers as a potential substrate for fuel-grade hydrocarbons production (Al-Hamamre *et al*., 2012; Caetano *et al*., 2013; Caetano *et al*., 2012; Jenkins *et al*., 2014; Akgün *et al*., 2014). For instance, Bio-Bean (FAME producing company, in the UK), has established that 1000 kg of SCGs can produce 108 L of fuel-grade hydrocarbons and 820 kg of heating pallets (Giller *et al*., 2017), these products are of great economic value. Figure 2.6 depicts the SCGs life cycle.

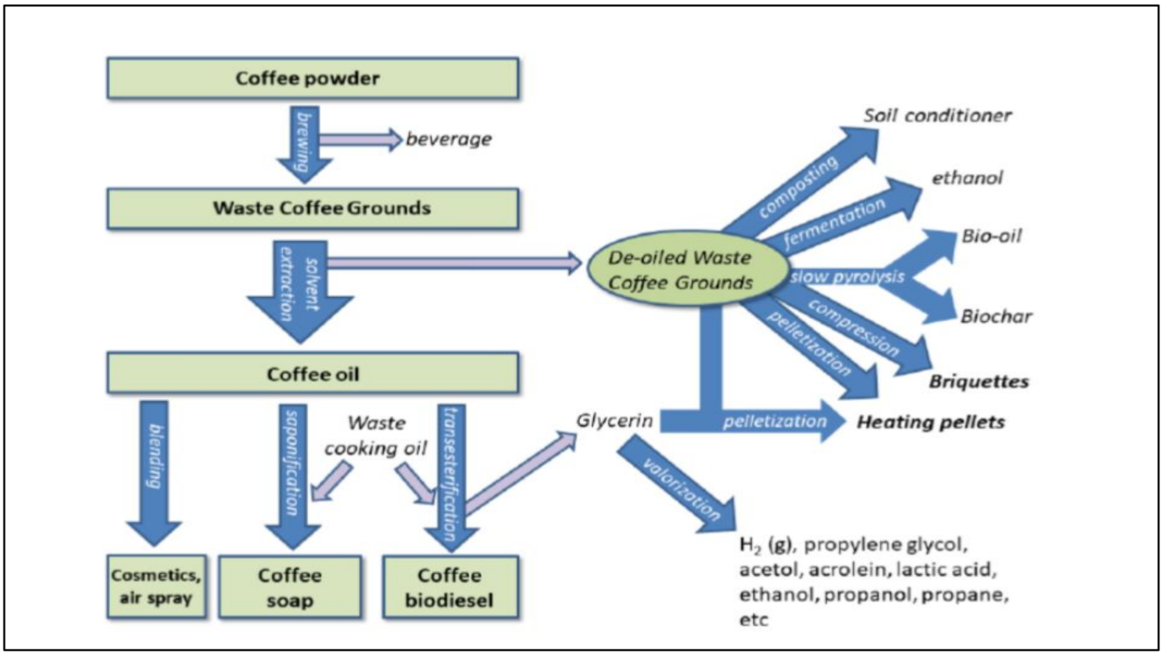


Figure 2.6: Flow chart depicting profitable and environmentally friendly life cycle of SCGs (Fadli, 2017).

Most recent studies have focused on using SCGs as a source of oil (Al-Hamamre *et al*., 2012; Abdullah and Bulent Koc, 2013; Raley, 2018) for fuel-grade hydrocarbon production. SCGs have also been suggested as a raw material for production of biochar, and bioethanol (Murthy and Naidu, 2012). Atabani *et al*. (2018), investigated the production of bio-gas, bio-oil from SCGs by pyrolysis. Relative to other biomass materials SCGs has a high energy content, high oil content and high carbohydrates thus making SCGs one of the most valuable biomass in the world (Raley, 2018).

2.4 Oil in SCGs

SCGs have been reported to contain between 6 – 27.80 wt% of oil on a dry basis, with most researchers reporting 10 – 18 wt% of lipids on a dry basis (Campos-Vega *et al*., 2015). SCGs from retail coffee shops have been reported to contain between 6 – 21.50 wt% of oil on a dry basis (Abdullah and Bulent Koc, 2013; Caetano *et al*., 2014; Akgün *et al.*, 2014; Go *et al*., 2016). SCGs from espresso machines have been reported to contain about 7.50 – 18.30 wt% of oil on a dry basis (Cruz *et al*., 2012; Pichai and Krit, 2015; Somnuk *et al*., 2017) and SCGs produced from instant coffee brewing have been reported to contain about 19.90 – 27.80 wt% of lipids on dry basis (Acevedo *et al*., 2013). The quantity of oil extracted from SCGs is strongly affected by the extraction method and the extraction conditions (Al-Hamamre *et al*., 2012; Caetano *et al*., 2014; Campos-Vega *et al*., 2015).

SCGs oil mainly contains triglycerides, usually above 80 wt% of the total oil and smaller and varying quantities of diglycerides and free fatty acids (FFA). The glycerides’ part accounting for 80− 95 wt% of the total oil (Campos-Vega *et al.*, 2015; Pichai and Krit, 2015). The remaining constituents of SCGs oil are made up of a relatively large proportion of unsaponifiable compounds such as phospholipids, glycolipids diterpenes (12.30 wt%), tocopherols, sterols (1.90 wt%), and waxes (Campos-Vega *et al.*, 2015). Jenkins *et al.* (2014), found that the unsaponifiable component of the oil extracted from the SCGs was on an interval of 0.1 − 40 wt% depending on the origin of the coffee beans, and different methods of harvesting and drying.

According to Al-Hamamre *et al.* (2012) oil extracted from SCGs contains antioxidants, which increase the stability of the oil thus prevent oil decomposition. This can be attributed to the nitrogenous, brown-coloured compounds of coffee, which are products of Maillard reactions. This shows the antioxidants capacity and the ability to hinder lipid peroxidation. The diterpenes kahweol ($C_{20}H_{26}O_3$) and cafestol ($C_{20}H_{28}O_3$) and phenolic compounds within the coffee lipids such as sinapic acid, p-coumaric acid, ferulic acid, vanillic acid, caffeic acid, and chlorogenic acid are also recognised for their antioxidant activity (Acevedo *et al.*, 2013; Campos-Vega *et al.*, 2015).

Free fatty acids are defined as those fatty acids which are not attached to any glycerol backbone and they can be found in oil recovered from SCGs, in different concentrations. FFA quantities ranging between 3 − 20 wt% are common (Vardon *et al.*, 2013; Kwon *et al.*, 2013; Haile *et al.*, 2013; *Go et al.*, 2016). However, values as low as 0.30 − 0.40 wt% have been reported by Pichai and Krit (2015), and values as high as 59 wt% have also been reported (Caetano *et al.*, 2012; Caetano *et al.*, 2013; Caetano *et al.*, 2014), suggesting a significant difference in the composition of the oil recovered from different SCGs with different extraction parameters. The free fatty acid level in the oil is an important quality factor. According to Al-Hamamre *et al.* (2012), high quantities of FFA increase the acid value, the kinematic viscosity of the oil, and makes it susceptible to oxidation thus accelerating the oil degradation rate.

Oil extracted from SCGs contains not only saturated but also unsaturated fatty acids (FA) and is primarily composed of palmitic, oleic, stearic, and linoleic acids in proportions different from those found in other common edible oilseed crops such as soybean and sunflower oil (Abdullah and Bulent Koc, 2013; Bulent Koc and Fereidouni, 2013; Haile, 2014; Jenkins *et al*., 2014). Eicosanoic and linolenic acids are also found in oil extracted from SCGs, while myristic and lauric acids are present in certain lipids depending on the geographic origin of the sample, processing, and oil recovery conditions used (Campos-Vega *et al*., 2015). In addition, in some SCGs oils, linoleic acid is present at the highest concentration of all the detected FA, while in some samples palmitic acids can be found in greater concentrations than that of linoleic acid. SCGs oils can be classified into two categories based on their FA composition, those with low palmitic (< 40%) and high linoleic (>40%) acid and those high palmitic (>40%) and low linoleic (< 40%) acids (Martín *et al*. 2001). These variations in compositions are probably caused by the differences in the origin of the coffee samples, especially the climatic conditions during the growth period of the coffee plant and the different mixtures of coffee that may have been used during brewing (Martín *et al*., 2001; Budryn *et al*., 2012).

Due to the quality, quantity, and composition of the oil extracted from SCGs, it is considered an attractive material by the food and pharmaceutical industries (Acevedo *et al*., 2013). Oil extracted from SCGs have some health benefits of the antioxidant's activity due to the polyphenols present (Ribeiro *et al*., 2013). The presence of palmitic acid in the oil extracted from the SCGs make it a suitable source for soap production. Furthermore, the SCGs oil has attracted attention from the cosmetic industry since palmitic acid provides good skin protection as a sun filter (Acevedo *et al*., 2013).

Physiochemical properties of SCGs oil such, as density, kinematic viscosity, saponification value, water, and sulfur content which are integral for utilisation of the oil in FAME production or as a direct fuel for diesel engines have been formerly studied (Abdullah and Bulent Koc, 2013). Oil density has been reported by Mebrahtu *et al*. (2013); Abdullah and Bulent Koc (2013) and Caetano *et al*. (2013) to range between 890 − 1149 kg/m^3 at 25 °C .The same authors reported the values of kinematic viscosity to range between 14.90 – 62 mm^2/s at 20 °C, water content has been reported to be in the interval of 0.03 − 1.78 wt%, sulfur content was reported to be very small (in most cases to be zero) and the saponification value was reported to range between 167.28 – 222.60 mg$_{KOH}$/g. High kinematic viscosity and density make the SCGs oil ineligible for direct use as fuel in diesel engines since it will polymerize and lead to formation deposits in the engine (Mebrahtu, 2014). The SCGs oil however has the potential of being used as a feedstock in FAME production. For a feedstock material to be considered viable for use in FAME production the raw material must be readily available; cheap, non-edible and must have high oil quantity, SCGs are said to meet all these requirements mentioned. Table 2.3 adapted from Binyam *et al*. (2018), depicts the oil quantities of different raw materials normally used in FAME production.

Table 2.3: Oil content of different raw materials (Binyam *et al*., 2018)

Material	Oil content (wt%)
Spent coffee grounds	11−20
Olives	10−30
Sunflower	22−36
Cotton seeds	22−36
Soybeans	20
Jatropha	25−40
Corn	2.8
Rapeseed and Palm	40

With regards to SA, taking the average oil content of SCGs as 16 wt% on dry basis and that 17 million kg of SCGs are recovered annually in SA, approximately 2.72 million kg of oil can be recovered, and 4.5 million kg of heating pellets can be produced per year (Frankson, 2019). SA is believed to have the largest unused biomass sources in the world (Bajaj *et al*., 2010). The FAME development in SA is still at its infancy stage but has provoked many debates amongst policymakers and development practitioners (Bajaj *et al*., 2010). Verda Waste a SA recycling company has taken the initiative, to investigate and invest in the utilisation of SCGs as a source of oil for fuel grade hydrocarbons and fire pellets production (Frankson, 2019).

2.5 Oil extraction techniques

Oil extraction is a vital step in the valorisation of SCGs since the methods used for the extraction does not only affect the oil yield but also the oil's physical and chemical properties (Al-Hamamre *et al*., 2012). Several oil extraction methods from SCGs have been studied, these methods include, microwave extraction, supercritical fluid extraction (SFE), ultrasound extraction, and Soxhlet extraction (solvent extraction). A summary of each technique is given below:"

i. Soxhlet extraction (Solvent Extraction):

This is the most used method for oil extraction from solids containing useful oil and several solvents have been studied for oil extraction from different oil-containing materials (Bhuiya *et al*., 2016; Binyam *et al*., 2018). The solvent extraction method recovers almost all the oil and leaves behind only 0.50 − 0.70 wt% residue oil in the raw material (Binyam *et al*., 2018). For spent SCGs, hexane has been successfully used in extracting the oil. Oil extraction of about 16 wt% has been recovered from SCGs with 12 wt% moisture (Al-Hamamre *et al*., 2012; Marchetti *et al*., 2017). The extraction temperature (65 °C) is normally set close to that of the boiling point of hexane. This process is referred to as leaching or solid-liquid extraction to distinguish it from Liquid – Liquid extraction. The concept of solid-liquid extraction is based on the selective nature of solute. In this case, oil from SCGs which is already in a liquid state dissolve into the solvent of the same polarity from the solid matrix (Bhuiya *et al*., 2016).

The leaching process involves three steps:(1) Penetration of the solvent into the walls of the oil-bearing material ;(2) Dissolution of the solute into the solvent; and (3) Transportation of the solute from the interior of the seed-bearing material to the solvent solid interface (Efthymiopoulos *et al*., 2019). The solute is dispersed into the bulk of the solvent through the diffusion process and agitation. Like any mass transfer process, the rate of mass transfer is determined by the length (barrier thickness) which the solvent must penetrate before interacting with the solute. This is strongly affected by the particle size (Al-Hamamre *et al*., 2012; Stroescu *et al*., 2015; Bhuiya *et al*., 2016). However small particle size will hinder the percolation of the solvent through the walls of the solid material walls, leading to fine particles of the solid material reporting into the desired solute. The mass transfer rate is also affected by the particle surface area, porosity of the material. Physical properties of the solvent, such as viscosity and diffusivity also affect the mass transfer rate (Stroescu *et al*., 2015). Therefore, selection of a suitable solvent is of great importance. To optimise the oil extraction process, the effect of five main factors should be considered. These factors include extraction temperature, solvent to solid ratio, extraction time, particle size, and solvent composition (Stroescu *et al*., 2015).

Oil extraction from spherical particles in excess solvent is best analysed by a dynamic model (Stroescu *et al*., 2015; Hatzilyberis *et al*., 2018). The oil extraction process occurs by moving the solute free phase interface towards the centre of the oil-bearing particles. Generally, the dynamic behaviour of oil extraction is governed by the shrinking core model (Stroescu *et al*., 2015). As a consequence of a shrinking core, it is assumed that the oil dissolution process is controlled by a kinetic process, which is of first order given by equation 2.1, and can be numerically solved.

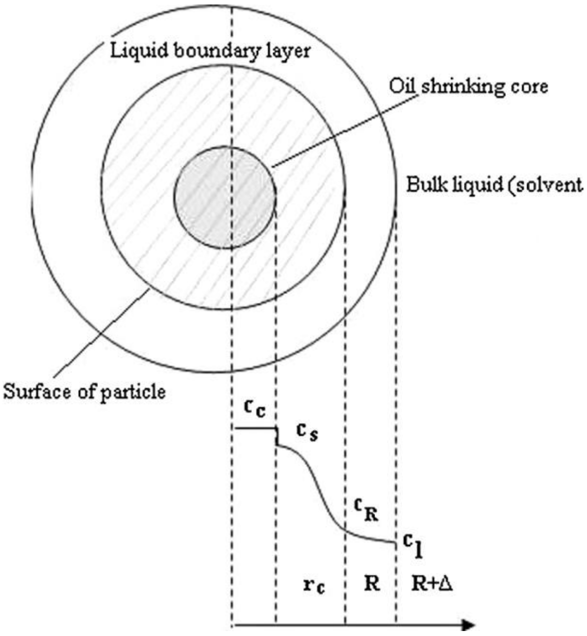


Figure 2.7: Schematic representation of oil extraction from a porous spherical seed (Stroescu *et al*., 2015).

The basic principle of the shrinking core model of oil extraction from a spherical oil-bearing particle is depicted in Figure 2.7. The dissolution rate of the oil into the extraction solvent is determined by the mass transfer rate of oil from the solid matrix into the solvent (Hatzilyberis *et al*., 2018; Hibbert, 2019). The flux of oil transpires because of the concentration gradient which occurs due to the oil concentration difference between the solid-liquid interface, described by Fick's law for steady state, and the isothermal process, given by equation 2.1. For in-depth reading on the shrinking core model, the reader is encouraged to refer to (Stroescu *et al*., 2015) and (Hatzilyberis *et al*., 2018).

$$\frac{dC_t}{dt} = kA(C_C - C_1) \qquad (2.1)$$

where C_1 = is the bulk oil concentration dissolved in a solvent.

C_c = is the oil concentration in centre of the particle.

k = is the average mass transfer coefficient.

A = is the particle surface are, which varies with the particle radius.

C_t = oil transfer rate from the particle

The highest possible oil concentration in the solvent is the oil saturation concentration (C_1) therefore it is imperative to keep the solvent to solid ratio as high as possible. This will ensure that the highest concentration of the oil, in the resulting solution will be below saturation when equilibrium is reached thus maximising the oil recovery. Equilibrium is reached when the concentration of oil is the same in the solvent and oil-bearing material. In industries, the oil extraction process is carried out in multiple stages with fresh or recycled solvent to achieve an oil concentrated solution (Seader and Henley, 2005; Berk, 2013). To reduce the number of extraction stages, the solute must be readily soluble in the selected solvent (Seader and Henley, 2005; Berk, 2013). The norm is that non-polar solvents are used for the recovery of non-polar solutes, conforming to the general chemistry principle, which states that like dissolves like.

With regards to the molecular process involved in the solvent recovery of oil from seeds. The non-polar triglycerides are initially desorbed from their sites from the oil-bearing sites, in an endothermic reaction and disperse through the organic part of the matrix to get to the matrix solvent interface (Mustafa and Turner, 2011; Freeman *et al*., 2011). Subsequently, the oil molecules diffuse into the solvent and energy is required to sever the solvent molecules to accommodate the solute molecules. Polar solvents requiring more energy than non-polar solvents, due to stronger intermolecular forces (Mustafa and Turner, 2011). In the final step, the solvent and oil molecules interrelate in an exothermic process, releasing high amounts of energy when a polar solvent is used. The oil molecules can only be dissolved in the solvent when the intermolecular forces of attraction between the solvent and the oil molecules, can overcome the intermolecular forces of the oil-solvent solution (Reichard and Welton, 2010).

Numerous studies have been conducted on oil extraction from oil-bearing seeds, using a Soxhlet and hexane as solvent (Deligiannis *et al*., 2011; Al-Hamamre *et al*., 2012; Abdullah and Bulent Koc, 2013; Binyam *et al*., 2018). Soxhlet extraction is commonly used as the baseline for most studies and a datum when other extraction methods are investigated. Soxhlet oil recovery involves the solubilisation of oil present in the SCGs by a liquid organic solvent and it is separated from the solvent wetted SCGs through multiple cycles of evaporation and condensation of the solvent (Efthymiopoulos *et al*., 2019). Hexane is considered to be the most effective solvent in studies that have been conducted (Al-Hamamre *et al*., 2012; Abdullah and Bulent Koc, 2013; Binyam *et al*., 2018). Table 2.3 depicts the oil yield obtained from SCGs using hexane as a solvent, including other information about the solid to solvent ratio, process duration, and FFA content.

Table 2.4: Soxhlet, hexane oil extraction yield on a dry basis with other related parameters.

References	SCGs to solvent ratio	Process duration(hr)	Oil yield(wt%)	Oil FFA content
Fadli (2017)	1:4	1	11.10	-
Al-Hamamre *et al*. (2012)	1:4.20	0.25 – 0.50	11.30	3.65
Caetano *et al.* (2012)	1:20	2.50 – 9.50	16.00	5.90
Binyam *et al*. (2018)	1:5.30	6.00	15.30	2.50
Boualdab (2016)	1:3.30	2.67	8.80	2.01

The differences in experimental conditions, such as extraction time, solid to solvent ratio, particle size, solvent composition, solvent pressure, and extraction temperature used by different researchers in their studies pose difficulties in comparing the results from previous studies. The effect of these conditions will be discussed in section 2.6. The advantage of this method (solvent Soxhlet) is that it is easy to handle and it is used as a traditional method for certification of standard materials thus it is a well-established method with cheap and good recoveries (Blinová *et al*., 2017). The drawbacks of this method that it requires a high volume of solvent, long extraction time, and thimble conditioning (Binyam *et al*., 2018).

ii. Supercritical fluid extraction (SFE):

This technique is relatively new, it is used to separate mixtures, sing a supercritical liquid as a solvent. This eliminates the problems associated with traditional solvent extraction processes. This method was initially developed for solid particle recoveries, but it can also be applied for liquids (Binyam *et al*., 2018). Carbon dioxide is the most used supercritical fluid, sometimes modified with a co-solvent such as ethanol or methanol. Carbon dioxide is used because it is cheap, non-flammable, safe, has a high oil extraction rate, and 100% oil extraction is achieved. However, the use of this method requires high-pressure equipment (78 bar minimum at 31.85 °C) Binyam *et al*. (2018). The other problem is that the oil containing material must be freeze-dried and have a moisture content < 20 wt% (Ahangari and Sargolzaei, 2013; Cardoso *et al*., 2013).

A study conducted by Couto *et al*. (2009) extracted oil from SCGs in the pressure range of 150 − 300 bar at temperatures in the intervals 39.85 − 59.85 °C and established that the oil extraction efficiency increased with pressure increase at a constant temperature. This coincided with the studies conducted by Ahangari and Sargolzaei (2013) and Akgün *et al*. (2014) who carried out SFE experiments with SCGs at similar temperatures 32.85 − 66.85 °C and pressures ranging between intervals 200 – 300 bar and 116 – 284 bar respectively. These observations were indistinguishable to those found during SFE of oil from food residues (Reverchon and De Marco, 2006), and can be attributed to the increased density of carbon dioxide at high pressures which results in increased capacity for solubilisation of lipids (Ahangari and Sargolzaei, 2013; Akgün *et al*., 2014).

The temperature effect is more complex since the temperature increase is accompanied by a decrease in the density of the supercritical fluid thus decreasing the oil extraction efficiency. But this also increases the dissolution of the oil (Couto *et al*., 2009). The effect of varying SFE temperature has been reported in previous studies and it has been observed that the lipid extraction efficiency decreased with an increase in temperature (Ahangari and Sargolzaei, 2013). A study conducted by Couto *et al*. (2013) advocated that the oil extraction efficiency increases with an increase in temperature, when the process pressure was in the interval of 250 – 300 bar. They observed decrease in oil extraction at 200 bar. The dissolution of oil has been reported to be independent of the supercritical fluid extraction temperature at pressures above 300 bar (Akgün *et al*., 2014).

Preceding studies that have investigated the use of SFE for recovering oil from SCGs concur that the addition of a co-solvent improves the oil extraction efficiency. This is likely caused by the increased solvent density (Couto *et al*., 2009; Ahangari and Sargolzaei, 2013). Moreover, Ahangari and Sargolzaei (2013) compared different liquids such as water, hexane, and ethanol as possible SFE co-solvents and found hexane to be the most effective in terms of oil extraction. Followed by ethanol and lastly water, with improvement in oil extraction observed with increase in co-solvent ratio.

iii. Ultrasound-assisted extraction (UAE):

This process is efficient in extracting oil from oil bearing seeds and has been applied in oil recovery from different seeds such as soybean and coffee seeds. Using high-intensity ultrasound with a two-phase oil recovery process can improve the oil recovery from oil-bearing seeds with high moistures (Al-Hamamre *et al*., 2012). The added advantage of this process is that the solvent can be recovered, under a moderate vacuum when the extraction process is complete and be used in the next oil extraction batch (Abdullah and Bulent Koc, 2013). The problem with this technique is that it is expensive and has a poor solvent recovery. On the bright side of this method is that, it has a short oil extraction time and low solvent usage, and is easy to use (Bhuiya *et al*., 2016).

UAE was tested by Rocha *et al*. (2014), they extracted oil from dry SCGs by suspended them in hexane, achieving 12 wt% oil recoveries. Abdullah and Bulent Koc (2013) tested oil extraction from wet SCGs using two-phase solvent extraction (methanol and hexane) amplified with ultra-sonication at room temperature and recovered 98 wt% of the available oil in 0.5 h. The oil extracted using this method is almost identical to that achieved by the Soxhlet (Efthymiopoulos *et al*. 2019). It has been reported that the use of UAE in Soxhlet extraction does not enhance the oil extraction efficiency from SCGs Caetano *et al*. (2014).

iv Microwave-assisted extraction (MAE):

This is a new technique for oil extraction, which combines microwaves and traditional solvent extraction (Hao *et al*., 2002). MAE has several advantages over other extraction methods, such as low costs, less solvent requirement, higher oil recovery rate, lower energy consumption, and shorter oil extraction time (Cardoso *et al*., 2013). This technique has shown a tremendous promise on feedstocks like pumpkin seeds, with 64.17 % oil recovery (Binyam *et al*., 2018). The disadvantage of this method is that it is a single-step extraction, which means un-extracted oil requires a new solvent for the same sample.

Hibbert *et al*. (2019), extracted oil from SCGs using the MAE method at different time intervals, while varying process parameters such as solvent volume, extraction temperature and found that each of these parameters had an effect of the oil extraction efficiency. Oil extraction of 11.54 wt% was achieved in 10 minutes, using 160 ml of hexane at 95 °C. MAE was successful in recovering more oil than the Soxhlet extraction and achieved a 24-fold decrease in oil extraction time relative to the Soxhlet extraction. The drawback of all these techniques is that they all require solid moistures < 10 wt%, which imposes significant costs on the process of financial feasibility since drying is a very expensive process.

2.6 Parameters affecting the oil extraction efficiency from SCGs

Several parameters must be optimised to achieve good oil recovery from SCGs. These parameters include the oil extraction period, solvent to solid ratio, SCGs moisture content, solvent composition, and SCGs particle size. These parameters are briefly discussed below:

i. Solvent to solid ratio:

The solvent-to-solid ratio is a critical parameter, since it affects both the economics of the process and the oil recovery efficiency. The amount of solvent used must not be more than the critical value, because this might lead to a high cost of solvent recovery which increases the operating costs of the process. Pichai and Krit (2015) investigated the SCGs-to-hexane mass ratio of 1:5.1 and 1:25 and observed a decrease in the SCGs to solvent ratio and improved lipid yield. This observation was attributed to improved diffusion and flow of oil through the surface of the SCGs for an increase in solvent quantity.

Najdanovic-Visak *et al.* (2017) conducted a study where the effect of SCGs to hexane ratio was investigated. The SCGs were suspended in a solvent at 60 °C and it was observed that a decrease in SCGs-to-solvent ratio from 1:80 − 1:15 wt% resulted in an improved oil yield. It was also observed that a further decrease in the SCGs-to-oil ratio to 1:25 wt% increased the oil yield significantly. In another study conducted out by Rocha *et al*. (2014) where they tested the effect of SCGs-to-solvent ratio on oil extraction efficiency. The same relationship was seen in an ultrasound-assisted extraction trial, where SCGs-to-hexane ratio was decreased from 1:20−1:40 w/v and 1:10−1:20 w/v respectively. It was also observed that the lowest of the tested ratios resulted in the highest oil recovery.

The effect of solids to solvent ratio on oil extraction efficiency was also studied with other oilseeds such as jatropha, soybean, sunflower, and cottonseeds with contrasting results (Sayyar *et al.*, 2009). Bulent Koc and Fereidouni (2011) investigated the effect of solids-to-solvent ratio on oil yield from soybean seed through an ultrasound-assisted Soxhlet extraction. They observed that the decrease in the solids-to-solvent ratio from 1:10 − 1:20 w/v increased the oil yield. Similar observations were made when extracting oil from sunflower seeds.

ii. SCGs moisture content:

High moisture content can have a significant disadvantage on the economic value of SCGs, as a potential feedstock for fuel-grade hydrocarbons production, especially in the oil extraction's point of view since most oil extraction methods require a dry feedstock (Al-Hamamre *et al*., 2012). Moreover, SCGs can be used to make fire pellets for home heating, therefore it needs to be dried to increase their calorific value and improve combustion efficiency (Gómez-De La Cruz *et al*., 2015). Normally SCGs have a high amount of water ranging between 75 − 85 wt% depending on the brewing process used (Al-Hamamre *et al*., 2012), although low moisture contents ranging between 18 − 45 wt% have been reported (Deligiannis *et al*., 2011). To reduce moisture content, SCGs are generally subjected to thermal drying at temperatures ranging from, 50 −105 °C for 24 to 48 h or left to dry at ambient temperature until the moisture content is fixed (Boualdab, 2016; Blinová *et al*., 2017). The relationship between SCGs drying time, drying temperature, and sample thickness was studied by Gómez-De La Cruz *et al.* (2015). Their investigation was carried out using a sample thickness ranging from 2 − 20 mm in a drying convective oven for a period of 4.20 h. They used a drying temperature range of 100 − 250 °C. They observed that the drying period decrease with an increase in temperature and increase with an increase in sample thickness (Efthymiopoulos *et al*., 2019).

Depending on the required moisture levels in the SCGs, the mechanical expression can also be used for dewatering the solids at ambient temperature or may be combined with the thermal drying process. The combination of these two drying processes is used when the solids being dried are for subsequent oil extraction or directly used as heating pellets (Efthymiopoulos, 2018). The mechanical expression has been used in dewatering of SCGs. Reducing the water content by 63 wt%, at 600 bars and ram press ram speed of 500 mm/min at room temperature (Efthymiopoulos *et al*., 2019). Once the moisture quantity has been reduced to acceptable levels, maximum oil can be extracted from oilseed crops or biomass.

Both oil and water can wet the solid part of the SCGs although the two have different affinities. Water has a relatively higher infinity than oil and wets particle surfaces faster than oil due to its polarity and absorption ability (Binyam *et al*., 2018). Some researchers have proved that solids are selectively wetted by liquids with lower surface tension at the interface thus water will tend to displace oil from the surface of the solid (Bajaj *et al*., 2010). According to Binyam *et al.* (2018) at a certain moisture content, the surface of the particles become saturated by water and oil has the freedom to move freely due to weakening molecular forces. Therefore, high moisture content increases the flow of the oil through the pores of the particles, thus the amount of oil in the particles and the bulk sample is reduced, resulting in an increase in oil yield, particularly in mechanical expression.

The effect of moisture content on oil extraction efficiency from SCGs treated with hexane using a Soxhlet has been studied by Caetano *et al*. (2014), with a moisture content of 65.70 wt% significantly inhibited the oil extraction process, leading to oil with higher density and viscosity compared to oil extracted from dried SCGs. In a study conducted by Najdanovic-Visak *et al*. (2017), SCGs with moisture content ranging between 0−50 wt% were suspended in hexane at 60 °C for 1 h and observed a decrease in oil extraction as moisture content increased. Abdullah and Bulent Koc (2013) successfully recovered lipids from SCGs with 67 wt% moisture content by using a two-step ultrasound-assisted extraction method and found no effect of water present in the SCGs on oil extraction efficiency.

Previous studies conducted on oil extraction from other oil-bearing seeds have shown that moisture contents of 9 −11 wt% resulted in maximum oil yields, with higher levels of moisture found to hinder solvent penetration and oil diffusion, specifically with hexane since it is highly insoluble in water. Feedstocks containing lower moisture content were observed to result in lower yields due to diminished solubility of phosphatides in the absence of moisture (Lawson *et al*., 2010). Ali and Watson (2014) investigated the Soxhlet solvent extraction of lipids using ethanol as a solvent from partially dried flax seeds with water content up to 12 wt% and reported a decrease in oil extraction efficiency with an increase in moisture content.

iii. Effect of particle size:

Particle size plays a crucial role in the yield of oil from solids. Oil yield from small particles tends to be higher. The reason is that larger particles have a small contact surface area, with high resistance to solvent penetration and oil diffusion towards the solvent. Therefore, less oil will be transferred from inside the larger particles into the bulk solution in comparison to the smaller ones. An increase in particle size decreases the oil yield but too fine particles will prevent the solvent from percolating through the mass (Binyam *et al*., 2018). Therefore, optimum particle size is to be maintained for the best extraction.

Go *et al*. (2016) carried out a study using SCGs, a Soxhlet with two samples of SCGs average particle size (diameter) of 430.50 − 32.30 µm and 374.70 − 8.30 µm and obtained yields of 16.51 − 0.73 wt% and 13.78 − 0.43 wt% respectively. Although the difference in oil yield may be attributed to other factors like the origin of the SCGs and the method used in coffee beverage making processing some reports have suggested that the oil yield is not affected by the method used during the coffee drinks making step. A study conducted by Sayyar *et al*. (2009) investigated oil extraction from jatropha seeds with different particle sizes and found that particle sizes ranging from 500 – 750 µm resulted in the highest oil yields.

iv. Oil extraction period:

The yield of oil is directly linked to the extraction time. The general perception is that the longer the extraction time the higher the yield of oil and the inverse is true. However, in a study conducted by Go *et al*. (2016) where oil was extracted from SCGs using the Soxhlet method it was found that 2 h of extraction was sufficient for maximum oil yield. It was also observed that extending the extraction duration time to 8 h did not increase the quantity of oil extracted. Pichai and Krit (2015), investigated the effect oil extraction period by suspending SCGs in hexane for 0.66 h and obtained oil yields ranging between 12.66 − 14.63 wt% at a constant solvent to SCGs ratio of 15:1 wt%. This showed a small benefit of increasing oil extraction period on the oil extraction efficiency. Sayyar *et al*. (2009) investigated the extraction of oil duration from jatropha seeds using a Soxhlet and observed that most oils were extracted after 6 h however a slight increase in oil yield was obtained after 8 h.

The effect of extraction period on oil yield obtained from other oil-bearing seeds such as sunflower, soybean, and cotton by Soxhlet solvent extraction have been previously studied, with oil extraction period between 3.50 − 5 h found to be the optimum range. A shorter extraction time reduced the oil yield. Increasing the extraction period beyond 5 h did not further increase the oil yield obtained (Lawson *et al*., 2010).

v. Effect of temperature:

Temperature plays a crucial role in the oil recovery process. It reduces the viscosity of oil and releases the oil from the solid cells. Temperature assists in speeding up the oil extraction process, reducing the moisture in the cell, further increasing the oil yield. At optimum temperature and minimum moisture content, individual oil droplets quickly come together to form a uniform layer (Binyam *et al.*, 2018). The impact of temperature on solvent extraction of oil from SCGs has been studied by Rocha *et al.* (2014), through ultrasound-assisted Soxhlet extraction. At temperatures between 20 − 60 °C, the highest yield can be achieved. Najdanovic-Visak *et al.* (2017), also observed the same correlation between temperature increase and oil extraction efficiency, through suspension of SCGs in hexane for a temperature range of 25 − 65 °C. In solvent extraction, the extraction temperature is dependent on the boiling temperature of the solvent used thus temperature cannot be taken as an exogenous parameter of the process.

Generally, an increase in temperature results in an increase in solubility of oil, thus resulting in high oil extraction. This is due to the high average kinetic energy of the solvent molecules, which increases the probability of effective collisions between the solute and solvent molecules. These effective collisions facilitate the excellent diffusion rate of the oil. Some reports suggest that high oil extraction temperatures 100 − 200 °C might potentially decrease the selectivity of the process, resulting in the extraction of bound oil, impurities, and cell wall constituents such as mannans and arabinogalactans (Campos -Vega *et al.*, 2015; Verhagen, 2018).

vi. Effect of solvent pressure:

Most oil extraction processes are carried out at atmospheric pressure, except microwave-assisted extraction. Which can be achieved at pressures higher than the atmospheric pressure (Efthymiopoulos, 2018). In general, the increase in pressure favours the penetration of the solvent into the matrix pores and improves solubility and desorption kinetics, resulting in improved oil extraction efficiency (Mustafa and Turner, 2011). Although the increase in pressure may increase solvent viscosity and surface tension (Mustafa and Turner, 2011). According to some studies, the effect of pressure is of no great importance, having only one advantage which is enabling the solvent to remain in the liquid phase at temperatures above its normal boiling point (Efthymiopoulos *et al.*, 2019).

The effect of pressure on oil extraction efficiency has been studied in the case of accelerated solvent extraction of lipids from pistachio and rice bran. The impact of pressure,10−150 bar on the extraction from pistachio oil with hexane at 60 °C was found to be of no significance (Sheibani *et al.*, 2008). However, Jalilvand *et al.* (2013) investigated the dynamic accelerated solvent extraction on rice bran oil with hexane at temperatures from 40 − 80 °C and pressure ranging from 20 −140 bars and observed that the oil yield increased significantly with the increase in pressure up to 75 bars, with further increase in pressure decreasing the oil extraction efficiency. Furthermore, pressurized fluid extraction of essential oil from Lavandula angustifolia using ethanol as a solvent at temperatures ranging between $60 - 100$ °C showed that pressure increased from $10 - 36$ bars increasing the oil extraction efficiency, with a further increase in pressure to 50 bars not affecting the oil extraction efficiency (Kamali *et al*., 2014).

vii. Effect of solvent composition:

In a study conducted by Al-Hamamre *et al*. (2012) pentane, hexane, toluene, chloroform, acetone, isopropanol, and ethanol were used in Soxhlet oil extraction from SCGs, they found that hexane recovered the highest amount of oil (15.28 wt%) with chloroform yielding the lowest oil recovery (8.60 wt%). It was also observed polar solvents generally resulted in lower oil yield relative to non-polar solvents, moreover polar solvents resulted in extraction of black gummy material. It was adjudicated that the gummy material might be made up of carbohydrates, proteins, and other constituents produced by complexes of fatty acids and carbohydrates breakdown which may hinder the oil extraction process (Al-Hamamre *et al*., 2012).

Somnuk *et al*. (2017) dipped the SCGs in hexane, methanol, and ethanol in an attempt to recover as much oil as possible and found hexane to be the most efficient with ethanol being the less efficient solvent, with yields of 14.70 wt% and 7.50 wt% respectively. The selected solvent has been observed to somewhat affect the density of the extracted oil, however significantly increased the kinetic viscosity of the oil (Al-Hamamre *et al*., 2012), this may be attributed to the increase in solubility of SCGs polar constituents in isopropanol.

In conclusion, non-polar solvents are suitable for oil extraction from solids compared to polar solvents, due to the absence of strong polar charges which allows for easier penetration of the solvent into the low polar matrix of SCGs (Akgün *et al*., 2014). The challenge with polar solvents such as alcohols tends to extract high amounts of FFA and other undesired by-products like proteins, Maillard reaction products, carbohydrates, phosphatides, and other continuities (Al-Hamamre *et al*., 2012).

The other challenge with polar solvents is that they have a high boiling point requiring a significant amount of energy, while low boiling point solvents are prone to significant losses during the extraction process. When selecting a solvent, the solvent availability and cost should be taken into account (Al-Hamamre *et al*., 2012). The solvent selection also affects the average chain length of the fatty acids and the number of ester bonds in the oil chain as given by the saponification value ranging from 173.90 − 222.60 mg_{KOH}/g and the ester value ranging from 166.60 − 213.50 mg_{KOH}/g, while slightly affecting the oil elemental composition (Ali and Watson, 2014).

2.7 Green solvents

For biofuels to be fully considered green and environmentally friendly, they must be solely produced from renewable components without harming the environment (Chemat e*t al*., 2019). Oil recovery from oil-bearing material for fuel grade hydrocarbons production, petroleum-based solvents such as hexane, propane, trichloroethylene, etc., are dominantly used and these solvents have a detrimental effect on the environment and are relatively expensive (Shanab *et al*., 2013). Utilisation of petroleum base solvents renders FAME as a partial green fuel, thus in-depth investigation into green solvents is required (Shanab *et al*., 2013). According to Chemat *et al*. (2019), an ideal solvent suitable for green oil extraction should meet the twelve criteria proposed in the principles of green chemistry. To list a few: (1) The solvent should have a high solvency rate, a high flash point with very low toxicity, and low environmental impact. (2) It must be eco-friendly and be obtained from infinite (non-petrochemical) resources at an economical price. (3) It should be easy to recycle without any detrimental effect on the environment and should be easy to produce. Therefore, finding a perfect solvent that certifies all the aforementioned requirements is a challenging task, such that the decision for the optimum solvent is likely to be compromised depending on the process requirements (Shanab *et al*., 2013).

Currently, there are five groups of chemical species thought to meet most of the aforementioned green solvent requirements namely supercritical water; supercritical carbon dioxide, ionic liquids, fluorous solvents, and bio-solvents (Shanab *et al*., 2013). However, some authors do not consider ionic liquids as green solvents due to the high energy demand and multiple steps required to make them (Jessop, 2011). The challenge of using supercritical water and supercritical carbon dioxide as solvents is that they require high temperatures and pressure to make, thus making them expensive. Water must be heated and kept at 374 °C at 221 bar and carbon dioxide must be heated and maintained at 31 °C at 78 bars to produce the supercritical solvents (DeSimone, 2002; Shanab *et al*. 2013), which limits their use. Fluorous solvents (solvents containing fluorine with a relatively large component in their molecule) are not widely used because of their high cost, environmental persistence, and biological half-lives, especially of C7- and C8-perfluoroalkyl group-containing compounds (Dobbs and Kimberley, 2002; Sheldon, 2005; Shanab *et al*., 2013). Bio-solvents have gained a lot of interest in recent years since they meet almost all the stipulated green solvent requirements apart from being mildly toxic (Bandres *et al*., 2011).

As the name indicates, organic solvents are produced from agricultural biomass. Depending on agricultural sources of the biomass used to manufacture these solvents, they can be mainly divided into four classes:(1) lignocellulosic (2) sugar and starch (3) protein and oil-based (4) other forestry and food waste (Calvo and María, 2018). The solvents recovered from these classes can be further categorized based on their functional groups (alcohols; ethers, terpenes, and esters) or based on the traditional petroleum-based solvents they were intended to replace (Lomba and Zuriaga, 2019) as depicted in Figure 2.8.

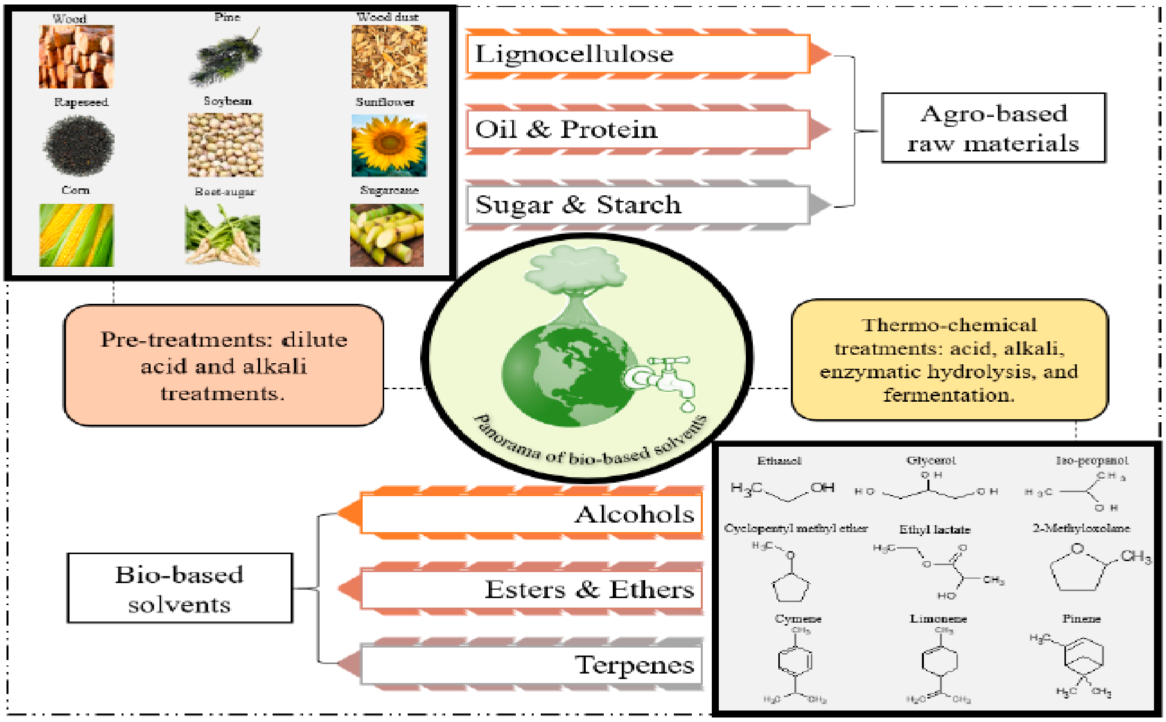


Figure 2.8: A re-view of bio-based solvents (Chemat *et al*., 2019).

The production of bio-based solvents or green solvents itself should not harm the environment. The agricultural biomass used as a feedstock in green solvent production has a rigid, fibrous structure and has to undergo a pre-treatment process and post-harvest before use. Pre-treatment coupled with the thermochemical process enables efficient processing of biomass thus making the biomass suitable for solvent production applications (Khoo, 2015).

For instance, in the production of 2-methyl tetrahydrofuran (2-MeTHF), the green solvents investigated in the current study involves three steps: (1) An acid treatment of lignocellulosic material to liberate pentose and hexose sugars, (2) Bio-refining process for conversion of sugars to furfural and levulinic acid and (3) Hydrogenation of levulinic acid with excess hydrogen (Chemat *et al*., 2019).

Chaabani *et al*. (2019) conducted a study where the quality and quantity of oil extracted from Pistacia lentiscus using 10 different green solvents, using the Soxhlet solvent extraction methods hexane as a datum solvent. The extraction period was set to 8 h for each solvent, near the boiling point of the respective solvent and conducted 3 extraction tests per solvent. It was observed that the oil quality and quantity extracted by hexane and 2-methyl tetrahydrofuran (2-MeTHF) were indistinguishable. Oil yields obtained from different solvents are depicted in Figure 2.9.

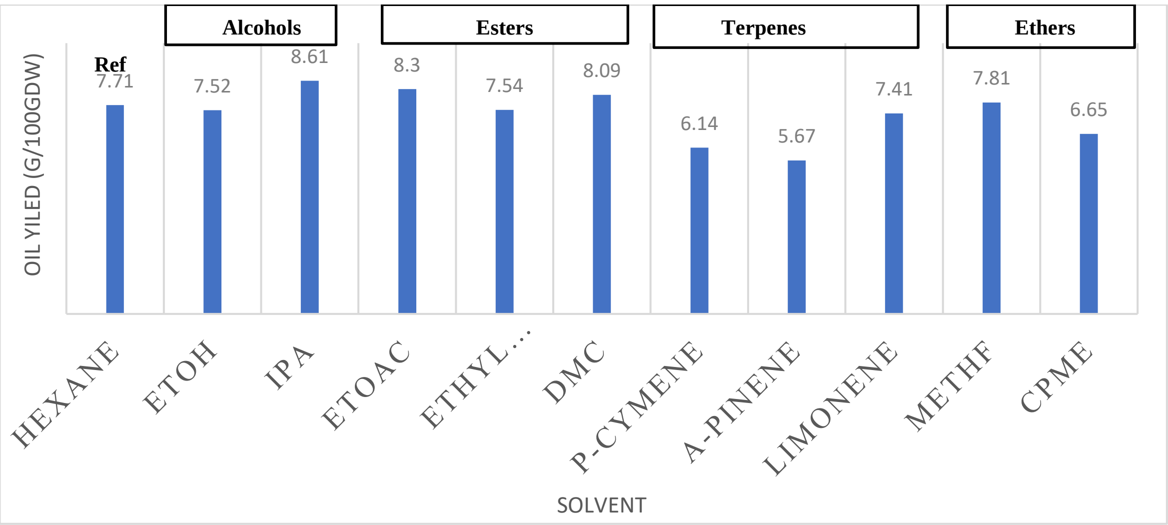


Figure 2.9: Comparison of oil extraction yield obtained by different bio-based solvents, relative to hexane (Chaabani *et al*., 2019).

Isopropyl alcohol (IPA) and dimethyl carbonate (DMC) had a high oil yield however the quality of the oil extracted by these two solvents was not as good as that of the reference solvent (hexane). Based on the quality and quantity of oil recovered by the 10 different green solvents, it was concluded that 2-MeTHF is the best green solvent to replace hexane as a solvent for edible oil extraction. This work aimed to study the capability of 2-MeTHF as a green novel solvent for oil extraction from SCGs.

2.8 SCGs oil as a substrate for fuel-grade hydrocarbons production

Oil extracted from SCGs has been suggested to be a promising substrate for cheap and high-quality fuel-grade hydrocarbons production (Al-Hamamre *et al*., 2012). The fatty acid (FA) composition of SCGs oil is strongly dependent on the moisture content of the SCGs, and the oil extraction method used. The FA composition of the oil determines the oil's fuel properties, such as oxidation stability, specific gravity, distillation characteristics, and cetane number. Once the oil is extracted from the SCGs its quality is assessed by determining the saponification, viscosity index, kinematic viscosity, density, acid value, calorific values, iodine number, water content, and elemental composition (Al-Hamamre *et al*., 2014). Oils with a high number of unsaturated bonds are prone to oxidation and formation of a slug when stored for a long time (Pandey, 2009).

The FA composition of certain oil samples is the quantity of different fatty acids present in the sample. The fatty acid composition or profile can be used to estimate both liquid and fuel properties of the FAME produced from that oil (Babajide, 2011). For instance, FAME derived from tallow, a highly saturated oil, tends to have a higher freezing point which inhibits cold flow properties. FA is described as carboxylic acids with long unbranched aliphatic chains, which are either saturated or unsaturated. FA occurs naturally in even numbers of carbon atoms from 4 to 28 (IUPAC, 1997). FA are normally obtained from triglycerides or phospholipids, when they are not attached to any molecules, they are called free fatty acids (FFA). A typical triglyceride (fat) molecule is depicted in Figure 2.10.

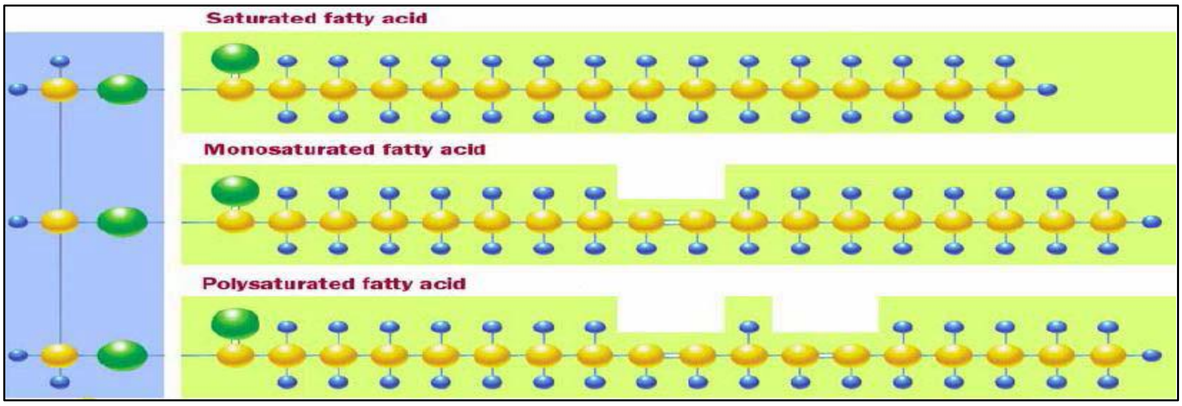


Figure 2.10: Example of a typical triglyceride molecule (Babajide, 2011)

According to Pandey (2008), vegetable oils have a relatively high viscosity (about 10 to 15 times higher that of mineral-diesel), higher flash points (about 3 to 5 times higher), and relatively lower calorific value (about 10 % less). Numerous laboratory engine tests and on-field vehicle trials have been conducted using straight chain vegetable oils as fuel in diesel engines with satisfactory results. However long-term operation of straight vegetable oil as fuel for diesel engines created problems in the combustion chamber of the engine. High oil viscosity and low vaporization characteristic of the vegetable oil resulted in combustion chamber deposition, oil ring sticking, thickening of the lubricating oil due to contamination by vegetable oil and more smoke was observed.

The atomisation of vegetable oil was observed to be poor due to its high viscosity thus affecting the spray pattern of the oil. To reduce the viscosity of vegetable oil to improve its atomization, spray pattern, and other combustion characteristics, the oil is blended with petroleum diesel, cracking of the oil microemulsion, and transesterification is used to reduce the viscosity of the oil (Tyson *et al*., 2004; Pandey, 2008). The transesterification process is the preferred method for reducing the viscosity of vegetable oil for commercial purposes (Abdullah and Bulent Koc, 2013).

Low-grade feedstocks such as waste cooking oil, animal fats, SCGs oil, etc., must undergo a quality test process before they can be used for FAME production. Due to their high phosphatides content most crude seed oils need to be degummed, this is the removal of phosphatides (Nolte, 2007; Al-Hamamre *et al*., 2012). The most critical parameters are acid and saponification values since they are directly linked to the acid quantity in the oil. The acid value indicates the total acidity or free fatty acid that is attached to the glycerol backbone. Oils with high free fatty acids (FFA >1%) need to undergo de-acidification (Mittelbach and Remschmidt, 2005). This entails the removal of excess FFA in the crude oil to less than 1mg_{KOH}/g equivalent (Nolte, 2007). FFA reduces the catalyst activity, especially the alkaline catalysts, and hinders the products separation process. Deacidification and degumming can be conducted concurrently by adding alkali catalysts like (NaOH, KOH) which reacts with the free fatty acid to form soap and in the presence of hot water causes the phosphatides to swell (Tyson *et al*., 2004).

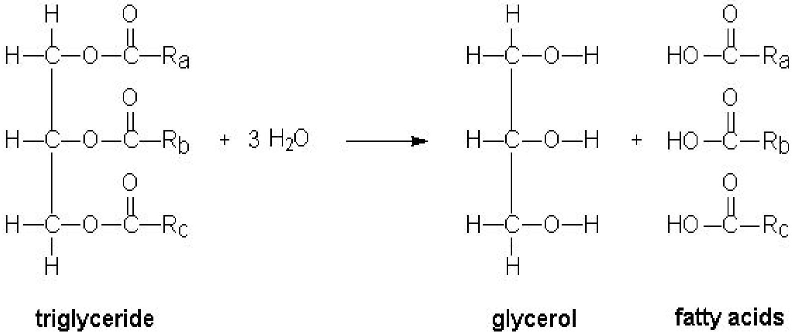
The degree of conversion of vegetable oils including SCGs oil into fuel-grade hydrocarbons is strongly affected by the quality of the oil, which is dictated by FFA quantity in the oil (Caetano *et al*., 2013; Al-Hamamre *et al*., 2013). These authors also established that an FFA content above 1−1.50 wt% on the oil hinders the alkaline methanolysis of the oil by forming stable soaps emulsion which makes the separation of products difficult (Deligiannis *et al*., 2011; Al-Hamamre *et al*., 2012). In addition, soaps bind with basic catalysts hence higher quality catalysts are required (Leung *et al*., 2010). The saponification of FFA with an alkaline catalyst, using NaOH as a catalyst is presented in equation 2.2.

$$\underset{\text{(FFA)}}{R-COOH} + \underset{\text{(catalyst)}}{NaOH} \rightarrow \underset{\text{(soap)}}{RCOONa} + \underset{\text{(water)}}{H_2O} \qquad (2.2)$$

These products can be precipitated. If the acid value of the oil is very high, such as in the SCGs oil (Al-Hamamre *et al*., 2013), the oil must be subjected to acid-catalysed esterification pre-treatment with methanol or ethanol (Mittelbach and Remschmidt, 2005; Blinová *et al*., 2017), as depicted by equation 2.3.

$$\underset{\text{(FFA)}}{R'-COOH} + ROH \xrightarrow{H^+} \underset{\text{(esters)}}{R-O-CO-R'} + \underset{\text{(water)}}{H_2O} \qquad (2.3)$$

Moreover, high FFA content in the oil increases the kinematic viscosity of the oil, which increases the power consumption when mixing the reactants during the oil transesterification process and leads to lower FAME yield (Babajide, 2011; Al-Hamamre *et al*., 2012). The water content of the oil to be used for FAME production must be < 0.30 wt%, since water can hydrolyse the triglycerides to diglycerides thus increasing the oil's FFA content (Leung *et al*., 2010). The glyceride hydrolysis is given by equation 2.4.



(2.4)

To reduce the water quantity in the oil, some researchers have recommended heating the oil to 100 °C to remove any traces of water before using it for the esterification process (Kondamudi *et al*., 2008). Figure 2.11 shows the effect of water on the esterification efficiency of oil. A small increase (0.10 %) in water greatly reduces the ester yield.

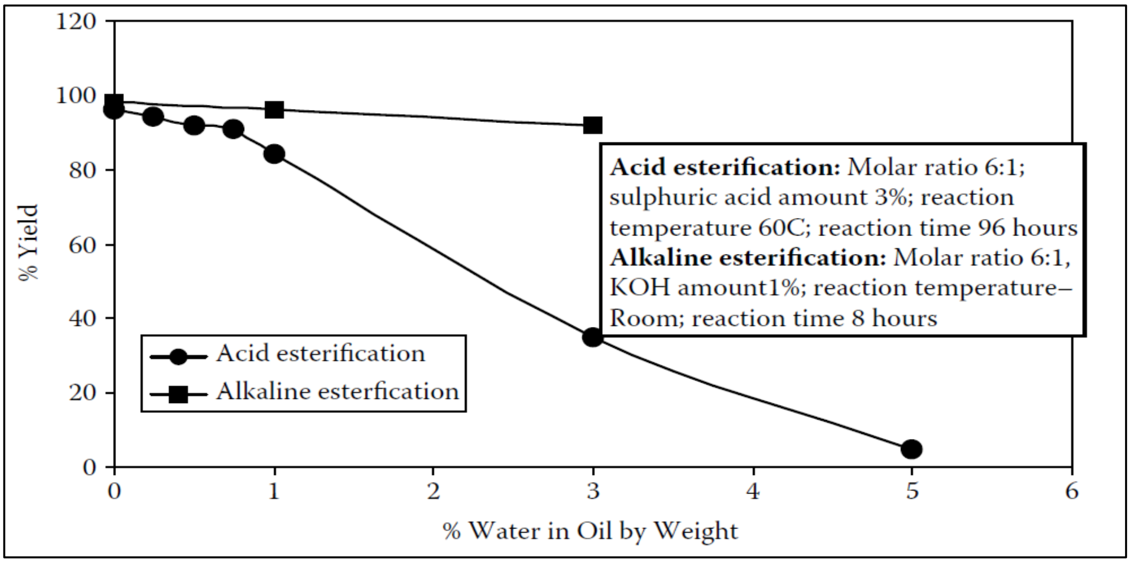


Figure 2.11: Effect of water on the oil and the yield of the process (Mittelbach and Remschmidt, 2005).

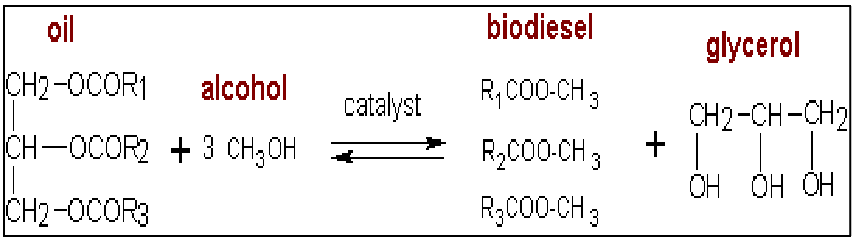
It has been reported that the increase in water in SCGs oil, greatly reduced the yield of esters. It was also reported that 0.50 % of water in the oil reduced the ester yield to 90 wt%. Most seed crude oils, except for soybean and palm oils can be used directly in transesterification reactions without any pre-treatment (Nolte, 2007). Excess alcohol (20:1) molar ratio, is generally required to ensure complete conversion of FFA (Boualdab, 2016; Binyam *et al.*, 2018). The final stage in the oil extraction process is the dehydration process, which is carried out to remove any traces of water in the oil. The water in the oil will decrease the conversion of alkaline catalysed transesterification reaction and harm the acid-catalysed reaction. Dehydration is carried out by passing a stream of nitrogen through the oil or by low-pressure distillation (Martins *et al.*, 2010).

2.9 Transesterification of SCGs oil

Several studies have been conducted on the properties of FAME produced from SCGs oil and its capability to replace mineral diesel (Deligiannis *et al.*, 2011; Caetano *et al.*, 2012; Jenkins *et al.*, 2014; Liu *et al.*, 2017). Transesterification is a chemical process of converting large, and branched triglyceride molecules of vegetable oils and fats into smaller, straight-chain molecules, almost similar in size to the molecules of the species present in mineral diesel fuel (Pandey, 2008). Glycerine is removed from the triglycerides (SCGs oil) by reacting with an alcohol to produce an ester and glycerol as a by-product (Bacovsky *et al.*, 2007; Binyam *et al.*, 2018). This method remains the best method for FAME production

(Blinová *et al.*, 2017). Different primary alcohols, such as ethanol, methanol propanol, and butanol have been used. Generally, methanol is used due to its low cost and that it reacts quickly with the triglyceride compared to other alcohols, and easily dissolves basic catalysts (Efthymiopoulos *et al.*, 2019). The main advantage of methanolysis compared to transesterification with higher molecular alcohols is that the two main products: glycerol and fuel grade hydrocarbons, are completely immiscible (Boualdab, 2016). Forming two distinct layers, the upper layer is mostly fuel-grade hydrocarbons, and the bottom layer is mostly glycerol.

The transesterification reaction can be carried out in the presence of a catalyst or in the absence of a catalyst. Non-catalytic transesterification is relatively slow, requires high temperatures and high pressure for the reaction to be completed (Bacovsky *et al.*, 2007). The use of different catalysts to speed-up the reaction and increase the yield of fuel-grade hydrocarbons has been intensively studied (Bacovsky *et al.*, 2007). Three types of catalysts can be used namely, heterogeneous, homogenous, and biocatalysts (enzymes). Traditionally the transesterification reaction is strongly dependent on process conditions such as reactor temperature, pressure, quality of feedstock (oil), residence time, reactant concentration, type of catalyst used, and the amount of the catalyst (Al-Hamamre *et al.*, 2012). Equation 2.5 shows the general reaction for transesterification.



(2.5)

The rate of formation of the FAME, glycerine, and consumption of the reactants is governed by reaction kinetics. FAME reaction kinetics are strongly dependent on the state (solid, liquid, gas), the concentration of the reactants, temperature, and the type of catalyst used to lower the activation energy required for the reaction to occur. The extent of the chemical reaction is limited by phase and reaction equilibrium. In the transesterification or alcoholysis reaction, one mole of triglyceride reacts with three moles of alcohol to produce three moles of FAME and one mole of glycerol (Amish and Vya, 2011). Reaction presented by equation 2.5, is a sequence of three conservative and reversible reactions where di-and mono-glycerides are formed as intermediates, as depicted by equations below (Bacovsky *et al.* 2007), as depicted by equations 2.6 to 2.8. Where R1. R2. R3 in the questions are FA.

Triglyceride + $R'H_3OH \rightleftharpoons$ diglycerides + FAME (2.6)

Diglycerides + $R'H_3OH \rightleftharpoons$ Monoglycerides + FAME (2.7)

Monoglycerides + $R'H_3OH \rightleftharpoons$ glycerol + FAME (2.8)

To shift the reaction equilibrium to the right, excess methanol is used in most commercial FAME plants (Mittelbach and Remschmidt, 2005; Bacovsky *et al.*, 2007; Pandey, 2008). The overall reaction kinetics varies with reactor temperature and pressure (Drapcho *et al.*, 2008). Noureddini *et al*. (1997), established that transesterification follows the pseudo-first-order kinetics and the reverse occurs is described by second-order kinetics. For conditions near the critical point of methanol, kinetics was considered as first-order (Drapcho *et al.*, 2008) given by the following equation 2.9.

$$\ln\left(\frac{C_f}{C_i}\right) = -kt \qquad (2.9)$$

where: C_f = Concentration of unreacted triglycerides (mol/m^3)

C_i = Initial concentration of triglycerides(mol/m^3)

k = is the first-order reaction kinetics (s^{-1})

t = is the reaction time(s)

The first order-reaction rate for esterification of FFA and transesterification of triglycerides in supercritical methanol ranges from 0.0002 – 0.10 s^{-1} in the temperature range of 240 – 290 °C (Noureddini *et al.*, 1997; Drapcho *et al.*, 2008). After the reaction constants were established, the Arrhenius equation was used to determine the activation energy given by equation 2.10.

$$\ln k_T = \ln k_{T_0} - \left(\frac{E_a}{RT}\right) \qquad (2.10)$$

where: E_a = is the activation energy (kJ/gmol)

R = is the universal gas constant (1.987 cal/gmol. K)

T = is the reaction temperature (K)

Activation energy is the minimum amount of energy that must be absorbed by the reacting species at their ground state to reach the activated complex thus forming the products. He *et al*. (2007) showed that activation energy at supercritical conditions was relatively higher than that of the normal transesterification conditions. From Figure 2.12, the activation energy of this region is determined by taking the slope of individual regions, supercritical and near supercritical. For supercritical conditions, the linear slope is: $-\frac{E_a}{R} = -5.66$ such that, Ea =11.20 cal/mol, the same is done for the near supercritical region: Ea = 9.20 cal/mol. The supercritical region and the near-supercritical region are depicted by the clear break in Figure 2.12 due to the distinctive reaction rates.

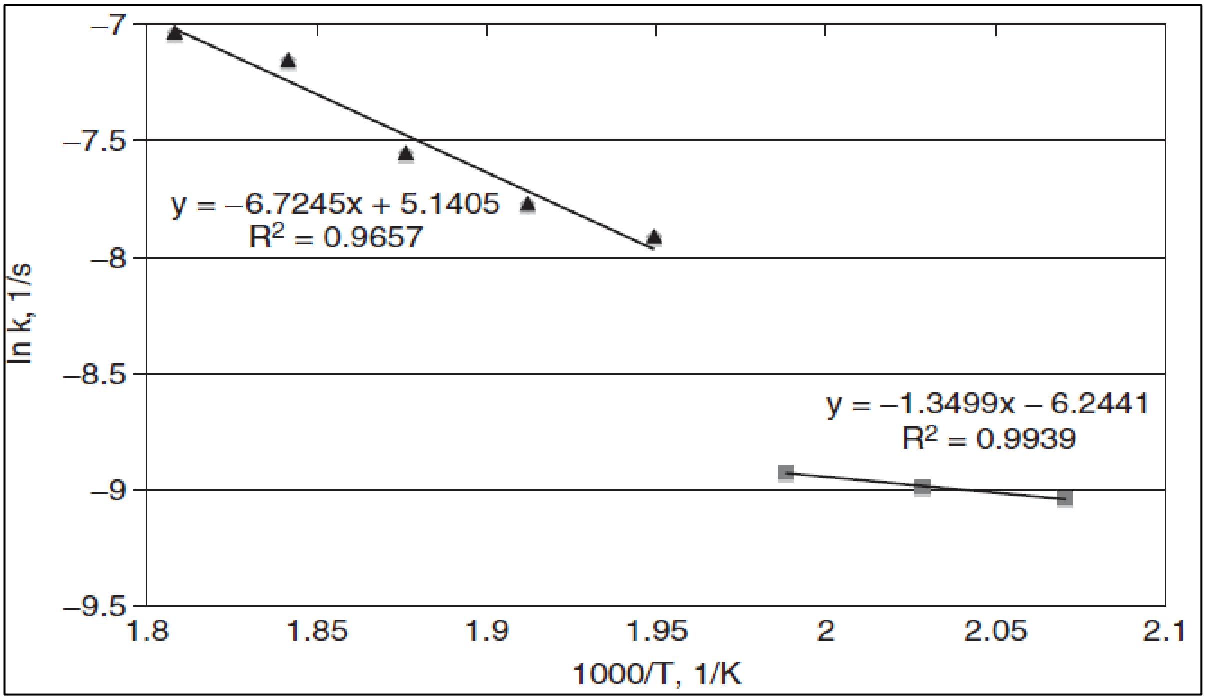


Figure 2.12: Arrhenius plot of transesterification of rapeseed oil with sub-and supercritical methanol (He *et al.*, 2007).

2.10 Production of FAME from SCGs oil process overview

According to Blinová *et al.* (2017), the rate of production of fuel-grade hydrocarbons from different types of oil is strongly influenced by the quality of the oil. The FFA content of the oil determines the process routes required to produce fuel-grade hydrocarbons from oil recovered from different sources. With regards to SCGs oil, the following processing routes can be used, depending on the process requirements and the FFA content of the oil.

1. One step alkali or Acid-catalysed transesterification
2. Two-step transesterifications

- ➢ Acid-catalysed pre-treatment
- ➢ Alkali-catalysed transesterification

3. In situ transesterification

The trans-esterified SCGs oil, which is fuel-grade hydrocarbons or esters has a reduced viscosity and increased volatility relative to the triglycerides present in SCGs oil (Abdullah and Bulent Koc, 2013). The schematic presentation of different FAME production routes from SCGs oil and other oil seed feedstock is represented in Figure 2.13.

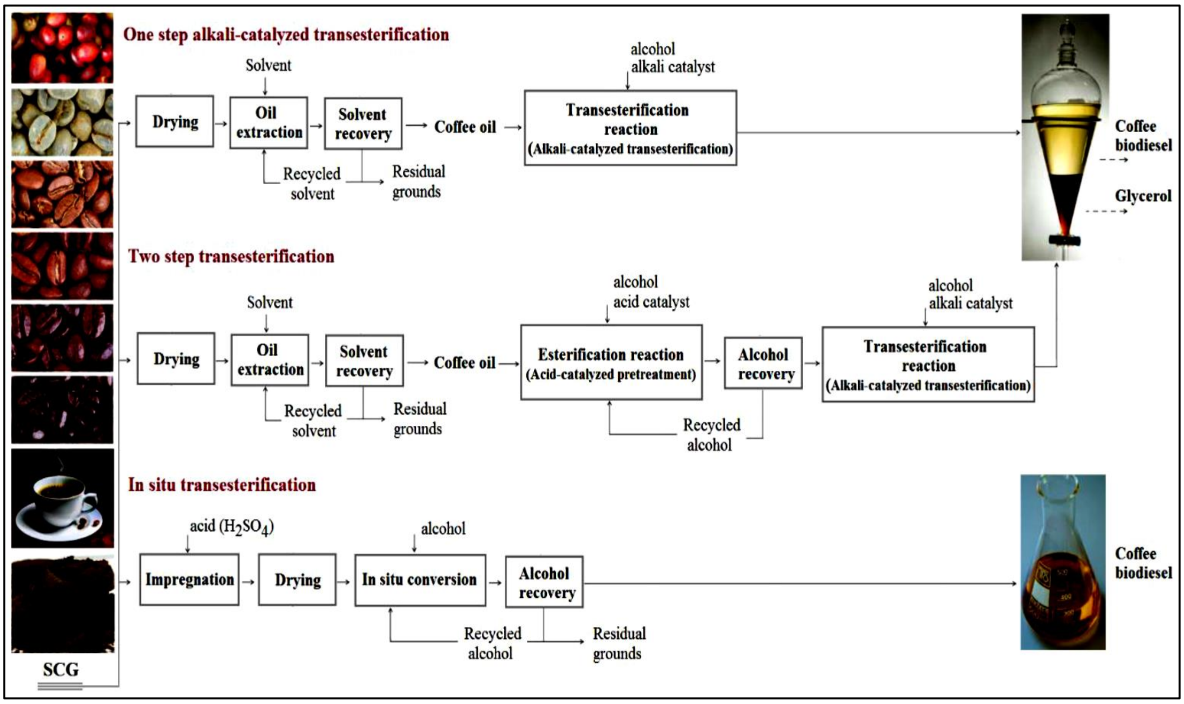


Figure 2.13: FAME production routes from SCGs oil (Blinová *et al*., 2017).

i. One step alkali-catalysed transesterification:

FAME production technologies can be categorised into single-feedstock and multi-feed stocks. According to Bacovsky *et al*. (2007), the so-called single feedstock technologies are utilised for half or fully refined oils, derived from edible seed crops. With these technologies the FFA content in the oil should be very low, thus the formation of soaps is limited (Bacovsky *et al*., 2007). Normally alkaline catalyst like sodium methoxide or potassium hydroxide is utilised. The formation of soaps can lead to the formation of emulsions which makes downstream processes like recovery and fuel-grade hydrocarbons purification difficult (Zhang, 2003; Mittelbach and Remschmidt, 2005). The soaps are formed as side products during the reaction. The soaps are either removed during the washing steps or recycled by esterification with acid catalysts after the work-up of the glycerol phase. FFA content above 0.25 wt% limits the use of one-step alkali-catalysed transesterification process, this corresponds to an acid value of (1 mg $_{KOH}$/g$_{oil}$) to 1 wt% FFA which corresponds to (2 mg$_{KOH}$/g$_{oil}$) of oil (; Martins *et al*., 2010; Al-Hamamre *et al*., 2012).

Ideally, the catalyst is not consumed in this process. It is recovered from the glycerol and water stream. In summary, the single feedstock technology has one major drawback, it is very sensitive to the purity of the reactants, especially water content and free fatty acid amounts (Zhang, 2003), which limits its application. In most single feedstock production plants, the glycerol phase is further processed to get pharmaceutical-grade glycerol. The yields for these single feedstock technologies are almost 100 % because side reactions like saponification are kept to a minimum due to low water and free fatty acid content in the starting material (Bacovsky *et al*., 2007).

Traditionally the reactor is charged with pre-treated oil (refined or semi-refined oil) and heated to about 50 − 60 °C with moderate stirring. Meanwhile about 0.5 − 1.0 wt% of anhydrous alkaline catalyst (NaOH or KOH) is dissolved into 10 −15 wt% methanol. This sodium hydroxide and methanol solution are mixed with oil in the reactor. The mixture is heated and stirred continuously for 0.50 − 0.75 h. The reaction is stopped, and the products are allowed to settle into two immiscible layers. The upper layer consists of FAME and the bottom layer is mainly glycerol and some impurities. The FAME layer is washed several times with water until the washing becomes clear. Traces of FFA, methanol, and catalyst in the glycerol layer can be processed in one or two stages depending on the number of impurities. A distillation column is required for excess methanol recovery, which is then recycled back to the reactor (Pandey, 2009; Ramon and Sorichetti, 2011). One-step alkaline transesterification was tested for oil extracted from SCGs, yielding promising results (Raley, 2018).

In a study conducted by Al-Hamamre *et al*. (2012) SCGs oil was esterified by anhydrous methanol in the presence of potassium or sodium hydroxide. The reaction was carried out at temperatures ranging between 60 − 85 °C, for a reaction period of 1− 4 h with the quantity of methanol and catalyst expressed in different ways thus making process efficiency comparison difficult. In the same study, Al-Hamamre transesterified SCGs oil containing 3.65 wt% FFA by mixing it with methanol and KOH (2.50 %) solution. Oil to methoxide molar ratios of 1:5 and 1:9 was used and observed an improvement in the oil conversion to FAME with a decrease in oil to methoxide ratio and longer reaction time 1 − 4 h. While increasing the reaction temperature from 65 − 85 °C reduced the reaction time. The reaction yield achieved in this study ranged from 55.50 − 85.50 wt% with the highest yield obtained after 4 h at 65 °C reaction temperature with the oil to methanol ratio of 1:9. Another study carried out by Deligiannis *et al*. (2011) used methanol to oil molar ratio of 9:1, with 1 wt%

of NaOH as a catalyst at 65 °C and achieved 92 wt% oil conversion to FAME in 1 h from SCGs oil with very low content of FFA (0.31 wt%). Generally, a molar ratio of triglyceride to methoxide of 1:6 is sufficient for complete conversion of the oil into FAME via alkaline-catalysed transesterification, while 1.50 wt% of NaOH concentration has been reported to be the optimum concentration in terms of FAME yield.

ii. One-step acid-catalysed transesterification:

Nonedible oils such as those extracted from SCGs contain more than 1 wt% FFA with animal fats containing from 5 – 30 wt% FFA. Some very low-quality feedstocks like trap grease can have up to 100 % FFA. It has also been established that the amount of water in the oil increases the acid value (Pandey, 2009). Oil extracted from SCGs containing 8.34−20 wt% FFA, has been used in a one-step acid-catalysed transesterification reaction to produce FAME. Since oil extracted from SCGs is not suitable for one-step alkaline transesterification due to high FFA content (Rocha *et al*., 2014). Acid-catalysed transesterification has been used either as a sole processing method or after saponification and acid hydrolysis.

In a study conducted by Canakci and Von Gerpen (2000) and Von Gerpen (2005), it was established that the standard conditions for carrying out the one-step acid transesterification reactions are 60 °C reactor temperature 3 wt% sulphuric acid 6:1 molar ratio of methanol to oil and a reaction period of 48 h. The oil conversion increased from 87.80 wt% to 95.10 wt% when the reaction time was increased from 48 to 96 h.

Kwon *et al*. (2013) conducted a study performing a one-step acid transesterification reaction, where methanol and ethanol were used in the presence of sulphuric acid for 48 h with oil containing 20 wt% FFA and achieved a FAME yield of 97.50 wt%. It was observed that the reaction with ethanol required higher temperature and alcohol molecular ratios relative to transesterification with methanol. Rocha *et al*. (2014) used SCGs oil containing 8.34 wt% FFA, initially carried out saponification with an alcohol solution of KOH in an ultrasonic bath followed by acid hydrolysis. Subsequently, ultrasound-assisted acid esterification with methanol to a fatty acid molar ratio of 9:1 in the presence of sulphuric acid (3.50 wt%) was performed for a period of 1 h at 60 °C, resulting in 97 wt% FAME yield. This study demonstrated the positive impact of ultrasound on the efficiency of one-step acid-catalysed transesterification.

Overall one-step acid-catalysed transesterification process when used as the only treatment for SCGs oil to produce FAME, high oil conversion is observed. However, it has two major drawbacks: (1) it requires a long reaction time, (2) high methanol to oil molar ratio (Drapcho *et al*., 2008).

iii. Two-step transesterification:

The two-step transesterification reaction is traditionally efficient in processing feedstock with high amounts of FFA. With this process, the feedstock undergoes a pre-esterification process first. Alternatively, the feedstock is directly fed into the transesterification unit operated under high pressure and temperature, thus converting all the fatty material directly to fuel-grade hydrocarbons (Khurshid, 2014). The reaction conditions can easily be changed to accommodate change in feedstock quality.

Two-step transesterification process was developed by Ramadhas, Jayaraj, and Muraleedharan in 2005 to produce fuel-grade hydrocarbons from crude rubber (Mittelbach and Remschmidt, 2005). This process is well suited to deal with oil derived from low-cost feedstocks such as animal fat, waste cooking oil, rendered fats, virgin vegetable oil, and oil derived from SCGs. Oil extracted from these feedstocks generally contains a high concentration of FFA that cannot be converted to biodiesel using an alkali catalyst (Canakcl and Van Gerpen, 2001; Vardon *et al*., 2013). Oil derived from non-edible seed crops and used cooking oil generally contain high levels of FFA (> 1 wt%) and animal fat contain about 5 − 30 wt% FFA (Mittelbach and Remschmidt, 2005; Duncan 2016). Some very low-quality feedstocks such as grease contain up to 100 wt% FFA. Moisture in vegetable oil or seed materials increases the acid value of the FFA of the extracted oil.

The oil extracted from SCGs contain high amounts of FFA (> 1 wt%) which prevent the direct base-catalyzed transesterification thus it requires the two-step process which includes acid-catalysed esterification, before the alkaline-catalyzed process (Al-Hamamre *et al*. 2014; Caetano *et al*., 2014). This process has been described as the most efficient technique for the conversion of oil extracted from low-grade feedstock into FAME. Oil extracted from SCGs has been found to contain high amounts of FFA ranging from 3.65 − 59.50 wt% which inhibit the use of one-step alkaline transesterification (Al-Hamamre *et al*., 2012). Making use of the two-step esterification process suitable for SCGs oil transesterification.

Al-Hamamre *et al*. (2012) initially converted FFA to esters by mixing SCGs oil containing 3.65 wt% with 20 % v/v methanol and 0.10 % v/v sulphuric acid for 4 h and transesterified the pre-treated oil with methanol (6:1 molar ratio to oil) and 1.50 wt% KOH for 6 h at 60 °C and achieved 99 wt% oil conversion. In the same study, a juxtaposition between the one-step alkaline and two-step transesterification was conducted with oil containing the same amount of FFA (3.65 wt%). It was observed that the two-step transesterification gave a higher biodiesel yield, with lower catalyst requirement compared to one-step alkaline transesterification due to the reduction of FFA.

In a study conducted by Vardon *et al*. (2013), SCGs oil containing 5.66 wt% FFA was treated with 35 % v/v methanol and 1 % v/v sulphuric at reflux for 4 h. Subsequently the pre-treated oil was mixed with methanol (6:1 methanol to oil molar ratio) and 0.50 wt% sodium methoxide (CH_3ONa), related to oil weight. This was done in a reflux condenser for 1 h and achieved 96 wt% FAME. Caetano *et al*. (2012) recovered oil from SCGs which contained 59.50 wt% FFA. The high FFA (59.50 wt%) oil was used in three successive esterifications reactions with 40 wt% methanol and1 % w/v sulphuric acid for 2 h at 60 °C. Thereafter performed the alkali-catalysed transesterification reaction with 40 wt% methanol and dissolved 1wt% NaOH at the same conditions. They obtained a relatively low FAME yield of 60.50 wt%. This suggested that the three step esterification reactions were not efficient in reducing the FFA in SCGs oil. The high FFA content in the SCGs oil resulted in the formation of soap during the transesterification step, which resulted in low FAME yield.

Oil from low grade feedstocks requires a pre-treatment step, where FFA are converted to esters, by the reaction of the FFA with alcohol (methanol) in the presence of an acidic catalyst (acid-catalysed pre-treatment). The pre-treatment step is used when the FFA concentration of the oil is >1 mg_{KOH}/g of oil (FFA > 2 wt%) (Al-Hamamre *et al*., 2012). In the next step (alkali-catalysed transesterification) the unreacted triglycerides are reacted with alcohol in the presence of a basic catalyst to produce methyl ester and glycerol (Blinová *et al*. 2017). The main advantage of this process rout is that the conversion of the fatty acid material to FAME is almost 100 % (Bacovsky *et al*., 2007). The highest FAME yield can be achieved. The remaining soaps in the glycerol layer are recycled by acidification of the glycerol and separation of the glycerol. The FFA are than recycled back into the pre-esterification step or transesterification step.

In conclusion, it has been found that the increase in the catalyst loading during the acid-esterification step, greatly decreases the amount of FFA with 5 wt% sulphuric acids performing well with oils containing 15−35 wt% FFA (Efthymiopoulos, 2018). It has also been established that the optimum methanol to oil molar ratio is 20:1 for oils containing 15 − 35 wt% FFA (Caetano *et al*., 2013). The other advantage of this process is that it can be fully automated. However, using two-step transesterification and recycling of the fatty acids produces side products during the reaction (Caetano *et al*., 2013). FAME yield of this process strongly depends on the quality of the oil fed into the reactor, but 100 % oil conversion to FAME is possible. There is no accumulation of solids or liquid during the FAME production process. The catalyst is converted into metal salts which can be used as fertilizers (Mittelbach and Remschmidt, 2005). Figure 2.14 depicts possible process routes depending on the amount of FFA present in the feed oil.

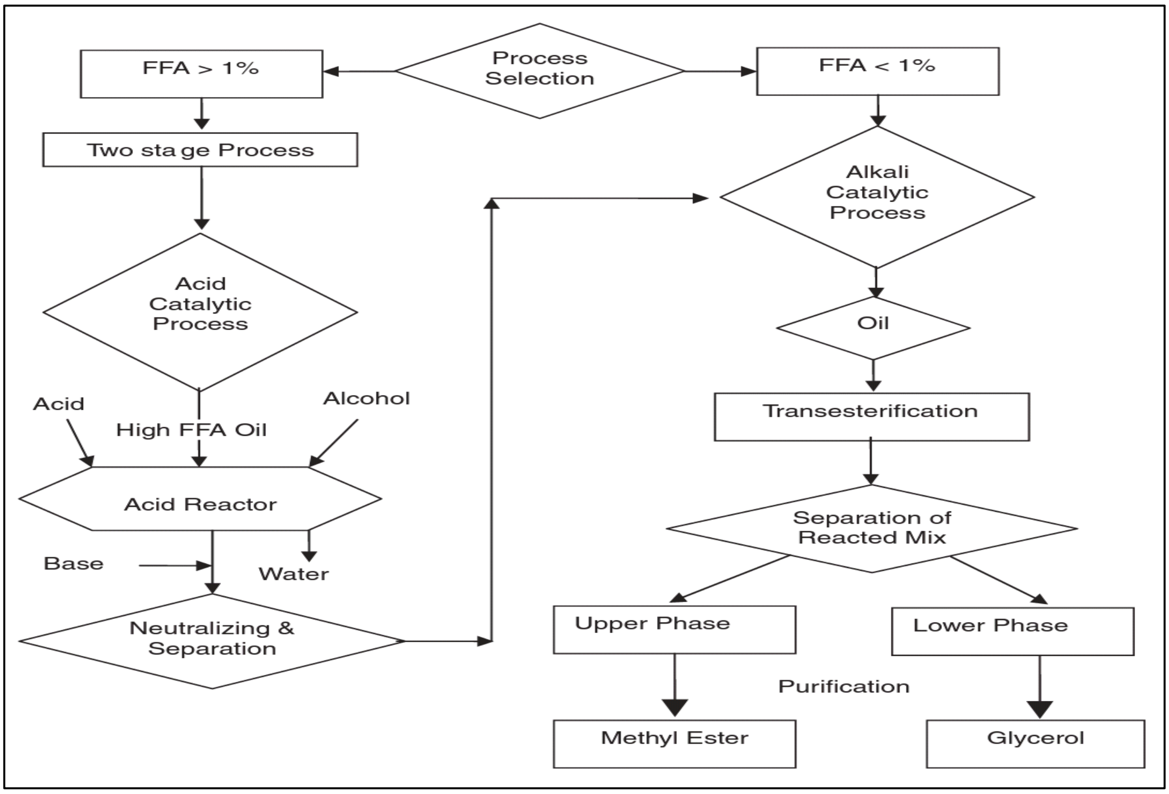


Figure 2.14: Process selection and steps for FAME production (Mittelbach and Remschmidt, 2005).

<u>iv. In-situ transesterification:</u>

Fuel grade hydrocarbons can be produced directly (in situ transesterification) from SCGs, without drying the SCGs, without oil extraction step and oil treatment step. This process combines the oil extracting step and the transesterification step into one step, saving on production costs. FAME produced using this technique is of similar quality and quantity to that produced using the other aforementioned techniques (Park *et al.*, 2016; Liu *et al.*, 2017). The other benefit of this process is that with a suitable catalyst the feedstock does not require drying (Park *et al.*, 2016).

The in-situ transesterification process is an understudy, with many researchers taking interest in this process due to its promise to deliver high quality and quantity FAME at a lower cost. Most studies utilise alkali catalysts such as sodium hydroxide, potassium hydroxide, or sodium methoxide, due to reduced corrosiveness and lower catalyst loading. The reaction time is also lower compared to the acidic catalysts (Liu *et al.*, 2017). This process also requires primary alcohol, mostly methanol or ethanol. Fuel grade hydrocarbons produced by the transesterification reaction must be purified, to ensure that the product complies with the stringent international standards and specifications (Blinová *et al.*, 2017).

A study conducted by Najdanovic-Visak *et al.* (2017), dry SCGs were added to a mixture of methanol and sodium hydroxide at 60 °C and achieved a maximum FAME yield of 96 wt%. In an investigation conducted by Liu (2017), SCGs were first impregnated with sulphuric acid because of the high FFA content in the SCGs oil. The impregnated SCGs were mixed with deionized water for homogeneous coating before thermal drying and transesterification with methanol at temperatures between 60 – 80 °C and obtained a FAME yield of 98.60 wt%. Tuntiwiwattanapun *et al.* (2017), conducted a study, where they first dried the SCGs and then washed the dry SCGs with methyl alcohol to reduce FFA content. They allowed the alcohol washed SCGs to dry. They added the dry SCGs to a mixture of methyl alcohol and NaOH for 3 h at a temperature between 30 – 60 °C and achieved a FAME yield > 80 wt%. A Filter was used to separate the solids from the liquid. Methanol was recovered using rotary evaporation, while fuel-grade hydrocarbons and glycerol were separated using liquid-liquid extraction.

Najdanovic-Visak *et al.* (2017), added dry SCGs to a mixture of methanol and sodium hydroxide at a temperature of 60 °C for 1.50 h and achieved a maximum FAME yield of 96 % w/w of the available oil. In a study conducted by Liu *et al.* (2017), SCGs were first impregnated with sulphuric acid ($H_2SO_{4(l)}$). This was done to reduce the high FFA content of SCGs oil. The mixer of SCGs and $H_2SO_{4(l)}$ was added into deionized water for homogeneous coating before thermal drying and transesterified with methanol.

In conclusion, in-situ transesterification of SCGs is a promising alternative processing route to produce fuel-grade hydrocarbons. Compared to solvent extraction the in-situ transesterification appears to have high FAME yield and comparable FAME quality (Liu *et al.*, 2017). The only drawback with this method is that it requires high methanol to solid ratio, high temperatures and the moisture content of the sample be relatively low to reduce methanol requirement and improve FAME yield unless special solvents like 1,8-diazabicyco [5.4.0] undec-7-ene are used (Najdanovic-Visak *et al.*, 2017). Temperatures between 60 − 80 °C, obtaining a maximum reaction yield of 98.6 wt%.

2.11 Catalyst

The primary function of a catalyst is to speed up the rate of reaction, without itself being consumed in the process. Currently, there are three types of catalysts used in fuel-grade hydrocarbons production namely, heterogeneous, homogenous, and enzyme catalysts. Several factors are considered when selecting a catalyst for FAME production, for instance: catalyst conversion rate, catalyst thermal stability, and catalyst deactivation (Rinaldi and Schuth, 2009).

i. Homogeneous catalyst

A significant amount of work has been done on homogenous acidic and alkaline catalysts, such as H_2SO_4, KOH, NaOH for the transesterification of lipids to FAME. Currently, most of FAME is produced using alkaline transesterification reaction for several reasons:(1) the reaction is carried out at low-temperature and low-pressure. (2) short reaction time. (3) high oil conversion (98 %) with minimal side reaction. The problem with using homogenous catalysts is that they cannot be reused or regenerated since the catalyst is consumed by side reactions and the recovery of the catalyst from the product is very difficult requiring more equipment which could lead to high process costs (Khurshid, 2014). Figure 2.15 depicts different catalysts that can be used in the production of fuel-grade hydrocarbons.

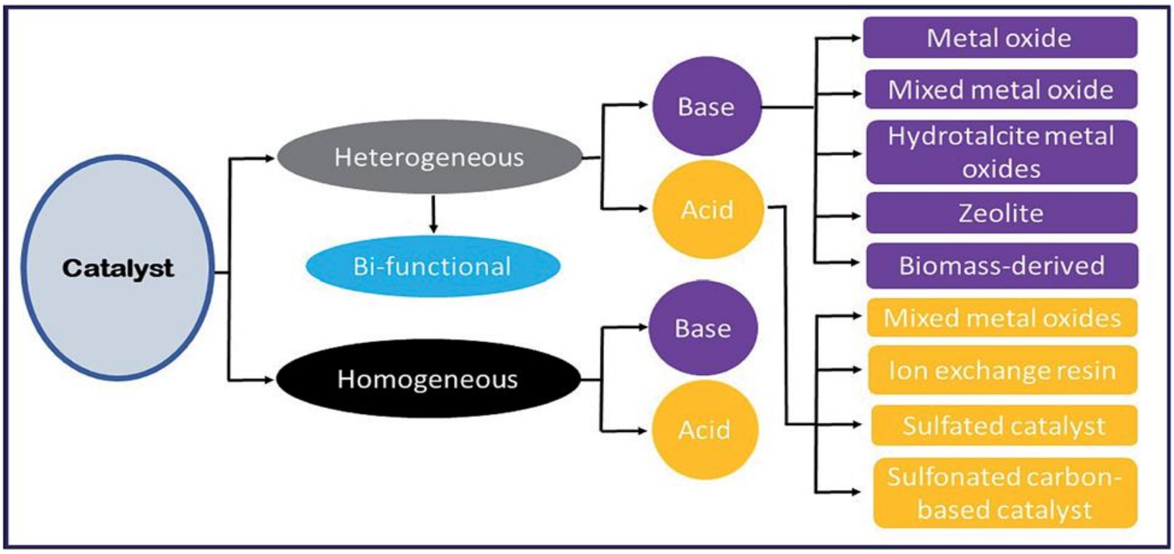


Figure 2.15: Catalysts classification for FAME production (Changmai *et al*., 2020)

Homogeneous acidic catalysts are normally used for the transesterification of high FFA feedstock. Water must be removed continuously during this process because water increase, decrease FAME yield. Temperatures above 100 °C, at ambient pressure with a continuous flow of an inert gas such as nitrogen, are used to remove water and increase FAME yield (Kusar, 2012). The challenge with using homogeneous acid catalysts is that they have a relatively low reaction rate, require high reaction temperatures. They also require high alcohol to oil molar ratio compared to homogeneous alkaline catalysts. Acid catalysts are associated with process equipment corrosion and environmental issues (Ranganathan *et al*., 2008; Helwani *et al*., 2009).

ii. Heterogeneous catalyst:

Although the homogeneous catalysts have their own merits, recently much attention has been given to chemical synthesis of heterogeneous catalysts. This heterogeneous catalyst can be for fuel grade hydrocarbons production. They can be fine-tuned, as per specific requirements and they can be easily recovered, thus enhancing reusability (Changmai *et al*., 2020). Homogeneous catalysts are not considered green catalysts because of the issues mentioned above. For catalysts to be considered green they must be eco-friendly, can be regenerated and can be used multiple times. This reduces the amount of waste produced during the production process. Heterogeneous catalysts are easy to separate from the products and can be reused multiple times thus reducing process waste and chemical consumption (Khurshid, 2014). Heterogeneous catalysts are non-corrosive and have high selectivity. Basic solids such as metal oxides ($CaO_{(s)}$) and zeolites as well as acidic solids like sulphated tin oxide are employed. The challenge of using a heterogeneous catalyst is that they are prone to mass transfer limitation due to a two-phase zone (solid-liquid). This challenge can be solved by mixing (Lotero *et al*., 2005; Khurshid, 2014). The reaction is generally carried out at a high temperature, with high alcohol to oil molar ratio, to overcome diffusion limitation and to shift the equilibrium towards the product side (Lu *et al*., 2009).

Many aspects of acid heterogeneous catalysts make them suitable for fuel-grade hydrocarbon production. For instance, they are insensitive to the presence of water and FFA content of the oil. They can be used for both batch and continuous systems. Acidic heterogeneous catalysts are relatively expensive compared to alkali heterogeneous catalyst. They also have fewer reaction sites therefore, are more affected by adsorption reactant rate. Surface reaction rate and products desorption rate are limited by the number of reaction sites. This reduces the fuel-grade hydrocarbons production rate (Khurshid, 2014). Currently, $CaO_{(s)}$ is the most used alkaline earth metal oxides for fuel-grade hydrocarbons production with 98% yield, during the first cycle (Singh and Sarma, 2011). According to (Khurshid, 2014), $Cao_{(s)}$ catalyst is modified by doping it with lithium (Li). This improves FAME yield because lithium improves the catalyst surface basicity and boost calcium glycerol formation (Singh Chouhan and Sarma, 2011). Many researchers have advocated that the use of heterogeneous catalysts both acid and alkaline have the advantages of being less costly, easy to separate, and is used multiple times (Gebremariam and Marchetti, 2017). Dell 'Anna *et al*. (2016) investigated the transesterification of polyunsaturated oil catalysed by recyclable polymer-supported palladium catalyst. They observed that heterogeneous catalysts display remarkable activity and was recycled for eight consecutive cycles. Sánchez *et al*. (2016) studied the effect of the reaction temperature, the oil to ethanol ratio and the amount of catalyst used on the transesterification of jojoba oil using $CaO_{(s)}$ as catalyst. They carried out the reaction in a pressurised (10 bars) reactor. They observed that oil to ethanol ratio and temperature were the most influential parameters on FAME yield. Whereas the increase in catalyst had a slight negative impact on the process. They also reported that the use of $CaO_{(s)}$ as catalyst reduced the reaction time from 10 to 5 h, achieving 96.30 wt% conversions of jojoba oil.

When heterogeneous catalysts are used the rate of reaction is strongly influenced by the internal and external diffusion desorption and adsorption and the surface reaction rate (Fogler, 2006). The overall reaction rate can be represented in terms of triglycerides conversion. The batch reactor design equation is coupled with the mass balance of the reacting species and the products to get the optimum system operating conditions. According to Khurshid (2014), the best way to model catalyst behaviour is to assume that the reactions follow the single site Eley-Rideal (ER) model. This model assumes that the reaction occurs at an active site of the catalyst as depicted in Figure 2.16. This model also assumes that the activity of the catalyst is heightened by increasing the number of active sites of the catalyst or by increasing the surface area of the catalyst.

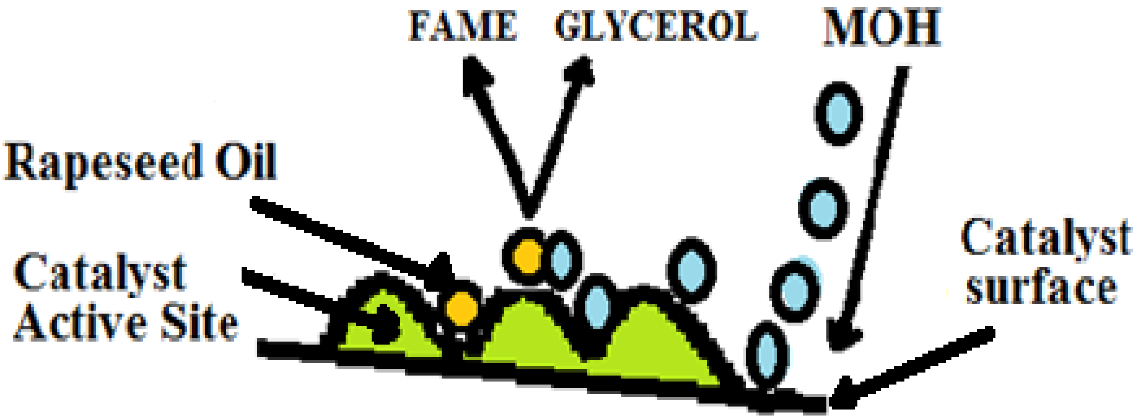


Figure 2.16: Particle catalyst surface (Khurshid, 2014).

The rate of adsorption can be computed by assuming that it is only affected by the diffusion of methanol diffusion on the catalyst active site (Khurshid, 2014). The catalyst activity is depicted by the set of equations below:

$$B + S \rightleftharpoons B.\,S \qquad (2.11)$$

Where: B = Methanol.

: S = Catalyst Active Sites.

: B.S = adsorbed alcohol on catalyst surface.

$$[N_B] = Y_B\, C_B\, [N_o] \qquad (2.12)$$

where: $[N_B]$ = Methanol Concentration at the Surface.

: Y_B = Adsorption Coefficient.

: C_B = Concentration of Methanol.

: $[N_o]$ = Fraction of Vacant Catalyst Sites.

The reaction rate on the catalyst active surface is computed from the alcohol adsorption rate when it reacts with oil in the liquid phase, and is given by:

$$B.S + G \underset{k2}{\overset{k1}{\rightleftharpoons}} M.S + F \quad (2.13)$$

where: B.S = Adsorbed Methanol at Catalyst Surface

: G = Oil

: M = Adsorbed Diglycerides or Monoglycerides

: F = Produced FAME

Therefore, the rate ($\mathbf{r_a}$) of surface reaction given by:

$$\mathbf{r}_a = k1\ [NB]\ C_G - k_2\ [N_M]\ C_F \quad (2.14)$$

The rate of desorption of di glycerides or mono glycerides is given by:

$$MS \rightleftharpoons M + S \quad (2.15)$$

$$[NM] = YM\ CM\ [NO] \quad (2.16)$$

Substituting equation (6) and (2) into equation (4):

$$\mathbf{r}_a = k_1\ Y_B\ C_B\ [N_O].C_G - k_2\ Y_M\ C_M\ [No]\ C_F \quad (2.17)$$

The total number of active catalyst site, [Ns], is the total number of empty catalyst sites $[N_o]$, the sites with alcohol at the surface $[N_B]$ and the sites with adsorbed diglycerides or mono glycerides $[N_M]$.

$$[N_S] = [N_O] + [N_B] + [N_M] \quad (2.18)$$

Substituting equation (6) and (2) into equation (8):

$$[N_S] = [N_O] + Y_B\ CB[N_O] + YM\ CM\ [N_O]$$

$$\text{Therefore: } [N_O] = \frac{N_s}{1+Y_B C_B + Y_M C_M} \quad (2.19)$$

Substitute equation (9) into equation (7):

$$\mathbf{r}_a = k_1 Y_B C_B \left(\frac{N_S}{1+Y_B C_B+Y_M C_M}\right) C_G - k_2 Y_M C_M C_F \left(\frac{N_S}{1+Y_B C_B+Y_M C_M}\right) \quad (2.20)$$

$$\text{Therefore: } \mathbf{r}_a = [k_1 Y_B C_B C_G - k_2 Y_M C_M C_F] \left(\frac{N_S}{1+Y_B C_B+Y_M C_M}\right) \quad (2.21)$$

The rate of adsorption is assumed to be negligible since it is much slower than the bulk concentration (Khurshid (2014) and Fogler (2006)), hence:

$Y_B C_B \gg Y_M C_M$.

$Y_M C_M = 0$

$$\text{Therefore: } \mathbf{r}_a = [k_1 Y_B C_B C_G] \left(\frac{N_S}{1+Y_B C_B}\right) \quad (2.22)$$

In a catalytic reaction, there are several limiting steps involved as shown in Figure 2.17. During the transesterification reaction, diffusion of the reactants i.e., methanol and oil (represented by A in the figure below) from the bulk fluid mixture to the external surface of the catalyst particle must occur (external mass transfer, step 1). The other limiting step is presented by the diffusion of the reactants from the pore opening through the catalyst pores into the immediate region of the internal catalytic surface (pore diffusion, step:2). Adsorption (step:3) of the reactants into the surface of the catalyst imposes another limiting step.

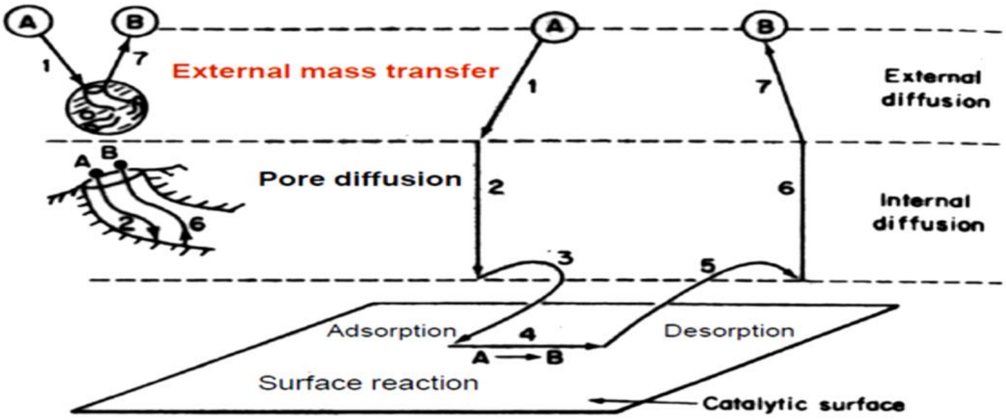


Figure 2.17: Steps in heterogeneous catalyst reaction (Fogler, 2006).

The reaction between the oil and the methanol takes place on the surface of the catalyst (step 4). The products face similar limiting steps as the reactants. Step:5 is the desorption of the products from the surface of the catalyst. Step:6 is the diffusion of the products from the interior of the solid particle to the pore mount at the external surface and step:7 is the mass transfer of the products from the surface of the particles into the bulk liquid mixture (Fogler, 2006).

The transesterification limiting steps can be summarised into mass transfer diffusion resistance and concentration difference across the boundary layer around the catalyst particle as depicted in the Figure 2.18. The mass transfer boundary layer is relatively big and limits the rate of reaction (Li, 2017).

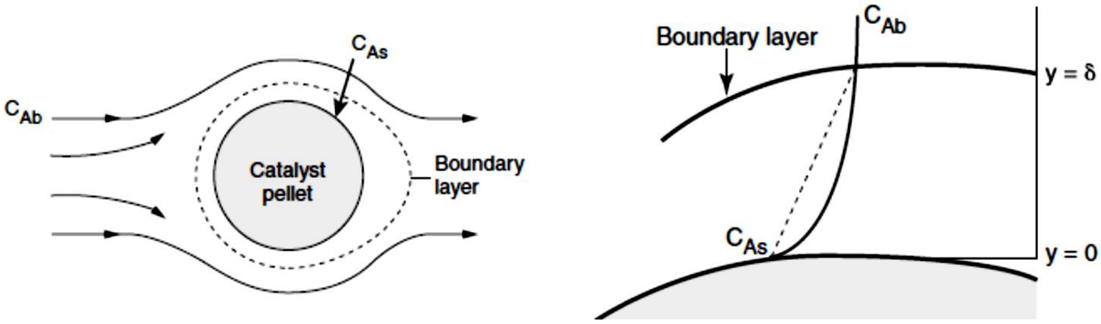


Figure 2.18: Diffusion through a stagnant film (Li, 2017).

At higher liquid mixture velocity, which is achieved by increasing the mixing rate, the stagnant film or boundary layer thickness decreases hence it no longer limits the reaction rate (Khurshid, 2014). At a certain mixing speed, the reaction limiting conditions can be improved by using a catalyst with a small particle size (Khurshid, 2014; Li, 2017). Reaction mechanisms and kinetics are vital in designing a suitable and efficient catalyst for FAME production. The solid acidic catalyzed mechanism for transesterification and esterification of FFA with methanol can be presented by two models namely, a single site Eley-Rideal (ER) model and dual-site mechanism Lagmuire Hinshelwood (LH) model (Endalew *et al.*, 2011).

iii. Enzyme catalyst:

In recent years' research has been focused on the use of the enzyme catalysts for FAME production. Lipases used in biotechnology are normally microbial in origin and are produced by fermentation. The use of lipases makes the reaction insensitive to the presence of FFA. Which is a problem with traditional FAME production processes (Khurshid, 2014). Different commercial lipases are available to be used as biocatalysts. Some are used as free powders, a majority are employed as immobilised preparation (Helwani *et al.*, 2009). Enzyme catalysts have several advantages: (1) they have high selectivity and a fixed running cost and reliable capital, (2) the process consumes low energy since it is operated at a low temperature and pressure, (3) with enzyme catalysts, there are no side reactions (saponification) compared to alkali esterification. However, enzyme catalysts have a low reaction rate thus a longer reaction period, high operating costs and low activity (Khurshid, 2014). These are considered drawbacks and affects the economic benefits of the process. Glycerol produced by the transesterification process covers the enzyme and reduce its efficiency thus requiring additives such as silica to remove the glycerol (Bajaj *et al*., 2010).

2.12 Effects of the transesterification reaction parameters

The main objective of the transesterification reaction is to reduce the viscosity of the feed oil. The transesterification reaction produces a low viscosity product (biodiesel) and a high viscous product (glycerol), which automatically form two immiscible layers. The fuel grade hydrocarbons produced are completely miscible with petrodiesel in any proportion (Binyam *et al*., 2018). Similar to the oil extraction step, the yield of FAME by transesterification reaction is affected by several process parameters, such as alcohol to oil molar ratio, reaction time, type and amount of catalyst used, process temperature, and oil quality. These process parameters are briefly discussed.

i. Effect of alcohol to oil molar ratio:

Alcohols such as methanol, ethanol, propanol, and amyl alcohols can be used in the transesterification reaction (Amish and Vya, 2011). However, methanol is the most used alcohol, since it is cost-effective, and the products formed are easy to separate. The use of methanol, KOH as a catalyst, and the alcohol to oil molar ratio of 6:1 have been reported to give a $90 - 98$ wt% yield of FAME depending on the temperature (Bacovsky *et al*., 2007; Nolte, 2007; Amish and Vya, 2011). The low alcohol to oil ratio is necessary to shift the reaction equilibrium to the direction of the products. Excess methanol accelerates the conversion of oil to fuel-grade hydrocarbons. However, it causes difficulties in products separation (Khurshid, 2014). Only the optimum molar ratio gives the higher yield of fuel-grade hydrocarbons and causes no problems during product separation.

ii. Amount and type of catalyst:

The yield of fuel-grade hydrocarbons can be influenced by the type and the amount of the catalyst used in the reaction. Alkaline catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) are mostly used. These catalysts increase the reaction rate several times faster than the acid catalysts (Mittelbach and Remschmidt, 2005). An alkaline catalysts concentration ranging from 0.5 − 1 wt% gives a yield of 94 − 99 wt% of fuel-grade hydrocarbons (Mathiyazhagan and Ganapathi, 2011; Boualdab, 2016). The increase in catalyst concentration does not improve yield but only adds to process costs and makes the process more complicated (Mittelbach and Remschmidt, 2005).

iii. Reaction time and temperature:

The transesterification reaction is strongly dependent on the reaction temperature. The reaction is generally carried close to the boiling point of the methanol, 60 − 70 °C, at atmospheric pressure (Al-Hamamre *et al*., 2012; Boualdab, 2016).This is also dependent on the quality of the oil. Some reports claim that an oil conversion of 78 % can be achieved at room temperature with a 1 h reaction time (Binyam *et al*., 2018). The increase in temperature is likely to result in methanol loss thus a reduction in FAME yield. It has been proven that the optimum reaction time at an optimum catalyst loading, 1 wt% of the oil and optimum alcohol to oil molar ratio (6:1) optimum reaction time is 1 h, (Boualdab, 2016). Higher temperatures also accelerate the rate of saponification of triglycerides (Mathiyazhagan and Ganapathi, 2011).

iv. Mixing intensity:

Oil and alcohols are not miscible thus the reaction can only take place in the interfacial region between the reacting species making the transesterification process relatively slow. According to Mittelbach and Remschmidt (2005), the mixing effect becomes significant during this slow period of the transesterification reaction and when a single phase is achieved mixing becomes irrelevant. Understanding the effect of mixing in the laboratory scale becomes significant in the scale-up and process equipment design. Generally, after adding alcohol, the catalyst mixture to the oil, stirring for 5 to 10 minutes is employed to speed up the reaction rate and products recovery. When oils with high viscosity are used as feed stock intense mechanical mixing is required to overcome the impediment of the mass transfer caused by the high viscosity of the oil (Bhuiya *et al*., 2016).

v. Oil purity:

The level of oil purity significantly affects the yield of the transesterification reaction. It is advised that before using any oil in the transesterification reaction, the oil must first be filtered to remove any solids. The oil settled at the bottom of a storage tank will have a lower conversion due to the deposition of impurities and wax (Mittelbach and Remschmidt, 2005).

2.13 Conclusion

SA generates about 37.87million kg of SCGs waste per annum, making SCGs one of the most plentiful oil-containing biomass in the country. Justifying their use as a potential FAME feedstock and other high-value products. The amount of the oil in the SCGs is not fixed. It varies depending on the origin of the coffee beans and the processing (roasting, treatment for instant coffee making) of the coffee bean before brewing. Water content of SCGs is mainly dependent on the coffee brewing method. SCGs with high water levels needs to be dry pressed for dewatering purposes before thermal drying since water inhibits oil extraction. Organic solvent (non-polar) extraction and SFE are the most studied methods for oil extraction from SCGs, with SFE shown to be less efficient in oil recovery. Oil extracted from SCGs using the SFE method tend to be inconsistent in fatty acid profile compared to the oil extracted using the Soxhlet solvent method.

In solvent extraction, the quantity of oil extracted from the SCGs is affected by several process parameters, such as SCGs to solvent ratio, oil extraction temperature, and solvent type. Decreasing the solids to solvent ratio increases the oil extraction efficiency. Setting the extraction temperature just below the boiling point of the solvent improves the oil extraction efficiency. The type of solvent used for SCGs oil extraction does not only affect the oil quantity but as well as the oil quality. The oil recovered using polar solvents have a higher amount of FFA relative to the non-polar solvent. Some researchers have observed black gummy material on the oil extracted using polar solvents. Generally, SCGs oil has a relatively high quantity of FFA. To produce high-quality fuel-grade hydrocarbons from SCGs oil, the two-step transesterification process should be used. The liquid and fuel properties of the fuel-grade hydrocarbons produced from SCGs oil vary depending on the origin of the oil source and the efficiency of the methanolysis process.

The main objective behind the production of FAME is that they are, only produced from renewable resources and they must not harm the environment during their production. However, most of the previous studies concerning the production of fuel-grade hydrocarbons from SCGs oil have only focussed on oil extraction and oil transesterification. The use of fossil-based solvents like hexane for oil extraction and the use of non-reusable catalysts for the transesterification of the oil like sodium hydroxide renders FAME a non-green fuel. The utilisation of green polar solvents for oil extraction from SCGs has not received any attention. The transesterification of SCGs oil in the presence of the chicken eggshell synthesised, $CaO_{(s)}$ as a catalyst has not been investigated. In an attempt to revolutionise the production of FAME more comprehensive studies must be conducted involving the development of green technologies. In addition, in-depth comprehension of the effect of oil extraction parameters on oil quality and yield as well as the effects of methanolysis parameters on the quality and yield on FAME is required to improve the valorisation of SCGs. The fuel properties of FAME derived from SCGs oil for use as fuel in existing diesel engines is equally vital for future industrialization for the production of fuel-grade hydrocarbons from SCGs.

CHAPTER 3

3.0 Introduction

This chapter details the experimental protocol for the work done to achieve the objectives of this study. This chapter also outlines the steps taken for spent coffee grounds sample collection, characterisation of the spent coffee grounds in terms of moisture content and particle size. Thereafter details the oil extraction process from the SCGs using the Soxhlet solvent extraction technique. Hexane was used as a datum solvent to measure the oil extraction efficiency of the green solvent 2-MeTHF. The parameters affecting the oil extraction were also investigated. The transesterification of the SCGs oil was carried out in a batch reactor in the presence of a renewable heterogeneous catalyst, calcium oxide ($CaO_{(s)}$) derived from chicken eggshells. The parameters affecting the oil conversion to FAME were also investigated. Figure 3.1 depicts the major process steps

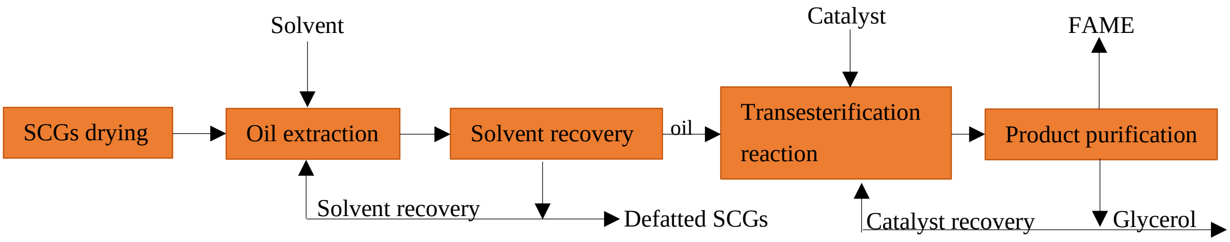


Figure 3.1: Process flow diagram showing all the major processes.

3.1 Spent coffee grounds sample collection

The spent coffee grounds used in this study were collected from three different coffee makers. Two samples were collected from a petrol station, a burger franchise and coffee franchise. However, information concerning the origin and upstream processing of the coffee beans used in this study was not available, but it was known that the samples were a by-product of brewed coffee. All wet SCGs samples were stored in a refrigerator to prevent deterioration, such mould formation as water promotes fermentation and mould growth. (Efthymiopoulos, 2018).

3.1.1 Materials for SCG oil extraction

Three different samples (SCGs1, SCGs2, SCGs3) of dry SCGs were used in the experimental work (10 kg of each sample), visual inspection indicated no noticeable differences between the samples. All samples had wet texture when felt by hand, and has a dark brown colour. The reagents and solvents used were potassium hydroxide, phenolphthalein, anhydrous ethanol (99.50 %), hydrochloric acid (99.99 %), hexane (99.99 %) and green solvent (2-MeTHF) > 99.50 % purity.

3.1.2 Solvents used for the extraction of oil from SCGs

Two solvents were used in this study, namely hexane and 2-MeTHF. Hexane was used as a reference solvent since it is the most used solvent for oil extraction from various oil-bearing seeds, hence its oil extraction efficiency is well understood. 2-MeTHF is a green solvent in this study, as its application allowed for the oil extraction from sunflower seeds and produced the same results as hexane. Thus, one of the objectives of this study was to investigate if 2-MeTHF would yield the same results when used to extract oil from SCGs (Chaabani *et al*., 2019).

Table 3.1 depicts the characteristics of the different solvents used in this study, such as solvent boiling point, molecular weight, dielectric constant, empirical polarity parameter, and solvent chemical formula.

Table 3.1: Chemical formulas and properties of the solvents used in the present study.

Solvent	**Chemical Formula**	**Boiling Point (°C)**	**Molecular Weight (g/mol)**	**Dipole moment[D] at 25°C**	**Dielectric Constant at 25°C**	**Polarity parameter E_T^N at 25°C**
Hexane	C_6H_{14}	68.70	86	0	1.88	0.009
2-MeTHF	$C_5H_{10}O$	80.20	86.13	1.38	6.97	0.207

It can be seen in Table 3.1. that hexane is a non-polar solvent while 2-MeTHF is a polar solvent. The use of non-polar and polar solvents allows the evaluation of the effect of solvent polarity on oil extraction efficiency.

3.2 Characterisation of SCGs

Moisture, oil content and particle size are the two factors that have a major impact on the oil extraction process. For efficient oil extraction the moisture content of the oil bearing solids must low. Knowing the maximum amount of oil that can be recovered from oil bearing solids is crucial for process equipment design. The efficiency of the oil extraction is strongly affected by the particle size distribution of solids.

3.2.1 Determination of moisture content.

To accomplish drying, 160 g of wet SCGs samples were weighed using an analytical balance Kern ALJ 220-4 for each drying run. A 6.50 mm sample thickens and dried in a vacuum oven (BHO Shatter) at 110 °C. The sample was removed from the oven and weighed every 0.5 h time interval. This was repeated until there was no observable change in the mass of the samples, and this occurred after 4 h of drying. The samples were kept in the oven for 5.50 h. The moisture content was calculated using equations 3.1 on a dry basis, and by equation 3.2, on a wet basis.

$$\%M_{db} = \left(\frac{W_o - W_f}{W_f}\right)100\% \tag{3.1}$$

$$\%M_{wb} = \left(\frac{W_o - W_f}{W_f}\right)100\% \tag{3.2}$$

where; W_o is the initial mass of the sample before being oven-dried W_f is the dried mass of the sample. The two moisture content expressions are related by the following equation 3.3:

$$\%M_{db} = \left(\frac{M_{wb}}{100 - M_{wb}}\right)100\% \tag{3.3}$$

The average initial moisture content for the SCGs used in this study was found to be 67.75 % (wet basis).

3.2.2. Particle sizing distribution of dry SCGs

Determination of particle size distribution (PSD) of various SCGs samples was undertaken using laboratory sieves with aperture sizes of 600 µm, 500 µm ,425 µm, 355 µm, 250 µm, 200 µm, 150 µm and 75 µm. The screens were mounted in a vibrating sieve shaker (Retsch sieve shaker), which was operated at a speed of 40 rpm for 1 h. Individual sieves were weighed on a balance (METTLER PJ3000) before adding the SCGs on the top sieve. The sieves were weighed before and after the shaking process, this was done to determine the estimated mass of the particles retained in each sieve. Figure 3.2 depicts the sieve setup used in the determination of the average particle size of the SCGs samples used during the investigation.

Figure 3.2: Sieves loaded with spent coffee grounds on a sieve shaker.

Equation 3.4 gives the percentage mass of SCGs particles of a specific particle size range:

$$x_i = \left(\frac{\mathrm{M_f} - \mathrm{M_i}}{\mathrm{M_{total}}}\right) \times 100\ \% \qquad (3.4)$$

where; x_i, M_f, M_i and M_{total} are the mass fractions of particular size particles retained in a particular sieve, the mass of the sieve prior to shaking, the mass of the sieve after shaking and total mass of SCGs used respectively. The mass mean particle diameter for each SCGs sample used was determined using equation 3.5:

$$\overline{D}_w = \sum_i^N x_i\, \overline{D}_{pi} \qquad (3.5)$$

Where: $\overline{D}_w$ and $\overline{D}_{pi}$ are the mass mean particle diameter and average particle diameter respectively.

3.3 Soxhlet oil extraction

The technique of Soxhlet oil extraction using hexane as solvent is widely used for laboratory-scale oil extraction from oil-bearing material as a datum method to measure the performance of new techniques and new solvents. In this study, oil was extracted from the oil bearing material semi-continuously with organic solvents, and is dependent on the solubility of the lipids in the solvents (Campos-Vega *et al*., 2015). The Soxhlet extractor (glassware) consists of a percolator that enables the circulation of the solvent, a thimble that contains the oil-bearing material, and a siphon mechanism, Figure 3.3 depicts the schematic representation of the Soxhlet extractor.

Samples of dried SCG1 (480.40 μm), SCG2 (482.95 μm), SCG3 (491.48 μm), (35 g) were placed in the cellulose extraction thimble and inserted into the Soxhlet apparatus along with a selected solvent in the distillation flask. The solvents were heated to their respective boiling point, 69 °C and 80 °C for hexane and 2-MeTHF, respectively, in the distillation flask to enable refluxing. The vapour rises through the distillation path of the apparatus during boiling. The solvent vapour floods into the chamber containing the SCGs. Any vapour that does not go into the thimble chamber will travel above the expansion adapter, cooled in the condenser and travels back down into the chamber which holds the solid material. The warm solvent slowly fills the thimbles chamber and dissolves the oil component of the SCGs, thus extracting the oil. When the thimble chamber is filled up to the siphon sidearm, draining of the thimble chamber will occur automatically and empty back into the distillation flask.

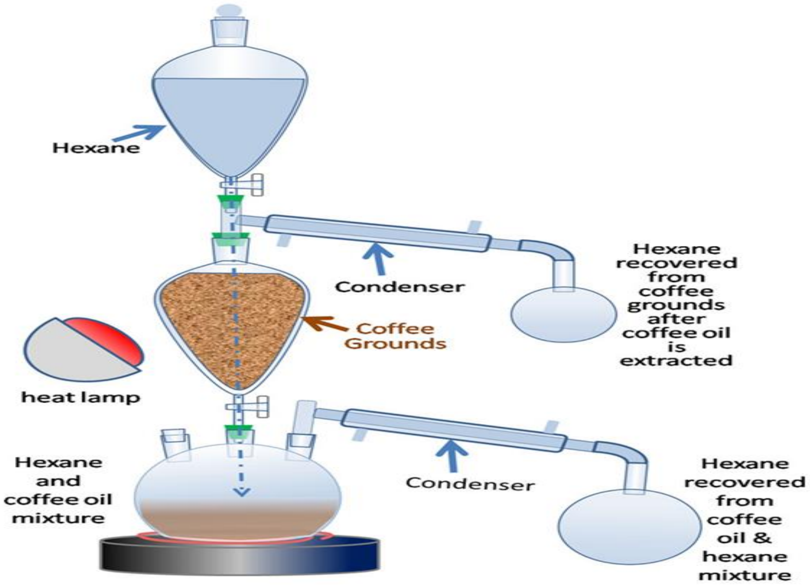


Figure 3.3: Schematic presentation of the Soxhlet extractor (Costello, 2007).

The distillation flask contains a mixture of oil and solvent, and since the oil has a higher boiling point than that of solvent, the refluxing of solvent can continue with the oil present.

This process was repeated until the condensed solvent and extracted oil mixture at the bottom of the thimble chamber became clear, taking approximately 0.83 h for hexane and 1.50 h for 2-MeTHF. The product mixture of solvent and SCGs oil was then placed in a rotary evaporator to separate the desired oil from the solvent. To investigate the effect of the solid-to-solvent ratio on oil extraction efficiency, the solids-to-solvent ratios of 5:1,10:1,15:1, 18:1, and 20:1 (v/w) were used. The use of different solids-to-solvent ratio would also assist in observing the benefits and the disadvantages of using low and high solids-to-solvent ratios. As aforementioned the solids-to-solvent ratio affects both the economics of the process as well as the oil recovery efficiency (Pichai and Krit, 2015).

To investigate the effect of the extraction period on the oil yield of each solvent. The solids-to-solvent ratio of 1:20 was selected for both solvents. The extraction period was varied from, 1 – 8 h since the optimum extraction time is said to be within this range (Lawson *et al*., 2010; Go *et al*., 2016). The extraction temperature was kept at the boiling point of the solvent in question. Figure 3.4 depicts the Soxhlet experimental setup used during the investigation.

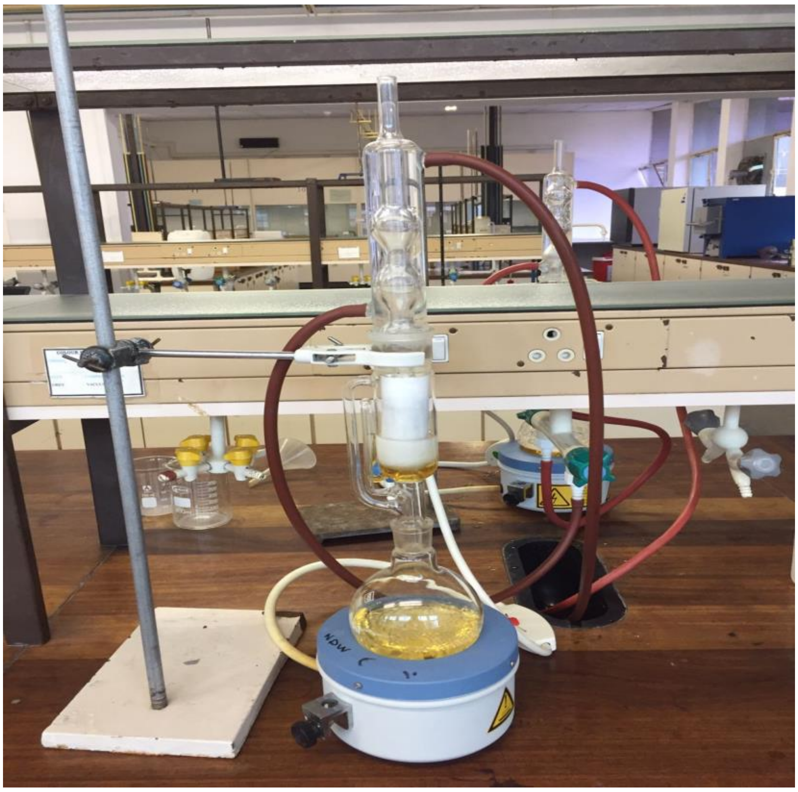


Figure 3.4: Soxhlet extraction apparatus experimental set-up.

A vacuum rotary evaporator system (RE-2000B) was used to separate the solvents and oil. The recovered solvent and extracted oil were quantified; and the solvents were re-used in the next extraction cycle.

3.3.1 Extracted oil quality and quantity

The oil extracted from SCGs was used to determine the amount of oil present in the SCGs from the local supply, thus indicating the possible quantity of fuel-grade hydrocarbons that can be produced. The oil physicochemical properties were determined (viscosity, density, saponification value, and acid value). This was done to determine the oil quality, for use of the oil directly as fuel in the traditional diesel engine, and for selecting a suitable fuel-grade hydrocarbons production route. The oil quality or properties were then compared to those found in the literature.

3.3.2 Determination of FFAs in the oil using the ASTM D 6751 limit method

After the oil was extracted from the SCGs, the oil's FFA content was tested. A sample (5 g) of oil was titrated with 0.1 M of KOH made with distilled water. The oil sample was added into a 250 ml conical flask and heated to 70 °C. Then 20 ml of anhydrous ethanol (99.50 %) and 5 drops of phenolphthalein were added into the titration beaker with the 5 g sample oil then mixed. Finally, the titration solution of 0.1 M of KOH was added until a colour of the oil mixture change to light orange. Once the colour changed from dark brown to pink the titration was stopped, and the volume of the solution used was measured. The volume of the solution used was used to compute the amount of FFA present in the oil. The FFA amount was calculated using equation 3.6:

$$\text{FFA value, mg}_{\text{KOH}}/\text{g}_{\text{, oil}} = \left(\frac{\mathrm{V} \times \mathrm{C} \times \mathrm{M_r}}{\mathrm{M_{oil}}}\right) \tag{3.6}$$

where: V, C, M_r, M_{oil} are solution volume used for titration, solution concentration (0.1mol/l), KOH molar mass (56.10 g/mol) and mass of oil (5 g), respectively. The FFA content for the oil to be used for fuel-grade hydrocarbons production must be < 1 wt% (Haile, 2014). Figure 3.5 depicts the experimental set-up for the determination of FFA from SCGs oil.

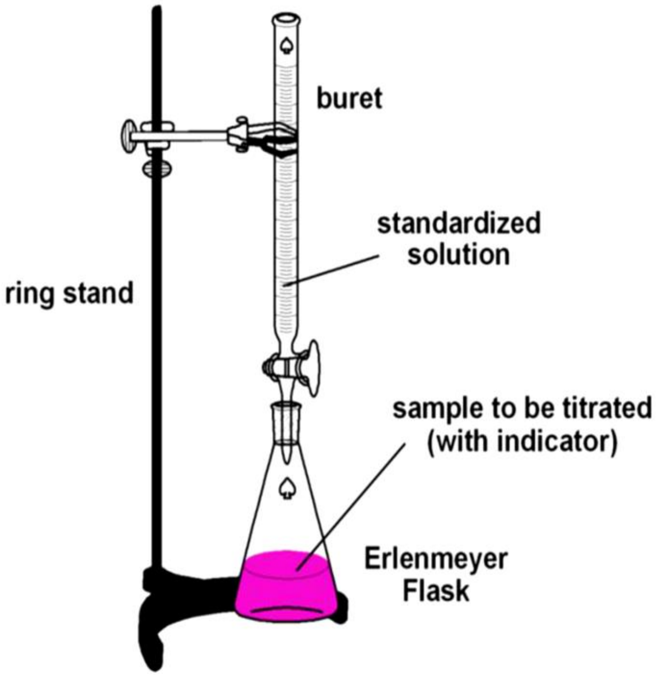


Figure 3.5: SCGs oil titration experimental set-up (Efthymiopoulos, 2018).

The FFA value was calculated to be greater than 5.35 wt% on average, therefore the oil required deacidification before the transesterification process.

3.3.3 Oil yield calculation using the ASTM method

The amount of oil extracted from the SCGs was calculated as depicted by equation 3.7.

$$\text{Oil yield } = \left(\frac{\mathrm{M_i}-\mathrm{M_f}}{\mathrm{M_i}}\right) \times 100\% \tag{3.7}$$

where; M_i is the initial mass of dry SCGs, and M_f is the mass of SCGs after oil extraction. The oil extraction ratio relative to the total oil available in the SCGs was calculated using equation 3.8.

$$\text{Oil extraction ratio} = \left(\frac{\text{mass of extracted oil}}{\text{mass of SCG used}}\right) \tag{3.8}$$

3.3.4 Determination of oil specific gravity using the ASTM D 4052 method

A sample of oil was filled into a graduated cylinder (10 ml), and then allowed to cool, to 25 °C. A hydrometer was used to measure the specific gravity (sg) of the oil at 25 °C. The oil-specific gravity was then used to determine the density of the oil, which was calculated using equation 3.9.

Density of oil: $\rho_{oi} = sg_{oil} \times \rho_{water}$ (3.9)

The density of SCGs oil is usually in the range of 890 – 1149 kg/m^3 at 25 ˚C, which is dependent on the method which was used to extract the oil (Caetano *et al*., 2013).

3.3.5 Determination of viscosity of the oil using the ASTM D 2270 method

A sample (20 ml) of oil was poured into a test tube and a viscometer was used to measure the viscosity at a temperature of 40 °C.

3.3.6 The oil acid value

The acid value (AV) of the oil was calculated using equation .3.10, (Efthymiopoulosm, 2018)

$$AV = 1.99 \times \%\ FFA \qquad (3.10)$$

3.3.7 Determination of saponification value

A sample (5 g) of the oil was placed in a conical flask to which 63 ml of ethanolic potassium hydroxide (0.1 M) was added and the mixture was allowed to boil gently for about 1 h with shaking at regular intervals of 5 minutes. Drops of phenolphthalein indicator, as specified by ISO 3657,1988 were added to the warm solution and then titrated with 0.5 M hydrochloric acid ($HCl_{(aq)}$). A similar procedure was used for the blank. The endpoint was reached when the pink colour of the indicator just disappeared. The saponification value (SV) was calculated using equation 3.11.

$$SV = 56.10\left(\frac{M(V_o - V_i)}{m}\right) \qquad (3.11)$$

where; V_o and V_i, is the difference in volume of HCl $_{(aq)}$ solution used for the blank test and m is the mass of sample.

3.4 Esterification experimental procedure

The oil extracted from the SCGs is converted to fuel-grade hydrocarbon in the presence of heterogenus catalysts, using a batch reactor. The process is depicted in Figure 3.6.

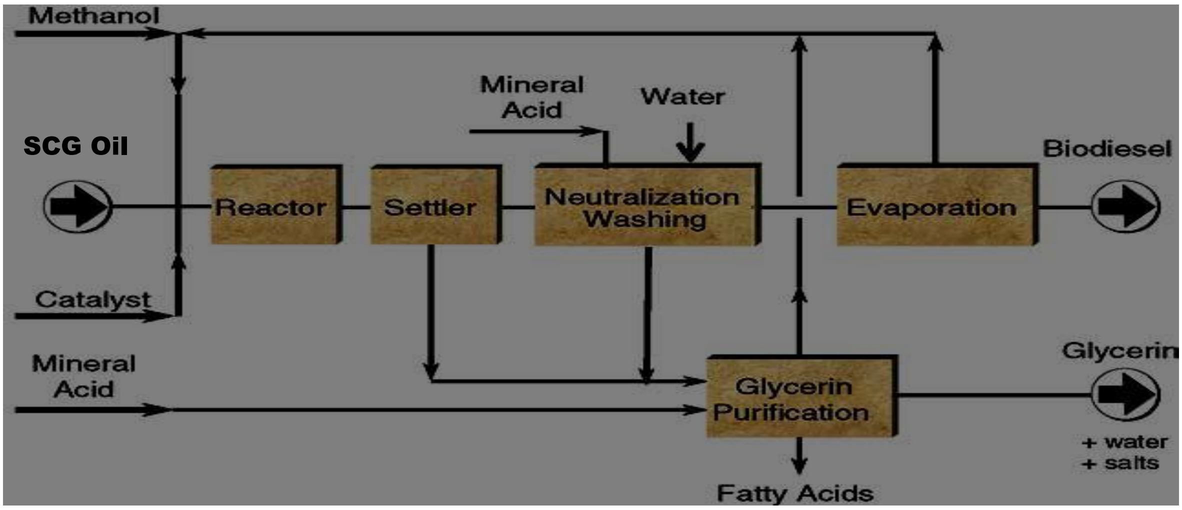


Figure 3.6: Flow chart for FAME production from SCGs oil (Khurshid, 2014).

3.4.1 Equipment and materials used for the transesterification

SCGs oil, chicken eggshells for calcium oxide, lithium oxide, methanol (99.95 % purity), distilled water, sulphuric acid (99.50 % purity), thermometer, glass condenser, temperature-controlled heating plate, magnetic stirrer, three-mouth round bottom flask (to use as a batch reactor), vacuum system, nitric acid (99.50 % purity), kiln (up to 1000 °C), and a separating funnel.

3.4.2 Catalysts

Calcium oxide ($CaO_{(s)}$) is widely used as a heterogeneous green catalyst in fuel grade hydrocarbons production. The conditions for catalyst synthesis such as temperature, pressure, and time of sintering influence the catalyst activity and then the yield of produced fuel-grade hydrocarbons. To produce $CaO_{(s)}$ from chicken egg shells, the egg shells were crushed and calcined at 900 °C for 5h as depicted in Figure 3.7. The decomposition reaction of calcium carbonate ($CaCO_3$) to produce $CaO_{(s)}$ is depicted by the reaction equation 3.12.

$$CaCO_{3(s)} + \text{heat} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{3.12}$$

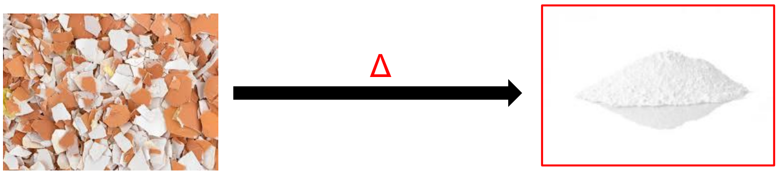


Figure 3.7: Chicken eggshells to calcium oxide.

The resulting calcium oxide was doped with lithium (Li-CaO$_{(s)}$) and used as a catalyst in 4 experiments. The catalyst was prepared by heating 99 wt% CaO$_{(s)}$ and 1 wt% lithium oxide at 600 °C for 4 h in the kiln.

3.4.3 SCGs oil transesterification experimental procedure

The SCGs oil was heated to 110 °C before feeding it to the reactor this was done to remove any traces of water in the oil. Figure 3.8 depicts the reactor set-up of the SCGs oil transesterification.

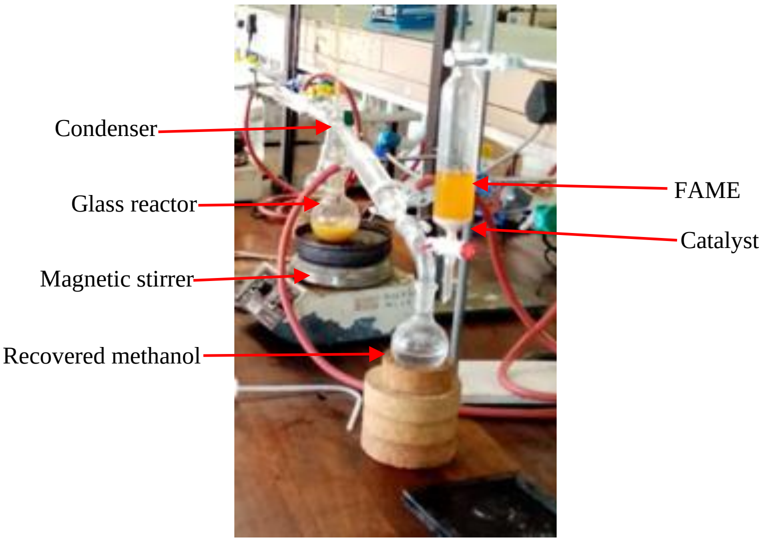


Figure 3.8: SCGs oil transesterification reactor set-up.

To investigate the effect of catalyst loading on FAME yield, SCGs oil and methanol, at a molar ratio of 1:12 were added into the batch reactor. The reactor was operated at 63 °C and 101.325 kPa. A catalyst weight ranging between 0.50 and 5 wt% of the oil used fed into the reactor for different experiments. The reaction was carried out for 1.33 h and a mixing speed of 165 rpm was used. Four experiments were conducted for each catalyst loading for statistical analysis, and repeatability test purposes.

To investigate the effect of reaction time on FAME yield, the reaction time was varied between 1 to 3 h. While keeping the reactor conditions the same as above, and using Li-CaO $_{(s)}$ as a catalyst at a loading of 5 wt% of the oil used, a mixing speed of 165 rpm and oil to methanol molar ratio of 1:12 was used. Once the reaction was complete, the reactor contents were discharged into a separating funnel and left to settle for 24 h.

The fuel grade hydrocarbons produced were washed three times: the first wash was with deionised water to remove any traces of un-reacted methanol and any other contaminants, the second wash with 2 wt% (aq) nitric acid to remove any traces of the catalyst, and the final wash was with deionised water to remove any traces of nitric acid from the previous wash. The washed fuel-grade hydrocarbons were centrifuged for removal of water, and finally dried in a heating plate at 120 °C for 0.5 h.

The products stream was analysed for unreacted feedstock (oil), methanol, FAME and glycerol. The FAME yield was calculated using equation 3.13.

$$\text{FAME yield} = \left(\frac{\text{Mass of FAME Produced(g)}}{\text{Mass of SCG Oil Used (g)}}\right) 100\% \qquad (3.13)$$

FAME produced was analysed for density, acid value, viscosity and saponification value, according to EN 14111 (Bondioli1 *et al*., 2011).

3.4.4 Experimental plan.

The design of experiments (DoE) is a method used to evaluate a relationship between parameters affecting a process and the process' outputs. In general, it's utilised to discover cause and-effect relationship. This information is required for monitoring process inputs and optimising the process output. In recent years, the use of DoE has drastically increased, and it has been used for the optimisation of a wide range of industrial processes, such machining, chemical mixing, and biochemical processes, to determine the best conditions. The most well-known method of DoE design is responses surface methodology (RSM), which was first introduced by Box and Wilson in the early 1950s (Draper, 1992). The central composite design (CCD) and the Box-Behnken design are the two most prominent forms of experimental designs for constructing second-order models among RSM designs. The benefits of using the Box-Behnken designs is that can generate higher order response surfaces using fewer required runs than a normal factorial technique.

RSM is used to determine the values of the process input parameters which will result in optimum process outputs. RSM is one of the optimisation approaches that is now being employed on a massive scale to describe the performance of biochemical processes and to discover the optimum of the desired responses. With respect to the process input variables, the optimum may be either the minimum or maximum of a certain function (Alfarjani, 2012). RSM is a collection of mathematical and statistical tool for experimental and process modelling and forecasting a response of significance that is influenced by a number of input variables, with the objective of optimising that response (Montgomery, 2019). RSM also specifies the links between one or more measured responses and the primary controllable input components. (Khuri and Cornell, 2018). Provided all independent variables are quantifiable and can be repeated with insignificant error, the response surface can be expressed using equation 3.14:

$$\mathrm{Y} = \mathrm{C_0} + \sum_{\mathrm{i=1}}^{\mathrm{k}} \mathrm{C_i X_i} + \sum_{\mathrm{i=1}}^{\mathrm{k}} \mathrm{C_{ii}}\, \mathrm{X_i^2} + \sum_{\mathrm{i=1}}^{\mathrm{k-1}} \sum_{\mathrm{i=i-1}}^{\mathrm{k}} \mathrm{C_{ij} C_{ij}} \tag{3.14}$$

With regards to the present study; Y (wt%) is the oil extraction yield or fuel grade hydrocarbons yield depending on the experiment being conducted, X_1, X_2 are process parameters to be optimised, C_o is the constant C_i the coefficients of the linear terms, C_{ii} coefficients for the quadratic terms and of C_{ij} is the coefficient of the interaction effects.

These major process parameters can be identified by reviewing previous literature or undertaking a preliminary investigation using a factorial or partial factorial design. For the extraction of oil from SCGs, parameters such as oil extraction time (X_1), solids-to-solvent (X_2) ratio and the type of solvents used plays a crucial role in the efficiency of the oil extraction process (Efthymiopoulos, 2018). Concerning the oil transesterification, process parameters such as catalyst loading (X_2), reaction time (X_1), reactor temperature and stirrer speed plays a crucial role in the in-process efficiency (Mathiyazhagan and Ganapathi, 2011).

Finding the limits of each factor:

With regards to SCGs oil extraction the minimum and the maximum process parameters were as follow:

- SCGs moisture content < 10 wt%.
- SCGs particles size distribution range: 430 – 750 µm.
- Extraction time: 1− 8 h.
- Solvent-to-solids ratio: 1:5 − 1:20 w/v

The first two parameters were only investigated for the purpose of characterisation of SCGs.

With regards to the SCGs oil transesterification process the minimum and the maximum process parameters were as follow:

- Reaction time: 1– 3 h.

- Catalyst loading: 0.50 – 5 wt%.

<u>Design-Expert experimental plan:</u>

RSM is commonly approached as a problem to be solved in a series of steps. In the instance of production of fuel-grade hydrocarbons from SCGs, the following process steps were followed to develop mathematical models for both SCGs oil extraction and heterogeneous transesterification of the SCGs oil.

- Identifying the critical process parameters for both oil extraction and transesterification process.
- Establishing the limits of each process parameter.
- Develop experimental design levels.
- Conducting the experiment.
- Recording the responses.
- Development of mathematical model.
- Estimation of the coefficients in the model.
- Testing the adequacy of the models developed.

The encrypted and non-encrypted levels of the Box-Behnken predictor variables are depicted in Table 3.2 and Table 3.3 for the SCGs oil extraction process and SCGs oil transesterification process preventively.

Table 3.2: Independent process variables and their experimental design levels for the SCGs oil extraction.

			levels		
Variables	**-1**	**-0.5**	**0**	**0.5**	**1**
Time (h)-X_1	1.00	2.50	4.50	5.50	8.00
SCG-to-2-MeTHF ratio (w/v)-X_2	0.20	0.10	0.067	0.056	0.05

A maximum of 14 experiments were predicted for both the SCGs oil extraction and the transesterification process.

Table 3.3: Independent process variables and their experimental design levels for the transesterification.

			levels		
Variables	**-1**	**-0.5**	**0**	**0.5**	**1**
Time (min)-X_1	60	90	120	150	180
SCG oil-to-Li-$CaO_{(s)}$ loading (wt%)-X_2	0.50	1.00	2.00	4.00	5.00

The first-order polynomial model is usually used until the system is found to have a curvature, and at this point the second-order polynomial model is employed. Generally, the probability value (p-value) is one of the major values investigated to determine the significance of an empirical model. A p-value less than 0.05 makes the model significant and the p-value for the lack-of-fit must be greater than 0.05 to make the model's lack-of-fit non-significant (Design Expert, 2005). The least-squares method is employed in determining the p-value of the model and the factors involved (Montgomery, 2017).

CHAPTER 4

4.0 Introduction

This chapter is divided into three sections. The first section presents the results from the inherent characteristics (moisture, oil content and particles size) of the three samples. The second section details the effect of solids-to-solvent on the oil quantity extracted from SCGs, and it also details the effect of extraction duration on the oil yield. In addition, the oil extraction efficiency of the green solvent was compared to that of hexane. The third section encompasses the selection and employment of a renewable catalysts to produce fuel-grade hydrocarbons from SCGs oil.

4.1 Characterisation of SCGs

Table 4.1. shows the summary of the average results obtained from each SCGs sample used. The SCGs moisture contents depicted in Table 4.1 are similar those reported by Abdullah and Bulent Koc (2013), i.e., 67 wt%. They were also found to be in a similar range to those reported by Efthymiopoulos *et al*. (2019), i.e., 64.20 to 69.90 wt% for SCGs obtained from retail coffee shops. The variation in the SCGs moisture content depicted in Table 4.1. can be attributed to different brewing methods which can drastically increase or decrease the moisture content of the resulting SCGs. According to Efthymiopoulos (2018), the initial inbound moisture content of the coffee bean samples can also affect the moisture content of the resulting SCGs.

Table 4.1: SCGs characteristics that affect the oil extraction process.

Samples	Moisture content on dry bases (wt%)	Average particle size (μm)	Oil recovered (wt%)	
			2-MeTHF	Hexane
SCGs 1	67.75	480.40	28.20	18.13
SCGs 2	67.81	482.95	25.19	17.77
SCGs 3	67.94	491.48	26.77	17.32

The particle size distribution was found to be slightly different for each sample, which could be attributed to the upstream coffee beans processing methods, and the coffee beverage brewing methods used. Three 35 g samples from each sample batch were subjected to an oil extraction process using 2-MeTHF as a solvent for 8 h. It was observed that the oil yield obtained did not exceed 28.20 wt%, while the SCGs flooding by the solvent suggests that the SCGs were getting saturated with the solvent after a prolonged extraction period. Figure 4.1 to 4.3, depicts the drying curves of the SCGs samples used in this study.

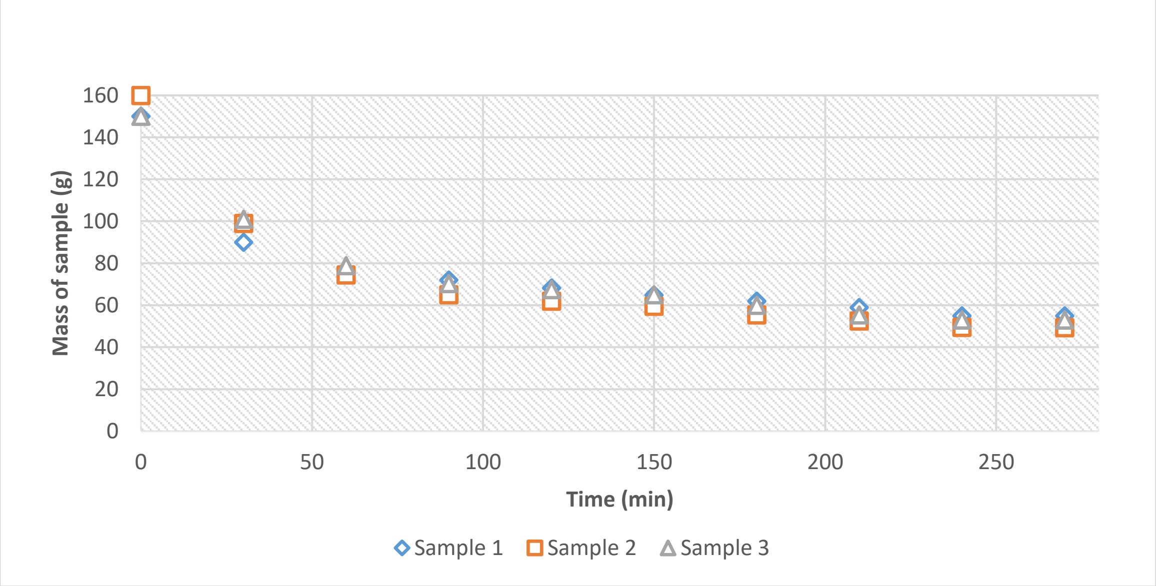


Figure 4.1: Mass vs dying time graphs for three different sub-samples taken from SCGs 1.

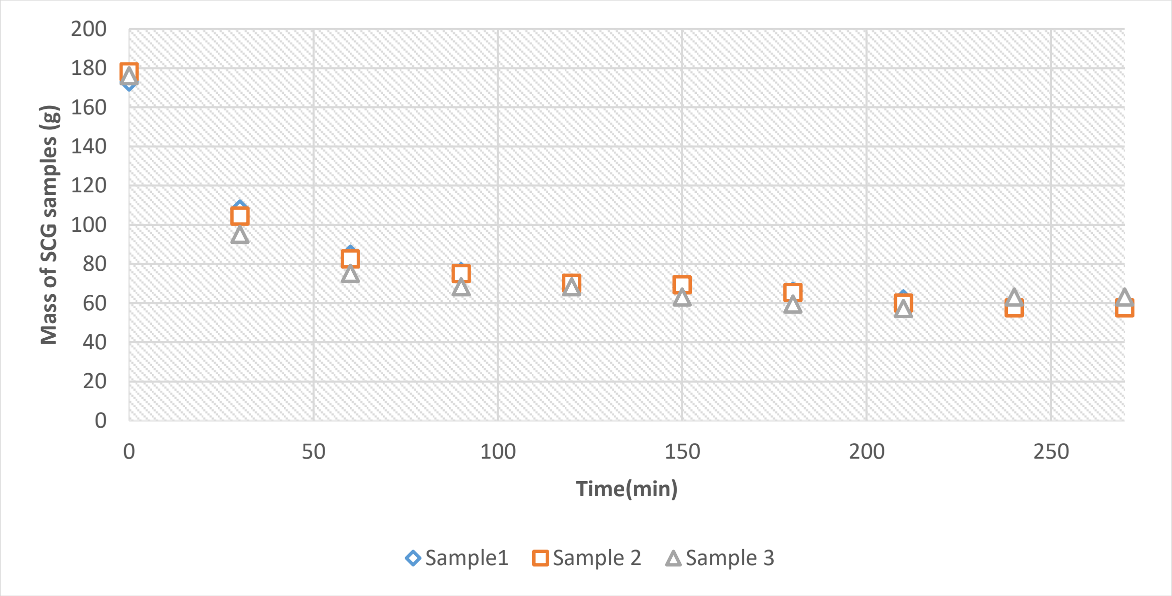


Figure 4.2: Mass vs dying time graph for three different sub-samples taken from SCGs 2.

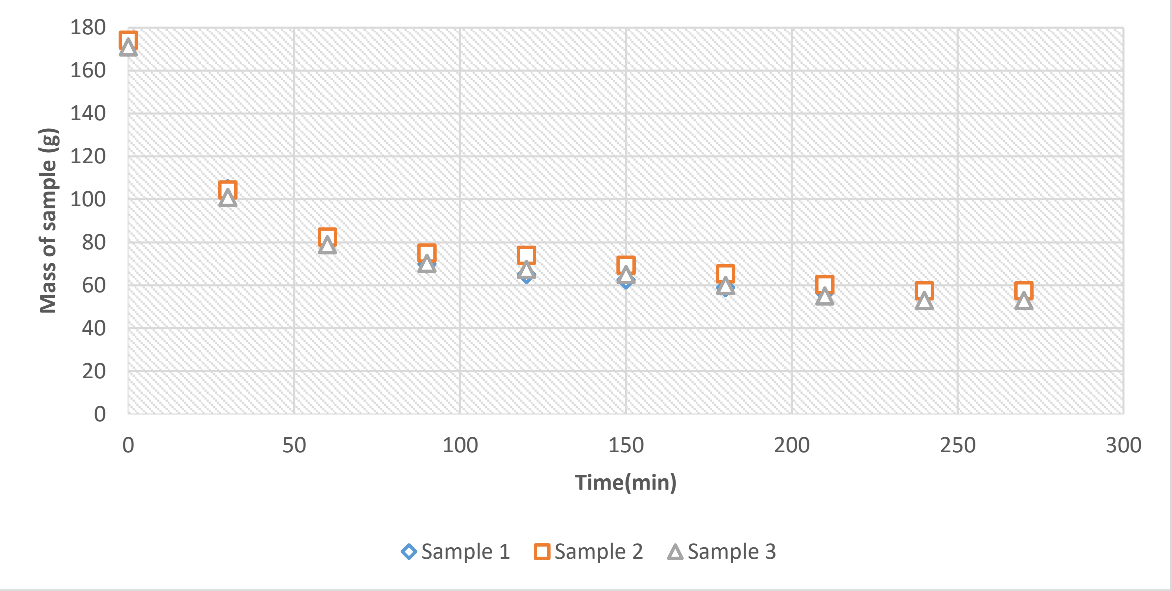


Figure 4.3: Mass vs drying time for three different sub-samples taken from SCGs 3.

It was observed that the three SCGs samples used in this work had similar drying curves. It was also observed that after 4 h in the drying oven at 110 °C using 6.50 mm sample thickness, the mass of the samples stopped decreasing, thus implying that most of the free moisture was removed.

In Figures 4.1 to 4.3, it is evident that most of the moisture was removed within the first 1 h, which was a similar observation made by Efthymiopoulos (2018). The high drying rate during the first 1 h of the drying process can be accredited to the removal of the unbound moisture, which is found between the SCGs particles. Considering these observations, it can be concluded that before oil extraction from retail SCGs samples, the samples need to be dried to bring the moisture content to the recommended value of < 10 wt%.

The average particle size of dried SCGs samples used in this investigation was found to be 428 µm, 401µm, and 490µm for the SCGs1, SCGs 2, and SCGs 3 samples, respectively. These values were calculated using equation 3.5. The variation in the particle size of the samples used (Table 4.1) can be attributed to different pressures applied during the treatment of the roasted coffee beans during the preparation of the coffee beverages (Efthymiopoulos, 2018). The average particle size of the samples depicted in Table 4.1 is outside of the optimum particle size of 500 – 750 µm as described by Sayyar *et al*. (2009). Before oil extraction, for the investigation of process parameters that affects oil yield. The three SCGs(1-3) samples were mixed to improve the average particle size of the samples, hence increasing the oil extraction efficiency.

The physcial characteristics of SCGs prior oil extraction,i.e., they were composed of fine particles and aggregate particles. They appeared as a dark brown powder as depicted in Figure 4.4 (a). After extration the SCGs changed to pale brown as depicted in Figure 4.4 (b). This colour change in SCGs indicated that some colour bodies from SCGs cells walls were being extrated by 2-MeTFH (Akgün *et al*., 2014).

Figure 4.4: SCGs before (a) and after (b) oil extraction using 2-MeTHF as a solvent.

Figure 4.5 depicts the scanning electron microscopy (SEM) images of the surface mophorlogy of the blended SCGs samples before oil extraction (Figure 4.5 a) and after oil extraction (Figure 4.5 b). There is an obvious difference between the two images. In Figure 4.5 (a), the surface of the SCGs appeared to have a rough texture,with a well defined thick suspension of oil embeded on the cell walls of the SCGs (Somnuk *et al*., 2017).The surface of Figure 4.5 (b), appeared smoother suggesting that the oil has been extracted from cell walls of SCGs, similar observations were made by Somnuk *et al*. (2017).

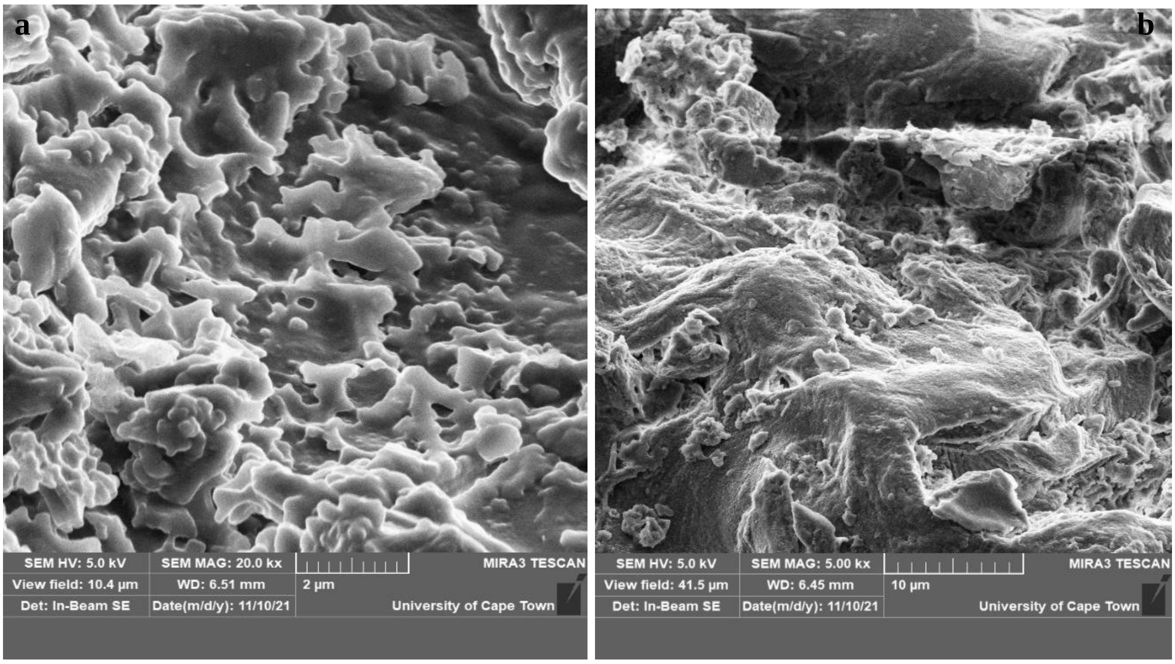


Figure 4.5: Scanning electron microscope of mixed SCGs before (a) and after (b) oil extraction.

The oil content of the SCGs were determined using both the solvents, with hexane giving an average oil yield of 17.77 wt% of the SCGs used, at 1:15 (w/v) solids-to-solvent ratio, for 5 h extraction time. These results are similar to those reported by Caetano *et al*. (2012), i.e, 16 wt% for the same extraction conditions and similar to those obtained by Mofijur *et al*. (2020), i.e., 17.23 wt% which they achieved using ultrasonic-assisted oil extraction technologies. The results obtained using hexane as a solvent, at 1:30 (w/v) solids-to-solvent ratio, for 0.57 h, were similar to those reported by Ahangari and Sargolzaei (2013), i.e, 16.70 wt% which they achieved using supercritical carbon dioxide. However, 2-MeTHF provided a much higher oil recovery of 26.87 wt%, on average, of the initial SCGs used for a short extraction time of 3 h. Similar results were obtained by Efthymiopoulos *et al.* (2019), i.e., 24.26 to 30.45 wt% oil using hexane as a solvent at 1:9 (w/v) solids-to-solvent ratio,for an extraction time of 8 h.

4.2 Effect of solvent extraction parameters on the oil extraction efficiency and SCGs oil properties.

After having determined the maximum amount of oil that can be extracted from the SCGs samples used in this study. This section investigates the effect of the two crucial parameters when extracting oil from oil-bearing solids, namely extraction time and solvent-to-solids ratio. This section also studied 2-MeTHF as a competitive novel green solvent for oil extraction from SCGs and results were compared to those obtained using the traditional solvent hexane under the same process conditions.

4.2.1 Effect of extraction time on the oil yield.

Figure 4.6 depicts oil yields obtained from the mixer of the dried SCGs while varying extraction time between 1and 8 h, and maintaining a solid-to-solvent ratio of 1:20 (w/v). This was done to investigate the effect of extraction duration on the oil extraction efficiency, for both the solvents in question.

The quadratic line of best fit describes the relationship between extraction time and oil yield for 2-MeTHF. The maximum oil extraction of 27.26 wt% of the initial SCGs used was compared to 19.85 wt% oil extracted by hexane for the same extraction conditions. The maximum oil extraction was achieved in 4 h for 2-MeTHF and in 8 h for hexane. However, it can be observed in Figure 4.6 that after 6 h the oil yield for hexane did not change significantly. This suggested that the 6 h extraction time was sufficient to recover most of the oil present in the SCGs. 2-MeTHF proved to be a more efficient solvent in extracting oil from SCGs when compared to hexane, since less extraction time was required to extract 8.41 wt% more oil than hexane.

The 4 h extraction period for 2-MeTHF was found to be within range, i.e., 3.50 to 5 h of the optimum oil extraction, from the oil-bearing seeds (Lawson *et al*., 2010). However, in Figure 4.6 it can be seen that increasing the extraction time for 2-MeTHF resulted in a decrease of the extracted oil. This decrease can be attributed to SCGs being saturated with the solvent, hence preventing further increase in oil extraction. The oil extracted with 2-MeTHF was observed to be darker than the oil extracted using hexane, which implies that other colour bodies were extracted, probably due to the high boiling point of 2-MeTHF (80 °C) and the polar nature of 2-MeTHF (Lawson *et al*., 2010).

Table 4.2 shows the average percentage and standard deviation of oil extracted from the combined SCGs samples using 2-MeTHF. The quadratic regression coefficient of 0.97 suggest that the quadratic model is an excellent fit for correlating extraction time and oil yield for 2-MeTHF. The low standard deviation per respective extraction time implies that for a given extraction conditions, such as extraction time, temperature, solvent-to-solids ration 2-MeTHF is capable of extracting oil at a consistent rate. This ability of 2-MeTHF to consistently extract the same amount of oil from SCGs per given extraction condition is important for process design.

Table 4.2: 2-MeTHF oil extraction yield from the combined SCGs samples at different extraction times and standard deviation.

Time (hr)	Run 1	Run 2	Run 3	Average (wt%)	Standard deviation
0	0.00	0.00	0.00	0.00	0.00
1	12.11	12.03	11.74	11.96	0.19
2	17.36	16.87	17.67	17.30	0.40
3	22.17	22.33	22.85	22.45	0.36
4	27.06	27.38	27.34	27.26	0.17
5	26.59	25.82	26.79	26.40	0.51
6	25.77	26.09	26.08	25.98	0.18
7	26.44	25.53	26.15	26.04	0.46
8	25.93	26.19	25.88	26.00	0.17

Table 4.3 shows the average and standard deviation oil extracted from SCGs using hexane as solvent.

Table 4.3: Hexane SCGs oil yield at different extraction period and standard deviation.

Time (hr)	Run 1	Run 2	Run 3	Average (wt%)	Standard deviation
0	0.00	0.00	0.00	0.00	0.00
1	12.62	12.87	12.88	12.79	0.15
2	14.65	14.31	14.69	14.55	0.21
3	15.77	15.81	16.03	15.87	0.14
4	17.58	17.88	17.69	17.72	0.15
5	17.91	17.69	17.71	17.77	0.12
6	19.11	19.12	19.04	19.09	0.04
7	19.30	19.07	19.14	19.17	0.12
8	19.89	19.75	19.91	19.85	0.09

The relationship between extraction time and oil yield, for hexane also appeared to follow a quadratic model. However, this quadratic relationship is not strong as that of 2-MeTHF.The quadratic regression coefficient for hexane model, i.e., 0.87 is 0.1, less than that of 2-MeTHF. Hexane was also able to repeatedly extract the same amount of oil from SCGs per given extraction condition.

In Figure 4.6 it is evident that 2-MeTHF has a better oil extraction than hexane, however, the 1 h extraction with hexane (12.78 wt%) gave a better oil recovery than 2-MeTHF (11.79

wt%). This can be attributed to the number of extraction cycles achieved by each solvent in each extraction period. It was observed that hexane took about 0.87 h to complete 5 extraction cycles, whereas 2-MeTHF took about 1 h to complete 5 extraction cycles. This may be the result of 2-MeTHF's high boiling point.

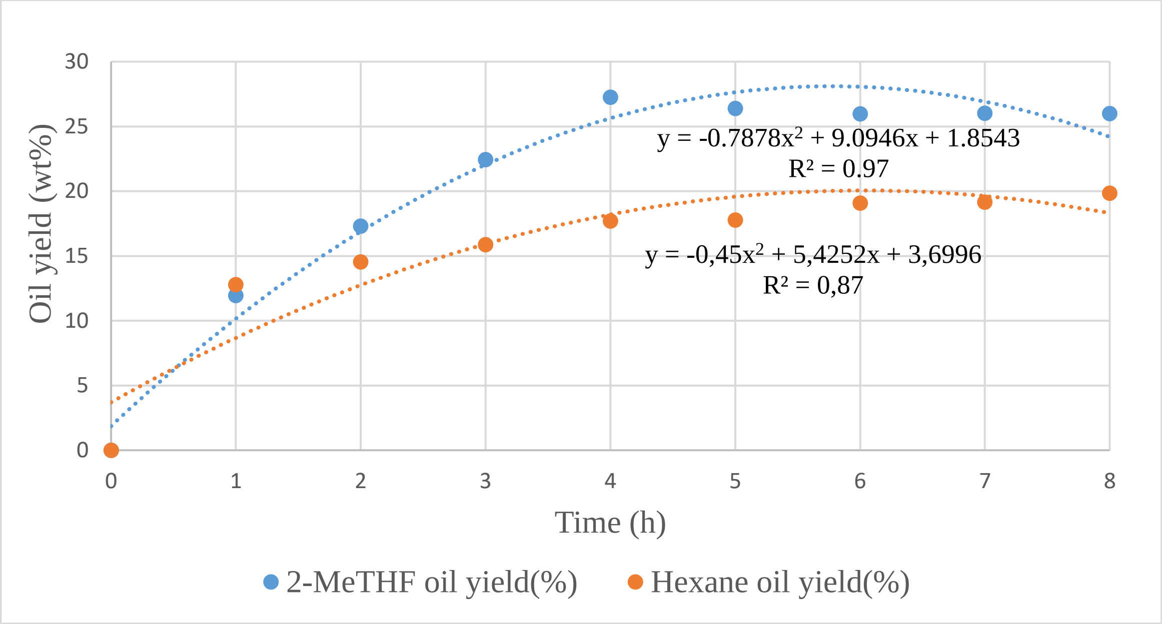


Figure 4.6: Oil yields per mass of dry SCGs achieved at different Soxhlet extraction time (1 to 8 h), for 2-MeTHF and hexane.

To examine the effect of solids-to-solvent ratio on oil extraction efficiency, and to determine which solvent performed better, the extraction time was fixed at 4.50 h. The solids-to-solvent ratio was varied as depicted in Figure 4.7 and Table 4.4. In a high solids-to-solvent ratio (1:5 or 0.20), the extraction efficiency of 2-MeTHF was somewhat lower compared to that of hexane for the same extraction period. This may be attributed to 2-MeTHF being quickly saturated with the crude extract as a result of high solids-to-solvent ratio. Similar observations were made by Efthymiopoulos *et al*. (2019), Najdanovic-Visak (2017), and Pichai and Krit (2015) when they used polar solvent for oil extraction from SCGs.

Table 4.4: Effect of solvent to solids ratio on SCGs oil yield for hexane and 2-MeTHF.

Solids-to- solvent ratio (0.20)	**Run 1**	**Run 2**	**Run3**	**Run 4**	**Average (wt%)**
Hexane	13.88	14.10	13.79	13.69	**13.87**
2-MeTHF	10.12	10.05	10.25	10.05	**10.12**
Solids-to- solvent ratio (0.10)					
Hexane	15.09	15.08	15.05	15.05	**15.07**
2-MeTHF	17.79	17.88	17.98	17.85	**17.88**
Solids-to- solvent ratio (0.067)					
Hexane	18.88	18.87	18.87	18.9	**18.88**
2-MeTHF	25.82	25.78	25.28	25.85	**25.68**
Solids-to- solvent ratio (0.056)					
Hexane	17.23	17.37	17.18	17.44	**17.31**
2-MeTHF	25.85	25.88	25.87	25.95	**25.89**
Solids-to- solvent ratio (0.050)					
Hexane	18.12	18.06	18.15	18.12	**18.11**
2-MeTHF	26.24	26.63	26.55	25.95	**26.34**

The averages in Table 4.4 are presented in Figure 4.7.

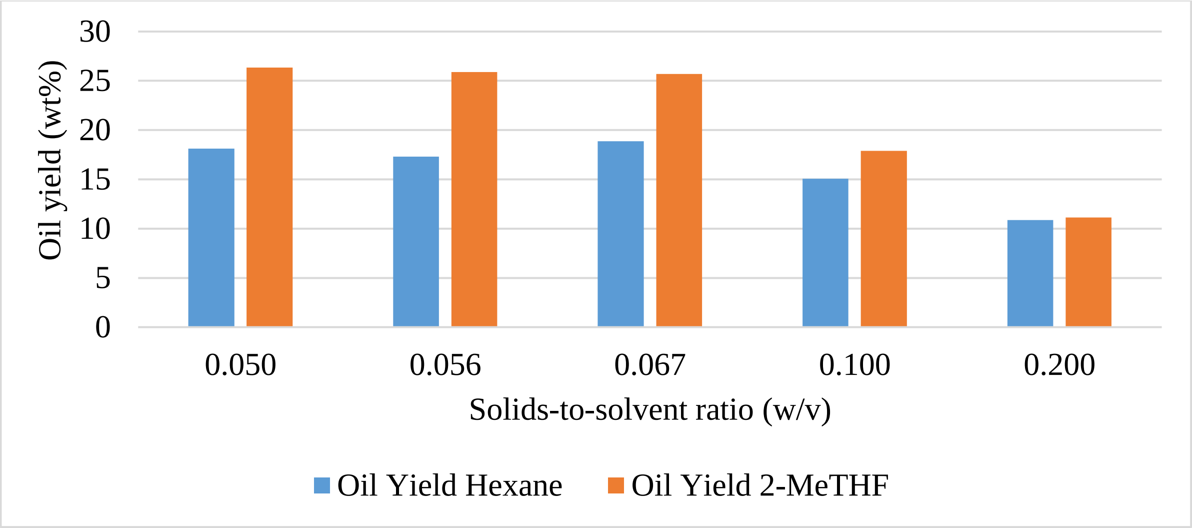


Figure 4.7: Oil yield per mass of dry SCGs achieved at different solids-to-solvent ratio for a constant extraction time (4.5 h), for 2-MeTHF and hexane.

In Figure 4.7 it is evident that despite the solids-to-solvent ratio used, 2-MeTHF has a better oil extraction compared to hexane. For 2-MeTHF the maximum oil extraction of 26.34 wt%

was obtained using the solids-to-solvent ratio of 1:20 or 0.05 (w/v). This agreed with the observations made by Rocha *et al*. (2014) and Pichai and Krit (2015) that the lowest solvent-to-solids ratio gives the highest oil extraction. For hexane, a maximum of 18.88 wt% was achieved using the solids-to-solvent ratio of 1:15 or 0.067 (w/v) instead of 1:20 or 0.05 (w/v) solids-to-solvent ratio. These observations contrast the general trend of low solids-to-solvent ratio which results in high yield of oil extraction. This could be attributed to the presence of relatively high moisture in the SCGs samples used, which inhibits the oil extraction process as reported by Najdanovic-Visak *et al*. (2017).

4.3 Extracted SCGs oil quality

Table 4.5, depicts the characteristics of the crude oil extracted from SCGs, i.e., the density and viscosity of the oil extracted using 2-MeTHF which are similar to those reported by Al-Hamamre *et al*. (2012), i.e., 1180.40 kg/m^3 and 53.06 mm^2/s, respectively. Figure 4.8 depicts the relationship between the oil mass and volume (density). The acid value (AV) and the saponification value (SV) are the chemical properties of the extracted oil. These chemical properties determine the quality of the extracted oil. AV corresponds to the FFA content of the oil and is defined as the amount of KOH required to neutralise the free acid within the oil. The saponification value was within range to those reported by as Al-Hamamre *et al*. (2012), i.e., 173.90 – 222.60 mg$_{KOH}$/g, and the FFA was like those reported by Vardon *et al*. (2013), i.e., 5.60 wt%. The SV of the oil extracted using 2-MeTHF was found to be 184.11 mg$_{KOH}$/g. This result was moderately higher compared to those reported by Muhammad *et al*. (2019), i.e., 176.40 mg$_{KOH}$/g.

Table 4.5: Characteristics of SCGs oil extracted using 2-MeTHF and hexane.

Solvent	Density (kg/m^3) @ 15 °C	Viscosity (mm^2/s) @ 40 °C	FFA Value (wt%)	SV (mg$_{KOH}$/g)
2-MeTHF	1162.83	50.24	5.53	184.11
Hexane	919.12	43.10	3.55	160.32

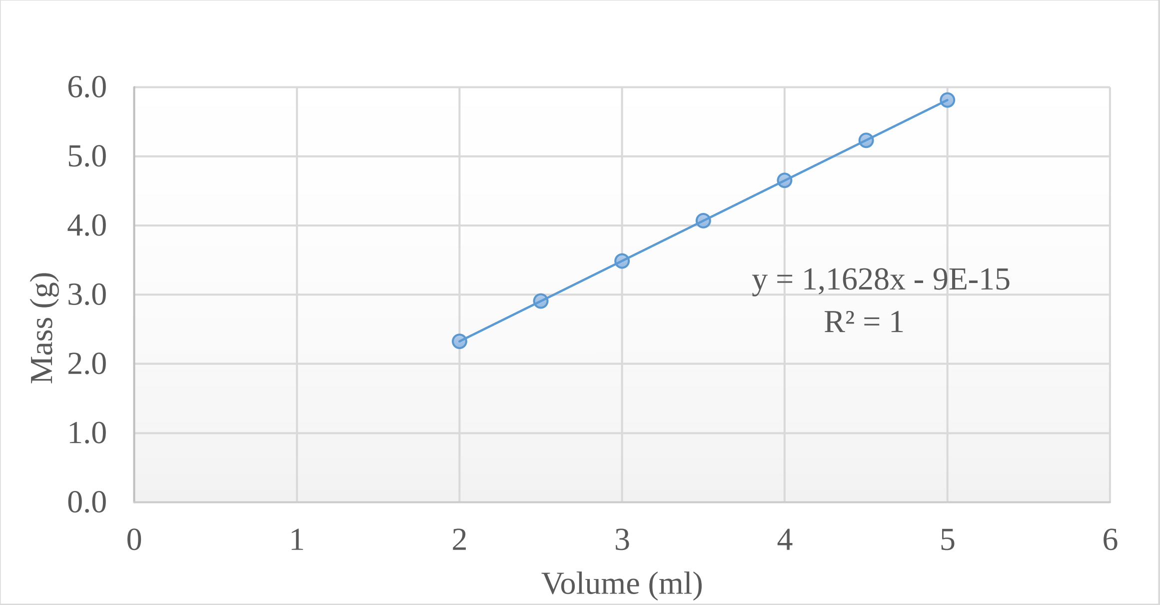


Figure 4.8: Relationship between mass and volume of SCGs oil extracted using 2-MeTHF.

The density (slope of the graph) of the oil extracted using 2-MeTHF was found to be 1.27 times higher than the density of the oil extracted using hexane. This observation was also made by Al-Hamamre *et al*. (2012), who observed that oil extracted from SCGs with polar solvents such as ethanol, acetone and isopropanol, had “gummy” material on it, and had a higher SV compared to oil extracted with non-polar solvents like hexane or heptane. This variation in the densities may be attributed to the “gummy” material observed in the oil extracted with 2-MeTHF (Akgün *et al*., 2014). The high density can be attributed to the “gummy” dark material which was observed when the SCGs oil was heated to elevated temperatures between 100 °C and 110 °C. This observation was also made by Al-Hamamre *et al*. (2012), who suggested that the material might be made up of carbohydrates, proteins, and other constituents produced by complexes of fatty acids. This could explain the high AV and high FFA content of the oil produced in this study. However, the oil yield was not reduced as Al-Hamamre *et al*. (2012), reported for polar solvents, such as ethanol and chloroform.

Figure 4.9 depicts the relationship between the volume and the mass of the oil extracted using hexane (density). It can be seen that the density (slope of the graph) of oil extracted using hexane is much lower than that of the oil extracted using 2-MeTHF. The other oil properties of the oil extracted with hexane were also lower than those of the 2-MeTHF extracted oil.

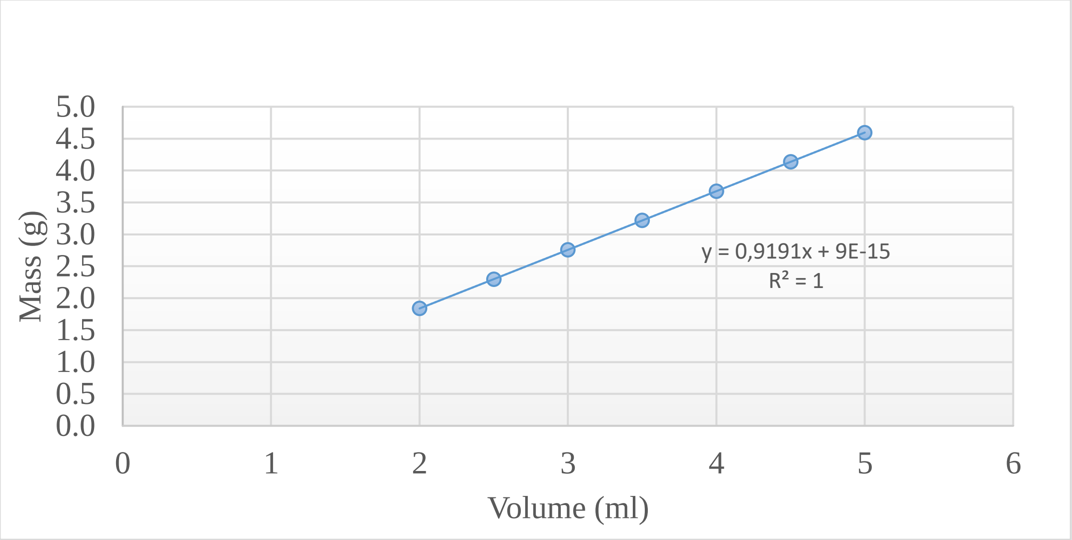


Figure 4.9: Relationship between mass and volume of SCGs oil extracted using hexane.

The density and viscosity of the oil extracted using hexane are similar to those reported by Caetano *et al*. (2012), i.e., 917 kg/m^3 and 22.23 mm^2/s. The SV of the oil was like those reported by Haile (2014), i.e., 167.28 mg$_{KOH}$/g, and the FFA value was like that reported by as Al-Hamamre *et al*. (2012), i.e., 3.65 wt%. The quality of the oil extracted using hexane was similar to those found in most literature (Vardon *et al*., 2013; Muhammad *et al*., 2019; Efthymiopoulos *et al*., 2019). Before SCGs oil can be used for fuel-grade hydrocarbons production, it should undergo mechanical purification. The oil should be filtered through screens to remove any solids. It was observed that the oil extracted using hexane had fine solid particles, and it was brighter than the oil extracted using 2-MeTHF.The bright colour of the oil extracted with hexane can be attributed to the low boiling point of hexane, which only allow extraction of non-polar oil components of the SCGs oil. This selective extraction of hexane prevents the extraction of colour compounds like caffeine, Maillard reaction products, carbohydrates, phosphatides, and other continuities (Al-Hamamre *et al*., 2012).

Figure 4.10. shows the SCGs oil extracted using 2-MeTHF (a) and the oil extracted using hexane (b). When the oil was heated to temperatures between 100 and 110 °C to remove water and traces of the solvents from the oil, a dark “gummy” residue was observed at the bottom of the flask for the oil extracted with 2-MeTHF. This dark material was not observed when the oil extracted with hexane at similar temperatures.

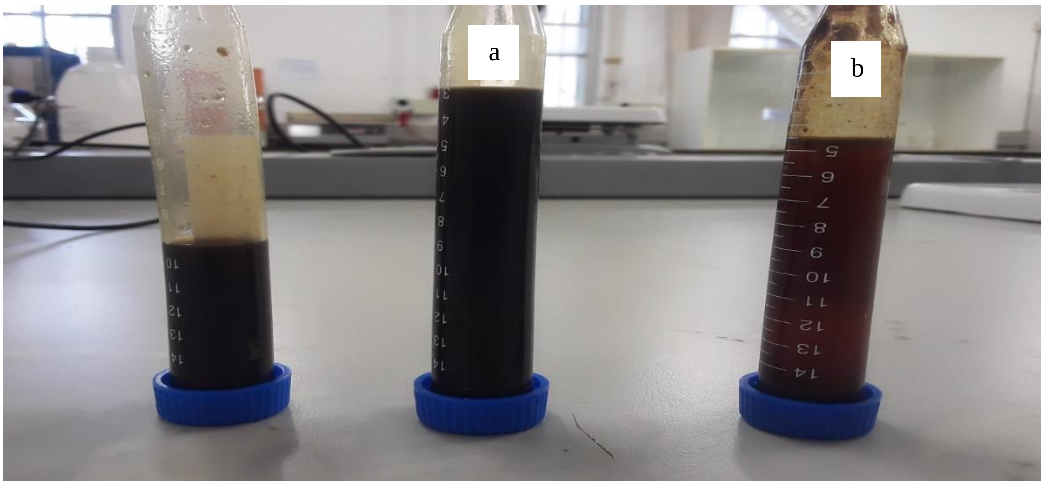


Figure 4.10: SCGs oil samples extracted using 2-MeTHF (a) and hexane (b).

It has been reported that temperatures between 100 and 200 °C tend to weaken the coffee cell wall structure of the coffee beans and increase the solubility of colour bodies, such as, *arabinogalactans* and *mannans* (Campos-Vega *et al*., 2015). The origin and up-stream coffee processing methods used, coupled with the high boiling point and polarity of 2-MeTHF may have contributed to the weakening, and extraction of polar molecules such as the SCGs cell wall, (which could be the contributing factor for the dark colour oil), and the inbound oil which improved the overall oil extraction yield.

4.4 SCGs oil extraction optimisation for 2-MeTHF.

In this investigation, the combined effect on the oil extraction efficiency of the two selected process parameter, SCGs-to-2-MeTHF ratio and extraction time was investigated. Table 4.6 presents the SCGs oil yields achieved from different combinations of the process parameters. Based on the number of process parameters that were to be simultaneously varied, DoE estimated that 14 experimental runs will be sufficient to assist determine a model for the process. Up on the analysis of the process outputs, a quadratic regression model was proposed. Table 4.6 depicts the results obtained after 14 experimental runs, which were obtained by employing the quadratic regression model. The yield of SCGs lipids is predicted by the quadratic model with coded variables, and the model is depicted by equation 4.1. Where, Y is the SCGs oil yield and X_1, and X_2 represent the extraction time (h) and SCGs-to-solvent ratio (w/v), respectively.

Table 4.6: Design of experiment for the optimisation of extraction of oil from SCGs.

Run	Time (hr)	SCGs-to-Solvent ratio (w/v)	Actual Yield (wt%)	Predicted Yield (wt%)
1	0	0	25.70	24.64
2	1	-1	15.40	14.95
3	0.5	0.5	24.60	25.09
4	-0,5	-1	13.10	14.69
5	0	0	26.10	24.64
6	0.5	-0.5	21.20	22.20
7	-1	-1	12.50	11.10
8	1	0	23.10	23.24
9	1	1	20.50	20.61
10	-0.5	1	17.10	18.23
11	-1	0	15.10	17.05
12	-1	0.5	17.40	16.52
13	-0.5	1	19.20	18.23
14	0	0	25.10	24.64

$$Y = (4.964 + 0.35X_1 + 0.26\ X_2 + 0.079X_1X_2 - 0.49X_1^2 - 0.62X_2^2\ )^2 \tag{4.1}$$

Figure 4.11 depicts the diagnostic graph for the model given by equation 4.1. Figure 4.11 gives the relationship between the oil yield predicted by the model versus actual values obtained from the experimental work. The observed linear relationship in Figure 4.11 shows a good degree of agreement between actual versus predicted oil extraction. This agreement in the actual and predicted oil yields suggest that the model can best describes the effect of the investigated process parameters on oil extraction efficiency from SCGs using 2-MeTHF as a solvent.

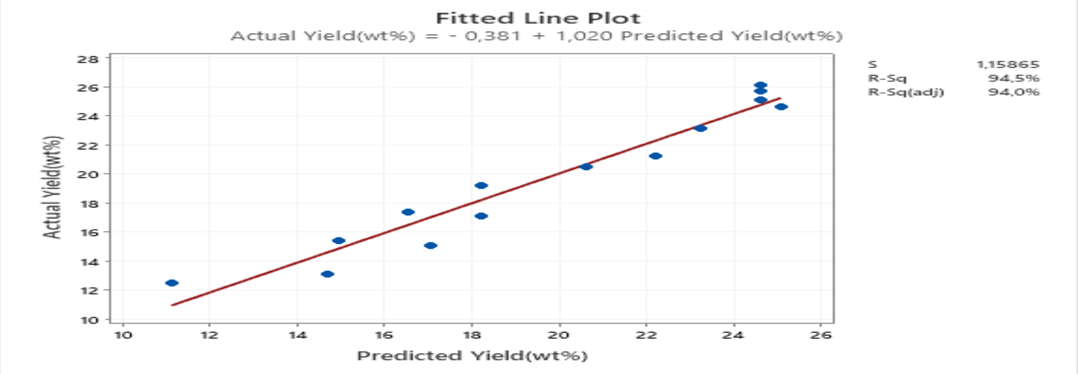


Figure 4.11: Actual vs predicted plot of SCGs oil yield using 2-MeTHF as a solvent.

The surface response of the qaudratic model was used to optimise the extraction of oil from SCGs using ANOVA. The out comes of this model are shown in Table 4.7.

Table 4.7: Analysis of discrepancies on the results for the quadratic regression model.

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	0.0359	5	0.0072	23.93	0.0001	significant
X_1-Time	0.0086	1	0.0086	28.73	0.0007	
X_2-SCG-to-Solvent ratio	0.0044	1	0.0044	14.61	0.0051	
X_1X_2	0.0002	1	0.0002	0.825	0.3904	
X_1^2	0.0057	1	0.0057	18.91	0.0025	
X_2^2	0.0105	1	0.0105	34.95	0.0004	
Residual	0.0024	8	0.0003			
Lack of Fit	0.0020	5	0.0004	3.47	0.1673	not significant
Pure Error	0.0004	3	0.0001			
Cor Total	0.0383	13				

The p-value of the parabolic model was 0.0001, which was < 0.05, indicating that the quadratic regression model was significant. The model terms are said to be significant if the p-values are 0.05 and the model terms are said to be insignificant if the p-value is 0.10. The lack of fit “F-value “was estimated to be 0.17, which indicated that the lack of fit was not significant when compared to the pure error. The adjusted R^2 value of 0.90 and the predicted R^2 value of 0.74 have a different value of 0.16, which is < 0.2. This indicated that there was a good estimation between the experimental data and the quadratic model. The SCGs oil yield at the optimal extraction conditions of 1:18 (w/v) SCGs-to-solvent ratio and 4.5 h extraction time was predicted by the model to be 25.10 wt%. The predicted optimal yield was confirmed experimentally, obtaining an oil yield of 26.71 wt% which was slightly higher but close to the prediction.

Figure 4.12 depicts the response surface plot for the oil yield for the combined investigated process parameters. As it can be seen in Figure 4.12 at high solids-to-solvent ratio and short extraction time the oil extraction efficiency of 2-MeTHF is low and increases as the solids-to-solvent ratio is decreased. At the lowest value of solids-to-solvent ratio and at the longest extraction time, the oil yield showed a similar behaviour smooth in increase, until the maximum oil yield was achieved. Figure 4.12 depicts possible combinations of process parameters that can be used to obtain a good oil yield. Based on the slope of the 3-D plot (Figure 4.12) and the coefficients of regression of the quadratic model (Table 4.7) the solids-to-solvent ratio was the more effective parameter on the oil extraction yield. A similar observation was made by Bokhari *et al*.(2012),whey they extracted oil from rubber seeds using hexane as a solvent.

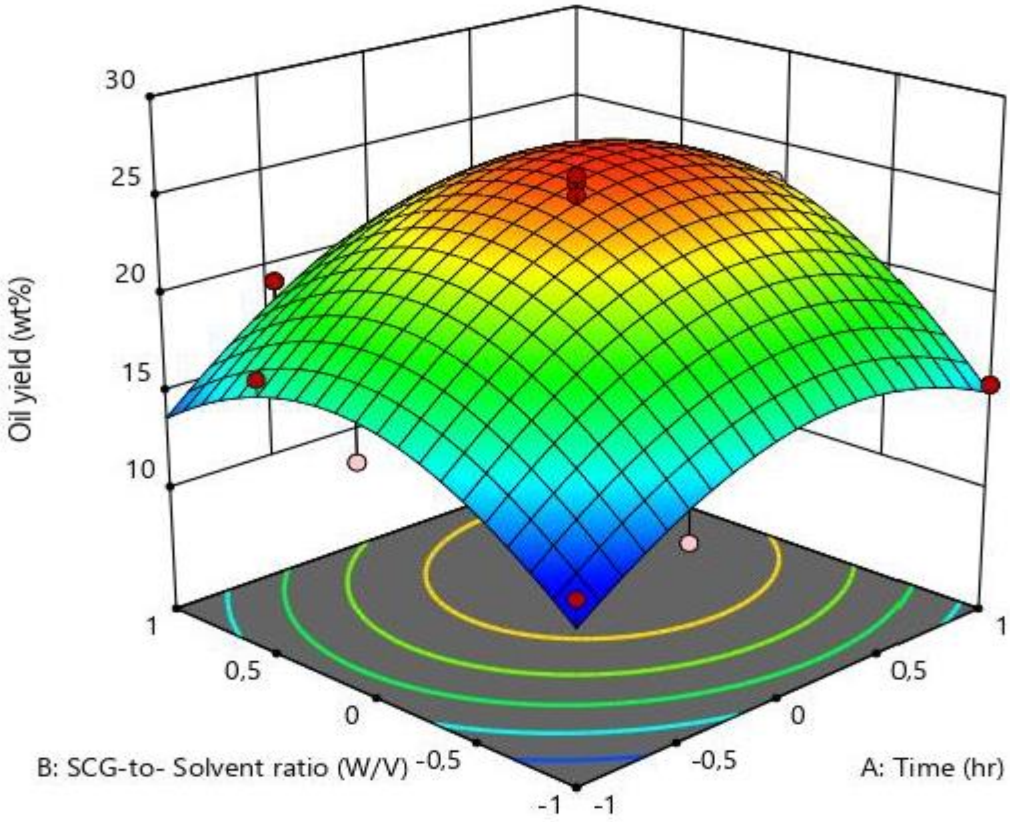


Figure 4.12: Three-dimensional surface plot depicting mutual effect of oil extraction time and SCGs-to-solvent ratio on the oil yield.

The increase in the oil extraction time results in more oil yield. At lower SCGs-to-solvent ratio the oil yield obtained is lesser, due to lower solubility of the oil in solvent (Bokhari *et al.*, 2012). As the solvent to seed ratio increased, the oil yield also increased because the amount of vapour contacted with the seeds increased. According to Son *et al*. (2018), the optimal extraction parameters reduce power consumption and avoid lipid degradation. However, the low solids-to-solvent ratio implies a high energy requirement for solvent recovery. The high solid-to-solvent ratio implies less oil extraction; thus, a trade-off must be made depending on process needs.

4.5 Conclusion

2-MeTFH was investigated as a potential green solvent for oil recovery from SCGs, and hexane was used as a datum solvent. The maximum oil extraction period was found to be between 3.50 and 4.50 h. The lowest oil yields were observed at extraction durations < 1.50

h, advocating that extraction period < 1.50 h were not suitable for oil extraction for both the solvents used in this investigation. It was also observed that increasing extraction period had a significant increase on the oil yield. Concerning the effect of SCGs-to-solvent ratio on the oil extraction efficiency, decreasing the ratio from 1:5 (w/v) to 1:20 (w/v) increased the oil yield considerably. SCGs were observed to get saturated with solvent, especially with 2-MeTHF at a low solids-to-solvent ratio for extraction periods > 5.5 h.

The optimal extraction conditions predicted and confirmed experimentally was 4.5 h for the extraction period, SCGs-to-solvent ratio of 1:18 (w/v) and 25.10 wt% oil yield. These results contrasted the general trend which is, longer extraction period and a low solvent to solid ratio confer higher oil yield. These conditions were tested experimentally and an oil yield of 26.71 wt% was achieved. The values predicted by the model were similar to those obtained experimentally suggesting that the model was a good fit.

The liquid properties such as density, viscosity, and the fuel properties such as FFA and SV of the oil extracted using 2-MeTHF on average were higher than those of the oil extracted using hexane. Moreover, the oil extracted using 2-MeTHF appeared darker compared to the oil extracted using hexane. However, the renewability and high oil yield of 2-MeTHF makes an excellent alternative solvent for oil extraction from oil bearing materials. Extraction duration longer than 5 h appeared to saturate the SCGs with 2-MeTHF and resulted in fine SCGs particles reporting to the oil-solvent mixture, causing a need for an additional oil filtration step. Overall, the 2-MeTHF proved to be a better SCGs oil recovery solvent than hexane, in terms of oil extraction efficiency and shorter oil recovery time. Hexane had a higher oil yield than 2-MeTHF for extraction period < 2 h due to short extraction cycle time compared to 2-MeTHF.

4.6 Transesterification of SCGs oil using eggshell derived $CaO_{(s)}$

This section presents the experimental results obtained by the transesterification of SCGs oil using Li-$CaO_{(s)}$ derived from chicken eggshells as a green catalyst. A model was developed to optimise the transesterification process using the DoE software.

4.6.1 Transesterification

The oil extracted from SCGs was subjected to mechanical cleaning, where solids particles as observed in Figure 4.9, were removed using a sieve mesh. The oil was heated to 110 °C to remove any traces of water. After the SCGs oil was cleaned, heterogeneously catalysed transesterification reaction experiments were conducted. The experimental conditions, for investigating the effect of time on the yield of fuel-grade hydrocarbons were those described in section 3.4.

Table 4.8: Transesterification of SCGs oil at different reaction times.

Time (min)	Run 1	Run 2	Run 3	Run 4	FAME Yield (wt%)	Stranded Deviation
60	82.71	82.38	83.55	84.71	83.34	0.51
90	95.68	89.61	90.45	91.68	91.85	0.13
120	96.97	97.74	96.90	97.42	97.26	0.13
150	95.27	95.00	94.13	95.73	95.03	0.14
180	96.34	96.55	96.97	96.70	96.64	0.16

As depicted in Table 4.8, four sets of experiments were conducted per reaction time. This was done for repeatability purposes. It can be observed in the results in Table 4.8 that the selected reactor conditions were capable of achieving consistent oil conversion per given time. The average SCGs oil conversion for the 60 minutes’ reaction time 5 wt% catalyst loading ,65 °C reactor temperature and a mixing speed of 165 rpm was found to be 83.32 wt%, with a standard deviation of 0.51. This relatively low standard deviation suggested that most of the experimental data points were clustered around the mean value of 83.32. For the similar reactor conditions, the average oil conversion for 90,120,150- and 180-minutes’ reaction times similar observations were made. The average SCGs oil conversions obtained were 91,85,97.26,95.03 and 96.54 wt% respectively, with a relatively low data standard deviation. Suggesting that the collected data was clustered around the mean conversion for the respective reaction time. The average oil conversion versus reaction time is depicted in Figure 4.13. The conversion of SCGs oil to fuel-grade hydrocarbons, with respect to the reaction time appeared to follow a quadratic model. The quadratic regression coefficient of the model was estimated to be 0.93 as depicted in Figure 4.13. The quadratic regression coefficient of 0.93 suggested a strong quadratic relationship between reaction time and fuel-grade hydrocarbons yield.

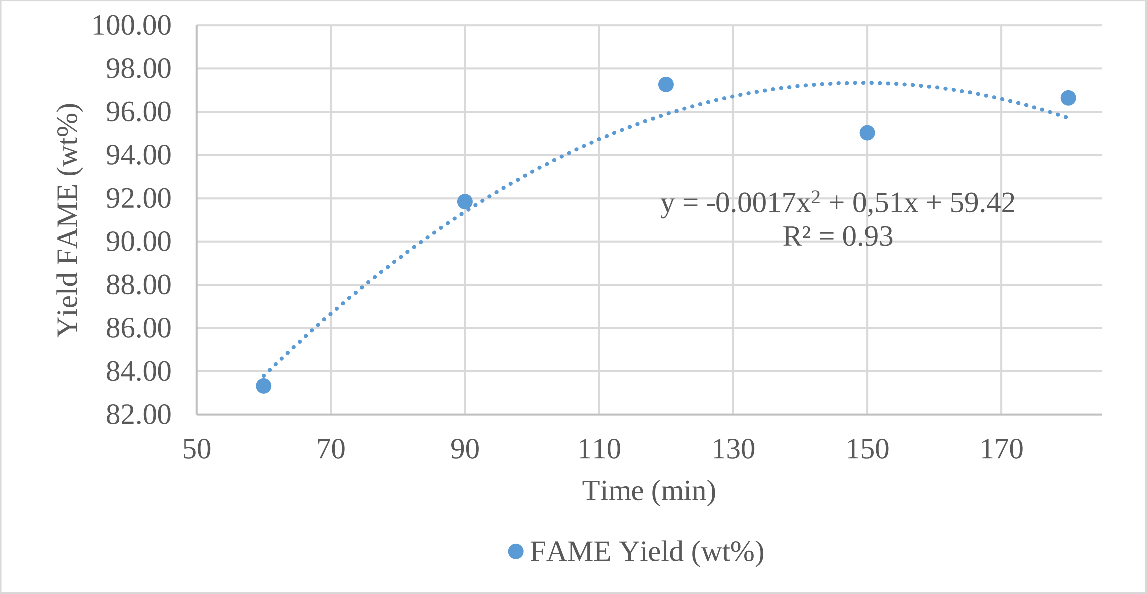


Figure 4.13: Heterogeneous-transesterification reaction yield vs reaction time.

It can be seen in Figure 4.13, that increasing extraction time had a positive impact on the conversion of SCGs oil to fuel-grade hydrocarbons, to a point. The conversion of oil to FAME increased from 83.32 wt% after 1 h of reaction time to 97.26 wt% after 2 h reaction time. Subsequently, decreasing after reaching the optimal value, i.e.,97.26 wt%. The decrease in oil conversion can be attributed to the formation of soap as a result of high catalyst loading and prolonged reaction time (Yesilyurt *et al*., 2018).

The conversions achieved were somewhat lower than those reported by Khurshid (2014), i.e., 98 wt% and Wang *et al*. (2012), i.e. 99 wt% for the same reaction conditions using jatropha oil with 8.50 wt% FFA, and waste cooking oil containing 6.78 wt% FFA. The relatively low conversion rate can be attributed to the presence of water in the oil, which not have been properly removed during the oil purification process. Catalyst poisoning may have also contributed to the low conversion, caused by the presence of FFA in the SCGs oil since a one-step transesterification was used. The presence of the un-reacted FFA in the oil also contributed to the low yield as they were part of the yield estimation as described by equation 3.13.

The effect of varying catalyst loading-to-oil mass is shown in Figure 4.14, while the logarithm best-fit regression line has been added. The experimental procedure was carried out as described in section 3.4.3.

Table 4.9: Transesterification of SCGs oil at different catalyst loadings

Catalyst Loading (wt%)	Run 1	Run 2	Run 3	Run 4	FAME Yield (wt%)	Stranded Deviation
0.50	55.10	54.85	55.13	54.92	55.00	0.14
1.00	58.13	58.21	57.76.	57.91	58.01	0.66
2.00	71.13	71.17	71.27	71.23	71.20	0.06
3.00	92.47	92.13	91.72	91.68	92.00	0.37
4.00	96.40	98.27	99.53	96.00	97.30	1.50
5.00	94.40	94.53	94.80	95.73	94.30	0.60

It can be seen in Figure 4.14 that at low catalyst loading-to-oil mass percentages of 0.50 and 1 wt% of the used oil were not sufficient to convert the to fuel-grade hydrocarbons. Only giving an SCGs oil conversion of 55 wt% and 58 wt%, respectively.

The relationship between the increase in catalyst loading and the yield of fuel-grade hydrocarbons appeared to follow a logarithm model. The logarithm regression coefficient was calculated to be 0.90, suggesting a strong logarithm correlation between the Li-CaO$_{(s)}$ and SCGs oil conversion to fuel-grade hydrocarbons. This contrast the observations made when the effect of time on fuel-grade hydrocarbons yield was investigated.

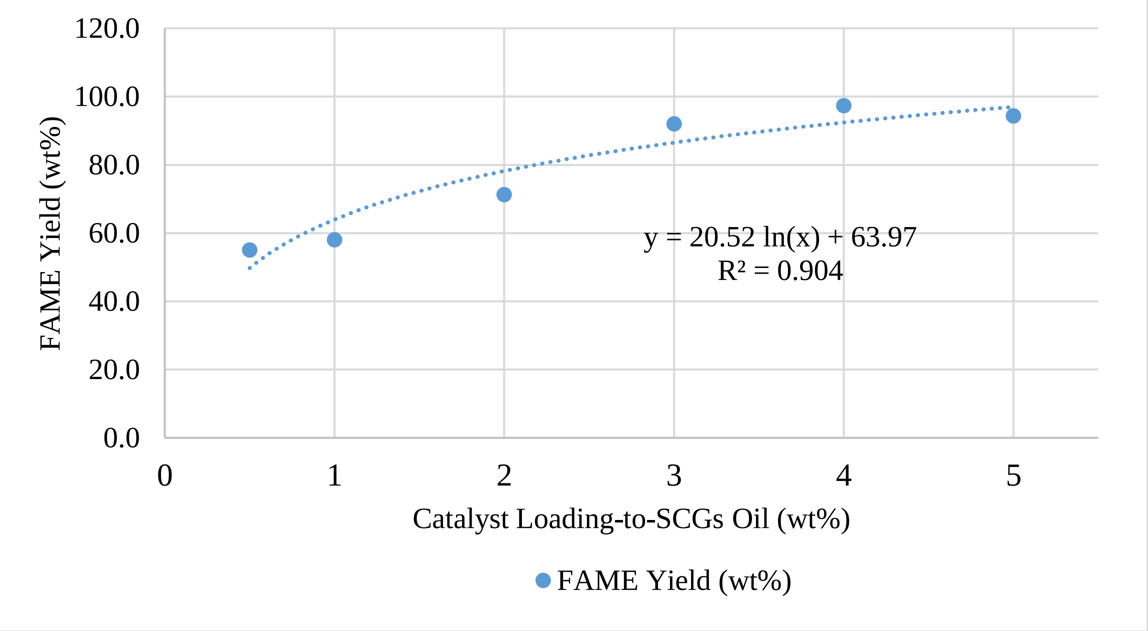


Figure 4.14: Heterogeneous-catalysed transesterification of SCGs oil vs catalyst loading-to-oil mass percentage.

However, further increasing the catalyst loading relative-to-oil mass percentage from 1 to 4wt%, significantly increased the conversion of the oil to fuel grade hydrocarbons, with 4wt% resulting in the highest oil conversion of 97.30 wt%. Catalyst loading higher than 4wt% of the oil led to a modest decrease in the conversion rate due to the formation of soaps. The high FFA (>2 wt%) content forms soaps which decrease the conversion of the oil to fuel-grade hydrocarbons when heterogeneous catalysts are used (Abdullah and Nolasco-Hipolito, 2014). The optimal catalyst loading-to-oil mass percentage was lower than those reported by Khurshid (2014), i.e., 5 wt% and Wang *et al*. (2012), i.e., 5 wt% of Li-CaO$_{(s)}$. Although the FAME yield obtained by Khurshid (2014), i.e,.98 wt%, was similar to those obtained in the present study at higher catalyst loading.

4.6.2 Fuel grade hydrocarbons properties

Table 4.10 shows the fuel (acid value) and the liquid (density and kinematic viscosity) values of the fuel-grade hydrocarbons resulting from the one-step transesterification of SCGs oil using Li-CaO$_{(s)}$ as a renewable catalyst. Figure 4.14 depicts the process undergone by the coffee beans to fuel grade hydrocarbons.

Figure 4.15: Coffee beans to fuel-grade hydrocarbons.

In Figure 4.15, it can be seen, that transesterification of the SCGs oil in the presence of Li-CaO$_{(s)}$ catalyst changed the oil's physical appearance from black to light brown. This physical change in appearance was accompanied by the change in the liquid and fuel properties of the oil discussed in section 4.2.1. The FAME liquid and fuel properties were like those reported by Efthymiopoulos *et al*. (2019), i.e., 835 kg/m^3 and 6.26 mm^2/s. Similar results were also reported by Haile (2014), i.e., 880 kg/m^3 and 5.4 mm^2/s. The transesterification reaction reduced the density of the SCGs oil from 1180.40 kg/m^3 to 850.10 kg/m^3 by converting the oil to fuel-grade hydrocarbons, on average. Table 4.10

depicts the average fuel and liquid properties of the fuel-grade hydrocarbons produced from SCGs oil.

Table 4.10: Liquid and fuel properties of FAME produced from SCGs oil

FAME	**Density @ 20 °C (kg/m^3)**	**Kinematic viscosity @ 40 °C (mm^2/s)**	**AV (mg $_{KOH}$/g_{oil})**
1	894.76	5.18	0.59
2	895.03	5.12	0.55
3	895.51	5.33	0.60
Average	**895.10**	**5.21**	**0.58**

The transesterification reaction also improved the kinematic viscosity of the SCGs oil from 50.24 mm^2/s to 6.89 mm^2/s. The density and kinematic viscosity were calculated as described in section 3.3.4 and 3.3.6. The density (895.01 kg/m^3) of the FAME was found to be within the range required by the EN 14214 standard limit of 860 to 900 kg/m^3 (BSI Standard, 2014).

The kinematic viscosity (5.21 mm^2/s), was similar to those reported by Deligianis *et al.* (2011), i.e., 5.61mm^2/s and by Haile (2014), i.e., 5.40 mm^2/s, however, these results were found to be slightly above the required range of 3.50 to 5.00 mm^2/s (BSI Standard 2014), which is a maximum viscosity for FAME, stipulated by the EN 14214 standard limit. The high viscosity may be assigned to the presence of triglycerides remaining to incomplete conversion. The high viscosity can also be attributed to high levels of FFA in the oil or to the presence of glycerol which was not removed during the purification process.

The acid value was estimated as described in section 4.4.5. The acid value of 0.58 mg_{KOH}/g_{oil} was found to be higher than the retried value of 0.5 mg_{KOH}/g_{oil} value set by EN 14214 standard (BSI-Standard, 2014). High AV were also reported by Caetano *et al.* (2012), i.e., 2.14 mg_{KOH}/g_{oil} and by Efthymiopoulos *et al.* (2019) , i.e., 0.55 mg_{KOH}/g_{oil}. The high AV can be attributed to incomplete oil transesterification, which is evident in relatively low yields obtained, which can be attributed to the presence of FFA in the oil.

4.7 SCGs oil transesterification optimisation.

In this investigation, the transesterification of SCGs oil was maximised by optimising two process parameters, namely, oil-to-catalyst loading and reaction time. The two parameters appeared to have the most effect on the conversion of SCGs oil to fuel-grade hydrocarbons, hence their optimisation. The quadratic regression model was proposed after regression analysis was performed on Box-Behnken exploratory design results. Table 4.11 shows the results obtained after 14 experimental runs, which were obtained by employing the quadratic regression model. The yield of SCGs oil is predicted by the quadratic model with coded variables, the model is depicted by equation 4.2. Y is the SCGs oil conversion, and X_1, and X_2 represent the extraction time in hours and SCGs oil-to-Li-$CaO_{(s)}$ loading (wt%), respectively.

Table 4.11: Analysis of discrepancies on the results for quadratic regression model.

Run	**Time (hr)**	**SCGs oil-to-Catalyst loading (wt%)**	**Actual Yield (wt%)**	**Predicted Yield (wt%)**
1	0	0	92.54	89.49
2	1	-1	59.91	60.22
3	0.5	0.5	90.82	97.02
4	-0.5	-1	55.80	60.22
5	0	0	84.82	89.49
6	0.5	-0.5	79.74	77.97
7	-1	-1	61.00	58.37
8	1	0	92.54	90.06
9	1	1	97.81	98.21
10	-0.5	1	95.84	92.54
11	-1	0	88.74	84.27
12	-1	0.5	81.00	89.49
13	-0.5	1	95.65	92.54
14	0	0	94.09	89.49

$$Y = (9.46 + 0.16X_1 + 0.98X_2 + 0.095X_1X_2 - 0.12X_1^2 - 0.66X_2^2)^2 \qquad (4.2)$$

Actual yield compared to predicted yield plot is demonstrated in Figure 4.16. It can be clearly seen that an acceptable correlation was obtained between predicted and actual data of SCGs oil, fuel-grade hydrocarbons.

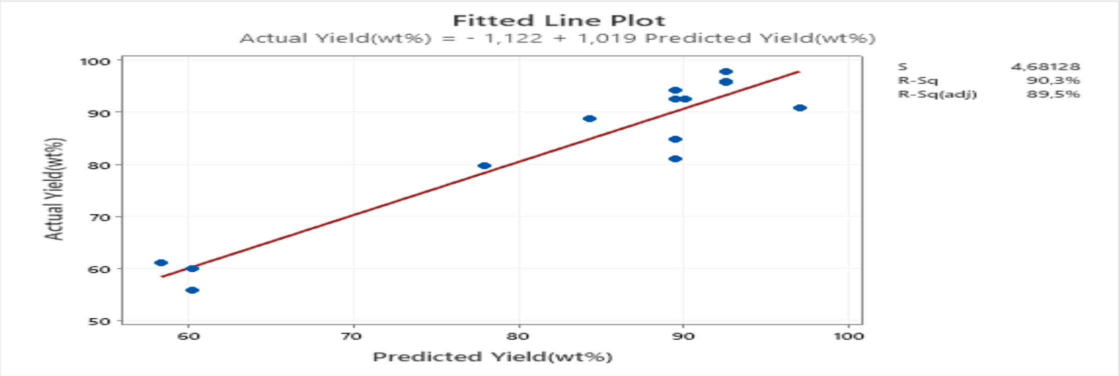


Figure 4.16: Actual vs predicted plot of fuel-grade hydrocarbons yield.

In addition, the line of (y = x) mentioned a better fitting of the model with experimental results,as indicated by the linear regresion coffecient of 0.903. The surface response of the quadratic model was to optimise the conversion of SCGs oil to fuel-grade hydrocarbons using ANOVA. The outcomes of this model are presented in Table 4.12.

Table 4.12: Analysis of discrepancies on the results for the quadratic regression model.

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	8.25	5	1.65	18.65	0.0003	significant
X_1-Time	0.1756	1	0.1756	1.98	0.1965	
X_2-SCG-to-Solvent ratio	6.30	1	6.30	71.25	< 0.0001	
X_1X_2	0.0363	1	0.0363	0.410	0.5399	
X_1^2	0.0365	1	0.0365	0.413	0.5384	
X_2^2	1.20	1	1.20	13.52	0.0063	
Residual	0.7079	8	0.0885			
Lack of Fit	0.5691	5	0.1138	2.46	0.2447	not significant
Pure Error	0.1388	3	0.0463			
Cor Total	8.96	13				

The p-value of the parabolic model was 0.0003, which was < 0.05, indicating that the quadratic regression model was significant. The model terms are said to be significant if the p-value is ≤ 0.05 and the model terms are said to be insignificant if the p-value is 0.10. The lack of fit “F-value “was estimated to be 2.46, which indicated that the lack of fit was not significant when compared to the pure error. The adjusted R^2 value of 0.87 and the predicted R^2 value of 0.77 have a different value of 0.11, which is < 0.2. This indicated that there was a good estimation between the experimental data and the quadratic model. The conversion of the SCGs oil at the optimal reactor conditions of 3 h reaction time and catalyst loading-to-SCGs oil of 4 wt% was predicted by the model to give a maximum oil conversion of 98.21 wt%. The predicted optimal yield was confirmed experimentally, using the following reactor conditions, 65 °C reactor temperature and a stirrer speed of 165 rpm, achieving a lipids conversion of 97.30 wt%, which was slightly lower than the predicted value of 98.21 wt%.

To visualise the correlation between the exogenous variables and the response, the 3-D response surface plot was generated. Figure 4.17 depicted the effect of reaction time and SCGs oil-to-catalyst loading on the conversion of the SCGs oil to fuel-grade hydrocarbons. It was observed that the SCGs oil conversion increased rapidly with the increase in reaction time as well as with the increase of catalyst loading.

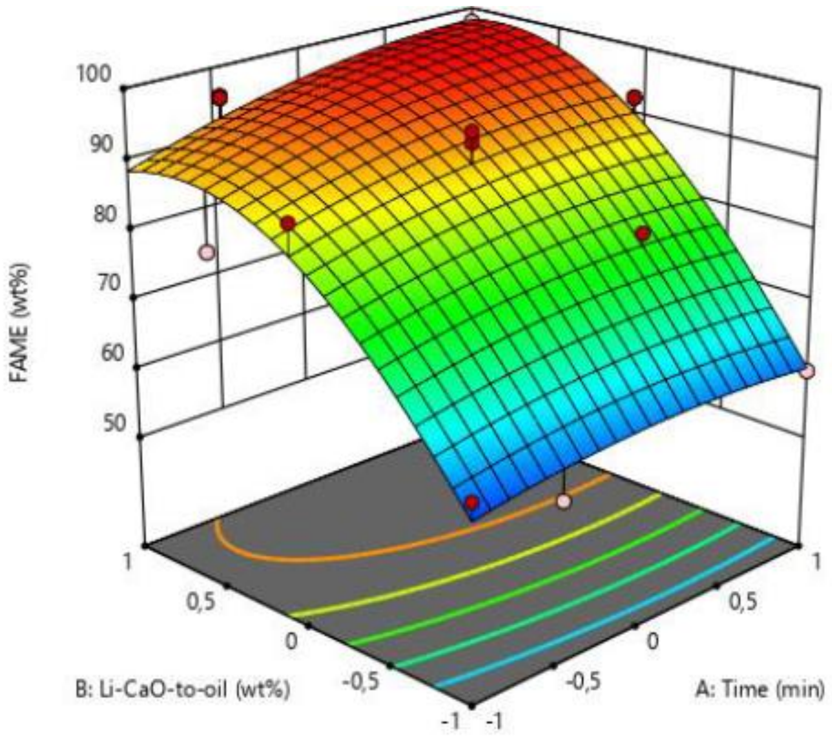


Figure 4.17: Three-dimensional surface plot depicting the mutual effect of reaction time (min) vs catalyst loading-to-SCGs oi (wt%) on FAME yield.

As seen in Figure 4.17, the reaction rate increases with the increase of reaction time. In the first moments, the reaction occurs slowly. In time, the reaction begins to accelerate and FAME yield is increases. Based on the slope of the 3-D plot, (Figure 4.17) and the coefficients of regression significance of the quadratic model in Table 4.8, the reaction time was the most significant factor in the conversion of SCGs oil to fuel grade hydrocarbons between the two studied parameters. The optimum conditions, i.e., 65 °C reactor temperature,165 rpm stirrere speed,4 wt% catalyst loading and 2 h reaction time, for the transesterification reaction were intended to maximise the fuel-grade hydrocarbons' yield. The optimal reaction parameters reduce power consumption and avoided FAME degradation, and provide the maximum yield of fuel-grade hydrocarbons ,i.e,. 97.81 wt%. There is relatively small deviation between the actual and predicted values. Therefore, the experimental results exhibited a good agreement with the predicted results. Also, the errors between the experimental and predicted data were calculated less than 1 %. It can be concluded that the high degree of compatibility was found between the predicted and experimental values.

4.7.1 Conclusion

In this section of this work, the oil extracted from SCGs in section 4.7 was converted to fuel-grade hydrocarbons in the presence of a heterogeneous green catalyst (Li-$CaO_{(s)}$). The $CaO_{(s)}$ was produced by the thermal decomposition of chicken eggshells. The effects of process parameters such as reaction time and catalyst loading on the conversion of SCGs oil were investigated.

The Box–Behnken design statistical modelling was utilised for the esterification process optimization. The optimum reactor conditions predicted by the model given by question 4.2, were catalyst loading of 4 wt% of the oil used, and 2 h reaction giving 97.81 wt% FAME yield. This yield was somewhat lower than the yields obtained by other researchers who utilised lithium-doped calcium oxide as a catalyst in the one-step transesterification of oil containing high free fatty acids, i.e., 98 wt%. The benefits of using calcium oxide derived from chicken egg shells as a green catalyst is that, the chicken egg shells are readily available and a renewable source of calcium oxide. In addition, calcium oxide derived from chicken egg shells have proven to be capable of converting high FFA oil to FAME.

The fuel properties of the produced fuel-grade hydrocarbons were examined; density (895.10 kg/m^3) was found to comply with the international standard ($860 - 900$ kg/m^3) for FAME. The kinematic viscosity (5.21 mm^2/s) and acid values (0.58 mg_{KOH}/g_{oil}) of the fuel grade hydrocarbons were found to be slightly higher than those stipulated by the international standards., i.e,. 3.50 to 5.00 mm^2/s kinamitic viscosity and 0.50 mg_{KOH}/g_{oil} FFA. The reason the relatively high kinematic viscosity and high acid values were attributed to incomplete transesterification and the presence of free fatty acids. To improve the conversion of SCGs oil, the use of two-step transesterification must be utilised. However, the use of waste eggshells synthesised catalysts to produce fuel-grade hydrocarbons from oil extracted from coffee was feasible. This work also showed that fuel-grade hydrocarbons production has the potential to be green process.

After confirmation that eggshell derived calcium oxide was able to convert the spent coffee grounds oil to fuel grade hydrocarbons, the design of experiment (DoE) software was used to develop a model and optimise the conversion of SCGs oil to fuel-grade hydrocarbons. The slope of the 3-D surface plot and the coefficients of the regression for the quadratic model showed that the reaction period had a significant impact on the conversion of SCGs oil to fuel grade hydrocarbons relative to catalyst loading.

CHAPTER 5

5.0 Recommendations for future work.

- This work has identified the possible use of 2-methyl tetrahydrofuran as a green solvent with a capability of replacing hexane as a solvent for the recovery of oil from SCGs, more understanding is required, regarding the quality of the oil extracted. Especially the effect of 2-MeTHF on the free fatty acid content of the oil. The effect of SCGs moisture content on the extraction of oil from SCGs yield requires some attention. The use of other bio-based solvents such as ethyl lactate since it is known to dissolve grease should be investigated (Aparicio & Alcalde, 2009), for extraction of oil from SCGs.
- The oil extraction of 2-MeTHF was relatively higher than that of hexane at the same extraction conditions, signifying not only glycerides and FFA were extracted. Identifying the other compounds extracted would be beneficial in understanding the nature of the SCGs oil.
- A techno-economic study on the valorisation of SCGs needs to be conducted in order to fully realise the economic benefits of using SCGs as a source of valuable chemicals. This techno-economic study will need to evaluate different green technologies that can be used to produced renewable fuels such as biobutanol, ethanol and FAME from SCGs.
- This work also showed that calcium oxide synthesised from chicken eggshells was capable of converting SCGs oil to fuel-grade hydrocarbons. The catalyst re-usability was not tested; thus, further work is required to establish the number of batches of FAME the catalyst can efficiently produce. The use of other waste materials such as boiler ash and cement dust from construction sites as a green catalyst for converting SCGs oil to fuel-grade hydrocarbons should also be considered.

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Appendices

Appendix A: SCGs moisture sample calculations

Table A1: SCGs 1 samples:

Time (min)	Sample 1 (g)	Sample 2 (g)	Sample 3 (g)
0	150.00	160.00	150.00
30	90.00	99.00	101.00
60	75.00	74.45	78.85
90	72.00	65.00	70.30
120	68.30	62.00	67.50
150	64.90	59.50	65.00
180	62.00	55.50	60.00
210	59.00	52.50	55,50
240	55.00	49,45	53.00
270	55.00	4940	53.00
Moisture Content(wt%)	**63.33**	**69.13**	**64.67**
AVE(%)		**65.71**	

Moisture content for sample SCGs1:M = $\left(\frac{\text{initial mass(g)}-\text{final mass(g)}}{\text{initial mass (g)}}\right) \times 100\% = \left(\frac{150-55}{150}\right) \times 100\% = 63.33 \text{ wt\%}$

Moisture content for sample SCG1:M = $\left(\frac{\text{initial mass(g)}-\text{final mass(g)}}{\text{initial mass (g)}}\right) \times 100\% = \left(\frac{160-49.40}{160}\right) \times 100\% = 69.13 \text{ wt\%}$

Moisture content for sample SCG1:M = $\left(\frac{\text{initial mass(g)}-\text{final mass(g)}}{\text{initial mass (g)}}\right) \times 100\% = \left(\frac{150-53}{150}\right) \times 100\% = 64.67 \text{ wt\%}$

Average moisture content for SCGs 1:$\overline{\mathrm{M}} = \frac{\sum_i \mathrm{M}}{\mathrm{n}} = \frac{63.33+69.13+64.67}{3} = 65.71\mathrm{wt\%}$

Table A2: SCGs 2 samples*:*

Time (min)	Sample 1 (g)	Sample 2 (g)	Sample 3 (g)
0	173.00	178.00	176.00
30	108.00	104.00	95.00
60	85.00	83.00	75.00
90	76.00	75.00	68.00
120	69.00	70.00	68.00
150	68.00	69.00	63.00
180	66.00	65.00	59.00
210	62.00	60.00	57.00
240	6.000	58.00	63.00
270	60.00	58.00	63.00
Moisture Content (wt%)	**65.28**	**67.70**	**64.24**
AVE (%)		**65.74**	

Average moisture content for SCGs 2:$\overline{\mathrm{M}} = \frac{\sum_i \mathrm{M}}{\mathrm{n}} = \frac{65.28+65.70+64.24}{3} = 65.74\ \mathrm{wt\%}$

Table A3: SCGs 3 samples:

Time (min)	Sample 1 (g)	Sample 2 (g)	Sample 3 (g)
0	171	174	171
30	105	104	101
60	80	83	79
90	70	75	70
120	65	74	68
150	63	69	65
180	59	65	60
210	57	60	55
240	55	58	53
270	55	58	53
Moisture Content (wt%)	**67.84**	**66.98**	**69.01**
AVE	**67.94**		

Average moisture content for SCG 3: $\overline{\mathrm{M}} = \frac{\sum_{\mathrm{i}} \mathrm{M}}{\mathrm{n}} = \frac{67.84+66.98+69.01}{3} = 67.94\mathrm{wt}\%$

The high SCGs moisture contents supported the need for first drying the SCGs before solvent oil extraction, since it is suggested that for good oil recovery from oil bearing solids the moisture must be less than 10 wt%.

Appendix B: SCGs particle size distribution

Table B1: Mass mean diameter of SCGs 1:

Sieve Size (µm)	**Mass Fraction (x_i)**	**Mass Mean Diameter ($\bar{D}_W$)**
600	0.26	156
425	0.44	226
355	0.14	55
250	0.12	36
150	0.040	8
Total	**1.00**	**480.40 µm**

$\bar{\mathrm{D}}_{600} = 600$ µm

$\bar{\mathrm{D}}_{\mathrm{W},600} = 600 \times 0.26 = 156$ µm

$\bar{\mathrm{D}}_{425} = 0.5(600 + 425) = 512.50$ µm

$\bar{\mathrm{D}}_{\mathrm{W},425} = 512.50 \times 0.44 = 226$ µm

$\bar{\mathrm{D}}_{355} = 0.5(355 + 425) = 390$ µm

$\bar{\mathrm{D}}_{\mathrm{W},355} = 390 \times 0.14 = 54.60$ µm

$\bar{\mathrm{D}}_{250} = 0.5(355 + 250) = 302.50$ µm

$\bar{\mathrm{D}}_{\mathrm{W},250} = 302.50 \times 0.12 = 36$ µm

$$\overline{\mathrm{D}}_{250} = 0.5(150 + 250) = 200\ \mu\mathrm{m}$$

$$\overline{\mathrm{D}}_{\mathrm{W},250} = 200 \times 0.04 = 8\ \mu\mathrm{m}$$

$$\boldsymbol{\overline{\mathrm{D}}_{\mathrm{W}} = \sum_{i}^{N} \overline{\mathrm{D}}_{\mathrm{W}} = 8 + 36 + 54.60 + 226 + 156 = 480.20\mu\mathrm{m}}$$

Table B2: Mass mean diameter of SCGs 2:

Sieve Size(μm)	**Mass Fraction (x_i)**	**Mass Mean Diameter ($\overline{D}_W$)**
600	0.26	156.00
425	0.48	246.00
355	0.12	46.80
250	0.06	18.15
150	0.08	16.00
Total	**1.00**	**482.95**

Table B3: Mass mean diameter of SCGs 3:

Sieve Size(μm)	**Mass Fraction (x_i)**	**Mass Mean Diameter ($\overline{D}_W$)**
600	0.30	180.00
425	0.45	230.63
355	0.13	50.70
250	0.06	18.15
150	0.06	12.00
Total	**1.00**	**491.48**

Appendix C: Solvent recovery system.

Figure C: Rotary vacuum evaporator.

The rotary vacuum evaporator was used to separate the SCGs oil and the extracting solvents. The vacuum evaporator allows the solvent to boil at temperatures lower than its normal boiling temperature by reducing the system pressure to below atmospheric pressure. This prevents the degradation of the oil, save on operating cost and also make the separation process faster than batch distillation. The solvents were then re-used in the next extraction cycle.

Appendix D: Determination of liquid densities

To determine the density of the SCGs oil and the density of the fuel grade hydrocarbons, different masses of the product in question were weigh, together with corresponding volumes. The mass was than plotted against the volume and the gradient of the resulting straight line was taken as the average density of that particular batch or product. The obtained density was than compared to the ones obtained using a density metre.

Table D1: Relationship between mass and volume for SCGs oil extracted using 2-MeTHF

Volume (ml)	Mass (g)
2.00	2.33
2.50	2.91
3.00	3.49
3.50	4.07
4.00	4.65
4.50	5.23
5.00	5.81

The average density of the SCGs oil extracted using 2-MeTHF was estimated to be:1162.80kg/m^3

Table D2: Relationship between mass and volume for SCGs oil extracted using hexane

Volume (ml)	**Mass (g)**
2.0	1.8
2.5	2.3
3.0	2.8
3.5	3.2
4.0	3.7
4.5	4.1
5.0	4.6

The average density of the SCG oil extracted using hexane was estimated to be:919.10kg/m^3

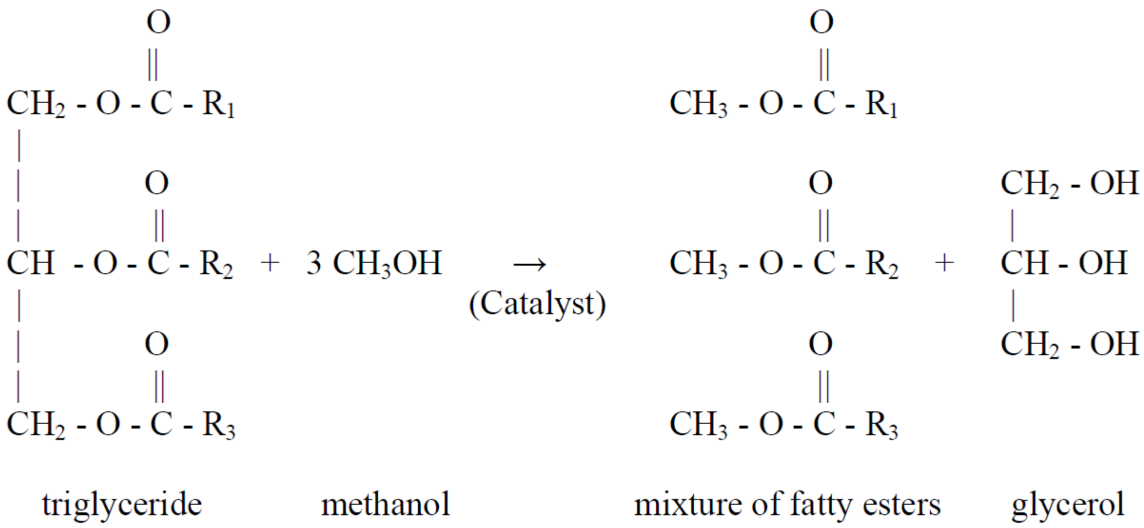
Table D3: Relationship between mass and volume for FAME

Volume (ml)	**Mass (g)**
2.00	1.70
2.50	2.13
3.00	2.55
3.50	2.98
4.00	3.40
4.50	3.83
5.00	4.25

The average density of the fuel grade hydrocarbons was estimated to be: 850.01kg/m^3

Appendix E: Methanol-to-oil molar ratio sample calculations:

Estimate the amount of methanol required:



Molar mass of coffee triglyceride: Mr (oil) = 885.45 g/mol

Molar mass of methanol: Mr (Meth) =32.04 g/mol

Mass of SCG oil used per run: m (SCGs) =15.50 g

Moles of oil used: n (oil) = $\frac{\text{Mass of SCG oil used}}{\text{Molar mass of SCG oil}} = \frac{\text{m(SCG)}}{\text{Mr(SCG)}} = \frac{15.50}{885.45}$ = 0.018 mol

Appendix F: Fuel grade hydrocarbons yield sample calculations & raw data.

The yield of FAME was estimated using question 22

$$\text{Biodiesel yield} = \left(\frac{\text{Mass of Produced(g)}}{\text{Mass of SCG Oil Used (g)}}\right) 100\% = \left(\frac{12.82}{15.50}\right) \times 100\% = 82.71\text{wt}\%$$

Transesterification of SCG oil at different reaction times.

Table F1: Raw data for 1 transesterification of SCG oil using 5wt% Li-$CaO_{(s)}$ as green catalyst.

60 min: Transesterification	**Run 1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.50	15.49	15.50	15.50
FAME weighed (g)	12.82	12.76	12.95	13.13
FAME Yield (wt%)	82.71	82.38	83.55	84.71
Average	**83.34**			

Table F2: Raw data for 1.50 h transesterification of SCG oil using 5wt% Li-$CaO_{(s)}$ as green catalyst.

90 min: Transesterification	**Run 1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.50	15.50	15.50	15.50
FAME weighed (g)	14.83	13.89	14.02	14.21
FAME Yield (wt%)	95.68	89.61	90.45	91.68
Average	**91.85**			

Table F3: Raw data for 2 h transesterification of SCG oil using 5wt% Li-CaO$_{(s)}$ as green catalyst.

120 min: Transesterification	**Run1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.50	15.50	15.50	15.50
FAME weighed (g)	15.03	15.15	15.02	15.10
FAME Yield (wt%)	96.97	97.74	96.90	97.42
Average	**97.26**			

Table F4: Raw data for 2.50 h transesterification of SCG oil using 5wt% Li-CaO$_{(s)}$ as green catalyst.

150 min: Transesterification	**Run1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.00	15.00	15.00	15.00
FAME weighed (g)	14.29	14.25	14.12	14.36
FAME Yield (wt%)	95.27	95.00	94.13	95.73
Average	**95.03**			

Table F5: Raw data for 3 h transesterification of SCG oil using 5wt% Li-CaO$_{(s)}$ as green catalyst.

180 min: Transesterification	**Run1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.00	15.00	15.00	15.00
FAME weighed (g)	14.33	14.44	14.71	14.65
FAME Yield (wt%)	96.34	96.55	96.97	96.70
Average	**96.64**			

Appendix G: Transesterification of SCGs oil at different catalyst loading.

Table G1: Raw data for transesterification of SCGs oil using 0.5 wt% Li-CaO$_{(s)}$ as green catalyst.

0.5 wt% Li-CaO$_{(s)}$-to-SCGs oil	**Run 1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.00	15.03	15.00	15.50
FAME weighed (g)	8.27	8.23	8.27	8.24
FAME Yield (wt%)	55.10	54.85	55.13	54.92
Average	**55.00**			

Table G2: Raw data for transesterification of SCGs oil using 1 wt% Li-CaO$_{(s)}$ as green catalyst.

1 wt% Li-CaO$_{(s)}$-to-SCGs oil	**Run 1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.00	15.00	15.00	15.00
FAME weighed (g)	8.72	8.73	8.66	8.69
FAME Yield (wt%)	58.13	58.21	57.76.	57.91
Average	**58.01**			

Table G3: Raw data for transesterification of SCGs oil using 2 wt% Li-CaO$_{(s)}$ as green catalyst.

2 wt% Li-CaO$_{(s)}$-to-SCGs oil	**Run 1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.00	15.00	15.00	15.00
FAME weighed (g)	10.67	10.66	10.69	10.68

FAME Yield (wt%)	71.13	71.17	71.27	71.23
Average	**71.20**			

Table G4: Raw data for transesterification of SCGs oil using 3 wt% Li-CaO$_{(s)}$ as green catalyst.

3 wt% Li-CaO$_{(s)}$-to-SCGs oil	**Run 1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.00	15.00	15.00	15.50
FAME weighed (g)	13.87	13.82	13.76	13.75
FAME Yield (wt%)	92.47	92.13	91.72	91.68
Average	**92.00**			

Table G5: Raw data for transesterification of SCGs oil using 4 wt% Li-CaO$_{(s)}$ as green catalyst.

4 wt% Li-CaO$_{(s)}$-to-SCGs oil	**Run 1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.00	15.00	15.00	15.50
FAME weighed (g)	14.31	14.74	14.93	14.88
FAME Yield (wt%)	95.40	98.27	99.53	96.00
Average	**97.30**			

Table G6: Raw data for transesterification of SCGs oil using 5 wt% Li-CaO$_{(s)}$ as green catalyst.

5 wt% Li-CaO$_{(s)}$-to-SCGs oil	**Run1**	**Run 2**	**Run 3**	**Run 4**
SCG oil (g)	15.00	15.00	15.00	15.50
FAME weighed (g)	14.16	14.18	14.22	14.36
FAME Yield (wt%)	94.40	94.53	94.80	95.73

Average	**94.31**