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**SYNTHESIS OF BIODIESEL FROM VIETNAMESE
SPENT COFFEE GROUND**

Development of Synthesis Method

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ABSTRACT

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<p>Fossil fuel is defined as a substance which can be burned to provide energy, heat and power. Therefore, it plays an essential part in human being's life. In recent years, fossil fuel has become a concerning problem because the excessive exploitation and usage of this resource. As a result, fuel not only exhausts rapidly but also impacts negatively on the environment. There is question that scientists are looking for an answer- "How can we find an alternative source of energy, other than fossil fuel, which provides lower life-cycle consumption and emits greenhouse for sustainable growth of fuel industry?".</p> <p>Biofuel, especially biodiesel, is one of the best answers for this question. Biodiesel can be produced from both vegetable oil and animal fat. Due to the characteristic of biodiesel, which is quite similar to diesel, it sparks the ability to replace diesel source. In many countries, edible oil-bearing crops such as coconut oil, sunflower oil, soybean oil, coffee oil are potential sources to produce biodiesel. Final products of them are non-edible oil.</p> <p>The main purpose of this final thesis is to develop a method to produce biodiesel from a non-edible oil which is named as "spent coffee ground oil" with high capacity. Spent coffee ground oil is high free fatty acid and impurities. Therefore, the procedure includes three stages: pre-treatment with alcohol, acid catalysed esterification and alkali catalysed transesterification in order to convert crude coffee ground oil to mono-ester. In addition, there are two main factors related to the conversion efficiency of process: molar ratio (oil/alcohol) and amount of catalyst. After that, by determining important properties such as density at 15°C, kinematic viscosity at 40°C, acid value (AV), the oxidation stability and cetane number, the quality of this biodiesel will be evaluated correctly. The results demonstrate that spent coffee ground will become a potential biomass source for industrial biodiesel production.</p>		

<p>Key words acid catalysed esterification, alkali catalysed transesterification, amount of catalyst, biodiesel, molar ratio (oil/alcohol), spent coffee ground.</p>

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CONCEPT DEFINITIONS

ASTM	American Society for Testing and Materials
AV	acid value
BHA	butylated hydroxyanisole
BHT	butylated hydroxytoluene
CFPP	cold filter plug point
CH ₃ OH	methanol
EN 14214	European Committee for Standardization
FAEE	fatty acid ethyl esters
FAME	fatty acid methyl esters
FFA	free fatty acid
FP	flash point
GC / MS	gas chromatography-mass spectrometry
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
NBB	National Biodiesel Board
PrG	propyl gallate
PUFAs	polyunsaturated fatty acids
rpm	round per minute
SCG	spent coffee ground
TBHQ	tert-butylhydroquinone
vitamin E	alpha-tocopherol
wt%	weight percent
%(m/m)	mass concentration of solution

ABSTRACT

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CONCEPT DEFINITIONS

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1 INTRODUCTION

Nowadays, biodiesel has substituted diesel in engines which is synthesized by from vegetable oils or animal fats with a certain alcohol such as methanol and ethanol (Gerpen 2005, 1097). Historically, in the 1900s, this oil was used to fuel engines. However, at this time, the oil sources were extremely cheap and they were necessary for human being. Until the price of fuel goes up significantly and worry about the lack of fuel (Sheehan et al 1998, 3). Therefore, finding alternative sources is essential.

Coffee bean and spent coffee ground become potential sources in researching biofuels. Indeed, Narasimharao, Kondamudi, Susanta Mohapatra and Manoranjan Misra in their research group Kondamudi at the University of Nevada (USA) said that it is possible and easy to produce biodiesel from spent coffee ground because this biodiesel is equivalent to the best biodiesel on the market. Furthermore, using this biodiesel for engines, it does not produce a smelly exhaust, only smell of coffee. The result of comparison emissions between biodiesel and diesel illustrates that the amount hydrocarbons in engine exhaust using biodiesel decreased by 65%, CO₂ decreased by 35%, particles smog reduced by nearly 40% (He et al 2009, 3657). After synthesizing biodiesel, the rest of the spent coffee grounds are used fertilizers and other practical applications.

Vietnam is the 2nd largest coffee export nation in the world after Brazil (Thanh, 2013, 2). In addition, coffee has become one of five key agricultural products with export volume is over 1 million tons / year. Utilizing coffee grounds not only solves biodiesel demands but also prevents environmental pollution and costs for disposing them. Simultaneously, it also contributes to the development of the country's economy.

2 OVERVIEW OF BIODIESEL

In this chapter the theory related to the thesis topic is outlined. In the beginning, the term 'Biodiesel' and characteristics are defined clearly. Next, there is a comparison biodiesel quality standard between Europe and America and explanation of key parameters which can be used to measure the quality of biodiesel. Finally, the advantages and disadvantages of using biodiesel are theoretically explained.

2.1 Definition of Biodiesel

Biodiesel is known as the type of fuel used for diesel engines and manufactured from vegetable oil or animal fat (Gerpen 2005, 1097). In fact, alkyl esters are main ingredient of biodiesel such as methyl esters. Moreover, biodiesel is often produced by transesterification reaction which is a reaction between triglycerides (main ingredient in vegetable oil or animal fat) and alcohol (FIGURE 1). The presence of catalysts (acid, base, ...) will accelerate the reaction process. In order to achieve a high conversion factor, the residual alcohol must be used because the transesterification reaction is a reversible process. (Demirbas, Ayhan 2009, 87.)

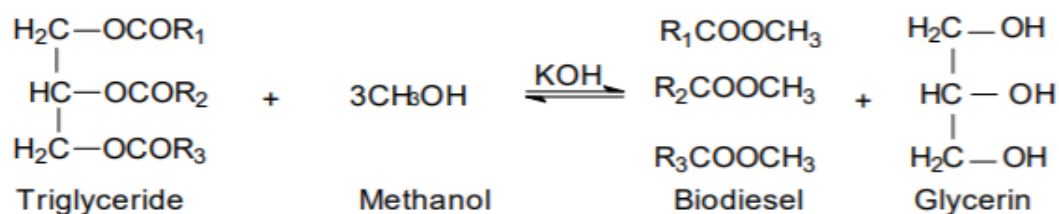


FIGURE 1. Transesterification reaction to synthesize biodiesel (Abdullah et al 2007)

Nowadays, biodiesel has become an attracted topic of scientists in the world because it has the ability to regenerate, manufactured and processed from vegetable oil and used in earlier diesel engines. In addition, biodiesel does not discharge toxic gases as diesel. Furthermore, biodiesel makes sense when used in standard diesel engines.

Biodiesel can be used alone or mixed with diesel oil. The mixture of biodiesel and traditional diesel is the most popular product that are distributed for using in the diesel fuel retail market. In the world, there is a classification system called "B" to specify the percentage of biodiesel volume in the fuel mixture (U.S Department of Energy 2006, 1). For example, 100% biodiesel is called B100, 20% of Biodiesel is

B20, 5% of Biodiesel is B5 and 2% of Biodiesel is B2. Obviously, the higher the biodiesel ratio is, the more environmentally friendly the fuel will be.

2.2 Cold flow property of biodiesel

When biodiesel is cooled at a certain point, some molecules will gather and form crystals. The beginning biodiesel has opaque sign as soon as the crystals become greater than a quarter of the wavelength of visible light - this is still the opaque point. Continuous to cool biodiesel, these crystals will become even bigger. The lowest temperature that biodiesel can pass through a 45 μm filter is called a cold-air filter plug point (CFPP). When biodiesel is further cooled, it will be gelatinized and then coagulated (Gaurav, Sharma 2014, 653). In Europe, there are differences in CFPP requirements between countries. At a certain temperature, pure biodiesel (B100) begins to gelatinize and depends on the combination of esters (U.S Department of Energy, 2006, 9). Therefore, the oil material is very useful in the production of biodiesel. For example, biodiesel produced from the erucic acid of rapeseed begins to gelatinize at approximately -10°C (14 F). Biodiesel produced from animal fats tends to gelatinize at approximately 16°C . (61 F). (Sanford et al 2009, 42.)

2.3 Contamination by water

Biodiesel can have problems when it contains a small amount of water (specification below 500 ppm (0.050 %)). Although it is not mixed with water but characteristic of biodiesel- hygroscopic (absorbs water from moist air) are the same as ethanol (Montero 2011, 25). Biodiesel can absorb water due to the durability of mono- and the remaining diglycerides from non-completed reaction. These molecules can act as an emulsifier which allow water to mix with biodiesel. The presence of water in biodiesel will affect the quality of biodiesel. Firstly, it reduces the combustion heat of a large amount of fuel. This means that there will be more smoke, it is harder for starting engines and productivity also decreases. Secondly, the presence of water in biodiesel can cause serious corrosion on the components of the fuel system such as pump fuel, injection pump and fuel flow. Thirdly, water and bacteria make filtration equipment in the system failed (upside down), thus, fuel pumps do not operate as expected by the absorption of the big element. Continuously, when biodiesel is in crystal form near 0°C (32 F), it makes the fuel freeze. These crystals set position for the formation of the nucleus and gelatinization of the residual fuel become faster. Furthermore, the presence of water in biodiesel will make bacteria grow

faster and can clog the fuel system. Finally, water can also cause gaps in the piston of the diesel engine (Montero 2011, 25.)

Previously, biodiesel contaminated with water was difficult to measure by taking sample, since water and oil are separated. However, now, water content can be measured by using water sensors in oil. Besides, it is possible to use certain chemical catalysts to participate in the production process, the contamination by water of biodiesel will significantly reduce because of the impact of catalyst base (high pH) such as potassium hydroxide. (US Department of Energy 2006, 12.)

2.4 Quality Standard

The production and widespread usage of biodiesel requires quality standards for biodiesel. In detail, Europe has the EN 14214 standard, at America, ASTM (Association America test and materials) also has specified standard for B100, ASTM D6751. When these standards are met, biodiesel can be mixed with crude diesel for using in diesel engines (Montero 2011, 1-7). As TABLE 1 below, main key parameters of biodiesel and diesel are demonstrated following the European biodiesel standards EN 14214, American ASTM D6751 and standards for diesel EN 590, ASTM D975.

TABLE 1: Summary of European biodiesel standards EN 14214 and American ASTM D6751 together with the standards for diesel EN 590 and ASTM D975 (Montero 2011, 1-7)

Standards	Method	EN 590	EN 14214	ASTM D975	ASTM D6751
Density at 15°C	ASTM D1298	820 – 845	860 – 900	–	–
Kinematic Viscosity at 40°C (mm ² /s)	ASTM D445	2.0 – 4.5	3.5 – 5.0	1.9 – 4.1	1.9 – 6.0
Flash point (°C)	ASTM D93	≥ 55	≥ 120	≥ 52	≥ 130
Sulfur (mg/kg)	ASTM D5453	≤ 50	≤ 10	≤ 50	≤ 50
Cetane value	ASTM D613	≥ 51	≥ 51	≥ 40	≥ 47
Water (mg/kg)	ASTM D2709	≤ 200	≤ 500	≤ 50 (% volume)	≤ 50 (% volume)
Ester content (%m)	EN 14103	–	≥ 96.5	–	–
Methanol (%m)	EN 14110	–	≤ 0.2	–	–
Monoglyceride (%m)	EN 14105	–	≤ 0.8	–	–
Diglyceride (%m)		–	≤ 0.2	–	–
Triglyceride (%m)		–	≤ 0.2	–	–
Free Glycerine (%m)	EN 14105/ EN 14106/ ASTM D6584	–	≤ 0.02	–	≤ 0.02
Total glycerine (%m)	EN 14105/ ASTM D6584	–	≤ 0.25	–	≤ 0.24

Indeed, the quality of biodiesel affects the operation of the engine, and the biodiesel, if some targets are not controlled at an allowable limit, it will cause the diesel engine to fail.

The most important factor of biodiesel is the metabolism of the ester transposition reaction. Even when the highest reaction efficiency is obtained, the biodiesel still contains a small amount of triglyceride, diglyceride and monoglyceride. This substance content has to be minimal because they can increase the viscosity, reduce oxidation resistance.

Glycerine is also a product of the synthesis of biodiesel, which is viscous liquid and can separate from B100, it forms sediment at the bottom of the fuel tank that can clogging of the fuel filters and worsening combustion in the engine. High glycerine content causes the clog of fuel injector and to limit this issue, ASTM D6751 requires maximum free glycerine content is 0.02 % (m/m). (Montero 2011, 5-6.)

The non-metabolism glyceride is known as the reason of clog fuel injector and create residues on the diesel engine cylinder. They also cause reduction of shelf life for both engines and incinerators. Indeed, about chemical structure, these are mono, di, and triglyceride compounds. This structure consists of main chain, which is the glycerine component connected to one, two or three fatty acid radicals by ester bonds. In order to protect engine, ASTM D6751 limits the maximum glycerine content (0.24 % (m/m)). This total glycerine content is the sum free glycerine content and associated glycerine content in mono, di and triglycerides. (Montero 2011, 6-8.)

2.4.1 Chemical composition

The elemental composition of biodiesel includes carbon, hydrogen and oxygen. Additionally, these elements slightly depend on the feedstock which is used to produce biodiesel. By determining the oxygen content, it can help to distinguish between biodiesel and diesel fuel composition which is from 10 to 13%.

In essence, biodiesel is free of sulphur. The composition of biodiesel comes from some fatty acid ethyl esters (FAEE) and fatty acid methyl esters (FAME) where their C number will depend on the feedstock used to produce biodiesel (between 6 and 17) (Shannon & Wee 2009, 41). In the composition of biodiesel, C, H and O atoms are the elemental composition of fatty acid methyl and ethyl esters and these form linear chain molecules with both single and double (carbon-carbon) bonds. In fact, the molecules with double bonds are unsaturated. Hence, fatty acid esters take the form of lipid number C(nc:nd) that the number of carbon atoms and double bonds in the fatty acid are respectively nc and nd. For example, 18:1 indicates that 18 carbon atoms and one double bond. The ester composition of biodiesel (methyl and ethyl esters) is C18:1, C18:2, C18:3, followed by C18:0. (Barabás & Todoruț 2010, 13.)

2.4.2 Cetane value

The cetane value is known as a dimensionless indicator which characterizes ignition quality of fuel used for compression ignition engines. In addition, cetane value also relates to the late ignition time when it is injected into the combustion chamber of the engine. The shorter the ignition time, the higher the cetane value. In fact, some properties: cetane value and density only depend on the properties of original material. Most of the remaining properties depend on the technical factors of manufacturing. (Montero 2011, 13.)

2.4.3 Oxidation stability

The quality of biodiesel can be affected by the oxidation which happened during storage (in contact with air). Recently, a requirement added to ASTM D6751 is oxidation stability. The oxidation can lead to acid corrosion as well as the formation of resins. In addition, it is the main reason for engine operation and combustion problems. Biodiesel contains products of polymerized unsaturated fatty acids such as C18:2 and C18:3 that are more easily oxidized in storage than diesel. Oxidative stability is also limited to a minimum of three hours by the EN 14112 method which called the oil stability value. Commercial biodiesel samples have a wide range of oxidative stability because of the difference in both total polymerization content of unsaturated fatty acids and antioxidant additives that are mixed. In the US, about 25% of B100 requests for addition these antioxidant additives to meet 3-hour oxidation stability cycle requirements. It is possible to improve the oxidation stability of biodiesel by using the appropriate additives. There are several special additives to enhance the storage stability of biodiesel such as tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG) and alpha-tocopherol (vitamin E). (Montero 2011, 24-25.)

2.4.4 Flash point

The flash point (FP) of fuel is defined as the minimum temperature and calculated to a barometric pressure of 101.3 kPa at which fuel ignites on application of ignition source with specified conditions. Moreover, FP is very useful in classifying fuel for transport, storage and distribution according to the hazard level. Practically, combustion is not affected directly by FP. If the FP is higher, it makes the fuel safer which regarded to storage, handling and transportation. For biodiesel, the flash point will have differences between countries in the world. For example, the minimum FP in US is 93°C, 100°C

in Brazil and 120°C in Europe (Montero 2011, 22). Besides, biodiesel has a higher FP than diesel. This is very helpful in transporting and the perversion of biodiesel.

2.4.5 Kinematic viscosity

The kinematic viscosity is known as one of the most important properties of biodiesel. There are some influences of kinematic viscosity such as the ease of starting the engine, the quality of spray, the size of particles, the penetration of the injected jet and the quality of the fuel-air mixture combustion (Alptekin and Canakci 2009, 75-80). If the kinematic viscosity is too high, it can cause operational problems at low temperatures because of the increasing of viscosity with decreasing temperature. The kinematic viscosity of biodiesel is much lower than that of vegetable oils or original animal fat. Therefore, it will not cause malfunctioning problems in diesel engines. Indeed, it has been discovered that the long chain of carbon, the increase saturation of the chain and the greater the ester oil group will increase the viscosity of biodiesel. Due to the existence of electronegative oxygen, biodiesel is more polar than diesel fuel. As a result, the kinematic viscosity of biodiesel is higher than that of diesel fuel.

2.4.6 Density at 15°C

The density (ρ) of fuel is the mass of unit volume measured in a vacuum. Due to the effect of temperature on density, the density quality standards of fuel will be determined at 15°C (Montero 2011, 17.) The density of fuel affects two factors: fuel performance and quality of atomization and combustion. Firstly, according to density, the performance of fuel, as some of the engine properties, can be identified clearly such as cetane number and heating value and viscosity. Secondly, the fuel quality of atomization and combustion also are affected by density. When diesel engine fuel systems such as pump or injectors measure fuel by volume, it leads to the alteration of density and affects the fuel mass that reaches the combustion chamber. Therefore, the energy content of the fuel dose will modify the fuel/air ratio and engine's power. For biodiesel, density is an important parameter in the manufacturing, storage, transportation and distribution process. The density of esters depends on four factors: the molar mass, free fatty acid content, water content and the temperature. Biodiesel has the typical density which is higher than diesel fuel and it also depends on fatty acid composition and purity. The density of biodiesel can be affected significantly by contamination which is known as an indicator of biodiesel density. (Montero 2011, 18.)

2.5 Advantages and disadvantages of using biodiesel

Nowadays, most of the energy in the world is consuming crude oil, coal and natural gas sources. In fact, these sources have limitation and with the high-speed usage of human beings, they will be exhausted completely by the end of the 21st century. Therefore, the exhaustion of crude oil source and environmental concern have led to researches and development of an alternative energy originated crude oil. Biodiesel is a potential replacement for diesel fuel. According to the properties of biodiesel, they have advantages and disadvantages for usage.

2.5.1 Advantages of biodiesel

Biodiesel has outstanding advantages related to environment, technical factors and economics. Firstly, regarding the environment, using biodiesel can reduce CO₂ emissions, soil, water environmental pollution and other emissions that cause the Greenhouse effect. In addition, biodiesel contains little sulphur compounds (less than 0.001% compared to 0.2% in diesel). Furthermore, biodiesel has the ability to self-decompose and is non-toxic. It can decompose 85/88% in water after 28 days and faster 4 times than diesel. Secondly, regarding technical factors, biodiesel is flexible to mix with diesel with any proportion. Biodiesel has a flash point that is higher than regular diesel, thus, it is burnt completely and safe in storage and usage. Biodiesel has good lubricity. (US Department of Energy 2006, 4-5). Finally, regarding economic, biodiesel help to promote the development of the agriculture which can utilize the available potential of the agricultural sector such as coffee, waste oil, animal fat, other less valuable oil used in food. It diversifies agriculture and increases incomes in rural areas. Moreover, biodiesel help to limit the import of diesel from foreign countries and contributes to budget saving for nation.

2.5.2 Disadvantages of biodiesel

In fact, besides the advantages, biodiesel also has many drawbacks that limit its widespread usage in industry and daily life. The freezing temperature of biodiesel depends on the raw material and it is higher than diesel. This greatly affects the usage of biodiesel in areas with cold weather. However, for tropical countries like Vietnam, the effect is not significant. Usage of fuels that contain more than 5% biodiesel can cause problem such as corrosion of engine components and appearance of resin in fuel tanks because the oxidation stability of biodiesel is low. Additionally, biodiesel absorbs water strongly, hence, it needs to have special storage solution to avoid it in contact with water. Furthermore, biodiesel is unstable,

easily oxidized and can cause difficulties in preservation. According to the NBB's recommendation, should not be used B20 after 6 months guarantee, while the expired date of diesel can be up to five years. (US Department of Energy 2006, 6.)

3 OVERVIEW OF COFFEE

Coffee (derived from café in French) is a black beverage that contains caffeine, produced and widely used by roasting coffee-beans from the coffee tree (Clifford and Willson 1985, 2). According to a legend which was recorded on paper in 1671, Goatherds in Kaffa (in Ethiopia nowadays) discovered that some goats in the herd after eating a branch with white flowers and red fruit ran tirelessly until the mid-night. When one of the goatherds tasted the red fruit, he confirmed its effect. Then, a lot of priests at the nearby institute reconsidered the area where the goats ate grass and discovered a tree with dark green leaves and fruit resembling cherry fruit. After drinking the juice from that fruit, they were of sound mind to pray until midnight. Thus, it can be considered that thanks to this herd of goats, humans got to know the coffee trees. After that, coffee spread to Egypt and Yemen, and by the 15th century, coffee appeared in Armenia, Turkey and North Africa. And then coffee came to Italy, the rest of Europe, Indonesia and US (Clifford and Willson 1985, 2-5). Today, coffee become one of the most popular drinks globally.

3.1 Characteristic of coffee

The origins of coffee tree are from sub-tropical Africa and southern Asia. It belongs to fruit-tree of the Rubiaceae family. It is a green shrub or small tree that can grow to 5 m without pruning. Its leaves are dark green and glossy, usually 10-15 long cm and 6.0 cm wide. The white flowers bloom with fragrant aroma. (Farah 2008.)

The shape of the bean has oval, about 1.5 cm long and green colour but gradually becomes yellow, then becomes red and black again. Each fruit usually has 2 seeds, 5-10% fruit has only 1 seed. The fruit usually blooms in 7-9 months. (Farah 2008.)

The coffee fruit consists of the following parts: exocarp, mesocarp, endocarp, silver skin, seed. It can be divided into two main parts including the skin part (exocarp, mesocarp) and seed part (endocarp, silver skin, seed).

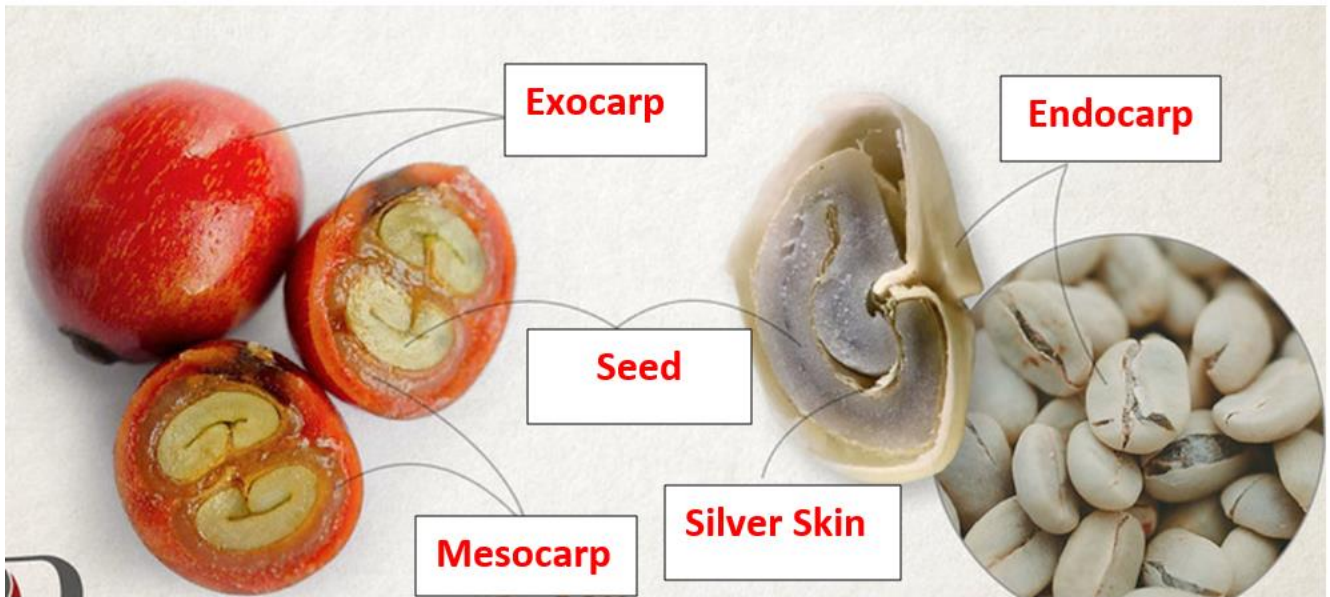


FIGURE 2. Composition of coffee fruit- Photo is taken from real coffee bean at TriAn factory (Nestle Vietnam)

The skin includes two layers, namely outer skin and pulp or mucilage. First of all, the outer skin is formed by a small layer of parenchymal cells (primary cells containing chloroplasts able to absorb water). The beginning of the endocarp colour is green because of the appearance of chloroplasts then it disappears when the fruit ripens. The color of mature exocarp depends on the variety of coffee but red or yellow are the most common. The red skin color (Coffee Typica) comes from anthocyanin pigments, while the yellow color is attributed to luteolin (Bourbon coffee). (Castro, Renato and Marraccini 2006, 175-180). Secondly, the pulp or mucilage, in immature coffee fruit, these are the hard tissue attached to the skin of the fruit. When these matures, the pectolytic enzymes break down the pectic chains which form sugars and pectin compounds (Borém 2008, 127-130) that make up a soft, succulent structure and has a high viscosity, thus, it is often called Mucilage. Indeed, mucilage is rich in fructose (27% on dry mass), glucose (21%), sucrose (9%) and organic acid (7.3%). Among them, there are three acids that are abundant such as malic acid, quinic acid and gluconic acid. (Koshiro et al 2015, 378-383.)

The seed includes silver skin, parchment and seed. In detail, parchment is the outer layer of the seed and directly in contact with the silver skin. Parchment is formed from three to seven layers of hardening cells (fiber cells play a major role in plants) and are known as endocarp. The cells that make up endocarp will harden during the maturation process of the coffee fruit; hence, it limits the final size of the coffee seed. In Arabica coffee, the average weight of endocarp with moisture 11% is about 3.8% of the total weight of the fruit. (Borém 2008, 131-140).

The name silver skin is derived from formation of nucellus and has silvery-white after drying. This skin is very thin and can be peeled off during the polishing process. Seed coffee is the innermost and most important part of the fruit which is responsible for extracting nutrients for the germination of the embryo. A regular coffee bean has two seeds. The chemical composition of seed is extremely important because it is considered as a precursor of flavour and aroma in roasted coffee. Chemical compounds found in endosperm include water-soluble compounds such as caffeine, trigonelline, nicotinic acid (niacin), at least 18 chlorogenic acid isomers, carbohydrate components (Mono-, di- and oligosaccharides), some mineral proteins and carboxylic acid and water-insoluble components include cellulose, polysaccharides, lignin and hemicellulose, as well as some proteins, minerals and lipids. (Borém 2008, 131-140.)

Next to the seed is embryos which consist of an embryo axis (hypocotyl) and two cotyledons 3-4 mm long (Wintgens 2009). When the seed starts to germinate, the embryo shaft will stretch and push the seed to the ground. The initial cotyledons are underground. After that, new cotyledons will be formed. Compared to the seed part, the endosperm has a moisture content about 51% with a high sucrose (8% on dry mass) and a low concentration of monosaccharides, while the most common organic acid (2.4%) is citric acid, malic acid and quinic acid. Additionally, trigonelline (1.0%) and caffeine (0.9%) concentrations in endosperm are higher than in mucilage but acetic acid concentration is lower. (Koshiro et al 2015, 378-383.)

3.2 Classification

Currently, coffee trees are grown in more than 50 countries around the world, including some exporting coffee countries. There are three main coffee trees namely *Coffea arabica*; *Coffea canephora* (Robusta) and *Coffea excelsa*. There are differences from quality or class of coffee which depend on each type of seed and place of planting. Robusta coffee is rated lower than Arabica coffee due to lower quality and cheaper prices. The most expensive and rare coffee in the world is Kopi Luwak (or "mink coffee") from Indonesia and Vietnam. This is not a coffee variety but a way of processing coffee by using the weasel digestive tract. The price for each type of coffee is about 20 million VND (1300 USD). Every year, only 200 kg of Kopi Luwak has been sold around the world. (Coffee Research Institute 2018.)

3.3 Influence of coffee

The effect of coffee has been known as stimulating nerves due to influence of caffeine. In addition, coffee has a sedative effect. It has been proven that, if you go to sleep for 15 minutes after drinking coffee, the sleep will be deeper because the blood in the brain has better circulation. But if you continue to hesitate, this effect will fade away, after that, the caffeine starts to work, you cannot sleep anymore. The sedative method has been used in many hospitals, especially for old patients because coffee will counteract the decline in breathing during sleep and help them sleep better. However, this delicious beverage can also have some negative effects on health. It dramatically increases the amount of insulin in the blood, loses body balance as well as affects on pancreas. If drink a high amount of coffee, it can cause swelling of the mucous membranes in the stomach. (Farah 2008, 100-106.)

The Japan National Cancer Centre in Tokyo conducted an experiment during ten years on 100,000 people who drunk coffee and found out that only 214 of them have kidney cancer. While people do not drunk coffee, this ratio was 547 / 100,000. According to the result, that concluded that antioxidant coffee has the ability to protect kidney cells from corrosion. (Manami et al 2005, 293-294.)

3.4 Coffee production and consumption in the world

Brazil is the largest coffee producing country in the world with an output of over 1.7 million tons per year and accounting for 25% of the international market. Other major exporting countries are Vietnam, Colombia, Indonesia, Côte d'Ivoire, Mexico, India, Guatemala, Ethiopia, Uganda, Costa Rica, Peru and El Salvador. The International Coffee Organization (ICO) forecasts global coffee production in the 2019-2020 will reach 167,4 million bags (60 kg bags). (International Coffee Organization- Coffee market report 2019, 1.)

Europe is the largest coffee market in the world, accounting for about 30% of the global coffee consumption. The specialty coffee market in Europe is growing strongly and bringing opportunities for high quality coffee suppliers. In detail, the specialty coffee segment is particularly growing in Northern Western Europe due to high income levels and consumer awareness as well as a more developed coffee culture. In Northern European markets, following to CBI Ministry of Foreign Affairs report, Finland has the highest coffee consumption rate in the world with about 66 million tonnes in 2015. There are two types of specialty coffee that are common in Finland: Coffee Arabica and Robusta (CBI Ministry of Foreign Affairs report 2017). The FIGURE 3 indicates large coffee consuming countries in Europe 2015.

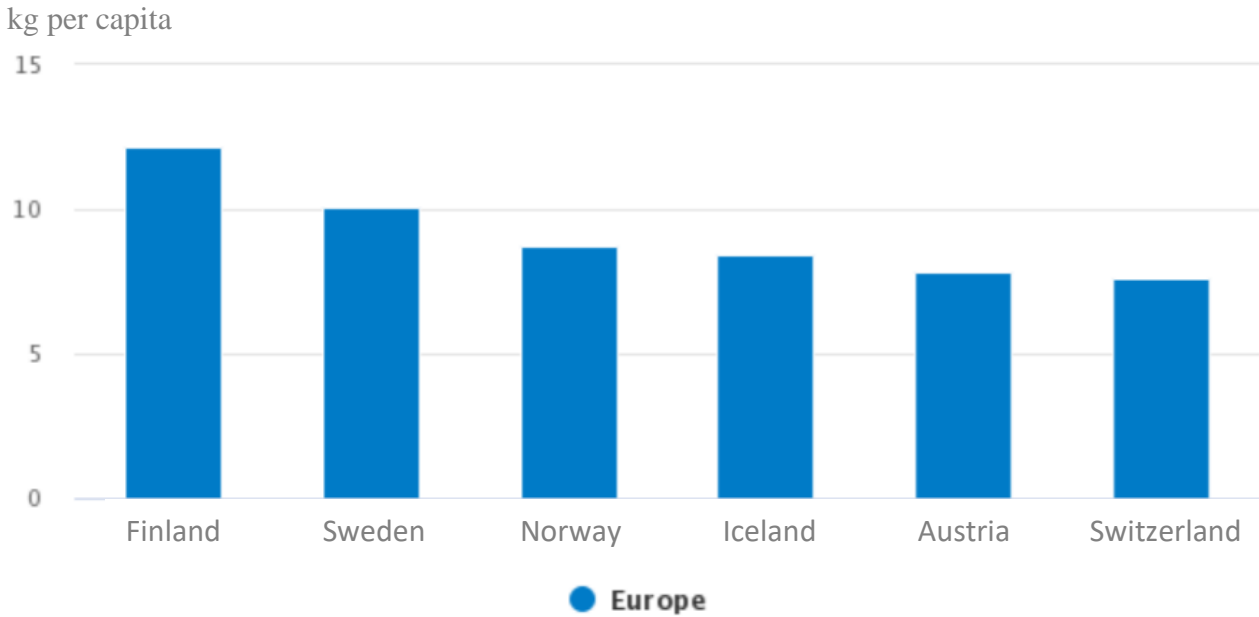


FIGURE 3. Largest coffee consuming countries (in kg per capita) in Europe 2015 (International Coffee Organization and own calculation 2016)

In Eastern Europe, the market for specialty coffee is smaller, but growing, especially in coffee culture cities like Krakow (Poland), Prague (Czech Republic) and Vilnius (Lithuania). The growth of coffee festivals, smaller scale roasters and coffee education institutions (such as the Coffee Embassy in the Czech) show the potential of these markets. (CBI Ministry of Foreign Affairs report 2017.)

3.5 Spent coffee ground

The coffee production and consumption in the world are growing gradually. In fact, with 50% green coffee output used to produce instant coffee, it has over 4,4 million SCG discharged from coffee industry. Almost SCG from instant coffee industry is collected to make fertilizer, gardening and bioenergy. In addition, SCG source contains a huge amount of organic compound such as fatty acids, lignin, cellulose, hemicellulose and another polysaccharide. Therefore, SCG can be applied to make more valuable products such as biofuel, producing activated carbon, fertilizer and absorbed metal ion chemical. Nowadays, SCG has become the main by-products which researched with active antioxidation bring several benefits for health.

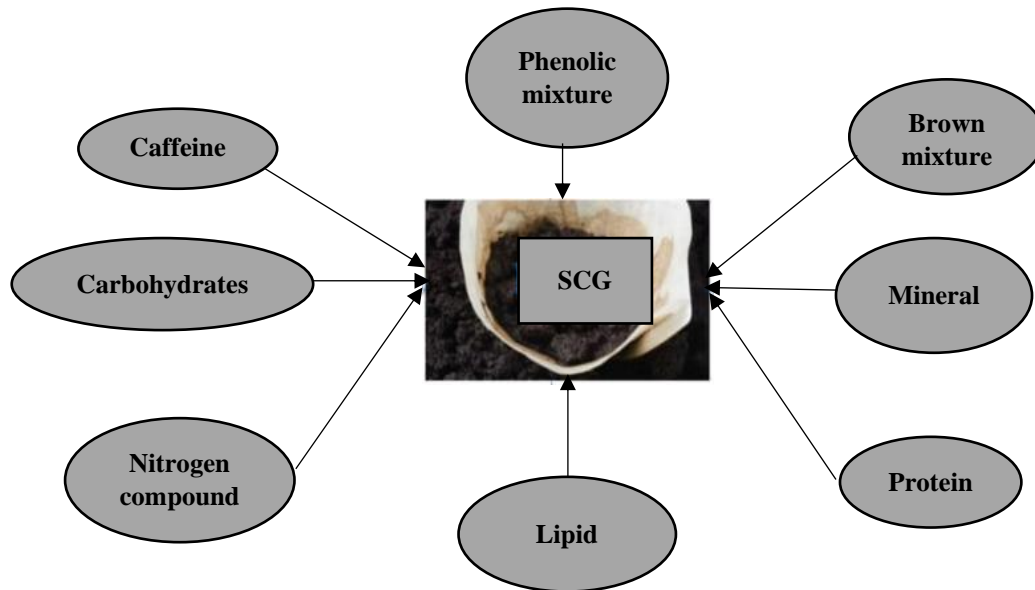


FIGURE 4. Main composition of SCG

As FIGURE 4 above shows SCG contains 8 main components such as phenolic mixture, carbohydrates, nitrogen compound without protein (caffeine, brown mixture), lipid, protein and mineral. SCG is known as potential source which can be applied for industrial branches ranging from medicine, cosmetic to fuel, food.

3.5.1 Carbohydrates

SCG source contains a high sugar (45.3% w/w). In detail, hemicellulose (mannose, galactose, arabinose) accounted for 36.7% and cellulose 8.6%. Mannose is the main polysaccharide 46.8%, galactose 30.4%, glucose 19% and 3.8% of arabinose (Mussatto et al 2010, 370-371). When making coffee, polysaccharides such as galactomannans and arabinogalactans will be extracted into coffee essence. However, there is a large amount of polysaccharide which still remains in coffee ground (Mussatto et al 2010, 368; Simoëa et al 2013, 81.)

Galactomannan has typical chemical properties which can be applied to food, pharmaceutical, biomedical and textile industries. Therefore, coffee ground can be used as a potential source to recover galactomannan. (Mussatto et al 2010, 368.)

Mannooligosaccharides are oligosaccharides which do not have digest ability, formed by mannose and can foster the growth of Bifidobacteria in intestinal tract as well as decrease stomach fat after drinking 300 ml of solution everyday which contains 3-6 g manooligosaccharides. (Takao et al 2006, 333-337.)

SCG includes neuter fibrous (45.2%) such as hemicellulose, cellulose, lignin mixture, acid fibrous matter (29.8%) (Vardon et al 2013, 1289). In addition, the fibrous property of coffee ground also performs antioxidation same as red wine 2.4 mM Trolox/100 g dry material.

3.5.2 Protein

SCG has a huge percentage of protein 13.6% w/w (Mussatto et al 2011, 369). The reason is the appearance of mixtures which contain nitrogen such as caffeine, trigonelline and acid amin. Essential amino acid accounts for 50% like leucine, valine, phenylalanine and isoleucine (Rogers et al., 1999). Furthermore, protein content in spent coffee ground is the source of arginine, glutamine and histidine which have a positive effect on the immune system. (Mussatto et al 2011, 369.)

3.5.3 Nitrogen compound without protein

In SGC, nitrogen compound without protein includes two main components: caffeine and brown mixture which can bring significant applications in agriculture. Caffeine (1,3,7- trimethyl-xanthine) is a purine alkaloid which is known as the most popular alkaloid in both coffee and products made from coffee. According to researchers, in coffee ground, the caffeine content accounts for 0.007-0.5% and depends on the extraction process and raw coffee (Cruz et al 2012, 7777-7779). Caffeine plays an important part in balancing the surface tension in oil-containing products, apply for producing several pharmaceutical and cosmetic products which made the skin soft and smooth. Additionally, caffeine is a nerve stimulant and applied to produce sedative and aspiring.

Browns mixtures in SCG are Mailard reaction between sugar and free amino products to form multi-product included melanoidins (Moreira et al 2012, 903-905). Malanoidins have high molecular mass and are the final products of Maillard reaction. These products can be used in functional foods and preservative because they have antioxidation ability and prevent lipid oxidation.

3.5.4 Lipid

The lipid content in SCG fluctuates from 9.3-16.2% (Cruz et al 2012, 1003). After making coffee, a huge amount of lipid remains in coffee ground (90.2%) that contains properties such as 84.4% triacylglycerols, 12.3% diterpene alcohol esters, 1.9% sterols, 0.1% sterol esters and 1.3% polarized mixture. (Ratnayake et al 1993, 263-269.)

Oil is a product of extraction SCG and divided into 2 groups. The first group has low acid palmitic content (<40%) and high acid linoleic (>40%). However, the second group has the opposite amount of palmitic and linoleic acid contents compared to the first group (Rudel et al 1995, 2101-2110). Oil from SCG can protect skin from UV, against cancer and anti-oxidation. Moreover, it is suitable to produce palmitic acid for shampoo technology. (Silva et al 2018, 1-5.)

3.5.5 Minerals

According to the analytical method ICP-AES, the ash content in SCG is 1.6% with main minerals such as potassium, phosphorus and magnesium (Mussatto et al 2011, 173-175). By extracting coffee with hot water, most of the minerals are found easily.

3.5.6 Phenolic mixtures

Phenolic mixtures (phenol or polyphenol) are the main factor which can decide anti-oxidation ability of plants. And SCG contains phenolic mixtures which bring benefits for the health such as antioxidation, resist bacterium, virus and prevention of cancer.

Phenolic mixtures can be extracted from SCG by a simple and effective method are extracted with ethanol solvent which is friendly to the environment. The maximum total polyphenol content which obtains in ethanol is 399 mg/g coffee ground. The high Chlorogenic acid and caffeine content indicate that the SCG has potential applications as a natural antioxidant. (Panusa et al 2013, 4162-4168.)

4 OVERALL OF FATTY ACIDS

Fatty acids contain free and parts of complex lipids which play an important role in metabolism. For example, they can function as a metabolic fuel for both storage and transport of energy. Moreover, they are a necessary component of all membranes and gene regulators. In addition, fatty acids have many industrial applications.

Lipids provide polyunsaturated fatty acids (PUFAs) that are precursors of powerful locally acting metabolites, i.e. the eicosanoids. As part of complex lipids, fatty acids are also important for thermal and electrical insulation, and for mechanical protection. Moreover, free fatty acids and their salts may function as detergents and soaps owing to their amphipathic properties and the formation of micelles. (Rustan & Christian 2005, 1.)

4.1 Lipids

Lipid is an ester of glycerol and fatty acid which are composed from three main elements C, H and O. In addition, lipids may contain other elements such as phosphorous and nitrogen. There are two important groups of lipids for biology and they are glycerol and sterol.

4.2 Fatty acids structure

Fatty acids are known as parts of complex lipids. They play a key role in metabolism, especially in metabolic fuel (Rustan & Christian 2005, 1). In addition, for thermal, electrical and mechanical protection, fatty acids are also important.

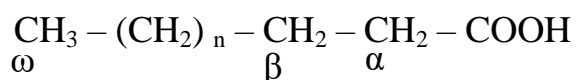


FIGURE 5. Nomenclature of fatty acids (Rustan & Christian 2005, 1)

Fatty acids are known as carbon chains which contain methyl group at one end of the molecule (omega, ω) and a carboxyl group at the other end (FIGURE 5). The carbon atom next to the carboxyl group is called the α carbon, and the subsequent one the β carbon. The letter n is also often used instead of the Greek ω to indicate the position of the double bond closest to the methyl end. The number of carbon

atoms in fatty acids is usually even (from 14 to 22 C). The ordinal number of carbon atoms in hydrocarbon chain of fatty acids is calculated from the carbon atom of the carboxyl group. (Rustan & Christian 2005, 1)

The carbon atoms in the group - COOH are numbered 1, the second atom is called carbon α and the third atom called carbon β . The carbon of the final methyl group is also called carbon ω .

The fatty acids in vegetable oil have a cis structure which are mainly palmitic acid (16:0), oleic acid (18:1 ω -9) and linoleic acid (18:2 ω -6). (Rustan & Christian 2005, 2). Fatty acids are divided into two types: saturated and unsaturated fatty acids.

Saturated fatty acids are called 'filled' (saturated) with hydrogen. The characteristic of saturated fatty acids is indicated by straight hydrocarbon chains with an even number of carbon atoms. 12–22 carbon atoms are contained in the most common fatty acids. (Rustan & Christian 2005, 1.)

Unsaturated fatty acids are classified into two groups monounsaturated and polyunsaturated fatty acids (PUFAs). Monounsaturated fatty acids contain one carbon–carbon double bond that can appear in different positions in a chain. Almost chain length of monoenes includes 16–22 and a double bond with the cis configuration. It means that on either side of the double bond, the hydrogen atoms will be oriented in the same direction. In detail, the appearance of a double bond can cause mobility restriction of the acyl chain at that point. Besides, the cis configuration gives a kink in the molecular shape. Compared to trans-forms, cis fatty acids are thermodynamically less stable and have lower melting points. (Rustan & Christian 2005, 1.)

Polyunsaturated fatty acids (PUFAs) are produced only from plants and phytoplankton which are essential to all higher organisms such as mammals and fish. Additionally, in the body, PUFAs are further metabolized by the carbon atoms addition and desaturation. In PUFAs structure, they contain the first double bond which can be occurred between the third and the fourth carbon atom from the α carbon that called ω -3 fatty acids. If position of is changed, between the sixth and seventh carbon atom, then they are called ω -6 fatty acids. The double bonds in PUFAs are separated from each other by a methylene grouping. (Rustan & Christian 2005, 1.)

5 PURPOSE OF RESEARCH, METHOD AND EXPERIMENTAL PROCEDURE

In this chapter, the intention of biodiesel extracted from SCG research is clarified. In addition, method of research, equipment, chemicals and the workflow of synthesis of biodiesel are demonstrated through experimental procedure.

5.1 Purpose of research

There are three purposes for this research. First of all, extract coffee oil from used coffee grounds by Soxhlet extraction method and then convert coffee oil into biodiesel by transesterification method with acid and alkali catalysts. Secondly, analyse the physical and chemical properties of biodiesel extracted from SCG. Finally, researching factors affecting biodiesel synthesis efficiency from coffee oil.

The extraction of coffee oil from SCG is conducted through two stages. Firstly, by Soxhlet method to extract mixture coffee oil from SCG and hexane solvent. Secondly, using rotary evaporator to separate coffee oil and hexane solvent.

5.2 Method of research

The most common method to reduce the viscosity of vegetable oil is to mix it with diesel, emulsification, heating, cracking and transesterification. As methods above, transesterification is the most suitable method because of the by-products of the process is glycerine which has a high economic value.

5.2.1 Transesterification method

Transesterification is a chemical reaction between triglycerides and alcohol, a catalyst plays a role to form the single ester. Long chain and branched triglyceride molecules are converted into single ester and glycerine. The transesterification process included a chain of three consecutive reversible reactions. It means that firstly, there is the conversion of triglycerides to diglyceride will be occurred and then convert diglyceride to monoglyceride. The glyceride is transformed into glycerine and produces one ester molecule at each step. The properties of these esters correspond to diesel. (Knothe G et al 2005, 34-36.)

According to the proportion equation, three moles of alcohol will react with one mole of triglycerides. However, practically the molar ratio (alcohol: oil) is often higher for better ester formation process. Esters are known as the main products of transesterification, but recovery glycerine is also an important issue because of its role in many industrial processes. Alcohol is usually used in short chains such as methanol, ethanol, propanol and butanol. The efficiency of the reaction depends on the type of alcohol, thus, the choice of one of these alcohols depends on the price and process nature. (Knothe G et al 2005, 34-36.)

Methanol is often used because it is quite cheap. Alkali metal hydroxides have the most efficient effect of transesterification reaction when compared with an acid catalyst. KOH and NaOH is the most commonly used alkali catalysts. Transesterification of vegetable oils with alkali catalyst is only feasible when the AV of the oil is less than 4. If AV of oil is higher, it will reduce efficiency of process. The purpose of this research is to develop a high AV conversion method. Especially, coffee oil is one of the most representative oils. First of all, checking the AV of oil is important for conducting synthesis in one stage or two stages. If the AV is low enough, it needs one stage to conduct. In this research, titration fatty acid in oil by solution KOH 0.05 M is carried out and then titrated to determine the AV. And for coffee oil, the AV value is high, so it performs at two stages. The process consists of two steps: esterified by acid and transesterification. The first step which reduces the FFA value of coffee oil down to 2% is called acidification ester. The next step is transesterification. After removing the impurities in the product of the first step, continue to convert into single ester of fatty acid with alkali catalyst. The parameters affect process such as ratio of molar alcohol / oil, amount of catalyst, temperature and reaction time. (Blinová et al 2017, 117-118.)

The biodiesel collection process can be continuous or cyclical. Practically, this process is usually done continuously through two stages. About 80% of the amount of alcohol and catalyst are used in the first reactor. The reaction mixture after separating the glycerine phase is put into second reactor to finish reaction with the remaining alcohol and catalyst. (Blinová et al 2017, 117.)

The glycerine is made after two reaction stages and separated from the ester phase in a centrifuge. Separation usually occurs easily because the glycerine is virtually insoluble in the ester. Amount of excess alcohol can slow the separation process because alcohol dissolves into both glycerine and ester. However, the excess alcohol cannot be removed before the phase separation process due to the equilibrium towards triglycerides. (Blinová et al 2017, 117.)

Oil, alcohol and the catalyst are mixed in the reactor with suitable time (1-2 hours) at a temperature 60°C. The ester after separating from glycerine is taken to neutral stage and through methanol separation tower. In the neutral stage, acids are used to neutralize the amount of residual alkali catalyst and amount of soap form as reaction (1) and (2) below



All residual catalyst, soap, salt, methanol and free glycerine are separated from biodiesel by using water to wash. Remember to neutralize with acid before washing with water in order to minimize the amount of soap and washing water needed. Thus, it can prevent the emulsion process (water in biodiesel with emulsifying agent is soap) which make a difficulty for separating water from biodiesel. Biodiesel is cleaned by water in the evaporator tower. (Blinová et al 2017, 118.)

Practically, biodiesel collection process can occur normally with a free fatty acid content is less than 0.5%. Then, an additional catalysis is required to neutralize free fatty acids. The amount of generated soap is within the allowable level. When the free fatty acid content is greater than 0.5%, the amount of generated soap can make the ester and glycerine phase separation. Besides, it significantly increases emulsion formation in washing by water. To reduce the content of free fatty acids, before the transesterification reaction, acid catalysts such as H_2SO_4 are used to convert free fatty acids into esters. (Blinová et al 2017, 118.)

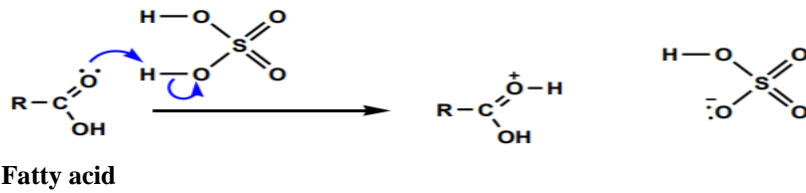


Therefore, the content of free fatty acids is the main factor in the technology selection for biodiesel production process.

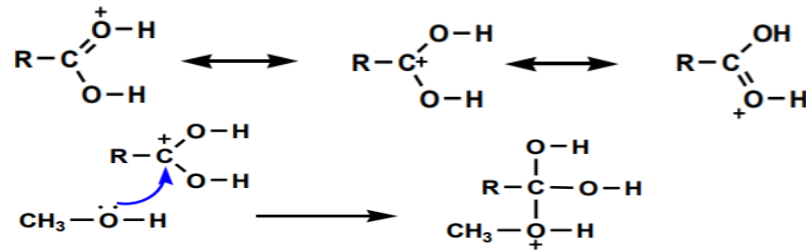
5.2.2 Catalyst for ester transposition

The esterification reaction with acid catalyst occurs through five steps

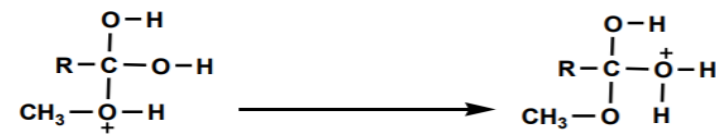
Step 1:



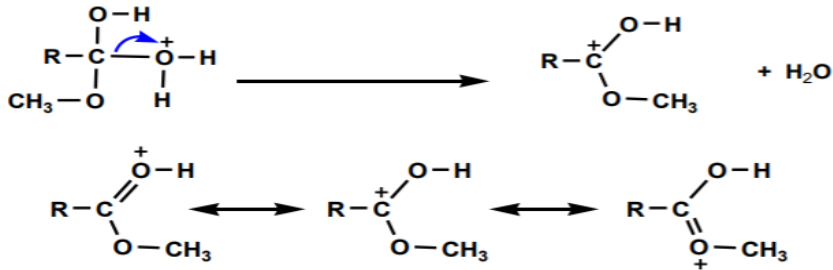
Step 2:



Step 3:



Step 4:



Finally

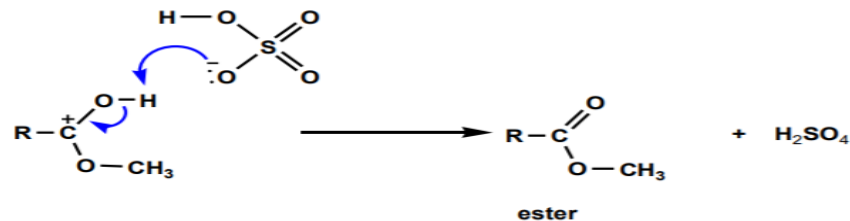
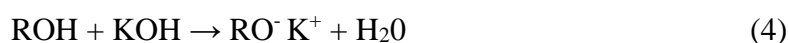


FIGURE 6. Five steps of acid catalyst esterification reaction (Jim 2019)

The catalysts for reaction can be acid or alkaline. However, in the homogeneous catalysis process, alkali catalyst promotes the reaction faster than acid catalyst. In the catalyst alkaline, the most common are NaOH and KOH which can help to obtain high quality biodiesel. In detail, KOH dissolves with CH₃OH more easily than NaOH and insoluble potassium sulphate salt is obtained during product cleaning which can be used as fertilizers.

The mechanism of esterification reaction is affected by alkali catalyst. The real catalyst is the anion RO⁻ (CH₃O⁻ in the case of CH₃OH), which is formed in alcohol solution (Knothe et al 2005, 37)



Anion RO^- attacks the positively charged centre of the $C^+ O^-$ bond, followed by the separation of the ester molecule from the triglyceride molecule and the formation of the diglyceride molecule (Knothe et al 2005, 38)

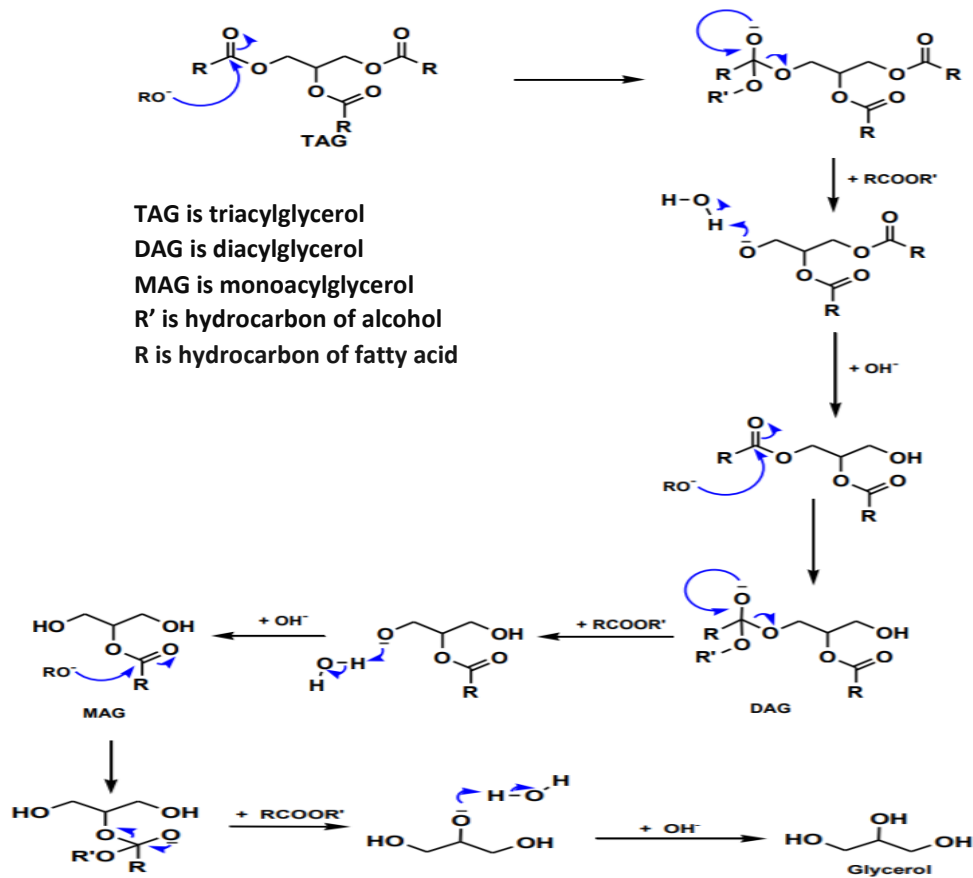


FIGURE 7. The alkali catalyst esterification reaction (Knothe et al 2005, 38)

This mechanism repeats until glycerine is formed. Through the reaction mechanism, the speed of reaction depends on the size of anion RO^- . Indeed, the bigger size of anion RO^- , the harder the anion will attack the CO bond; thus, the reaction occur slower. Therefore, the reaction with methanol occurs more easily than other alcohols. (Gerpen 2005, 1103.)

Besides, the main cause of the reaction rate reduction is the difficulty of dissolution of methanol into oil. In order to increase this solubility, it is necessary to increase the temperature and the level of stirring (especially at the starting point of the reaction during the cycle) or using an intermediate solvent. If the reaction takes place at room temperature, it takes 4-8 hours to complete the reaction. In detail, at 40°C , it takes 2-4 hours and at 60°C , it takes 1-2 hours. Higher temperatures will reduce the reaction time but it needs to be done under pressure conditions to keep methanol in liquid state. Practically, the process is carried out mainly at 60°C . The reaction efficiency is calculated according to the formula below (Blinová et al 2017, 114-119.)

$$H\% = \frac{\text{mass of biodiesel}}{\text{mass of raw material}} * 100$$

5.3 Experimental procedure

Equipment, chemicals and raw materials that are used in this experiment listed in TABLE 2

TABLE 2. List of equipment, chemicals and raw materials for experiment

Equipment	Chemicals	Raw material
Burette	Methanol	The biomass source (SCG) of this experiment comes from TriAn Factory-Nestle Vietnam
Erle	KOH anhydrous	
Circulating module kits	Concentrated H ₂ SO ₄	
Soxhlet extraction kits	Na ₂ SO ₄ anhydrous	
Electric oven	Phenolphthalein	
Glass flask	Hexane	
Glass cup	Absolute Ethanol	
Rotary evaporators	Diethyl ether	
Measuring cylinder, dropper		
Extracted funnel, filtered funnel		

The workflow synthesis of biodiesel from SCG is occurred through three stages: extraction of coffee oil from both SCG and hexane, esterification reaction with sulfuric acid catalyst and esterification reaction with alkaline catalyst.

5.3.1 Stage 1- Coffee oil extraction from SCG and hexane

The oil extraction process from SCG will be followed to four steps. Step 1: Make spent coffee ground to be dry, dehumidify (50% wt%) in a drying oven and a desiccator. Step 2: Separate oil from coffee grounds by Soxhlet extraction kit and reflux distillation device. Weigh 16 g of coffee grounds into the Soxhlet device's filter cup. Pour 90 ml of n-hexane solvent into a flask at the bottom of the Soxhlet machine. Step 3: Boil the solvent at the bottom of flask. The hexane will vapor and go through the duct to the circulation system. Then, it is cooled into drops that go down into the coffee grounds filter bag below. The coffee oil is pulled out by the hexane until it reaches the lower limit of the tube and will be pushed to the flask below. Next, collect the mixture of coffee and hexane in the flask. Repeat the procedure every hour.

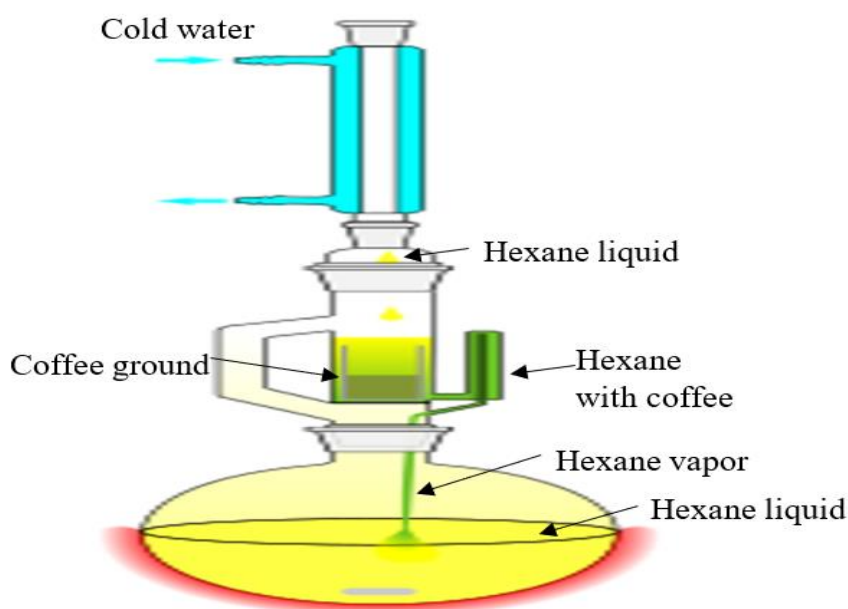


FIGURE 8. Simulation Soxhlet extraction system in Paint 3D program

Step 4: After separating sufficient amount, use a rotary evaporator to evaporate the hexane from the mixture, stirring speed at 500 rpm and a temperature from 60°C to 67°C until the sample solution turns brown. Carry out the recovery of hexane solvent to use for the next extraction. Collect coffee oil to take away for reaction.



PICTURE 1. Rotary evaporator equipment

5.3.2 Stage 2- Esterification reaction with sulfuric acid catalyst.

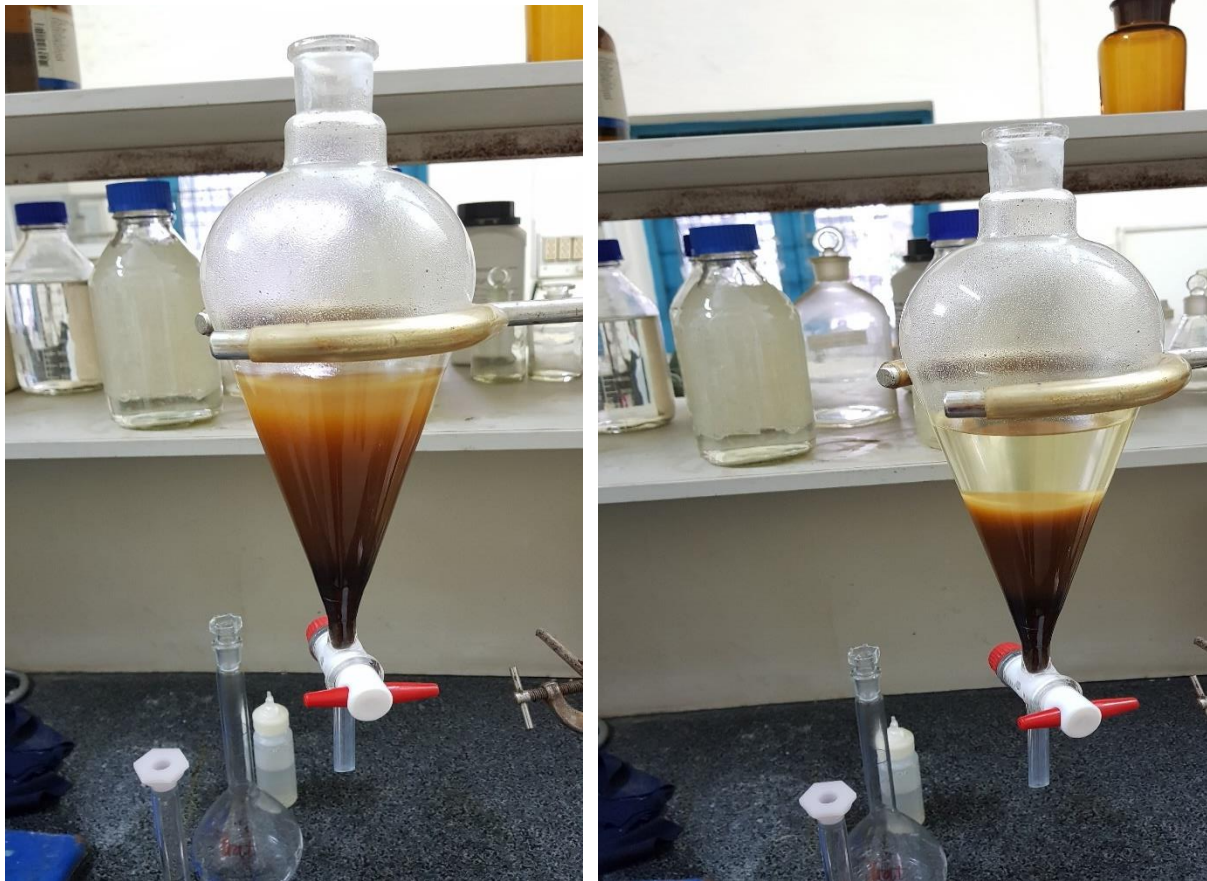
For esterification with sulfuric acid catalyst, 1 liter of crude coffee oil requires 600 ml of methanol. The amount of methanol is about 60% of the oil. Then, coffee oil is poured into flasks and heated to 60°C. Methanol is also added to the coffee oil, heated and stirred for a few minutes. After that, add 1% (mass of oil) sulfuric acid. Continuously heat and stir the mixture within 4 hours at normal pressure. When reaction completes, the product is poured into an extracted funnel to separate phases. Residual alcohol with sulfuric acid and impurities in the upper phase are removed. The stage one finishes, the bottom phase is separated and used for the next stage (transesterification). The AV is 1.05 which measured at stage 2.

The amount of acid catalyst also affects the metabolism of the process. The catalyst will vary in about 1%. It means that the percentage value is the volume of coffee oil required for this reaction. The acid catalyst process can achieve maximum efficiency when sulfuric acid is 1% original mass of oil. In addition, it is noted that during the experiment, adding more sulfuric acid will make the product more darken.

5.3.3 Stage 3- Esterification reaction with alkaline catalyst

The transesterification uses an empirical setting of the pre-treatment stage by acid catalyst. The product of stage 2 is heated to the required temperature for the reaction about 60°C in the flask. Meanwhile,

KOH is dissolved in methanol and poured into the flask. The mixture is heated and stirred for about 2 hours. At the end of the process, the product is poured into an extracted funnel to separate into two layers. The lower layer contains mainly impurities and glycerine are removed. The ester is still in the upper layer. Methyl ester is washed to remove residual impurities and glycerine. Water is sprayed on the surface of ester layer and then stir gently. The lower layer is removed, and the top layer which have yellow- brown colour (biodiesel) is separated.



PICTURE 2. Extracted funnel contains coffee oil which is separated before and after 30 minutes

Influence of molar ratio of methanol / oil: the amount of methanol required for transesterification is analysed through ratio molar of methanol / oil. According to the proportion equation, the necessary molar ratio is 3: 1. In fact, to increase the reaction efficiency, a higher molar ratio will make the reaction toward creating products with faster speed.

The influence of alkaline catalyst: alkali catalyst (KOH) concentration varies about 0.5-1.5% (mass of KOH / mass of oil) which is used in this experiment. Maximum conversion efficiency can be achieved when the concentration of KOH is 1%. The amount of catalyst added to increase the ability to create emulsions. Similarly, this increases the viscosity and leads to gel formation. Transesterification takes

place ineffectively when the amount of KOH is not enough. The result is obtained in final stage with mass of oil to weigh for reaction: 20g

6 RESULTS

After the extraction SCG by Soxhlet method and going through two reactions: esterification reaction with sulfuric acid and alkaline catalysts, the product: biodiesel from SCG is analysed with important quality parameters and compared to diesel.

6.1 Physical and chemical properties of biodiesel extracted from SCG

Biodiesel extracted from SCG is assessed for quality through values of basic physical and chemical criteria at the Vietnamese Institute of environment and resource. Results are shown in TABLE 3

TABLE 3. Comparison of the physical chemistry properties of Biodiesel extracted from SCG to both standard (ASTM) and Diesel (The quality parameter results is analysed at Vietnamese Institute of environment and resource)

Analytical parameters	Analytical method	ASTM	Diesel	Biodiesel
Total Methyl ester content (%)	EN 14103	96.5	-	96.63
Density at 15 °C (g/cm ³)	ASTM D 1298	0.875 - 0.900	0.85	0.892
Kinematic viscosity at 40°C (mm ² /s)	ASTM D 445	1.9 - 5.0	3.2	4.1
AV (mg KOH/g)	ASTM D 974	0.5 max	-	0.36
Cetane value	ASTM D 613	47 min	45	49.7
Oxidation Stability	ASTM D2274	3 min	6	2.53
Corrosion copper leaf (50°C, 3h)	ASTM D 130	N° 1	1a	1a

According to ASTM standards, the lowest limit of ester content (in proportion to the difference biodiesel yield) of biodiesel is 96.5%, from the results in TABLE 3. The ester content of biodiesel extracted from coffee ground is 96.63% which indicates that almost all coffee oil has been converted into ester. However, the efficiency can be higher if the crude oil is initially refined. (O'Brien et al 2000, 20-25.)

Secondly, the density at 15°C of biodiesel extracted from coffee ground is approximately same to diesel which shows that these products are suitable to density range standard of fuel and related to volatility in the air.

Thirdly, the kinematic viscosity at 40°C of biodiesel is higher than diesel. This is one of the main reasons why biodiesel extracted from coffee ground or vegetable oil and animal fats should be synthesized before

used and cannot be used directly as diesel fuel. If viscosity is out of standard, it affects on the ability pumping and injecting fuel into the combustion chamber. Therefore, thanks to process of converting to esters, biodiesel extracted from SCG have similar properties as diesel.

Continuously, by observing the colour of SCG, the AV of biodiesel extracted from coffee ground can be questioned. For example, if coffee ground has light brown, AV is about 10 mg KOH / g, conversely, if coffee ground is dark brown, the AV range is from 20 to 80 mg KOH / g (A.S.Ramadhas et al 2008, 980-983). In addition, the AV also depends on other factors such as time and storage because the oil is easily oxidized at ambient air. Furthermore, hydrolysis will occur due to presence of water molecules in the oil. In this experiment, the biodiesel extracted from coffee ground was yellow and AV was about 0.36 mg KOH / g. It means that the lower the AV, the easier transesterification reactions because less amount of free fatty acids react with the alkali catalyst to form soap and thus it is possible to separate this oil out of glycerol.

Next, the only difference between gasoline and diesel engines is the ignition mechanism. While gasoline engines need an ignition device to ignite the combustion process of gasoline-air compressed air mixture, the diesel engine operates following the explosive principle. When diesel-air carburettor is compressed at high pressure (high compression ratio), heat is generated that will trigger the process of self-ignition. It is this feature that makes the efficiency of diesel engines are higher. The specification of diesel is also different from gasoline. While gasoline uses an octane detonation value, diesel uses cetane detonation value. The cetane value is one characteristic quantity of the self-igniting ability of diesel or biodiesel in an internal combustion engine. The higher the cetane value, the shorter the delay time and good burning fuel. However, the lower the cetane value, the harder it is for the engine to start, make noise and create lots of emissions. Practically, diesel engines will operate better which fuels which have cetane value is greater than 47 (US Department of Energy 2006, 21-22). In this research, the cetane value met the requirements of ASTM (49.7) and is higher than the cetane value of diesel. It means that biodiesel extracted from coffee ground has better combustion characteristics than diesel.

Most biodiesel synthesized from vegetable oil and animal fat does not meet the standard on oxidation stability. This is one of the biggest disadvantages of biodiesel. They are extremely sensitive to oxidizing agents such as: air, light and temperature. Biodiesel is essentially esters of fatty acids, in which, unsaturated fatty acids dominate the highest percentage, they are easily affected by oxidizing agents in order to form free radicals and continuously form peroxides, aldehyde and finally they form acids (mainly short-chain acids). The formation of these acids is the main cause of engine erosion effects (DunnRobert

O 2008, 657-662). The oxidation stability of biodiesel extracted from coffee ground is no exception. There are lots of ways for biodiesel to meet oxidation stability requirements, among them, usage of an antioxidant to increase the oxidation resistance is the simplest way.

Metal corrosion is a concerned problem of biodiesel because it damages diesel engines. Under the influence of high temperature conditions, the oxidation process of biodiesel will be accelerated. As the result, the process forms short-chain organic acids, in which, formic acid, acetic acid, propionic acid and caproic acid make up the majority. Copper is one of metals which corroded easily by these acids. At the end, the reaction process will form the metal salts of these acids which are accumulated gradually to turn into fouling and can lead to serious problem with nozzles. (US Department of Energy 2006, 13.)

As the result of the physical chemistry properties in TABLE 3, biodiesel extracted from SCG is a potential biomass source for biodiesel production. However, it needs to improve some parameters to meet ASTM standard.

6.2 Factors affect the performance of catalysed transesterification

When synthesis of biodiesel totally complete, the results of all biodiesel extracted from spent coffee ground process are recognized with keys parameters such as concentration KOH%, mol (oil/methanol), efficiency H% and acid value through TABLE 4.

TABLE 4. Summary results of all biodiesel extracted from SCG process

Concentration KOH % (m KOH/oil)	Mol (oil/methanol)	H%	Acid value
0.5	1:4	44.1	0.47
	1:5	47.2	0.47
	1:6	57.36	0.43
	1:7	31.27	0.47
	1:8	43.86	0.47
0.75	1:4	47.62	0.47
	1:5	50.47	0.47
	1:6	59.46	0.43
	1:7	51.82	0.47
	1:8	46.12	0.47
1.0	1:4	56.31	0.46
	1:5	61.2	0.46
	1:6	74.88	0.36
	1:7	62.34	0.46
	1:8	47.37	0.46
1.25	1:4	55.37	0.47
	1:5	67.55	0.47
	1:6	70.38	0.43
	1:7	65.12	0.47
	1:8	57.56	0.47
1.5	1:4	58.42	0.47
	1:5	59.76	0.47
	1:6	66.85	0.47
	1:7	59.97	0.43
	1:8	56.76	0.47

Following TABLE 4 above the synthesis of biodiesel extracted from SGC get the highest efficiency (74.88%) with the AV is 0.36 when this synthesis combines concentration KOH % (1%) and ratio mol of oil/methanol (1:6)

After extraction spent coffee ground oil and synthesis them by transesterification method, the final product - biodiesel is collected (PICTURE 3) which physical properties and colour are quite similar to diesel. The SGC before and after extraction has different colour (PICTURE 4). In detail, the colour of SCG before extraction is black brown but SCG after extraction has yellow brown. It means that, almost oil in SGC is extracted by Soxhlet equipment.



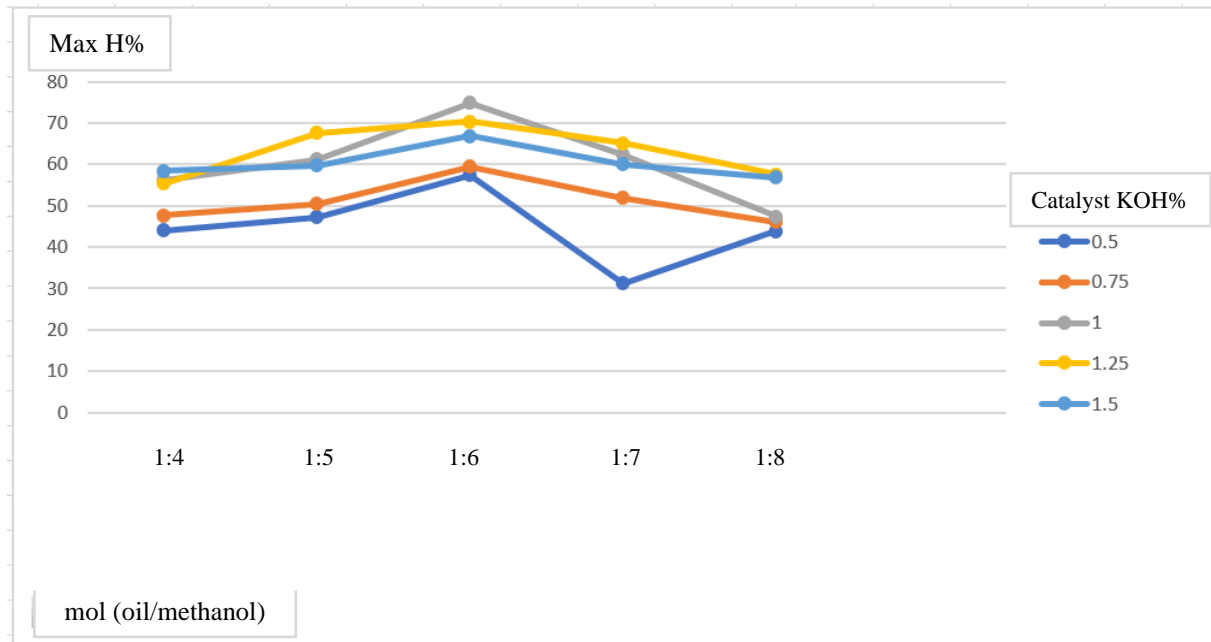
PICTURE 3. Final product: Biodiesel



PICTURE 4. SCG before and after extraction

6.2.1 The molar ratio (oil/methanol) affecting the performance of catalysed transesterification

The molar ratio (oil/methanol) ratio is one of the most important factors which affects the reaction performance. In this research, a series of experiments is conducted that has a molar oil/methanol ratio from 1: 4 to 1: 8 and the results are demonstrated in GRAPH 1

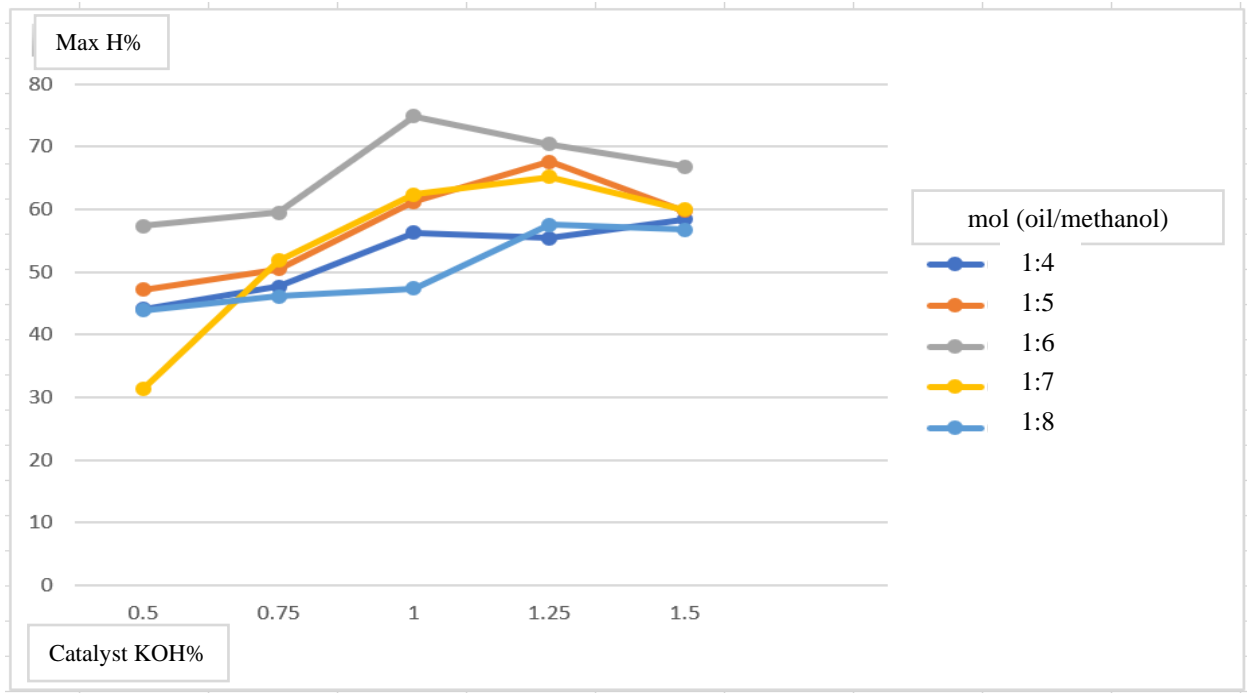


GRAPH 1. The effect of oil/methanol ratio on biodiesel generation efficiency

If the molar oil/methanol ratio is gradually made lower, the synthesis biodiesel efficiency increases. The molar ratios are lower than molar ratio oil/methanol in theory transesterification reaction (1:3), the speed of ester formation gets faster (Fukuda et al 2001, 405-410). When the molar ratio is 1:6, the efficiency is highest (%). However, if the molar ratio is lower than 1:6, the efficiency will decrease gradually. It can be explained as methanol contains polar OH group which plays a part as an emulsifier (Umer Rashid et al 2008, 265-270) which has the ability to increase solubility of glycerine in reaction solution. The rest of glycerine in the reaction solution will make the equilibrium displace following to the opposite direction and creates mono ester and the performance will decrease. The second reason is that methanol can dissolve both glycerine and alkyl ester, hence, an amount of alkyl ester and methanol will enter the glycerine phase and thus reduces the efficiency.

6.2.2 Catalyst KOH affects performance of catalysed transesterification

With the purpose to research the effect of catalyst (KOH) amount, the experiments are conducted with the KOH catalyst concentration change from 0.5% to 1.5% (compared to oil mass) and also change of molar ratio oil/methanol from 1:4 to 1:8, the temperature is fixed at 60°C, stirring speed is at 500 rpm, reaction time is 2 hours and GRAPH 2 shows the results.



GRAPH 2. The effect of catalyst KOH% on biodiesel generation efficiency

With the concentration of catalyst (KOH) 0.5%, the reaction has lowest performance due to amount of KOH is not enough to react completely. Next, when it increased to 0.75%, the performance begins to increase quite well. When the concentration of the catalyst (KOH) is 1%, reaction gets the highest efficiency. On the contrary, when the KOH concentrations are greater than 1%, efficiency of reaction decreases gradually because soap will be formed when increase the amount of catalyst and then reduce the product efficiency. It means that the additional amount of catalyst can create emulsions. Similarly, this increases the viscosity and leads to gel formation. Transesterification takes place ineffectively when insufficient KOH level.

Finally, optimal conditions for the transesterification reaction are found as follows: KOH catalyst content is 1% (compared with oil mass), molar ratio (oil / methanol) is 1:6, reaction temperature at 60°C, reaction time is in 2 hours and stirring speed is 500 rpm.

7 DISSCUSION AND CONCLUSION

This research is conducted with the purpose is to produce high quality biodiesel from the low value materials with high FFA content. It can be seen that with high FFA materials, the esterification reaction by the same procedure as an existing alkali catalyst is not happened. The main reason is that alkali catalysts will react with free fatty acids to form soap and prevent the phase separation of glycerine and ester. Thus, the esterification process includes two stages to convert high FFA oil into its ester.

Firstly, the Soxhlet method is applied to extract the coffee oil from SCG. Secondly, coffee oil is converted into alkyls ester of fatty acid by transesterification with methanol in the presence of alkali catalyst (KOH). In order to obtain biodiesel after extracting coffee oil, it had to be conducted through two-step process. The first step (esterification reaction with acid catalyst) helps to reduce FFA content in coffee oil to below 2%. The added sulfuric acid is too much and darken the product. The second step is the esterification with alkali catalyst by initial ester and glycerine formulations. As a result, the efficiency of two steps is affected by molar methanol / oil ratio. The molar ratio of oil/methanol is 1:6 can convert into ester better within 2 hours, at a temperature 60°C and the stirring speed is 500 rpm. According to GC / MS analysis results, the oxidation stability of biodiesel extracted from SCG is quite good because of two reasons. The first reason shows that lower poly-containing component compared to some biodiesel obtained from some other biomass sources. The second reason is that in coffee oil antioxidants exist such as polyphenols, phenolic acid so it can be asserted that coffee ground is a potential biomass source.

Besides, the final product of the experiment is glycerol which is a valuable product and it needs to be refined before using. Furthermore, it also adds more value for synthesis of biodiesel from SCG.

According to the CBI Ministry of Foreign Affair report, Finland has the highest coffee consumption rate in Northern European markets, about 66 million tonnes in 2015. Thus, a huge amount of spent coffee ground is released every day. In addition, the Finnish government focuses on using biomass sources to produce biofuel. Two reasons above indicate that it is an opportunity for Finland in order to produce biodiesel from spent coffee ground (biomass source). In the future, the thesis can contribute to research and development biodiesel extracted from spent coffee ground which is possible to use widely in commercial fuel market.

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REQUIREMENTS FOR BIODIESEL (B100) BLEND STOCK AS LISTED IN ASTM D6751-03
(U.S Department of Energy 2006, 10)

Property	ASTM Method	Limits	Units
Flash Point	D93	130.0 min.	°C
Water and Sediment	D2709	0.050 max.	% vol.
Kinematic Viscosity, 40°C	D445	1.9 - 6.0	mm ² /s
Sulfated Ash	D874	0.020 max.	% mass
Sulfur*	D5453	0.0015 max. (S15) 0.05 max. (S500)	% mass
Copper Strip Corrosion	D130	No. 3 max.	
Cetane Number	D613	47 min.	
Cloud Point	D2500	Report to Customer	°C
Carbon Residue**	D4530	0.050 max.	% mass
Acid Number	D664	0.80 max.	mg KOH/g
Free Glycerin	D6584	0.020 max.	% mass
Total Glycerin	D6584	0.240 max.	% mass
Phosphorus Content	D4951	0.001 max.	% max.
Distillation Temperature, 90% Recovered (T90)***	D1160	360 max.	°C

FATTY ACID PROPERTIES OF BIODIESEL (U.S Department of Energy 2006, 21)

Chemical formula	Name	Molecular mass	%
C ₁₅ H ₃₀ O ₂	Methyl tetradecanoate	242,40	0,08
C ₁₇ H ₃₄ O ₂	Hexadecanoic acid, methyl ester	270,45	9,09
C ₁₇ H ₃₂ O ₂	9-Hexadecenoic acid, methyl ester, (Z)-	268,43	0,16
C ₁₉ H ₃₈ O ₂	Methyl stearate	298,51	9,56
C ₁₉ H ₃₆ O ₂	11-Octadecenoic acid, methyl ester	296,49	1,22
C ₁₉ H ₃₆ O ₂	11-Octadecenoic acid, methyl ester	296,49	2,64
C ₁₈ H ₃₂ O ₂	9,12-Octadecadienoic acid, methyl ester	280,45	37,6
C ₂₁ H ₃₆ O ₂	11,14,17-eicosatrienoic acid methyl ester	320,51	16,98
C ₁₅ H ₃₄ O ₂	Hexadecanoic acid, 15-methyl-, methyl ester	284,27	0,39
C ₂₁ H ₄₀ O ₂	11-Eicosenoic acid, methyl ester	324,54	0,20
C ₂₃ H ₄₆ O ₂	Docosanoic acid, methyl ester	354,61	0,08

COMPOSITION OF VARIOUS BIODIESEL FEEDSTOCKS

(U.S Department of Energy 2006, 16)

