BIOFUEL PRODUCTION FROM SPENT COFFEE GROUNDS BY SUPERCRITICAL ETHYL
ACETATE

Miss Wirasinee Supang

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Fuel Technology
Department of Chemical Technology
FACULTY OF SCIENCE
Chulalongkorn University
Academic Year 2020
Copyright of Chulalongkorn University

การผลิตเชื้อเพลิงชีวภาพจากกากกาแฟคั่วบดโดยเอทิลแอซีเทตภาวะเหนือวิกฤต

น.ส.วิลาสินี ศุภางค์

Thesis Title	BIOFUEL PRODUCTION FROM SPENT COFFEE GROUNDS BY SUPERCRITICAL ETHYL ACETATE
By	Miss Wirasinee Supang
Field of Study	Fuel Technology
Thesis Advisor	Professor Somkiat Ngamprasertsith, Ph.D.
Thesis Co Advisor	RUEANGWIT SAWANGKAEW, Ph.D.

Accepted by the FACULTY OF SCIENCE, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Science

--- Dean of the FACULTY OF SCIENCE

(Professor POLKIT SANGVANICH, Ph.D.)

THESIS COMMITTEE

--- Chairman

(Associate Professor PRASERT REUBROYCHAROEN, Ph.D.)

--- Thesis Advisor

(Professor Somkiat Ngamprasertsith, Ph.D.)

--- Thesis Co-Advisor

(RUEANGWIT SAWANGKAEW, Ph.D.)

--- Examiner

(Associate Professor Chawalit Ngamcharussrivichai, Ph.D.)

--- External Examiner

(Sasithorn Sunphorka, Ph.D.)

วิลาสินี ศุภางค์ : การผลิตเชื้อเพลิงชีวภาพจากกากกาแฟคั่วบดโดยเอทิลแอซีเทตภาวะเหนือวิกฤต. (BIOFUEL PRODUCTION FROM SPENT COFFEE GROUNDS BY SUPERCRITICAL ETHYL ACETATE) อ.ที่ปรึกษาหลัก : ศ. ดร.สมเกียรติ งามประเสริฐสิทธิ์, อ.ที่ปรึกษาร่วม : ดร.เรืองวิทย์ สว่างแก้ว

งานวิจัยนี้ศึกษาการผลิตเชื้อเพลิงชีวภาพจากกากกาแฟคั่วบดโดยเอทิลแอซีเทตภาวะเหนือวิกฤต กากกาแฟเป็นของเสียจากอุตสาหกรรมกาแฟที่มีแนวโน้มเพิ่มปริมาณมากขึ้นอย่างต่อเนื่องทุกปี เพื่อเพิ่มมูลค่าของกากกาแฟ การใช้เอทิลแอซีเทตเป็นตัวทำละลายเพื่อสกัดและทำปฏิกิริยาในการผลิตเชื้อเพลิงชีวภาพผ่านปฏิกิริยาอินเทอร์เอสเทอริฟิเคชัน การวิเคราะห์องค์ประกอบของกากกาแฟแสดงให้เห็นว่า ความชื้นในกากกาแฟสดมีค่าประมาณร้อยละ 56 โดยน้ำหนัก เมื่อผ่านการอบความชื้นของตัวอย่างกากกาแฟลดลงเหลือร้อยละ 12.76 โดยน้ำหนักเพื่อยืดระยะเวลาในการกักเก็บรวมถึงลดผลกระทบของปฏิกิริยาไฮโดรไลซิสในปฏิกิริยาอินเทอร์เอสเทอริฟิเคชัน ขั้นตอนการทำแห้งมีความจำเป็นต่อการลดปริมาณน้ำในตัวอย่างกากกาแฟ ปฏิกิริยาไฮโดรไลซิสทำให้ค่ากรดของเชื้อเพลิงชีวภาพที่ผลิตได้สูงขึ้น เอทิลแอซีเทตเป็นตัวทำละลายที่เหมาะสมเนื่องจากสามารถสกัดน้ำมันจากกากกาแฟได้ในปริมาณสูง (ร้อยละ 22.74) สารตั้งต้นในการผลิตเชื้อเพลิงชีวภาพคือ ของผสมระหว่างน้ำมันกาแฟและเอทิลแอซีเทตที่อัตราส่วนโดยโมล 1 ต่อ 30 สกัดที่อุณหภูมิและความดันบรรยากาศ ในการผลิตเชื้อเพลิงชีวภาพตัวแปรที่ศึกษาในงานวิจัยนี้ ได้แก่ อุณหภูมิที่ใช้ในการทำปฏิกิริยา (275, 300, 325, และ 350 องศาเซลเซียส) และ อัตราการไหลของสารที่ใช้ในการทำปฏิกิริยา (2, 2.5, และ 3 กรัมต่อนาที) ทำการทดลองภายใต้ความดัน 15 เมกะพาสคัล ปริมาณเอทิลเอสเทอร์ของกรดไขมันตรวจวัดด้วยเครื่องแก๊สโครมาโทกราฟ จากการทดลองพบว่าภาวะที่เหมาะสม คืออุณหภูมิที่ 350 องศาเซลเซียสและควบคุมอัตราการไหลของสารที่ 2.5 กรัมต่อนาที ให้ผลิตภัณฑ์เป็นเชื้อเพลิงชีวภาพที่มีปริมาณเอทิลเอสเทอร์ของกรดไขมันร้อยละ 86.44 ของน้ำหนัก ซึ่งสามารถสรุปได้ว่ากากกาแฟเป็นวัตถุดิบที่เหมาะสมในการผลิตเป็นเชื้อชีวภาพในเอทิลแอซีเทตภาวะเหนือวิกฤต เป็นหนึ่งในทางเลือกที่สามารถเพิ่มมูลค่าให้กับกากกาแฟ

สาขาวิชา	เทคโนโลยีเชื้อเพลิง	ลายมือชื่อนิสิต ....
ปีการศึกษา	2563	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
		ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

6172063123 : MAJOR FUEL TECHNOLOGY

Wirasinee Supang : BIOFUEL PRODUCTION FROM SPENT COFFEE GROUNDS BY SUPERCRITICAL ETHYL ACETATE. Advisor: Prof. Somkiat Ngamprasertsith, Ph.D. Co-advisor: RUEANGWIT SAWANGKAEW, Ph.D.

In this work, spent coffee grounds (SCGs) was used as the feedstock for biofuel production by supercritical ethyl acetate. The SCGs is waste obtained from coffee industrial that is continuously increasing every year. To make SCGs becomes more valuable, utilization of ethyl acetate as the extracting and reacting solvents for biofuel production via interesterification reaction. The characterization of SCGs sample showed that the moisture content of fresh SCGs was around 56 wt%. After oven drying, the moisture of SCGs was reduced to 12.76 %wt. To prolong the shelf-life of the sample and to minimize impact of hydrolysis on interesterification reaction, the drying step is required to reduce the water in SCGs. Ethyl acetate was a suitable solvent for coffee oil extraction from SCGs due to high recovery of coffee oil (22.74 wt%). The feedstock for biofuel production was the mixture of coffee oil and ethyl acetate at molar ratio of 1:30 that extracted at room temperature and atmospheric pressure. In biofuel production, two parameters were investigated for optimal condition. Temperature (275, 300, 325, and 350℃) and feed flow rate (2, 2.5, and 3 g/min) were controlled under pressure at 15.0 MPa. The amount of fatty acid ethyl ester (FAEE) in the product was measured by gas chromatography. The optimal condition was found at temperature of 350℃ and feed flow rate of 2.5 g/min. The highest yield of FAEE is 86.44 wt%.

Field of Study:	Fuel Technology	Student's Signature ....
Academic Year:	2020	Advisor's Signature ....
		Co-advisor's Signature ....

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

LIST OF TABLES

LIST OF FIGURES

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

CHAPTER I

INTRODUCTION

1.1 Background

Biofuel is one of alternative energies which can compatibly use same as fossil fuel but in term of emissions, biofuel can give a less of emitted greenhouse gas when compare to the fossil fuel. Also, the growth of population is increasing worldwide then a require of energy consumption still high. Biofuel can use in many forms such as biogas or bio-oil but the type of biofuel that mostly known is biodiesel. It is derived from various kind of feedstocks such as palm oil, animal fat, and waste cooking oil. Biodiesel is produced by chemical reaction, transesterification reaction as shown in figure 1.1. Glycerol is the by-product of the transesterification reaction. Because the demand for biodiesel is high enough to make the increasing of biodiesel production that led to the overproduction of glycerol. Due to the large amount of glycerol led the price of glycerol decline [1] and become a waste which can be burden to the environmental and biodiesel producer.
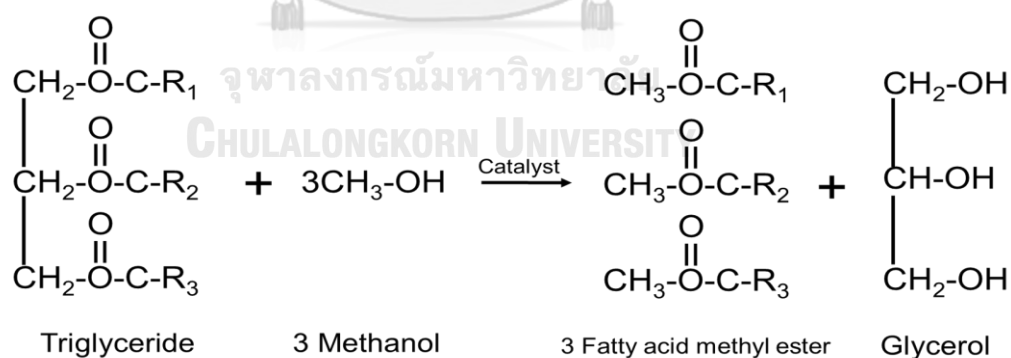
Figure 1.1 Transesterification reaction

Since the biodiesel still be the popular alternative fuel, to investigate the new reaction for biodiesel production is important for avoid the generation of glycerol. Interesterification reaction [2] produces biodiesel by replacing the carboxylate ester instead of the alcohol which normally use as reactant in transesterification reaction.

The co-product in this reaction is triacetin unlike glycerol, which still needs the separation steps in downstream process. Triacetin can use as fuel additive for improve cold flow properties in biofuel [3]. Because of this reason, triacetin was needless to separate from the main product which is biodiesel. Interesterification reaction also reduces the cost of the biodiesel production since there was no need for separation step in the downstream process.

Supercritical ethyl acetate is the solvent that can use in biodiesel production via interesterification reaction. The production of ethyl acetate was came from ethanol which obtain from the fermentation process [4]. It can conclude that the biodiesel which is produced by using ethyl acetate as the reactant is truly came from the renewable resource. Moreover, the feedstock that use for biodiesel production was also important. There are many types of feedstock that can be used in the process but to make the process become more sustainable, feedstock that came from waste was the preferred choice to use. This work focuses on using spent coffee grounds (SCGs) which is the one type of waste that came from coffee beverage industry. Since coffee is the most popular drinks around the world, the amount of SCGs was increase annually. Although SCGs is waste, there are some useful materials that contain in SCGs such as protein, carbohydrate, antioxidant, and lipid.

To produce the biodiesel, the feedstock must contain oil which use to react in chemical reaction. Amount of lipid in SCGs are quite enough for use it as the feedstock. Normally, the coffee oil in SCGs contained around 13%wt of dry biomass [5] and the fatty acids in coffee oil were also similar to palm oil. Therefore SCGs is suitable as feedstock for biodiesel production which can reduce the amount of waste from coffee industry. This process can make SCGs become more valuable. However, the extraction step for extract coffee oil in SCGs still required. The amount of extracted coffee oil depends on the type of solvent and the extraction methods [6].

This work aims to use SCGs for biofuel production by supercritical ethyl acetate via interesterification reaction. The extraction part to obtain the coffee oil as feedstock for biofuel production, ethyl acetate still used as the solvent to extract coffee oil from SCGs. The extraction part was performed at room temperature and atmospheric pressure by submerged SCGs in ethyl acetate. The mixture of coffee oil and ethyl acetate was fed into tubular reactor for biofuel production in the supercritical condition. The pressure was constant at 15 MPa. Temperature and feed flow rate were the parameters that concern to investigate for the highest fatty acid ester content at the optimum condition.

1.2 Objectives

    1.2.1   To extract the coffee oil from spent coffee grounds by using ethyl acetate at ambient pressure and temperature.

    1.2.2   To produce biofuel from coffee oil by supercritical ethyl acetate in a tubular flow reactor.

1.3 Scope of thesis

    1.3.1   The amount of extractable coffee oil when using ethyl acetate as a solvent at ambient temperature and pressure base on the amount of extracted coffee oil content in SCGs after using Soxhlet extraction with ethyl acetate.

    1.3.2   The effect of temperature in range 275°C to 350°C on interesterification reaction for coffee oil conversion to fatty acid ethyl ester in supercritical state.

    1.3.3   The effect of feed flow rate which were 2, 2.5, and 3 g/min on interesterification reaction for coffee oil conversion to fatty acid ethyl ester in supercritical state.

1.4 Expected beneficial outcome from thesis

    To obtain optimal condition for biofuel production from spent coffee grounds oil by supercritical ethyl acetate.

1.5 Research plan

1.5.1 Literature review and formulate the problem in the research.

1.5.2 Extraction of coffee oil by ethyl acetate.

1.5.2.1 Moisture content of SCGs will be analyzed. Soxhlet extraction of SCGs by ethyl acetate will be performed to obtain the maximum oil content in SCGs sample.

1.5.2.2 Optimization of the extraction time to find the optimal time for recovery SCGs oil by using ethyl acetate. The sample will collect every hour to observe the oil content in the mixture. The extracted mixture will be analyzed by filtration and solvent evaporation.

1.5.2.3 Optimization of the SCGs extraction by ethyl acetate, to obtain the molar ratios of the final extracted mixture of 1:30.

1.5.2.4 Coffee oil analysis by gas chromatography to obtain the fatty acid profile.

1.5.3 Biodiesel production from SCGs by supercritical ethyl acetate.

1.5.3.1 Optimization of the reaction temperature. To find the best condition for biodiesel production the temperature which are 275 ℃, 300 ℃, 325 ℃, and 350 ℃ will be investigated. The maximum FAEE yield is defined as the indicator.

1.5.3.2 Optimization of the feed flow rate. To find the best condition for biodiesel production, the feed flow rate will be 2 g/min, 2.5 g/min, and 3 g/min. The optimal condition will be justified by the maximum FAEE yield.

        1.5.3.3 Collect the products from the continuous reactor for analysis.

        1.5.3.4 Product analysis by gas chromatography.

1.5.4   Discuss and compare the results to find the optimal condition for the process.

1.5.5   Conclude all the data.

1.5.6   Write the thesis.

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Biofuel

The biofuel is mostly known as one type of renewable energies. This type of energies has various forms to use such as biogas or biochar but the most useful state of biofuel that usage in worldwide is liquid biofuel. The biofuel was produced to handle the global warming problem which comes from the combustion of fossil fuel [7]. Since the biofuel has low of the carbon intensity when compare to fossil fuel, the biofuel can be the alternative energy which made for people who concern about environmental.

To produce biofuel, many types of biomass that come from plants or animals is used as feedstock. They could be converted in different ways to produce the desired final product. The application of the products is shown in figure 2.1 [8]. Even though biomass can convert into assorted products, the interest of liquid fuel still highly demand. Biorefinery is adopted for producing biofuel and chemicals comparable to the petroleum refinery to solve the increasing of energy demand nowadays.

The developing or investigating new technology for biorefinery attend to make the new process or new source for biofuel production. To describe the origination of biofuel briefly, the type of biofuel feedstock can be divided into three generations which the detail of each generation was shown in this part.
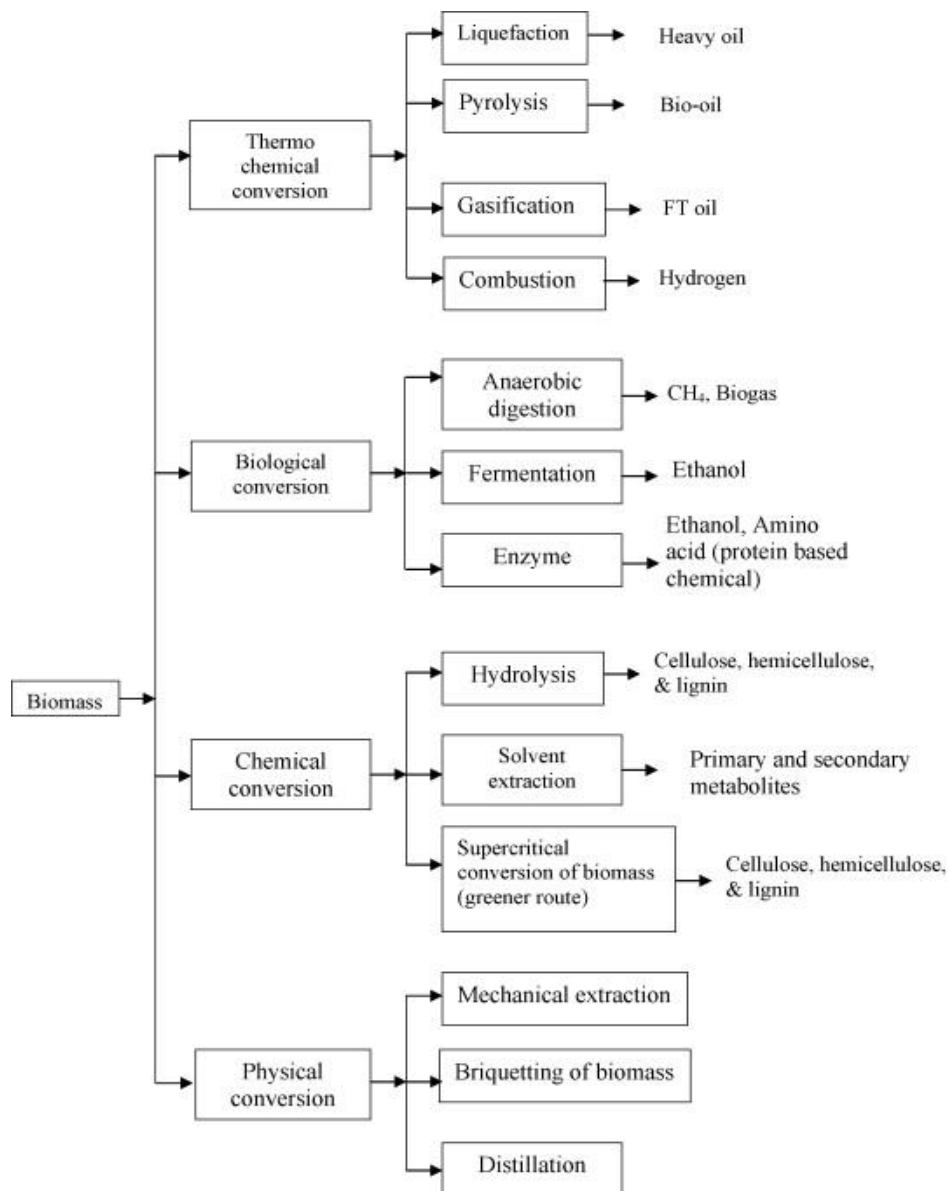
Figure 2.1 The conversion of biomass for biofuel production [8]

2.1.1 First-generation biofuel

In the first-generation of biofuel production, the edible plants, or crops are usually used as feedstock for biofuel production in this generation. The trendy feedstock is the plant-based source such as palm oil, sugarcane, and cassava [9, 10]. The biodiesel is produced from vegetable oils or edible oils e.g. soybean, palm, and sunflower. Although the conventional process of biodiesel production is mainly used edible plants as the feedstock, the growth of population still increases annually led

the consumption of the food raised. The production of biofuel from edible crops can affect to the food supply [11]. The first-generation biofuel also impacts to the land field which need to uses for harvesting the crops and causes the loss of relative species of the other plant [12].

2.1.2 Second-generation biofuel

The problem in the first-generation biofuel is the source of feedstock mostly come from edible crops which can affect to the food supply. In second-generation biofuel, the non-edible plant, the lignocellulosic crops or wastes which come from animal product or plant residues such as wood chips, waste cooking oil, and animal fat are used as feedstock to produce biofuel. This generation is more sustainable than conventional fuel which come from fossil fuel when compared in term of carbon released during the process of biofuel production [13]. Also, the amount of feedstock in this generation are massive enough for support the demand of biofuel production. These abundant wastes become more valuable and decrease the amount of waste which come from agricultural and community.

The conversion of biomass in the second-generation when compare with first-generation, the feedstock in the second-generation need to pretreatment before use in the biofuel production process. The main component in the feedstock is lignocellulose as shown in figure 2.2 [8]. Although the complexity in the second-generation feedstocks is higher than that of the first-generation, the technology for support the producer of the feedstock is modernizing. These feedstocks still provide a new type of product or increase the amount of desired product depend on the method of the process [14].
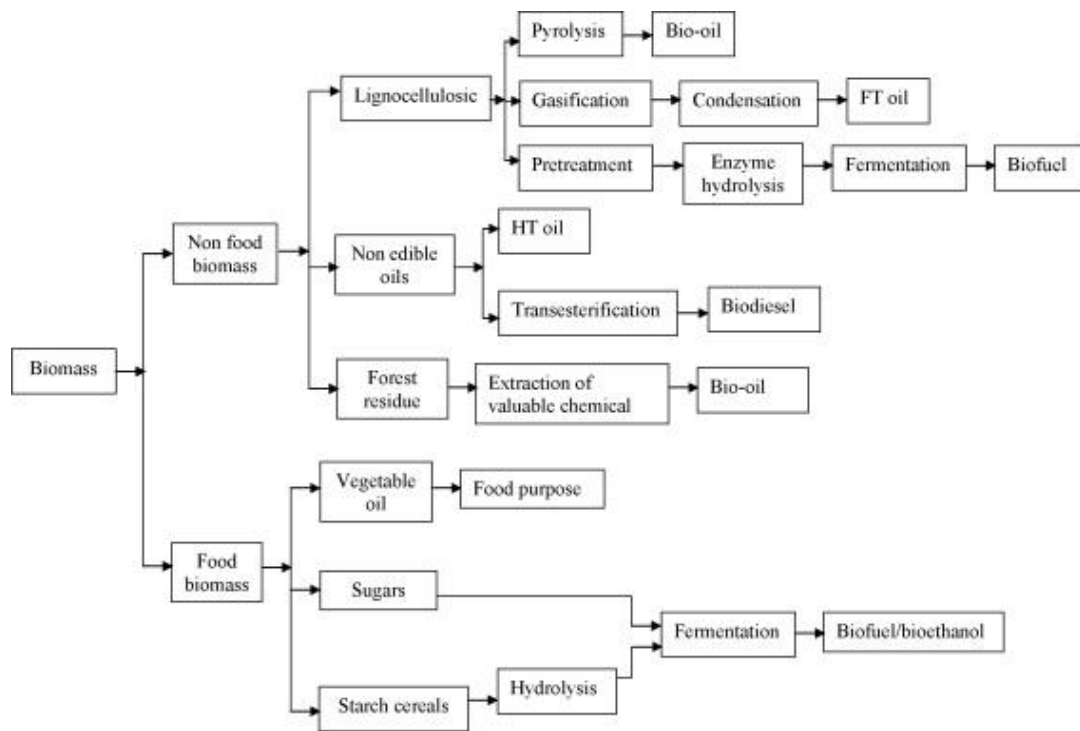
Figure 2.2 The conversion of non-food and food biomass to biofuels and biochemicals [8]

2.1.3 Third-generation biofuel

Nowadays, the requirement of liquid biofuel is still high led to the production of liquid biofuel lack of feedstock to produce. Microalgae is the alternative feedstock in this generation because of the properties in term of the high lipid content. The growth rate of the microalgae is rapid more than the other plants. This feedstock needs the less of land field when compare to the first- and the second-generation feedstock. The microalgae has higher result in environmentally friendly than both of previous generation biofuel [13, 15].

Although microalgae seem to be a promising feedstock for biofuel production in the future, this feedstock still needs the additional technology to make it give the high efficiency for the recovery oil. The oil extraction part from cultivated microalgae is the problematic part when compare to the other step in the biofuel production process, especially in term of environmental impact [16].

2.2 Biodiesel production

In among of biofuel products, biodiesel is the well-known biofuel that has been used in various ways such as transportation, industrial process, or blend with the petroleum diesel for diesel engines [17].

Biodiesel is the mixture of the long chain fatty acid alkyl ester (FAAE). This type of biofuel can be obtained from the oil-based feedstock; thus, biodiesel is the product that affect to the environmental less than using the petroleum fuel. It becomes the alternative biofuel for support the demand of energy consumption from population growth [18].

There were many kinds of the process or reaction for the biodiesel production but the most recognized process is using the chemical reaction between triglycerides in the feedstock and the various type of reactants. The description of two major reactions are given below.

2.2.1 Transesterification reaction

Transesterification reaction is the universal reaction for biodiesel production which has a different method to produce biodiesel. Each method gives the same products which are biodiesel and glycerol as by-product. The operation in the method is different depending on the reactant and the condition. The methods can be divided into catalytic and non-catalytic reactions.

2.2.1.1 Catalytic transesterification reaction

This reaction can operate in the mild condition with the presence of the acidic or basic catalysts in the different forms. The chemical reactants are usually alcohols, especially, methanol or ethanol because the price of these chemicals is low. Amount of the production for these chemicals is available enough for the biodiesel production.

The mechanism of transesterification is shown in figure 2.3 [19]. Triglycerides from the feedstock react with the alcohol (e.g. methanol or ethanol) to produce the di and mono-glycerides which were intermediate products in the reaction. The final products of this reaction were fatty acid alkyl esters (FAAE) which the alkyl group will change depend on the type of alcohol.
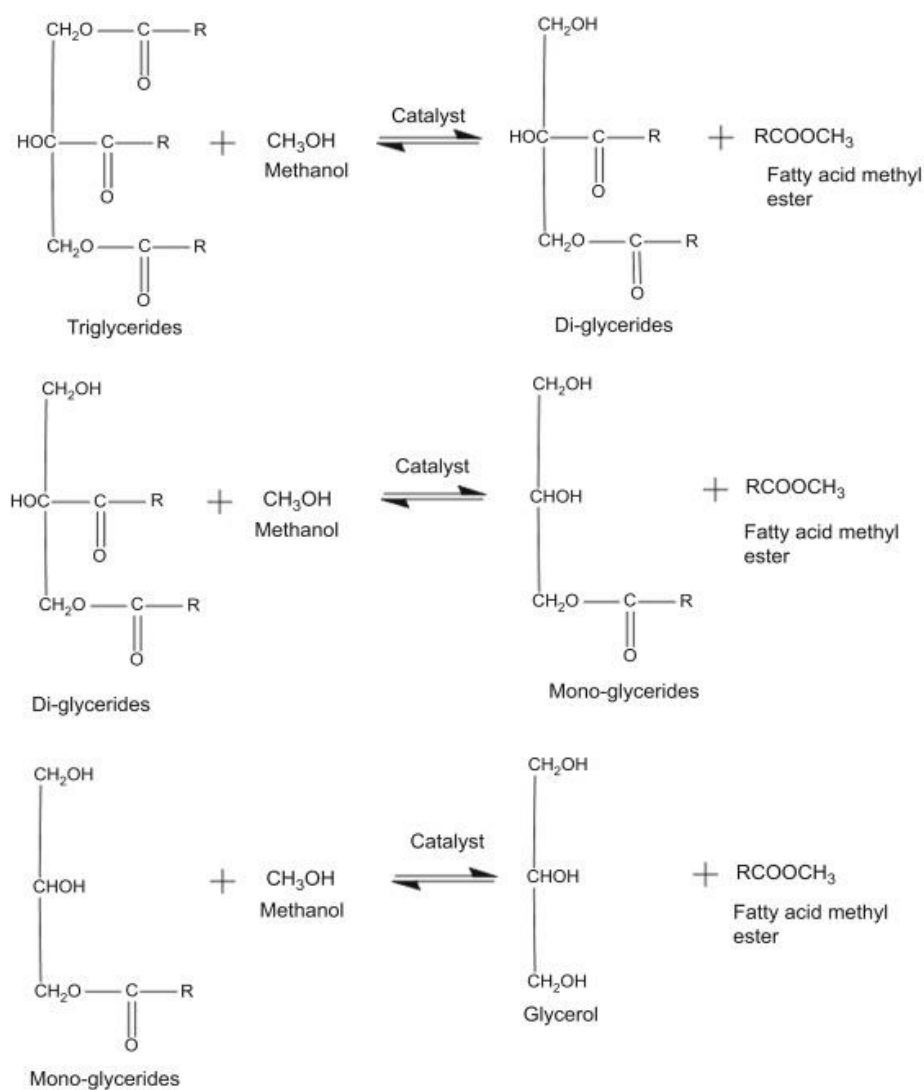
Figure 2.3 The mechanism of catalytic transesterification reaction [19]

There are many types of the catalyst used in the reaction (figure 2.4). In the conventional process for biodiesel production via transesterification reaction, the homogeneous basic catalytic process is the method that the producer choose because the operation is simple and low cost of operation [20].
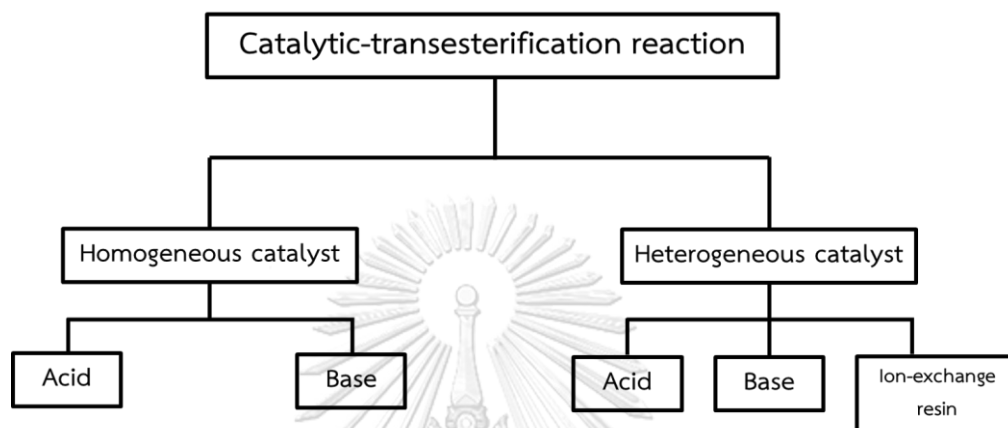
Figure 2.4 Types of catalyst in catalytic transesterification reaction

Another option for the catalytic transesterification reaction is the heterogeneous catalyst which has both of acidic and basic catalysts. The ion-exchange resin was brought to use in the production process due to the highly active and selective properties [21]. Since the heterogeneous catalysts are not soluble in alcohol, these catalysts can give the advantage to the user in term of separation and reusability. Unlike the homogeneous catalyst, separation of the catalyst in the downstream process by water washing is not necessary. The wastewater could be significantly reduced when the heterogeneous catalyst is applied to biodiesel production process.

2.2.1.2 Non-catalytic transesterification reaction

Using homogeneous catalyst in the transesterification gives the high yield but in term of the environmental impact [22], the biodiesel production process is facing the huge problem of wastewater treatment. The contamination of fat and soap resists the precipitation of activated sludge in wastewater treatment plant. The wastewater from biodiesel production plant has very high pollution level a very polluting wastewater (i.e. the COD up to 35000 and the BOD up to 30000 mg O_2/L) [23] To reduce the environmental problem from the downstream process, there were some researches that investigate the alternative way to produce biodiesel via transesterification reaction without using the catalyst.

Supercritical fluid (SCF) technology is the way for the biodiesel production without using catalyst. The properties of SCF which is the intermediate between liquid and gas. The phase diagram of the SCF region was shown in figure 2.5 [24]. When the pressure and temperature rise above the critical state of the material or at supercritical state, the viscosity of the material defines as gas state, in contrast the density of the substance defines as liquid state.
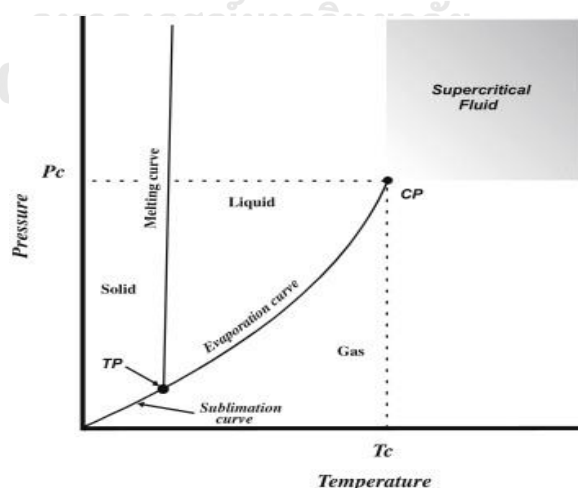
Figure 2.5 Phase diagram of pure substance [24]

TP: Triple point; CP: Critical point, T_c: Critical temperature; P_c: Critical pressure

Since the properties of SCF is useful for chemical synthesis without catalyst, this method is used as the new promising way for biodiesel production. Moreover, SCF is the technology which can use on variety of feedstock such as waste cooking oil unlike the alkaline-base catalyst. The type of feedstock used in the alkaline-base process needs to be refined due to the sensitivity of the catalyst. SCF technology is environmentally friendly when compare to the catalyst-base process because this technology generates less of waste than the conventional method [25].

2.2.2 Conventional process for biodiesel production

Since, the biodiesel is the alternative fuel which can blend or use on the diesel engines directly without modified engine, the demand of the biodiesel is increasing annually. The production process becomes a commercial scale worldwide. Figure 2.6 shows the diagram process of the biodiesel production by using the catalytic transesterification reaction. The catalyst in the process is the homogeneous basic catalyst such as NaOH and KOH. The biodiesel producer prefers to use the homogeneous basic catalyst in the production process because of the low price of the catalysts, widely available, and the readiness of the technology. The homogeneous basic catalyst gives the high conversion in the short time and it can operate in the mild condition which easier to control than using other methods [26].
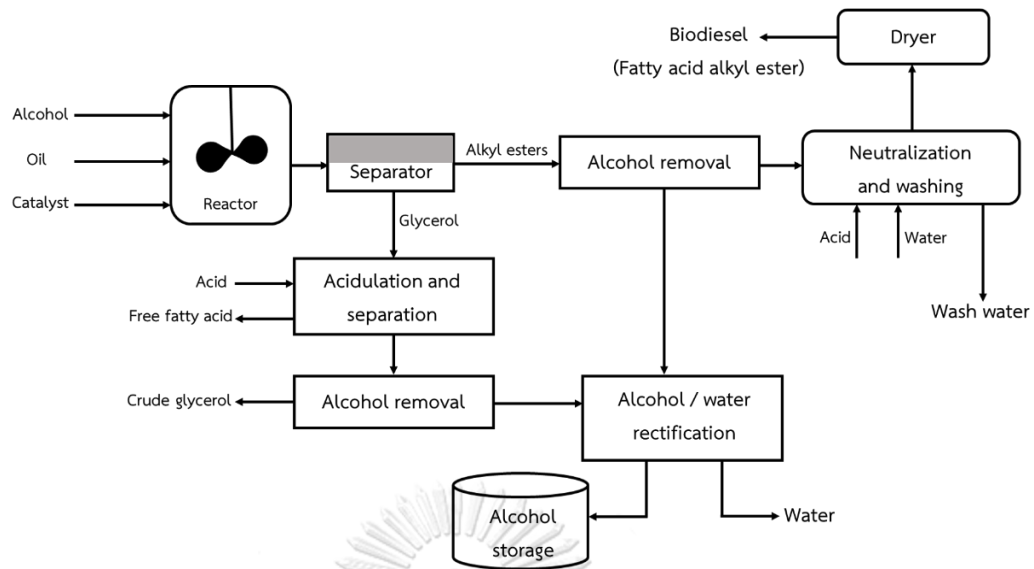
Figure 2.6 Flow diagram of conventional biodiesel production

In the production process, catalyst and alcohol are dissolved before fed into the reactor to react with oil. The industrial scale commonly uses the stirred-tank reactor because the simple of operation. After the feed are stirred and well-mixed under the condition around 60°C for an hour, the product is mainly FAAE and the by-product is glycerol. The FAAE is split from the glycerol in the separator and subjected to alcohol removal process. Around 50 percent of glycerol is separated in this step along with some alcohol. To refine the separated glycerol, acid is used to split the soap which generate from the excess used of alcohol. This soap is an impurity that mixed in the glycerol phase.

After adding the acid into glycerol, the soap will split into free fatty acid and salt. This makes the phase of glycerol turn into three layers [27]. The upper layer is the free fatty acid, the middle layer is the glycerol, and the bottom layer is the salt. The free fatty acids can recycle or remove as shown in the figure 2.6. The type of salt depends on the catalyst that used in the process. For example, potassium hydroxide is the base catalyst and phosphoric acid is utilized in the acidulation. The salt in the process is potassium phosphate which can use as the plant fertilizer.

The mixture of glycerol after separated free fatty acid and salt pass into the alcohol stripper (e.g. methanol stripper) to remove the remaining alcohol. The crude glycerol is obtained as the final product. For the FAAE, after separated from the glycerol in the separator, the product is fed into alcohol stripper before pass to the neutralization and washing steps.

The recycling alcohol might contain the water from the process. To make it be usable, the membrane separation or the distillation process is used to remove the water from the alcohol. After removed the water, the alcohol will be fed into the alcohol storage for reuse.

After remove the excess alcohol from the product (FAAE), the product is fed into the neutralization step [28], this step will make the FAAE easy to wash with water in the washing step. These steps aim to remove the remained catalyst or impurities that might contain in the product. Then, the product will be fed into dryer to remove the remaining water and obtain the final biodiesel product.

Although this commercial production of biodiesel is widely well-known and acceptable, there are some problems that the biodiesel producer must concern such as the regulatory requirement in the environmental and human safety. Since the conventional process of biodiesel production still used ton of chemical that can be generated a ton of waste as well.

2.2.3 Alternative reaction for biodiesel production

Because the awareness of the global warming problem still be the topic that people concern, the demand of the production of biofuel had risen. The biofuel is the alternative fuel that can reduce the need of the fossil fuel. The main cause on the global warming problem is the released carbon from the combustion of fossil fuel [29].

Although biofuel can reduce released carbon, the production of biofuel still generates a ton of waste. In the biodiesel production process, the glycerol by-product became oversupply and the price of glycerol was plummeted [30]. To diminish the amount of glycerol during the biodiesel production, Fadjar et al. [2] was introduced the chemical reaction that can produce biodiesel without generating glycerol as a by-product. This chemical reaction called 'interesterification reaction' (figure 2.7). The alcohol in transesterification reaction is replaced by carboxylate ester. The interesterification produces triacetin as a by-product.
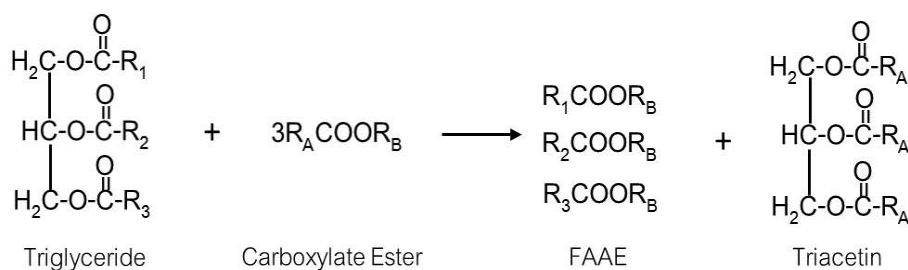
Figure 2.7 Interesterification reaction between triglyceride and carboxylate ester [2]

R_1, R_2, R_3; hydrocarbon residues

R_A; Alkyl residue in acyl moiety, R_B; Alkyl residues in alcohol moiety

Triacetin which is the by-product in this reaction can use as fuel additive to improve the cold flow properties in the biofuel [3]. Since the by-product can dissolve in the biofuel unlike the glycerol, the interesterification reaction is the alternative way to avoid the generation of glycerol. In addition, this chemical reaction can decrease the production cost in the purification step or glycerol separation step of the process.

Nowadays, interesterification reaction is the new promising chemical reaction for biodiesel production. Due to the quantity of the product which can include the by-product as the fuel additive that can give the efficiency of the reaction higher

than the transesterification reaction [31]. The interesterification reaction can conduct in various methods such as using homogeneous catalyst, using heterogeneous catalyst, and using supercritical condition. This reaction gives the new way to produce biofuel which is environmentally friendly than transesterification reaction, especially in term of reducing the glycerol waste.

2.3 Biodiesel production by supercritical fluid technology

Supercritical fluid technology is one of the many methods which can make the production process become greener due to the using the less amount of chemical solvent. In the biodiesel production, using SCF was also use as the alternative way to produce biodiesel which has less environmental impact. The SCF can use in different chemical reaction for biodiesel production including the acceptability in the various type of feedstock.

In SCF, the reactant is marked to make it become a supercritical fluid. Since the condition of the process is in high temperature and high pressure, the reaction that used for biodiesel production is mostly no need of the catalyst. This is the main advantage of using this technology instead of the conventional method.

Nowadays, many researchers were used SCF to improve the biodiesel production via different chemical reactions or solvents, including the feedstock to make the process become more environmentally friendly. The examples of these research are described below.

2.3.1 Biodiesel production via SCF Transesterification reaction

Since transesterification reaction is the well-known reaction for the biodiesel production, this reaction has continuously improved by many researchers using SCF. The main problem of transesterification reaction by a homogeneous catalytic process is a ton of wastewater generated during the downstream process which impact to the environment and the production cost [32].

Methanol is the common alcohol that biodiesel producer uses in the production process, there are some research that using supercritical methanol in the transesterification reaction without the presence of the catalyst. The side reactions from using the basic catalyst (e.g. saponification reaction) that might generate during the process are eliminated. The producer can obtain the high quality of the biodiesel while using SCF technology.

There are various types of feedstock in research that was used to produce the biodiesel by supercritical methanol. For example, Salar-García et al.[33] used *Jatropha* oil for biodiesel production in the supercritical methanol. The reaction gave the highest conversion of 99.5% at 350°C with molar ratio methanol to oil of 42 : 1 in 90 mins of reaction time. Tobacco seed oil was also used for biofuel production by supercritical methanol, the maximum yield of the product was 92.8% when operated the reaction at 300°C and 90 min with fixed molar ratio of oil to methanol at 1:43 [34] or using the crude castor oil in similar operating condition which molar ratio of feedstock was 1:43 of oil to methanol, 300° C and 90 min for reaction time that can give the high conversion of the product which was 96.5% [35]. Using supercritical methanol could reduce the amount of waste that comes from the using of basic catalyst and gives the high quality of biodiesel.

In term of heterogeneous catalytic transesterification, the benefit of using this catalyst while compare with homogeneous catalyst is the purity of the products (biodiesel and glycerol), the reusability, and the reduction of downstream process [36]. Although using heterogeneous catalyst for biodiesel production is the alternative way, it still has the problems such as the reduction of active sites while using the feedstock contaminated with a high free fatty acid. The heterogeneous catalysts must be synthesized via the prudent conditions which are sensitive with

many parameters such as concentration, temperature, and pH. The scale-up of heterogeneous catalyst preparation is the challenge topic in this research field.

The SCF could combine with heterogeneous catalytic transesterification for improve the performance of the biodiesel production process. Lamba et al.[37] used the integrated pathway which was the combination of heterogeneous catalyst (Zinc oxide) and supercritical methanol for biodiesel production from Mahua (*Madhuca longifolia*) oil. The SCF technology can significantly enhance the rate of the reaction and the heterogeneous catalyst can reduce the optimal temperature and pressure as well. The production process becomes more effective and generates less impact to environmental.

2.3.2 Biodiesel production via SCF Interesterification reaction

The interesterification reaction is the suitable reaction to solve the overproducing of glycerol problem which can be burden to the environmental and the biodiesel producer. Using SCF for interesterification reaction will enhance the production process to become green process. The biodiesel production do not need of the catalyst when using SCF technology. The interesterification reaction generates the triacetin as the by-product, instead of glycerol.

The reactant that used in the interesterification is carboxylate ester for avoiding the generation of glycerol from the alcohol which is the reactant in the transesterification reaction. Fadjar et al. [2] used the various types of carboxylate ester to find the most suitable solvent for the biodiesel production from rapeseed oil. The list of carboxylate ester group is shown in table 2.1. The results revealed that in the supercritical state, methyl acetate is the reactant which can give the highest conversion of the triglycerides to the products around 97.7 wt% (this value included biodiesel and triacetin as a product).

Table 2.1 Various carboxylate esters used for biodiesel production in supercritical treatments [2]

Carboxylate Esters	Critical point		Reaction pressure at 350°C (MPa)	Molar ratio of solvent to oil (vol, ratio)	Theoretical maximum (wt%)	
	$(T_C, °C)$	(P_C, MPa)			FAAE	Triacetin
Methyl carboxylates						
Methyl acetate	234	4.6	17.8	42(3.4)	100	25
Methyl propionate	258	4.0	15.4	42(4.1)	100	29
Methyl butyrate	281	3.5	11.2	42(4.9)	100	34
Ethyl carboxylates						
Ethyl acetate	250	3.9	16.3	42(4.2)	100	23
Ethyl propionate	273	3.4	14.5	42(4.9)	100	28
Ethyl butyrate	293	3.1	10.9	42(5.7)	100	32
Propyl carboxylates						
Propyl acetate	276	3.2	14.2	42(4.9)	100	22
Propyl propionate	305	3.0	10.4	42(5.7)	100	27
Propyl butyrate	327	2.7	4.6	42(6.4)	100	31
Butyl carboxylates						
Butyl acetate	306	3.1	9.2	42(5.7)	100	22
Butyl propionate	322	2.8	7.4	42(6.4)	100	26
Butyl butyrate	339	2.6	3.1	42(7.1)	100	30

To make the interesterification reaction become the well-known reaction as transesterification reaction, Fadjar et al. [38] also investigated the optimal condition for the biodiesel production by using supercritical methyl acetate. The highest biodiesel yield was 96.7 wt% and 8.8 wt% of triacetin yield at 350°C with pressure 20 MPa and reaction time was 45 min with the molar ratio of methyl acetate and oil at 42: 1. This results indicated that using interesterification reaction can give the high quantity of the desired products.

Impurities in the feedstock such as water and free fatty acids still the limitation of the biodiesel production when using homogeneous catalytic transesterification reaction. For the interesterification reaction, it was reported that water enhances the performance of the reaction. In 2014, Fadjar et al. [39] used water as the additive to see the effect in the biodiesel product by supercritical methyl acetate. The results showed that added water into system can give the higher conversion of biodiesel. Thus, the low-cost feedstock is acceptable for interesterification without ruining the production process.

Although supercritical methyl acetate can give the high conversion in the interesterification reaction, it is still be the harmful solvent when compare to the ethyl acetate. Since ethyl acetate obtained from the ethanol that produces from the fermentation process, the produced biodiesel truly comes from renewable resource. Ethyl acetate is the good choice of the solvent for interesterification since the solvent gave the conversion of biodiesel highest inferior to methyl acetate [2].

When using the supercritical ethyl acetate in biodiesel production from palm oil [40], added water into system can increase the %yield of products (biodiesel and triacetin) from 90.9 wt% to 101.5 wt%. This result confirm that both solvents (methyl acetate and ethyl acetate) have the similar effects of impurity in the feedstock. Using

ethyl acetate in the interesterification reaction can promote the reaction as same as using methyl acetate.

2.4 Spent coffee grounds as the promising feedstock for biofuel production

Besides the chemical reactions for biofuel production, the type of feedstock is an important parameter for controlling the quality of the product. The second-generation biofuel which used the non-edible oil plants or the wastes still popular for the biofuel production as the feedstock.

Spent coffee grounds (SCGs) is one of interested wastes that suitable for biofuel production. Coffee is the most popular drink in the world and it have a second largest traded commodity after the petroleum [41]. SCGs is obtained from coffee brewing in both coffee shops and instant coffee factory. The cycle of the coffee production is shown in Figure 2.8 [42] that shown the formation of the SCGs which is the waste of the production of coffee beverage.
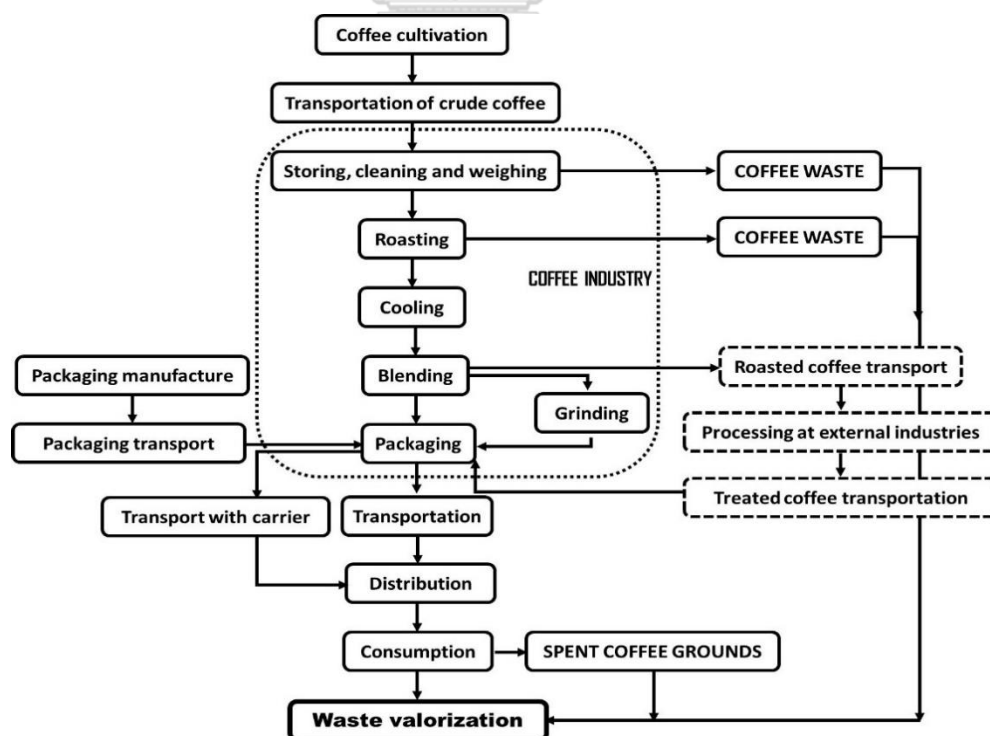
Figure 2.8 Coffee life cycle show the formation of spent coffee grounds [42]

One gram of the ground coffee can produce the 0.91 gram of the SCGs in average. The amount of SCGs still increases annually due to the requirement of the coffee drinks in the population nowadays [43]. To make SCGs becomes more valuable, many researchers was interested to investigate the characteristic of the SCGs. SCGs has been use in the different ways to decrease the amount of SCGs and to made SCGs into the value-added products.

2.4.1 Characteristic of spent coffee grounds

Since SCGs is obtained from a natural product, the composition in SCGs depends on the various parameters such as the type of the coffee bean and the climate even the soil condition for the coffee plant [44].

In 2014, Ballesteros et al. [45] studied on the composition in the SCGs and the coffee silver skin. The list of the component in SCGs is shown in table 2.2

Table 2.2 Chemical composition of SCGs and coffee Silver skin [45]

Chemical components	Composition (g/100 g dry material)	
	Spent coffee grounds	Coffee silverskin
Cellulose (Glucose)	12.40±0.79	23.77±0.09
Hemicellulose	39.10±1.94	16.68±1.30
Arabinose	3.60±0.52	3.54±0.29
Mannose	19.07±0.85	1.77±0.06
Galactose	16.43±1.66	3.76±1.27
Xylose	nd	7.61±0.02
Lignin	23.90±1.70	28.58±0.46
Insoluble	17.59±1.56	20.97±0.43
Soluble	6.31±0.37	7.61±0.16
Fat	2.29±0.30	3.78±0.40
Ashes	1.30±0.10	5.36±0.20
Protein	17.44±0.10	18.69±0.10
Nitrogen	2.79±0.10	2.99±0.10
Carbon/Nitrogen (C/N ratio)	16.91±0.10	14.41±0.10
Total dietary fiber	60.46±2.19	54.11±0.10
Insoluble	50.78±1.58	45.98±0.18
Soluble	9.68±2.70	8.16±0.90

Results are expressed as mean ± standard deviation ; n=3. nd not detected

The result showed that the most abundant components in SCGs are polysaccharide. They are polymerized into cellulose and hemicellulose. This result is similar to the research in 2011 [46]. Mussatto et al. studied on the compositions in SCGs and found that the main chemical composition in SCGs were 36.7 wt% of hemicellulose.

Bioactive compound is the compound that mostly found in the plant. Polyphenols are the main of bioactive compounds that can be found in SCGs. These compounds can be useful in many ways, for instance, use to prevent the cancer formation. Balzano et al. [47] studied on spent espresso coffee grounds to find the bioactive compounds. The natural phenolic antioxidant called "tyrosol" was first detected and it had the highest amount contained in the SCGs sample. The other interested compounds such as vanillin, caffeic acid, and 4-hydroxybenzoic acid which can give a high potential treatment for a human lung carcinoma cell. Those bioactive compounds make the SCGs more valuable.

Another valuable component in SCGs is the coffee oil. The amount of coffee oil will depend on the type of coffee bean and roasting level, but the coffee oil content in SCGs is around 7 to 15 wt% in average [44]. This high amount of oil in SCGs can be a promising result to make the SCGs become a potential feedstock for biodiesel production. Although the coffee oil in SCGs is enough to use as a feedstock for biofuel production, the problem on extraction of coffee oil out of SCGs is the first task before using it as the feedstock.

Somnuk et al. [5] studied the various types of the solvent to extract coffee oil form SCGs and analyzed the fatty acid profile of extracted oil. The results can indicate that SCGs sample can be extracted coffee oil around 14.7 wt% when using solvent extraction method. This result also proved that the type of extraction solvent is one of the parameters for the coffee oil extraction. The different solvents that used in the experiment can give the distinctive amount of extracted coffee oil. For example, methanol gave the lowest yield of 7.5 wt% while n-hexane provided the highest yield of 14.7 wt%. The fatty acid profile in the extracted coffee oil was shown in Table 2.3.

Table 2.3 Composition of fatty acid profile in extracted coffee oil [5]

Common name	Fatty acid	Content (wt%)
Caprylic acid	C8:0	0.01
Nonanoic acid	C9:0	0.00
Capric acid	C10:0	0.01
Lauric acid	C12:0	0.02
Myristic acid	C14:0	0.09
Pentadecanoic acid	C15:0	0.00
Palmitic acid	C16:0	34.44
Palmitoleic acid	C16:1	0.04
Stearic acid	C18:0	0.00
Oleic acid	C18:1	7.74
Linoleic acid	C18:2	43.12
Alpha linolenic acid	C18:3	1.18
Arachidic acid	C20:0	2.83
Paullinic acid	C20:1	0.27
Behenic acid	C22:0	0.59
Erucic acid	C22:1	0.19
Lignoceric acid	C24:0	0.29
Nervonic acid	C24:1	0.01

wt% = percent by weight

The main fatty acids that contain in coffee oil were linoleic acid (C18:2) and palmitic acid (C16:0), respectively. These types of fatty acids were also similar to fatty acid profile of the palm oil which is the main feedstock for the biodiesel production (Table 2.4) [48].

Table 2.4 Fatty composition in palm oil [48]

Fatty acid	Composition (wt%)
C12:0	0.4
C14:0	0.8
C16:0	37.4
C16:1	0.2
C18:0	3.6
C18:1	45.8
C18:2	11.1
C18:3	0.3
C20:0	0.3
C20:1	0.1

To make the higher amount of the extracted coffee oil, Leal et al. [49] investigated the new technology which can enhance the amount of extracted coffee oil from SCGs. They used the non-thermal plasma in the pre-treatment state of the SCGs extraction. The increasing of extracted coffee oil yield was around 30% when compared to the ultrasound pre-treatment method.

These can show that using SCGs is a suitable feedstock for producing the alternatives energies. The SCGs has the promising compound for many industrial especially, the fatty acid for biofuel production.

**2.4.2 Biodiesel production from spent coffee grounds**

SCGs is a candidate as the new source for the second-generation biofuel, there are many reports that showed SCGs is suitable source for biorefinery such as bioethanol [50] or biopolymer [51]. Biodiesel production is one of the useful ways to make SCGs become more valuable. There are some researches reported that using SCGs as the feedstock give the high quality of biodiesel like the other sources in the second-generation biofuel feedstock.

In 2014, Rocha et al.[52] used ultrasound technology to make SCGs as feedstock for biodiesel and ethanol productions. The obtained extracted coffee oil yield was 12 wt% when used the solvent (n-hexane) to SCGs sample ratio at 4 ml/g at 60°C for 45 min. The extracted coffee oil was used as feedstock for transesterification reaction by sonicated with mixture of alcohol and homogeneous base catalyst for 30 min at room temperature (the ultrasonic bath was setup at 40 kHz, 160 watt). The result showed that the FAME yield was 97 wt%. On the other hand, the defatted SCGs were hydrolyzed with diluted sulfuric acid to obtain the glucose. The high amount of glucose at 192 mg/g_{SCGs} was observed. When fermented with *Saccharomyces cerevisiae* for 10 hours, the process generated ethanol yield around 19 g/l.

Moreover, the biodiesel production by using SCGs become less of complexity, Liu et al. [53] used the direct transesterification reaction from SCGs. This research was not using solvent for extracting coffee oil from SCGs but using methanol and sulfuric acid as the catalyst in the transesterification to avoid the side reaction which is saponification reaction. This can be assumed that this method is the one-step transesterification reaction from SCGs without solvent extraction. The flow diagram for comparing the one-step of biodiesel production and the conventional process for biodiesel production from SCGs was shown in Figure 2.9.
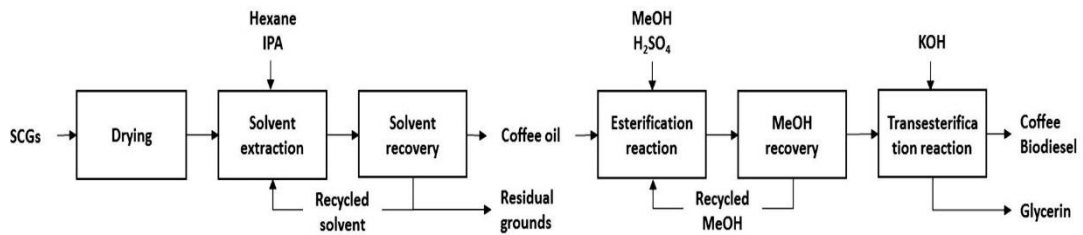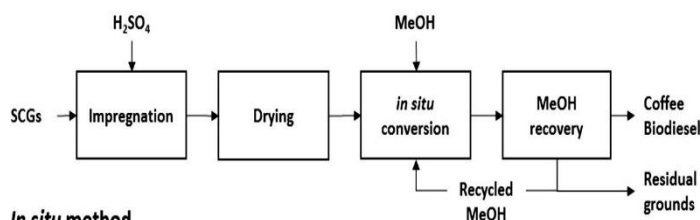
Figure 2.9 Flow diagram of conventional and direct transesterification process for

biodiesel production from SCGs [53]

At the concentration of sulfuric acid of 20 wt% and reaction temperature of 70°C for 12 hours, the direct transesterification reaction can give the FAME yield of 98.61 wt% or around 17.08 wt% yield of the dried SCGs sample. This process become less required of the production steps which can reduce the cost of production also the energy consumption in the process when the quality of the product still high.

There was the research that aim to reduce the step in the process of biodiesel production from SCGs. Normally, SCGs is the feedstock that has the high of moisture content, to use SCGs as the feedstock, the producer must remove the moisture out of the SCGs before applying in the process. Park et al. [54] investigated the wet in-situ transesterification reaction which can use wet SCGs directly with the alcohol and catalyst for biodiesel production. This method can extract the coffee oil from wet SCGs and used it for transesterification reaction at the same time to reduce the energy consumption in the process and the production cost. The conversion of the SCGs oil from wet in-situ transesterification reaction shown that the yield of the

product was over 15 wt% when using sulfuric acid or hydrochloric acid as catalyst at 95°C.

Wet in-situ transesterification reaction was used with supercritical fluid technology for biodiesel production from SCGs. Son et al. [55] used the combined methods for using wet SCGs as feedstock in transesterification reaction. Supercritical methanol and subcritical water were employed in this process to improve the efficiency of the process by enhanced the surface area of SCGs. The SCGs oil was efficiently extracted by using supercritical methanol. The conversion of the product was established at 86.33 wt% of SCGs coffee oil sample at the optimal condition. The reaction temperature was 270°C and pressure was 9.0 MPa for 20 min of reaction time with the molar ratio of methanol to SCGs of 5:1. Moreover, this research was found that the space loading is the important parameter for this method. Since the system was operated in the supercritical state, the space loading affected to the efficiency due to the lower of the pressure from overload the sample. The less of space loading decreased the conversion as well. This research found the optimal space loading for this system was 58.4 ml/g. The results also showed that adding subcritical water into the system provided the positive result on the conversion. First, subcritical water can hydrolyze triglyceride to become free fatty acid. There was the result proved that adding water up to 60% in the system can improve the yield of the product [56]. It could be concluded that using combine technology for biodiesel production from SCGs improve the efficiency of the biodiesel production process.

CHAPTER III

EXPERIMENTAL APPARATUS AND METHOD

The objective of this research is to investigate the biofuel production from spent coffee grounds (SCGs) by using supercritical ethyl acetate both in oil extraction and interesterification reaction and to find the optimum condition which are temperature and feed flow rate.

3.1 Materials

Spent coffee grounds (SCGs) was obtained from Starbuck coffeehouse, Square One, Bangkok, Thailand to use as feedstock for biofuel production.

Analytical-grade ethyl acetate (99.8%) was supplied by RCL Labscan limited, Thailand used as solvent for coffee oil extraction and biofuel production via interesterification reaction.

For sample analysis part by using gas chromatography (GC), analytical-grade n-heptane (99.5%) was provided by Fisher Scientific.

For the external standard, analytical-grade ethyl palmitate (≥99%) and ethyl oleate (98%) was purchased from Sigma Aldrich.

3.2 Experimental equipment and methods

This study has divided the experiment into three parts, each part has used a different method and equipment which all the experiment are specified in this part.

3.2.1 SCGs characterization

3.2.1.1 Moisture content

After obtaining SCGs from source, 1.0 g of SCGs was taken out as sample to determine the moisture in SCGs. The sample was placed in the shelter for 72 hours at room temperature (30 ℃) for removing the outer surface water in the sample. For the inner surface water, the sample was divided into three replicates (6.0 – 8.0 g) for evaluate the moisture content. All the samples were weighted before dried in the oven as shown in Figure 3.1 at 105℃ for 24 hours, then the dried samples were weighted again to calculate the water loss in the sample.

Figure 3.1 The oven for drying SCGs samples

3.2.1.2 Extracted coffee oil content

Dried SCGs (DSCGs) was used for oil extraction by using ethyl acetate as a solvent. Soxhlet extractor was selected to use in this part to identify the maximum oil content in DSCGs. The DSCGs was weighted 20 g for using as sample for coffee oil extraction. The sample was filled into cellulose thimble then placed in the

Soxhlet extractor chamber. The 200 ml of ethyl acetate was heated in the round bottom flask to extract coffee oil from the sample. The temperature of the process was set at 80°C and extraction time was 6 hours which long enough to make the color of the cellulose thimble turn back to white color.

3.2.1.3 Coffee oil characterization by GC-MS chromatography

After obtaining extracted coffee oil by using ethyl acetate as solvent from Soxhlet extractor, the sample was evaporated the excess ethyl acetate by nitrogen stripping. The n-heptane was used as solvent to dilute the coffee oil sample, the concentration of the sample was set at 500 ppm for analysis by gas chromatography-mass spectrometry (GC-MS). The condition for GC-MS was described in the table 3.1 [57].

Table 3.1 the GC-MS condition for coffee oil analysis

Condition	Value
Molecular weight scan range	50-500 m/z
Detector temperature	280°C
Oven initial temperature	150°C (Hold 3 min)
Oven heating rate	2°C/min
Oven final temperature	250°C (Hold 5 min)
Injection part temperature	250°C

3.2.2 Coffee oil extraction for biofuel production

After collected the data from the Sections 3.2.1, the rest of DSCGs was used as feedstock for coffee oil extraction. DSCGs were drowned in ethyl acetate to obtain the molar ratio of DSCGs to ethyl acetate of 1: 30 then soaked for 24 hours. The coffee oil content in the micellar phase was calculated by take some sample mixture to evaporate the solvent. The fresh DSCGs was replaced in the mixture

instead of the extracted DSCGs after the coffee oil contained in micellar phase was saturated.

When the mixture of coffee oil and ethyl acetate has the proper amount of coffee oil that attribute to the Soxhlet extraction part, the mixture was filtrated to separate SCGs out of the mixture. The coffee oil-ethyl acetate mixture as shown in Figure 3.2 was obtained and become a feedstock for biofuel production by supercritical ethyl acetate.

Figure 3.2 The mixture of coffee oil and ethyl acetate after filtrated the SCGs

3.2.3 Biofuel production from coffee oil by supercritical ethyl acetate

The process diagram of the reactor was shown in Figure 3.3. The mixture of coffee oil-ethyl acetate was fed into the preheater part of tubular reactor by high pressure liquid pump which purchased from Jasco, model PU-1580. Since the feed flow rate was also the one of the investigated parameters, the decrease of the feed mass was collected in actual time by using the electronic scale (AMPUT, model

APTP457A series) to determine the feed flow rate to make sure that the condition of the experiment was steady.

The preheater of the reactor is the coiled stainless steel (SUS316) tube with 500 cm. length, 3.17 mm. of outer diameter, and 0.71 mm. of the thickness. The coiled tubular reactor made of stainless steel (SUS316) tube with 300 cm. length, 9.52 mm. of outer diameter, and 0.88 mm. of the thickness. All part of the reactor was placed in the fluidized sand bath (OMEGA, model FSB-3, USA) which heated by the electrical heaters.

The K-type thermocouples (VSC advance Co., Limited, Thailand) were used to monitor the temperature of the process. The temperature controller was used to control the temperature in the fluidized sand bath. For the reaction pressure, a back-pressure regulator (Swagelok, UK) was equipped to increase and decrease the pressure in the reactor. All the process apparatus was shown in Figure 3.4.
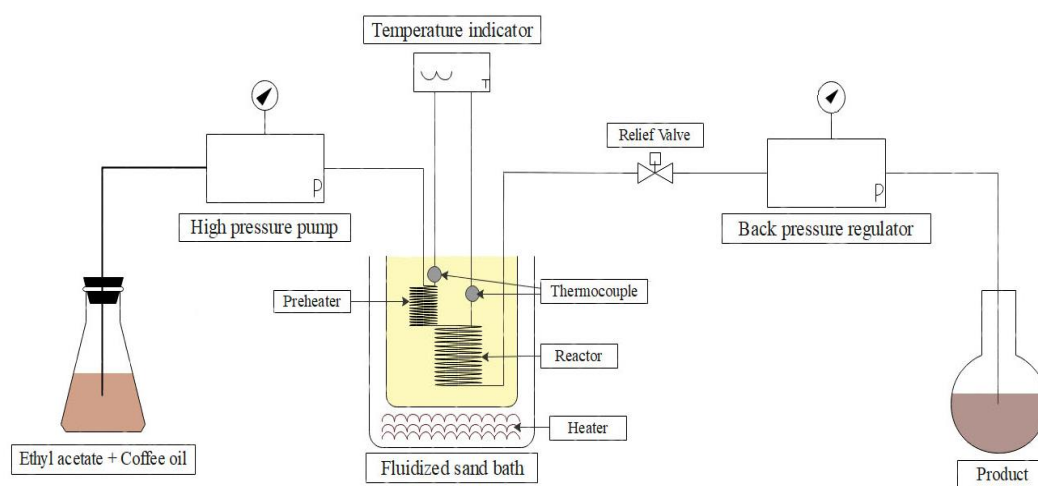
Figure 3.3 Process diagram for biofuel production from SCGs
by using supercritical ethyl acetate

Figure 3.4 The continuous reactor (tubular reactor) which compact in

fluidized sand bath and equipped with cooling system

To obtain the product, the external cooling system was connected to the
outlet of the reactor to cooldown the product. The liquid product was filled into the
flask and evaporated the excess ethyl acetate in the product by nitrogen stripping.
The condition of the process in this part was shown in Table 3.2.

Table 3.2 The condition for the biofuel production from SCGs

Parameters	Unit	Range
Temperature	℃	275, 300, 325, 350
Feed flow rate	g/mins	2, 2.5, 3
Pressure	MPa	15

3.2.3.1 Biofuel analysis by gas chromatography

The samples obtained at each condition were subjected to gas chromatography analysis. Ethyl palmitate and ethyl oleate was used in weight 0.625 to 0.1 g then diluted in n-heptane to generate the external standard calibration curve. For the sample analysis, 0.1 g of the sample was dissolved in 0.9 g of n-heptane. The quantitative analysis of the fatty acid ethyl ester (FAEE) in the sample was achieved by gas chromatography (Agilent technology, model 6890N) which equipped with capillary column (DB-FATWAX, length of 30 m and external diameter of 0.25 mm) and flame ionization detector (FID). The condition of the gas chromatography for quantifying FAEE in the sample was shown in Table 3.3.

Table 3.3 Condition of gas chromatography (GC) for FAEE quantity analysis

Condition	Value
Carrier gas (He) flow rate	1.3 ml/min
Detector temperature (FID)	280°C
Split ratio	1: 25
Injection part temperature	260°C
Inject volume	1 µl

For the qualitative analysis, GC-MS was used to analysis the component in the biofuel sample to confirm the conversion of the product. To prepare the 500 ppm of the sample, 0.05 g of the sample was dissolved in 0.95 g of n-heptane. The condition of the GC-MS for qualifying the sample was shown in Table 3.4 and Table 3.5 [57].

Table 3.4 Condition of gas chromatography-mass spectrometry (GC-MS) for FAEE

quality analysis

Condition	Value
Molecular weight scan range	33-600 m/z
Solvent delay	2 min
Transfer line temperature (Aux heater)	320°C
EI Source temperature	250°C
EI Voltage	70 eV
Injector volume	1 µl
Inlet temperature	270°C
Split ratio	7:1

Table 3.5 Oven condition for FAEE detection on GC-MS

Oven	°C/min	°C	Hold (min)
Initial		60	2
Ramp1	4	320	3
Ramp2			
Ramp3			
Ramp4			
Total			70
Post run		320	5

CHAPTER IV

RESULTS AND DISSCUSSION

4.1 Characterization of SCGs

After obtained SCGs sample from the source, some of SCGs were divided for the characterization to find the moisture content in the sample, extractable coffee oil, and components in the extracted coffee oil. The results in each experiment were described in further section.

4.1.1 Moisture contents in SCGs

To prevent the formations of bacteria and molds in the sample, the excess water in fresh SCGs was removed by drying at ambient temperature for 72 hours. The samples were calculated the moisture content after remove the excess water (three replicates) which shown in Table 4.1.

Table 4.1 SCGs sample weight and moisture content before and after drying at room temperature for 72 hours

SCGs sample	Before drying (g)	After drying (g)	Loss water (g)	Moisture content (%)
1	1.0375	0.4606	0.5769	55.60
2	1.0333	0.4546	0.5787	56.01
3	1.0677	0.4703	0.5974	55.96

It was reported that the average moisture contain of the fresh SCGs were between 55 to 80% [58]. However, the moisture contains in fresh SCGs sample were around 56% of biomass weight in this study. The average moisture of the fresh SCGs revealed that the high moisture of the fresh SCGs is suitable for the

growth of the bacteria and molds. It is noticed that the drying process was required to remove the outer surface water in order to prevent the degradation of coffee oil by microbes and to prolong the shelf-life of the SCGs.

The oven for drying the fresh SCGs sample was set at 105°C to remove the inner surface water. The SCGs samples were used for the calculation of the moisture content in dry SCGs (DSCGs). Table 4.2 was shown the result of the weight and the moisture content in the three SCGs samples after dried in the oven at 105°C for 24 hours.

Table 4.2 SCGs sample weight and moisture content before and after drying at 105°C for 24 hours

SCGs sample	Before drying (g)	After drying (g)	Loss water (g)	Moisture content (%)
1	7.5366	6.6072	0.9294	12.33
2	6.7965	5.8856	0.9109	13.40
3	8.3175	7.2726	1.0449	12.56

The average moisture content of DSCGs was around 12.76%. Removal of the inner surface water of the sample can completely prevent the growth of the bacteria and the molds. It can give the longer of the SCGs sample storage time as well. The results showed that the inner surface water of SCGs sample was lower than 15% that had the less impact on the biofuel production by the interesterification reaction.

Since the interesterification reaction is similar to transesterification reaction, the hydrolysis reaction induces the high acid value of the product when the feedstock contains the high amount of water [59]. Furthermore, the acetic acid hydrolyzed from triacetin led to significantly increase of the acid value in the product.

4.1.2 Extracted coffee oil from SCGs by ethyl acetate

The 20 grams of DSCGs sample were used to determine the amount of extractable coffee oil when using ethyl acetate as the solvent. The results showed that the amount of coffee oil was 22.74 wt% after extracted for 6 hours. The amount of extracted coffee oil depends on the type of the solvent. Hexane was the popular solvent that use for extracting the coffee oil in many studies. The highest amount of coffee oil around 12.5 wt% when using Soxhlet extraction [60]. The results in this study show that ethyl acetate is the suitable solvent for coffee oil extraction from DSCGs due to the higher coffee oil recovery than that of hexane.

4.1.3 Characterization the composition in extracted coffee oil

The extracted coffee oil was used to analysis the components in the coffee oil by using GC-MS. The result showed the various of chemical components in coffee oil such as Caffeine, 3,5,7-Pregnatrien-2O-one, and 2-(1,2-Dimethyl-1H-indol-3-ylmethyl)-4-nitrophenol. The important components in extracted coffee oil were palmitic acid (n-Hexadecenoic acid) and linoleic acid (9,12-Octadecadienoic acid). It could be implied that coffee oil is a suitable feedstock for biofuel production. The full GC-MS results are given in Appendix A.

4.2 Effect of temperature on biofuel production from DSCGs

In the part of biofuel production, the mixture contained ethyl acetate and coffee oil was fed into a tubular reactor. The optimal condition was located by the highest yield of FAEE in the product.

Because the reaction temperature is the crucial parameter that can affect to the %FAEE content in the supercritical condition, the studies were conducted slightly above the critical point of ethyl acetate (260°C). After collected the products from each condition and analysis the amount of the FAEE content in the products, Figure 4.1 shows the yield of FAEE in the product when operated at 275°C.
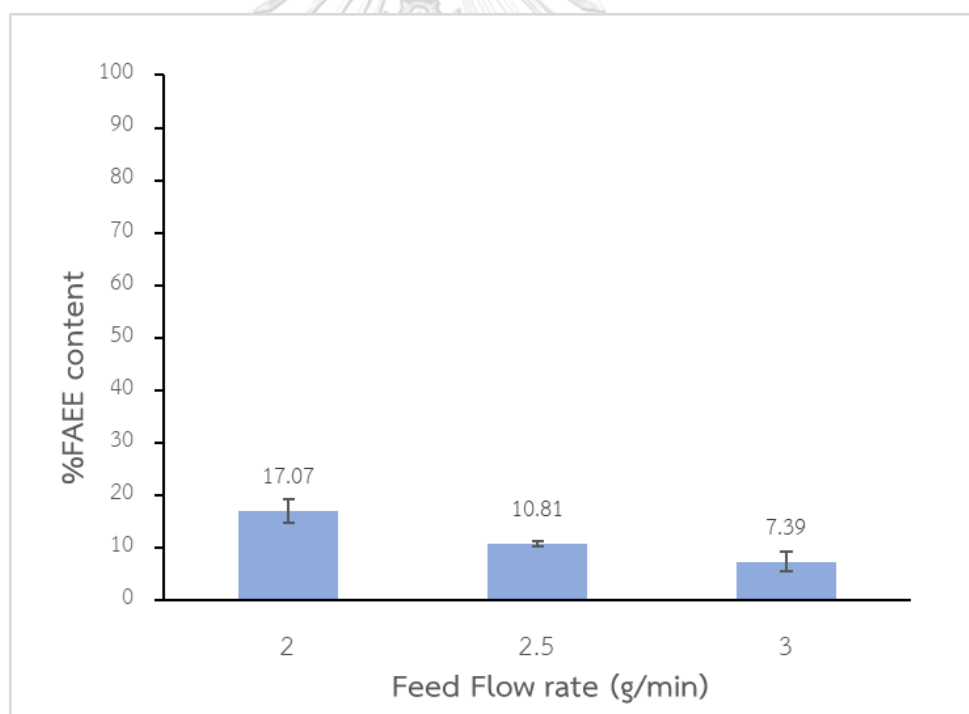
Figure 4.1 %FAEE content in product obtained at temperature 275°C, 15.0 MPa, and ethyl acetate to oil molar ratio of 30:1

The results after obtained from three replicates found that the maximum yield of FAEE was 17.07 wt% at feed flow rate of 2.0 g/min. It is indicated that the interesterification reaction of coffee oil in supercritical ethyl acetate took

place at temperature of 275°C. Thus, the reaction was further investigated at the higher temperature.

Figure 4.2 showed the conversion of the coffee oil at 300°C in various feed flow rates. The %FAEE content increased twice when compared to the reaction at 275°C at all feed flow rates. At 275°C and 300°C, the maximum %FAEE content was found at the feed flow rate of 2.0 g/min. It could be deduced that the decreasing in %FAEE content at 275°C and 300°C with the increasing of feed flow rate is a result of insufficient of residence time.
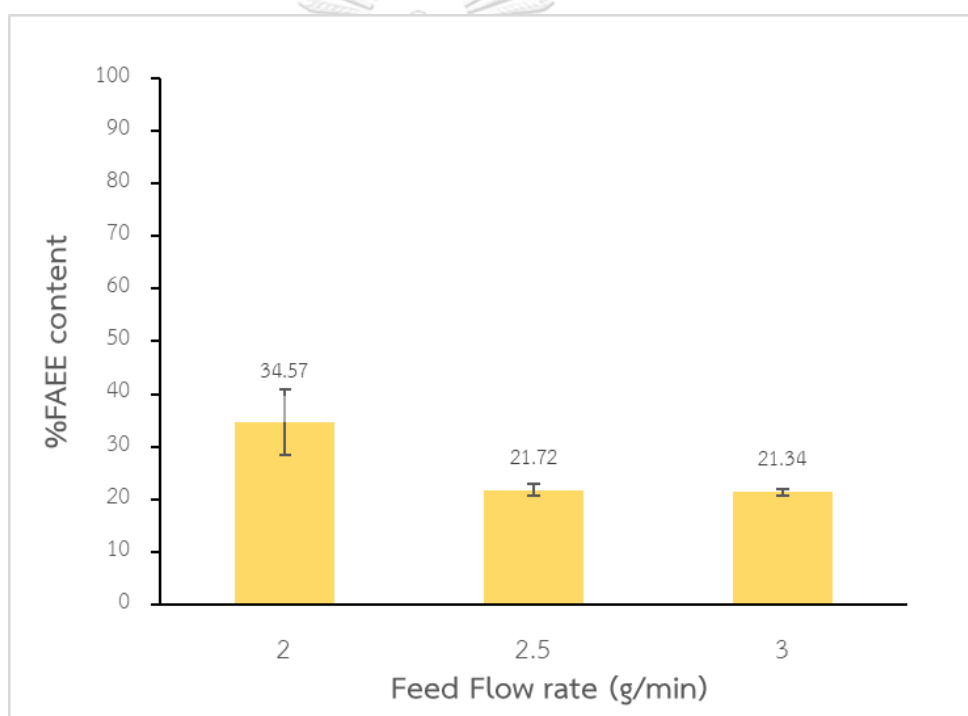
Figure 4.2 %FAEE content in product obtained at temperature 300°C, 15.0 MPa, and ethyl acetate to oil molar ratio of 30:1

Figures 4.3 and 4.4 depict the %FAEE content in product obtained at 325°C and 350°C. These results show that the increasing of temperature from 325°C to 350°C significantly affects to the FAEE yield. At the operated temperature of 325°C and 350°C, the FAEE yields were maximized at feed flow rate of 2.5 g/min.

This indicated the degradation of FAEE at feed flow rate of 2.0 g/min because of the surplus of residence time.
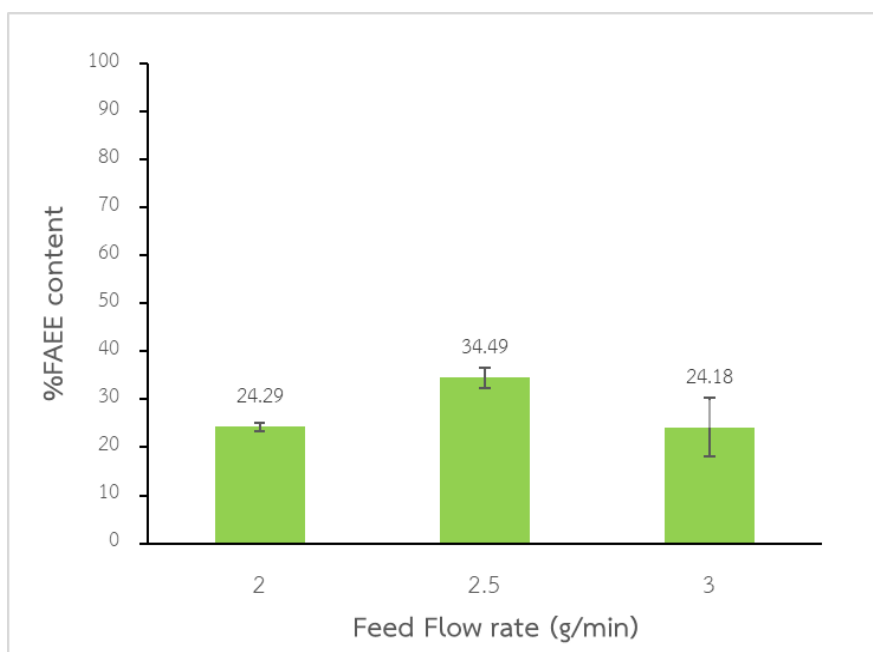
Figure 4.3 %FAEE content in product obtained at temperature 325℃, 15.0 MPa, and ethyl acetate to oil molar ratio of 30:1
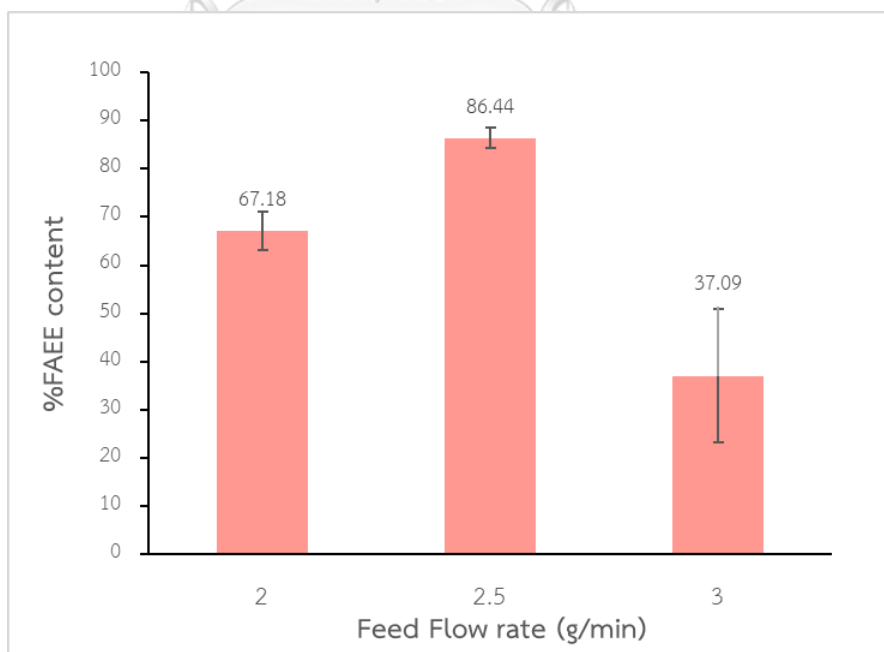
Figure 4.4 %FAEE content in product obtained at temperature 350℃ , 15.0 MPa, and ethyl acetate to oil molar ratio of 30:1

The maximum FAEE yield of 86.44 wt% was obtained at 350℃. Although the increasing of the temperature improves the conversion of coffee oil, the thermal decomposition of oil was reported in biofuel production in supercritical condition [61]. In this study, the fume of the product was observed at the reactor outlet when the reaction took place at 375℃ and feed flow rate 3 g/min. Because of the high viscosity of ethyl acetate-coffee oil mixture, the HPLC pump could not smoothly operate at flow rate above 3 g/min. Thus, the maximum temperature conducted in the experiment was kept at 350℃.

Unlike alcohols, ethyl acetate is the solvent that can extract coffee oil from DSCGs that mean using this solvent in the supercritical state was not aimed to make the feed and solvent become miscible. The rate of the interesterification reaction improves in supercritical condition. The reaction is initiated by the thermal decomposition of carboxylic esters. When compared to supercritical methyl acetate, the supercritical ethyl acetate process give the conversion lower than that of supercritical methyl acetate when using rapeseed oil as the feedstock [2].

All the results showed that increasing of the temperature led to improve the conversion of the coffee oil in supercritical ethyl acetate. The optimal temperature for the biofuel production from SCGs was 350℃ which indicated by the highest yield of 86.44 wt%. The optimal temperature probably depends on the type of feedstock and the solvent that used in the reaction. However, the effects of feed flow rate or the residence time was not clearly, the further study would be performed in Section 4.3.

4.3 Effect of the feed flow rate in biofuel production from SCGs

At constant temperature and pressure, feed flow rate controls the residence time in the continuous tubular reactor. In this section, the different feed flow rate was presented to find the optimal feed flow rate which can give the highest yield of FAEE in product. The calculation of residence time shows in appendix B [62].

Feed flow rate at 2 g/min was the minimum flow rate that applied in the experiments with the temperature range of 275°C to 350°C. The results are shown in Figure 4.5. The residence times for the reaction temperature of 275°C, 300°C, 325°C, and 350°C are 41.5 min, 38.2 min, 34.9 min, and 31.6 min, respectively.
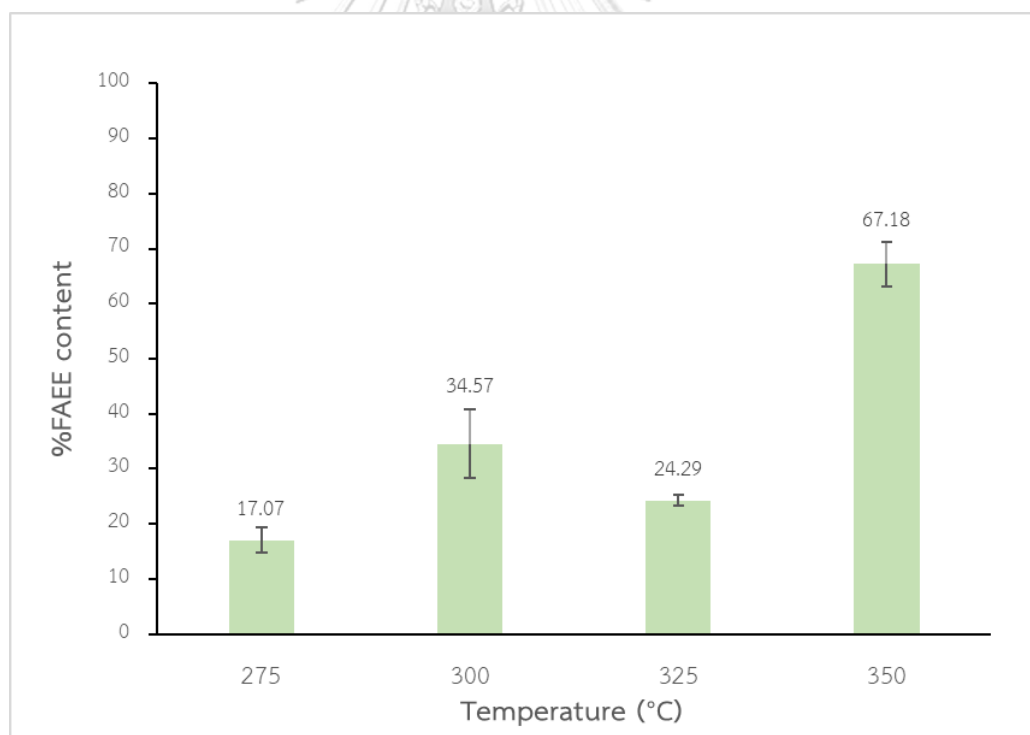
Figure 4.5 %FAEE content in product obtained from various temperatures at feed flow rate 2 g/min, 15.0 MPa, and ethyl acetate to oil molar ratio of 30:1

The maximum product yield was 67.18 wt% when operated the feed flow rate of 2 g/min (residence time of 31.6 min) at 350°C. This result showed that the high residence time can give the mixture of the feed interacted with the heat which can improve the conversion rate of the reaction.
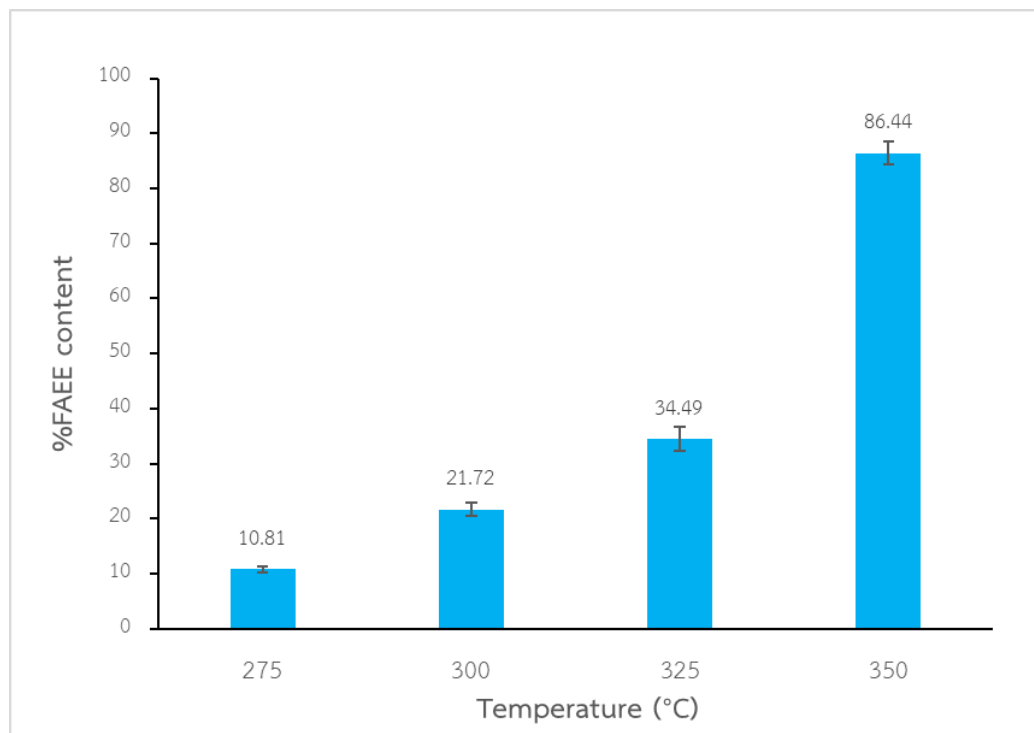
Figure 4.6 %FAEE content in product obtained from various temperatures at feed flow rate 2.5 g/min, 15.0 MPa, and ethyl acetate to oil molar ratio of 30:1

At the feed flow rate at 2.5 g/min, the results are shown in figure 4.6. The residence times at 275°C, 300°C, 325°C, and 350°C are 33.2 min, 30.6 min, 27.9 min, and 25.2 min, respectively. In this part, the maximum %FAEE yield of the product was 86.44 wt% which higher than the previous feed flow rate. The trend of the product yield is higher than the product at the feed flow rate 2.0 g/min. These results indicate that the higher residence time can reduce the yield of the product which came from the thermal decomposition at high temperature (350°C). Thus, the yield of FAEE increased when the feed flow rate was increased because the residence time was reduced.

The maximum feed flow rate of this study was 3 g/min which can calculate the residence times of 27.7 min, 25.5 min, 23.3 min, and 21.0 min for temperature at 275°C, 300°C, 325°C, and 350°C respectively. The results are shown in Figure 4.7. The results were proved that feed flow rate can effect the conversion because of the reducing of the residence time.
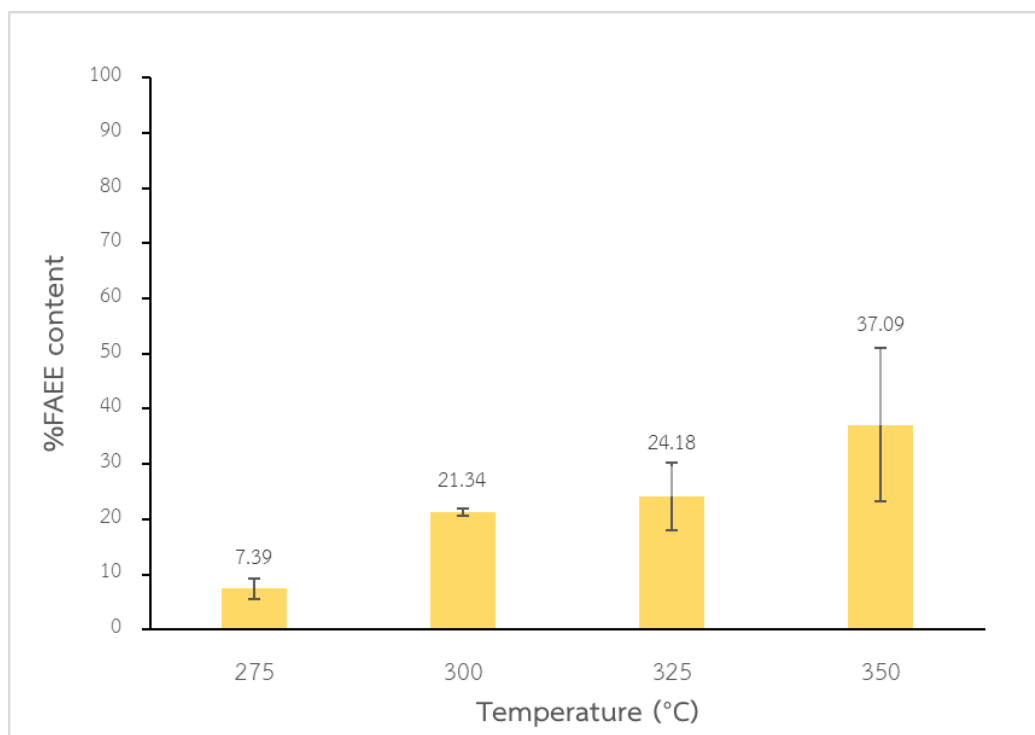
Figure 4.7 %FAEE content in product obtained from various temperatures at feed flow rate 3.0 g/min, 15.0 MPa, and ethyl acetate to oil molar ratio of 30:1

The maximum yield of the product was 37.09 wt% when operated at feed flow rate 3.0 g/min. The lowest product yield when compared with the yield at the same temperature. This can conclude that the optimal condition was obtained at temperature of 350 °C feed flow rate of 2.5 g/min or residence time of 25 min which can give the highest yield of the FAEE in the biofuel product.
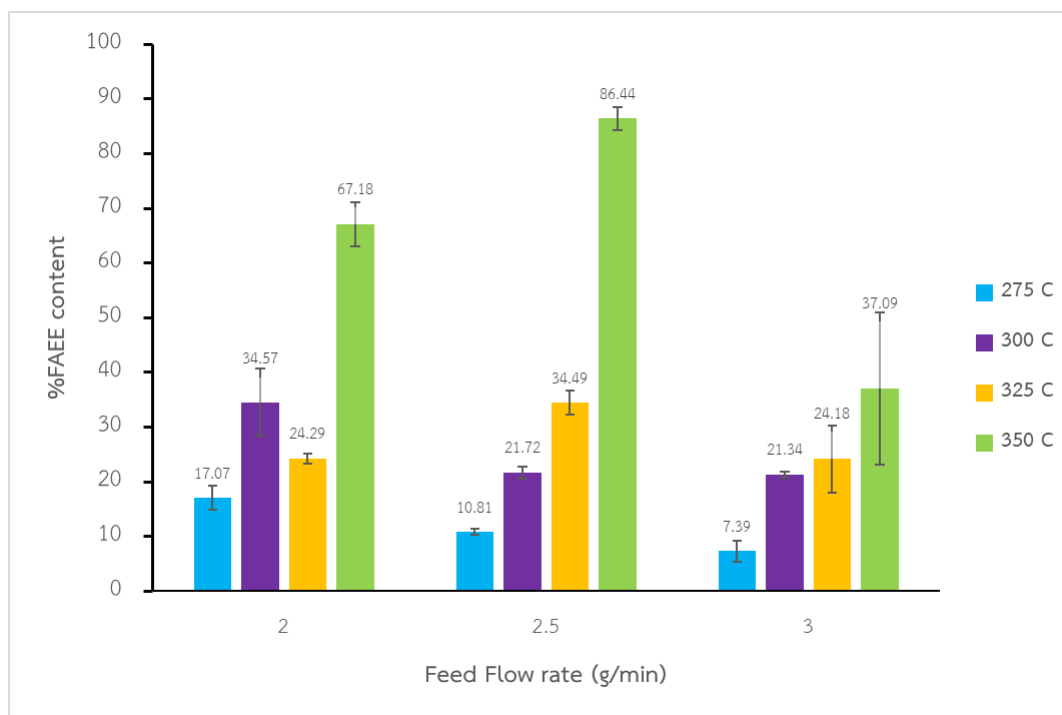
Figure 4.8 Coffee oil conversion by supercritical ethyl acetate in different temperature and feed flow rate

Figure 4.8 reveals the overall results at various temperature and feed flow rate. All the results showed that residence time of the process was one of parameters which affected to the extent of reaction. At constant temperature, the long residence time (over 30 min at 350 °C) can cause the thermal decomposition of the product which made the yield of the product declined. The FAEE content did not decrease at 275 °C and 300 °C (see Figure 4.9) with the residence time up to 41.5 min. The thermal degradation initiated at 325 °C because the decreasing of FAEE was observed at residence time of 34.9 min. In contrast, the short residence time (below 20 min at 350 °C) also reduce the conversion of the product because the insufficient of residence time. It can be concluded that the optimal condition for biofuel production from SCGs by using supercritical ethyl acetate at pressure 15.0 MPa was 350°C with feed flow rate of 2.5 g/min which can give the highest FAEE yield of 86.44 wt%.
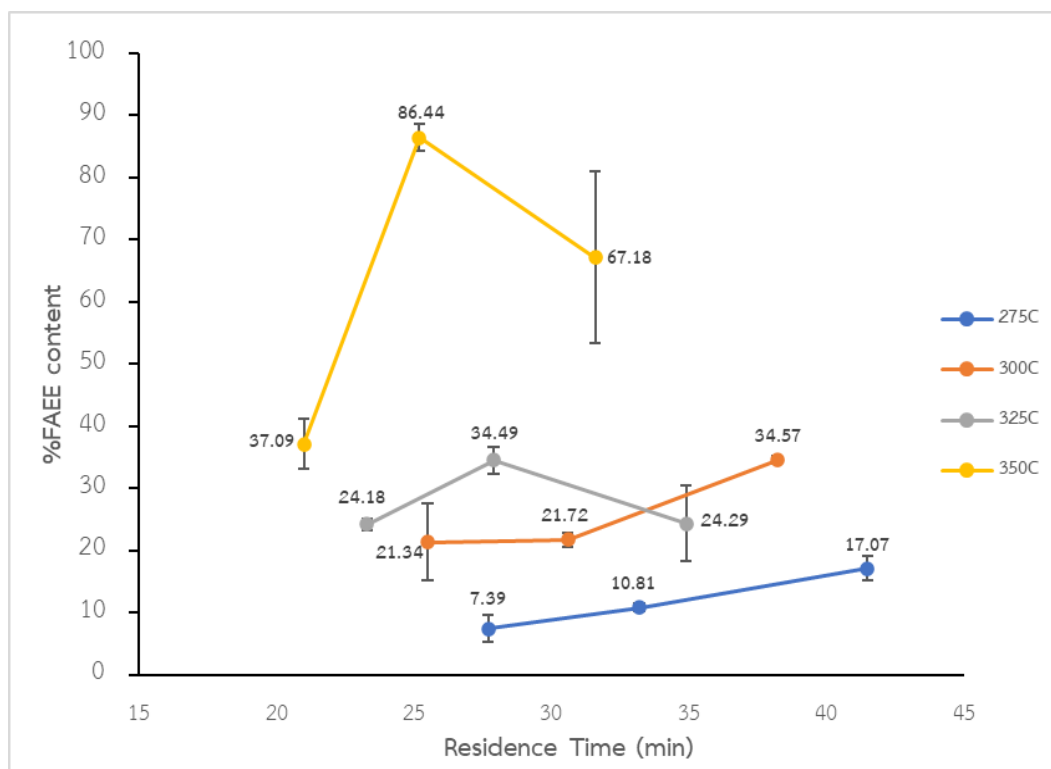
Figure 4.9 %FAEE content of coffee oil conversion by supercritical ethyl acetate at
various residence time and temperature

The effects of residence time for biofuel production from SCGs by supercritical ethyl acetate was shown in Figure 4.9. The method of residence time calculation is demonstrated in Appendix B. The residence time at 25 min give the highest yield of FAEE at 86.44 wt% when operated at the temperature of 350°C. These results also proved that the increasing in residence time lead to decrease the yield of FAEE when the temperature is higher than 300°C. Furthermore, increasing in the reaction temperature decreased the residence time but it delivers the higher yield of FAEE than that obtained at lower temperature. On the other hand, the longer of residence time at the high temperature can induce the thermal decarboxylation of FAEE content as shown in Figure 4.9 at 325°C and 350°C. The confirmation of hydrocarbons is shown in Section 4.4.

4.4 Biofuel product analysis by GC-MS

The results from GC-MS can confirm the composition of biofuel as demonstrated in Figure 4.10. Caffeine (Rt. 25.316 min) was found in the biofuel. Triacetin (Rt. 9.128 min) was detected in the sample which can prove that biofuel production by supercritical ethyl acetate was conducted via interesterification. The main fatty acids in coffee oil were palmitic and linoleic acids. They were consequently converted to FAEE. Ethyl palmitate (Rt. 30.459 min) and ethyl linoleate (Rt. 35.402 min) were detected by GC-MS. There were not found glycerol formation in the sample. In addition, the small molecules of hydrocarbon were detected at the retention time in range of 41-56 min. The revealed hydrocarbon (C22-C30) molecules illustrate the thermal decarboxylation and polymerization of fatty acids. This GC-MS result can show that the interesterification reaction in biofuel production process truly reduced the amount of glycerol by-product. The full GC-MS results of produced biofuel are given in Appendix C.
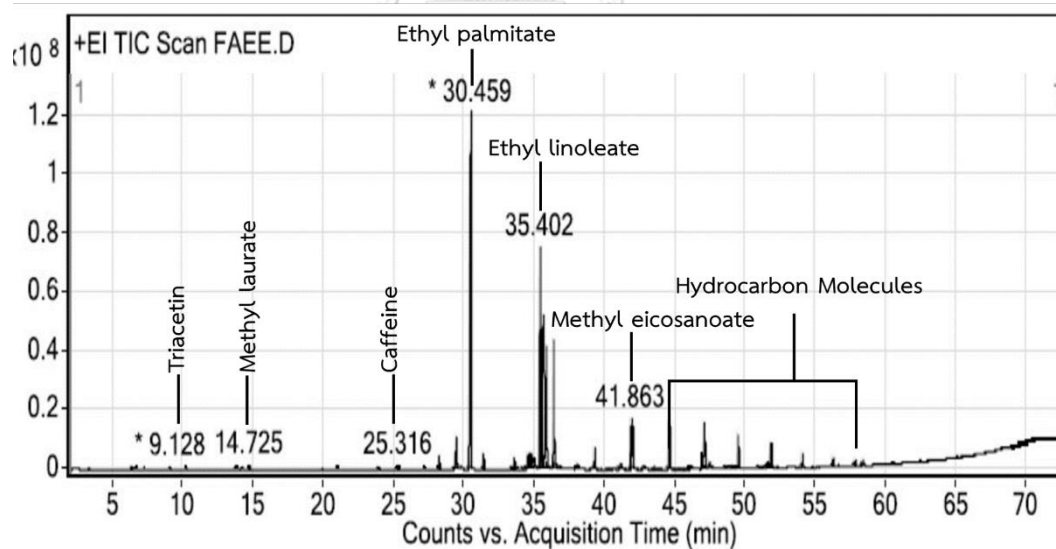
Figure 4.10 GC-MS chromatogram of the biofuel product obtained at 350°C, 15 MPa, and 1:30 of coffee oil to ethyl acetate molar ratio

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

Spent coffee grounds (SCGs) is the abundant waste that increased in amount sharply. To make SCGs more valuable, using SCGs as the feedstock for biofuel production is one of many ways to make the green biofuel that can relieve the effects of global warming.

Ethyl acetate is the promising solvent that can be used for extracting coffee oil in SCGs. The extraction of coffee oil by conventional solvent, e.g. hexane requires the solvent removal before producing the biofuel. It is the limitation of using SCGs for biofuel production. Furthermore, ethyl acetate can use as the reactant in the interesterification reaction for biofuel production. This alternative reaction produces the triacetin as by-product instead of glycerol. Because of the continuously growth of biodiesel industry, the oversupply of glycerol creates the declining of its world market price. On the other hand, triacetin is the fuel additive that can be mixed with produced biofuel. The increasing in fuel yield and the reducing of the downstream process are simultaneously obtained when using ethyl acetate as extracting and reacting solvent.

Using supercritical technology for biofuel production reduce the amount of chemical waste that generated during the process. Supercritical ethyl acetate to produce biofuel from SCGs is the green process that could cure the environmental problem. The conversion of SCGs to biofuel instantaneously solved problems from waste management and energy resource.

In this research, characterization of SCGs is the important step to prove that the obtained SCGs is suitable for biofuel production by supercritical ethyl acetate. Since SCGs is the natural biomass, the fresh SCGs moisture content is around 56% of biomass weight. The high moisture content is suitable for the growth of bacteria and molds. Removing the moisture from SCGs essentially required to prevent the formation of microbes. After drying the SCGs in the atmospheric condition, the moisture content of the sample is reduced to 12.68 wt%. This moisture content has less impact on the interesterification reaction.

The amount of coffee oil in SCGs directly depends on the source of the coffee bean and the type of extraction solvent. First, ethyl acetate was used to determine the amount of extractable coffee oil by using Soxhlet extraction at 80°C for 6 hours. The amount of extracted coffee oil was 22.74 wt%. The extracted oil was subjected to GC-MS to confirm it contained the palmitic and linoleic acids. The results shown that coffee oil is a suitable the feedstock for biofuel production.

To reduce the amount of chemical used, ethyl acetate was used as the solvent for extracting coffee oil from SCGs and acted as the reactant for the biofuel production. To extract the coffee oil from dried spent coffee ground (DSCGs), it was submerged in ethyl acetate. The coffee oil-ethyl acetate mixture was filtrated after the molar ratio of oil to ethyl acetate of 1:30 was obtained. Next, the mixture was fed into tubular reactor for biofuel production.

Temperature and feed flow rate were parameters that can affect to the conversion of the FAEE in the product. The results indicate that increasing in the temperature reaction can rise the conversion. The optimal condition in this research was 350°C and feed flow rate at 2.5 g/min representing the residence time of 25 min which provided the highest yield of FAEE at 86.44 wt%.

The product was confirmed the generation of FAEE by GC-MS. The result proved that using interesterification reaction instead of transesterification reaction can reduce the formation of glycerol which becomes abundant waste nowadays. Triacetin was detected in the sample as the by-product of the interesterification reaction. Ethyl palmitate and ethyl linoleate also detected in the sample which proved that using coffee oil as the feedstock for biofuel production can give the FAEE as the product by using supercritical ethyl acetate as the reactant.

5.2 Recommendation

1. This study employed the SCGs from the same coffee shop as the sample. However, the components in SCGs depends on various factor such as the species of the coffee bean, roasting level, and the brewing method. The further characterization of the SCGs is the important step to know its composition before use it as the feedstock. The variation of the composition in SCGs is the interesting topic as well.

2. The limitation of using SCGs for biofuel production is the user must extract the coffee oil from SCGs sample. The amount of coffee oil depends on the method of extraction or the type of the solvent. The process that can give the maximum amount of coffee oil but reduce the energy consumption during the process is the ultimate goal. The biofuel production from SCGs become more efficiency and environmentally friendly.

3. To investigate the co-solvent such as ethanol in the biofuel production from SCGs by using supercritical ethyl acetate might improve the performance of the process in term of the conversion of the product which can make the yield of the product increase.

4. The biofuel production from SCGs by supercritical ethyl acetate is suitable for the instant coffee factory where the cost of logistic is eliminated. Since the SCGs generated in the coffee shop is only a few kilograms per day, the drying and collecting are cost and labor intensive. This work used the Arabica SCGs obtained from Starbuck coffee house because it has a constancy in quality and accessible. Furthermore, the other coffee shops did not separate the SCGs from other wastes, e.g. spent tea waste, tissue napkin, and syrup cap. Although the SCGs in the instant coffee factory is Robusta bean, the results from this study could be implied. Therefore, the further study on the SCGs obtained from the instant coffee factory is a challenge topic. Techno-economic and life-cycle assessment could be applied for this process as well.

REFERENCES

[1]   M.R. Monteiro, C.L. Kugelmeier, R.S. Pinheiro, M.O. Batalha, A. da Silva César, Glycerol from biodiesel production: Technological paths for sustainability, Renewable and Sustainable Energy Reviews 88 (2018) 109-122.

[2]   F. Goembira, K. Matsuura, S. Saka, Biodiesel production from rapeseed oil by various supercritical carboxylate esters, Fuel 97 (2012) 373-378.

[3]   P.A. Leggieri, M. Senra, L. Soh, Cloud point and crystallization in fatty acid ethyl ester biodiesel mixtures with and without additives, Fuel 222 (2018)   243-249.

[4]   A.J. Kruis, M. Levisson, A.E. Mars, M. van der Ploeg, F. Garcés Daza, V. Ellena, S.W.M. Kengen, J. van der Oost, R.A. Weusthuis, Ethyl acetate production by the elusive alcohol acetyltransferase from yeast, Metabolic Engineering 41 (2017) 92-101.

[5]   K. Somnuk, P. Eawlex, G. Prateepchaikul, Optimization of coffee oil extraction from spent coffee grounds using four solvents and prototype-scale extraction using circulation process, Agriculture and Natural Resources 51(3) (2017) 181-189.

[6]   I. Efthymiopoulos, P. Hellier, N. Ladommatos, A. Kay, B. Mills-Lamptey, Effect of Solvent Extraction Parameters on the Recovery of Oil From Spent Coffee Grounds for Biofuel Production, Waste and Biomass Valorization 10(2) (2019) 253-264.

[7]   F. van der Ploeg, Untapped fossil fuel and the green paradox: a classroom calibration of the optimal carbon tax, Environmental Economics and Policy Studies 17(2) (2014) 185-210.

[8]   S.N. Naik, V.V. Goud, P.K. Rout, A.K. Dalai, Production of first and second generation biofuels: A comprehensive review, Renewable and Sustainable Energy Reviews 14(2) (2010) 578-597.

[9]   Y. Dahman, K. Syed, S. Begum, P. Roy, B. Mohtasebi, 14 - Biofuels: Their characteristics and analysis, in: D. Verma, E. Fortunati, S. Jain, X. Zhang (Eds.), Biomass, Biopolymer-Based Materials, and Bioenergy, Woodhead Publishing2019, pp. 277-325.

[10]   P.A. Fokaides, E. Christoforou, 3 - Life cycle sustainability assessment of biofuels, in: R. Luque, C.S.K. Lin, K. Wilson, J. Clark (Eds.), Handbook of Biofuels Production (Second Edition), Woodhead Publishing2016, pp. 41-60.

[11]   S. Saha, A. Sharma, S. Purkayastha, K. Pandey, S. Dhingra, 14 - Bio-plastics and Biofuel: Is it the Way in Future Development for End Users?, in: S.M. Al-Salem (Ed.), Plastics to Energy, William Andrew Publishing2019, pp. 365-376.

[12]   P.M.F. Elshout, R. van Zelm, M. van der Velde, Z. Steinmann, M.A.J. Huijbregts, Global relative species loss due to first-generation biofuel production for the transport sector, Glob Change Biol Bioenergy 11(6) (2019) 763-772.

[13]   V.K. Garlapati, S. Tewari, R. Ganguly, Chapter 19 - Life Cycle Assessment of First-, Second-Generation, and Microalgae Biofuels, in: M. Hosseini (Ed.), Advances in Feedstock Conversion Technologies for Alternative Fuels and Bioproducts, Woodhead Publishing2019, pp. 355-371.

[14]   M. Uyan, F.M. Alptekin, D. Cebi, M.S. Celiktas, Bioconversion of hazelnut shell using near critical water pretreatment for second generation biofuel production, Fuel 273 (2020).

[15]   F. Alam, S. Mobin, H. Chowdhury, Third Generation Biofuel from Algae, Procedia Engineering 105 (2015) 763-768.

[16]   S. Dutta, F. Neto, M.C. Coelho, Microalgae biofuels: A comparative study on techno-economic analysis & life-cycle assessment, Algal Research 20 (2016) 44-52.

[17]   T.M.Y. khan, A.E. Atabani, I.A. Badruddin, A. Badarudin, M.S. Khayoon, S. Triwahyono, Recent scenario and technologies to utilize non-edible oils for biodiesel production, Renewable and Sustainable Energy Reviews 37 (2014) 840-851.

[18]   A.K. Azad, M.G. Rasul, M.M.K. Khan, S.C. Sharma, M.A. Hazrat, Prospect of biofuels as an alternative transport fuel in Australia, Renewable and Sustainable Energy Reviews 43 (2015) 331-351.

[19]   V. Thangarasu, R. Anand, Chapter 17 - Comparative evaluation of corrosion behavior of Aegle Marmelos Correa diesel, biodiesel, and their blends on aluminum and mild steel metals, in: A.K. Azad, M. Rasul (Eds.), Advanced Biofuels, Woodhead Publishing2019, pp. 443-471.

[20]   R. Guzatto, T.L. de Martini, D. Samios, The use of a modified TDSP for biodiesel production from soybean, linseed and waste cooking oil, Fuel Processing Technology 92(10) (2011) 2083-2088.

[21]   A. Al-Ani, N.E. Mordvinova, O.I. Lebedev, A.Y. Khodakov, V. Zholobenko, Ion-exchanged zeolite P as a nanostructured catalyst for biodiesel production, Energy Reports 5 (2019) 357-363.

[22]   Z. Sajid, F. Khan, Y. Zhang, Process simulation and life cycle analysis of biodiesel production, Renewable Energy 85 (2016) 945-952.

[23]   K. Mozaffarikhah, A. Kargari, M. Tabatabaei, H. Ghanavati, M.M.A. Shirazi, Membrane treatment of biodiesel wash-water: A sustainable solution for water recycling in biodiesel production process, Journal of Water Process Engineering 19 (2017) 331-337.

[24]   M. Saito, History of supercritical fluid chromatography: instrumental development, J Biosci Bioeng 115(6) (2013) 590-9.

[25]   D. Wen, H. Jiang, K. Zhang, Supercritical fluids technology for clean biofuel production, Progress in Natural Science 19(3) (2009) 273-284.

[26]   O.M. Ali, R. Mamat, M.G. Rasul, G. Najafi, Chapter Eighteen - Potential of Biodiesel as Fuel for Diesel Engine, in: M.G. Rasul, A.k. Azad, S.C. Sharma (Eds.), Clean Energy for Sustainable Development, Academic Press2017, pp. 557-590.

[27]   S.S. Win, T.A. Trabold, Chapter 6 - Sustainable Waste-to-Energy Technologies: Transesterification, in: T.A. Trabold, C.W. Babbitt (Eds.), Sustainable Food Waste-To-energy Systems, Academic Press2018, pp. 89-109.

[28]   I.M. Atadashi, M.K. Aroua, A.R.A. Aziz, N.M.N. Sulaiman, Refining technologies for the purification of crude biodiesel, Applied Energy 88(12) (2011) 4239-4251.

[29]   M.L.N.M. Carneiro, F. Pradelle, S.L. Braga, M.S.P. Gomes, A.R.F.A. Martins, F. Turkovics, R.N.C. Pradelle, Potential of biofuels from algae: Comparison with fossil fuels, ethanol and biodiesel in Europe and Brazil through life cycle assessment (LCA), Renewable and Sustainable Energy Reviews 73 (2017) 632-653.

[30]   T.A.Z. de Souza, C.J.R. Coronado, J.L. Silveira, G.M. Pinto, Economic assessment of hydrogen and electricity cogeneration through steam reforming-SOFC system in the Brazilian biodiesel industry, Journal of Cleaner Production 279 (2021).

[31]   M.S. Dhawan, S.C. Barton, G.D. Yadav, Interesterification of triglycerides with methyl acetate for the co-production biodiesel and triacetin using hydrotalcite as a heterogenous base catalyst, Catalysis Today (2020).

[32]   F.E. Kiss, R.D. Micic, M.D. Tomić, E.B. Nikolić-Djorić, M.Đ. Simikić, Supercritical transesterification: Impact of different types of alcohol on biodiesel yield and LCA results, The Journal of Supercritical Fluids 86 (2014) 23-32.

[33]   M.J. Salar-García, V.M. Ortiz-Martínez, P. Olivares-Carrillo, J. Quesada-Medina, A.P. de los Ríos, F.J. Hernández-Fernández, Analysis of optimal conditions for biodiesel production from Jatropha oil in supercritical methanol: Quantification of thermal decomposition degree and analysis of FAMEs, The Journal of Supercritical Fluids 112 (2016) 1-6.

[34]   N. García-Martínez, P. Andreo-Martínez, J. Quesada-Medina, A.P. de los Ríos, A. Chica, R. Beneito-Ruiz, J. Carratalá-Abril, Optimization of non-catalytic transesterification of tobacco (Nicotiana tabacum) seed oil using supercritical methanol to biodiesel production, Energy Conversion and Management 131 (2017) 99-108.

[35]   C. Román-Figueroa, P. Olivares-Carrillo, M. Paneque, F.J. Palacios-Nereo, J. Quesada-Medina, High-yield production of biodiesel by non-catalytic supercritical methanol transesterification of crude castor oil (Ricinus communis), Energy 107 (2016) 165-171.

[36]   B.K. Uprety, W. Chaiwong, C. Ewelike, S.K. Rakshit, Biodiesel production using heterogeneous catalysts including wood ash and the importance of enhancing byproduct glycerol purity, Energy Conversion and Management 115 (2016) 191-199.

[37]   N. Lamba, R. Gupta, J.M. Modak, G. Madras, ZnO catalyzed transesterification of Madhuca indica oil in supercritical methanol, Fuel 242 (2019) 323-333.

[38]   F. Goembira, S. Saka, Optimization of biodiesel production by supercritical methyl acetate, Bioresource Technology 131 (2013) 47-52.

[39]   F. Goembira, S. Saka, Effect of additives to supercritical methyl acetate on biodiesel production, Fuel Processing Technology 125 (2014) 114-118.

[40]   C. Komintarachat, R. Sawangkeaw, S. Ngamprasertsith, Continuous production of palm biofuel under supercritical ethyl acetate, Energy Conversion and Management 93 (2015) 332-338.

[41]   P.S. Murthy, M. Madhava Naidu, Sustainable management of coffee industry by-products and value addition—A review, Resources, Conservation and Recycling 66 (2012) 45-58.

[42]   S.K. Karmee, A spent coffee grounds based biorefinery for the production of biofuels, biopolymers, antioxidants and biocomposites, Waste Manag 72 (2018) 240-254.

[43]   L. Blinová, M. Sirotiak, A. Bartošová, M. Soldán, Review: Utilization of Waste From Coffee Production, Research Papers Faculty of Materials Science and Technology Slovak University of Technology 25(40) (2017) 91-101.

[44]   R.W. Jenkins, N.E. Stageman, C.M. Fortune, C.J. Chuck, Effect of the Type of Bean, Processing, and Geographical Location on the Biodiesel Produced from Waste Coffee Grounds, Energy & Fuels 28(2) (2014) 1166-1174.

[45]   L.F. Ballesteros, J.A. Teixeira, S.I. Mussatto, Chemical, Functional, and Structural Properties of Spent Coffee Grounds and Coffee Silverskin, Food and Bioprocess Technology 7(12) (2014) 3493-3503.

[46]   S.I. Mussatto, L.M. Carneiro, J.P.A. Silva, I.C. Roberto, J.A. Teixeira, A study on chemical constituents and sugars extraction from spent coffee grounds, Carbohydrate Polymers 83(2) (2011) 368-374.

[47]   M. Balzano, M.R. Loizzo, R. Tundis, P. Lucci, O. Nunez, D. Fiorini, A. Giardinieri, N.G. Frega, D. Pacetti, Spent espresso coffee grounds as a source of anti-proliferative and antioxidant compounds, Innovative Food Science & Emerging Technologies 59 (2020).

[48]   N. Viriya-empikul, P. Krasae, W. Nualpaeng, B. Yoosuk, K. Faungnawakij, Biodiesel production over Ca-based solid catalysts derived from industrial wastes, Fuel 92(1) (2012) 239-244.

[49]   A. Leal Vieira Cubas, M. Medeiros Machado, R. Tayane Bianchet, K. Alexandra da Costa Hermann, J. Alexsander Bork, N. Angelo Debacher, E. Flores Lins, M. Maraschin, D. Sousa Coelho, E. Helena Siegel Moecke, Oil extraction from spent coffee grounds assisted by non-thermal plasma, Separation and Purification Technology 250 (2020).

[50]   A. Burniol-Figols, K. Cenian, I.V. Skiadas, H.N. Gavala, Integration of chlorogenic acid recovery and bioethanol production from spent coffee grounds, Biochemical Engineering Journal 116 (2016) 54-64.

[51]   G.O. Coelho, M.J.A. Batista, A.F. Ávila, A.S. Franca, L.S. Oliveira, Development and characterization of biopolymeric films of galactomannans recovered from spent coffee grounds, Journal of Food Engineering 289 (2021).

[52]   M.V. Rocha, L.J. de Matos, L.P. Lima, P.M. Figueiredo, I.L. Lucena, F.A. Fernandes, L.R. Goncalves, Ultrasound-assisted production of biodiesel and ethanol from spent coffee grounds, Bioresour Technol 167 (2014) 343-8.

[53]   Y. Liu, Q. Tu, G. Knothe, M. Lu, Direct transesterification of spent coffee grounds for biodiesel production, Fuel 199 (2017) 157-161.

[54]   J. Park, B. Kim, J.W. Lee, In-situ transesterification of wet spent coffee grounds for sustainable biodiesel production, Bioresour Technol 221 (2016) 55-60.

[55]   J. Son, B. Kim, J. Park, J. Yang, J.W. Lee, Wet in situ transesterification of spent coffee grounds with supercritical methanol for the production of biodiesel, Bioresour Technol 259 (2018) 465-468.

[56]   J. Park, B. Kim, J. Son, J.W. Lee, Solvo-thermal in situ transesterification of wet spent coffee grounds for the production of biodiesel, Bioresour Technol 249 (2018) 494-500.

[57]   A.L.d. Oliveira, P.M. Cruz, M.N. Eberlin, F.A. Cabral, Brazilian roasted coffee oil obtained by mechanical expelling: compositional analysis by GC-MS, Ciência e Tecnologia de Alimentos 25(4) (2005) 677-682.

[58]   F.J. Gómez-de la Cruz, F. Cruz-Peragón, P.J. Casanova-Peláez, J.M. Palomar-Carnicero, A vital stage in the large-scale production of biofuels from spent coffee grounds: The drying kinetics, Fuel Processing Technology 130 (2015) 188-196.

[59]   K.T. Tan, K.T. Lee, A.R. Mohamed, Prospects of non-catalytic supercritical methyl acetate process in biodiesel production, Fuel Processing Technology 92(10) (2011) 1905-1909.

[60]   B.H.H. Goh, H.C. Ong, C.T. Chong, W.-H. Chen, K.Y. Leong, S.X. Tan, X.J. Lee, Ultrasonic assisted oil extraction and biodiesel synthesis of Spent Coffee Ground, Fuel 261 (2020).

[61]   H.-Y. Shin, S.-M. Lim, S.-Y. Bae, S.C. Oh, Thermal decomposition and stability of fatty acid methyl esters in supercritical methanol, Journal of Analytical and Applied Pyrolysis 92(2) (2011) 332-338.

[62]   C. Komintarachat, R. Sawangkeaw, S. Ngamprasertsith, Density of Ethyl Acetate-Palm Oil Mixture in Supercritical Condition, Engineering Journal 19(2) (2015) 29-39.

APPENDIX A

THE COMPOSITIONS IN EXTRACTED COFFEE OIL BY GC-MS
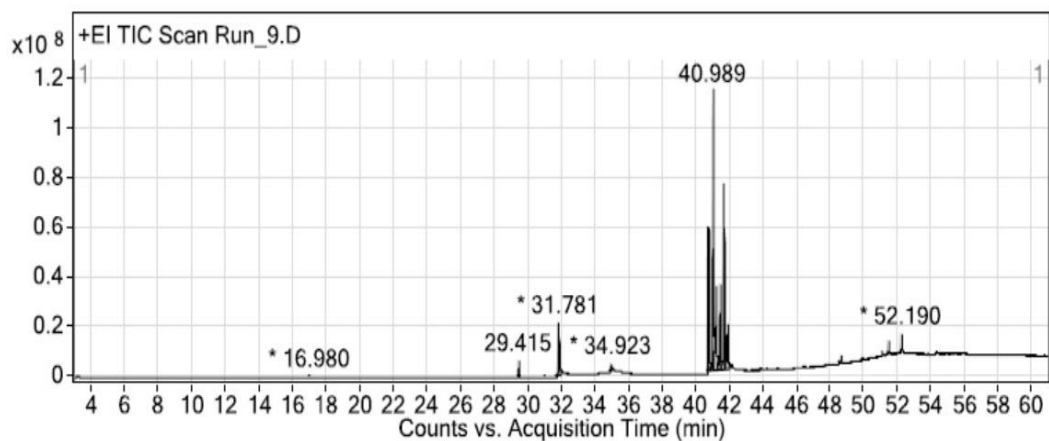
Figure A1 Chromatogram of extracted coffee oil detected by GC-MS

In figure A1 shown the chromatogram of extracted coffee oil sample which can detect the compositions of coffee oil as show in this section.
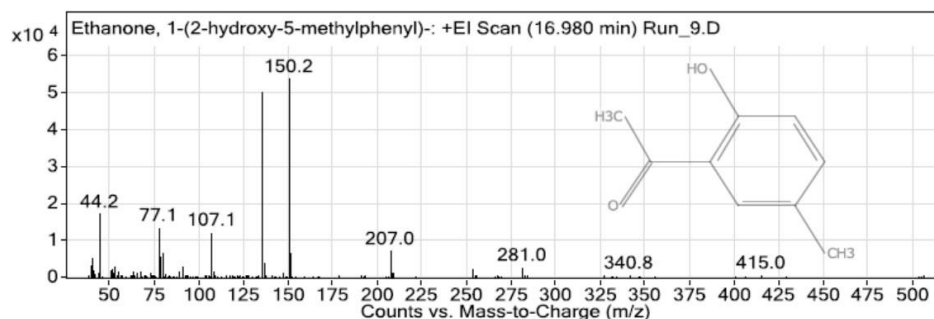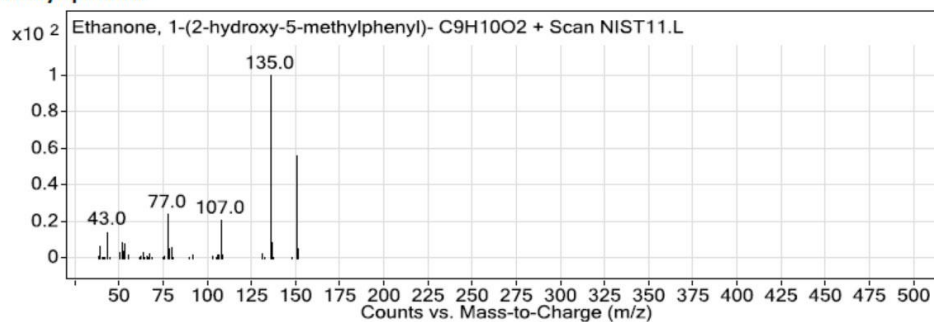
Figure A2 Ethanone, 1-(2-hydroxy-5-methylphenyl) detected by GC-MS

compare to library spectrum
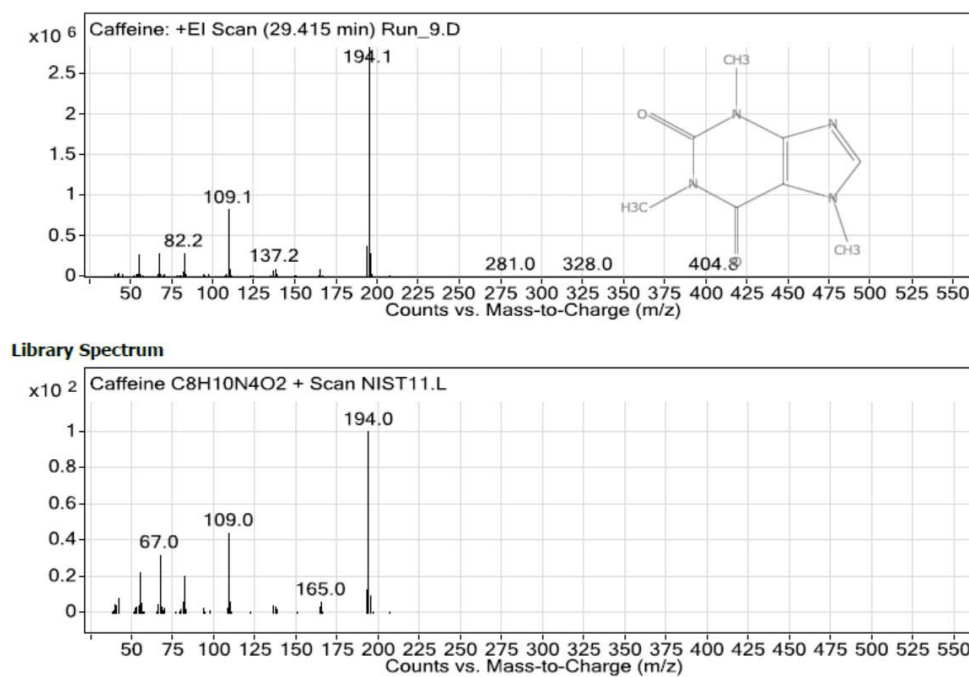
Figure A3 Caffeine detected by GC-MS detected by GC-MS compare to library spectrum
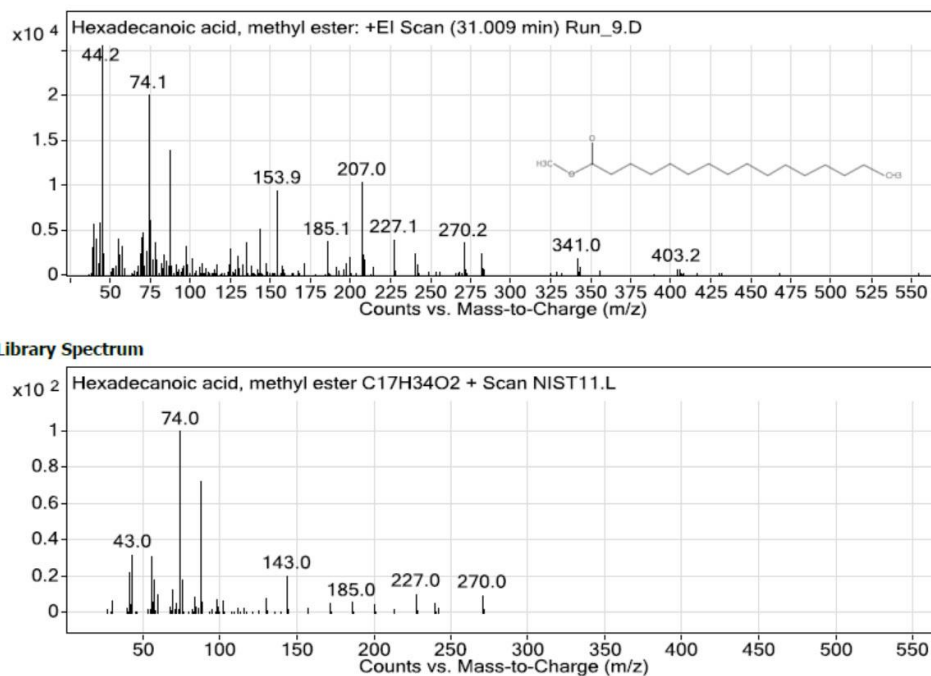
Figure A4 Hexadecanoic acid, methyl ester detected by GC-MS compare to library spectrum
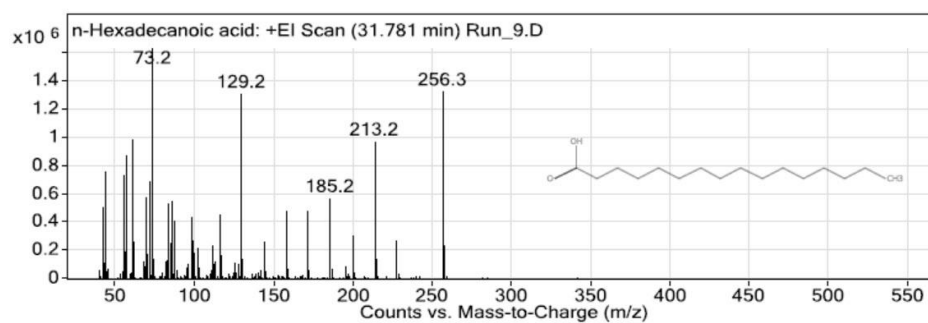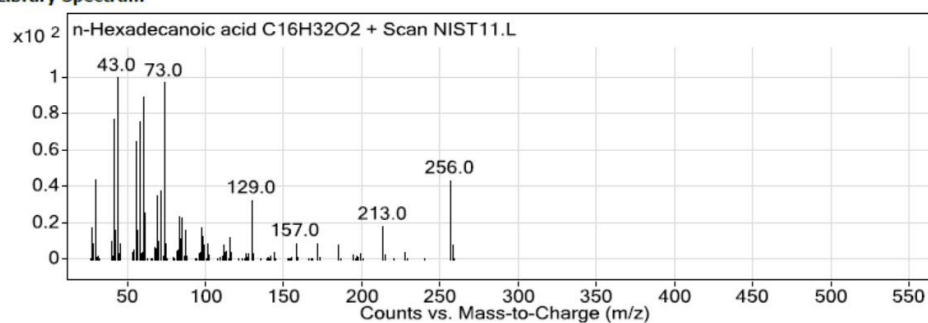
Figure A5 n-Hexadecanoic acid detected by GC-MS compare to library spectrum
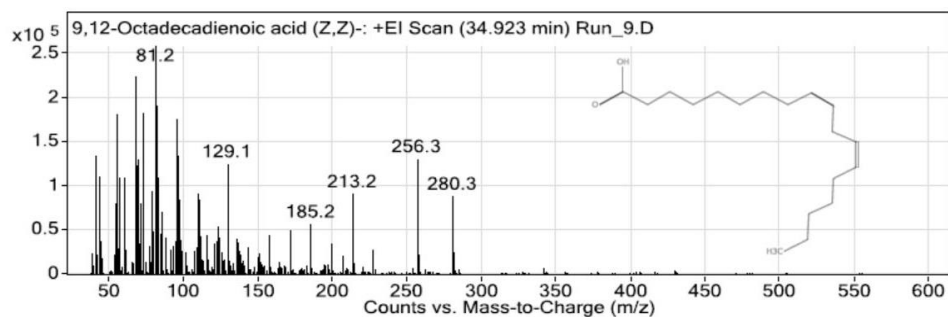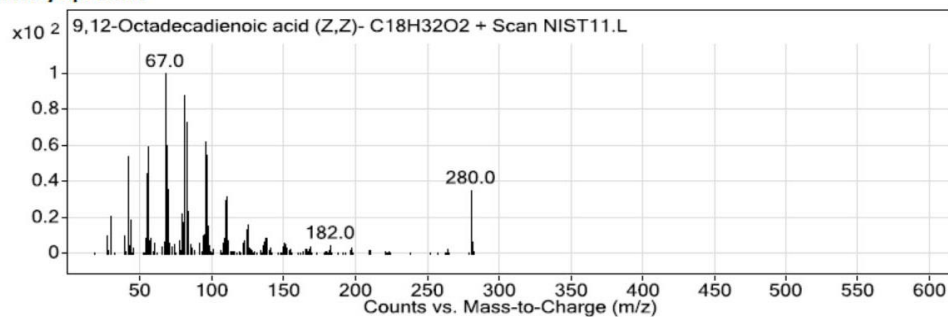
Figure A6 9,12-Octadecadienoic acid (Z,Z) detected by GC-MS compare to library spectrum
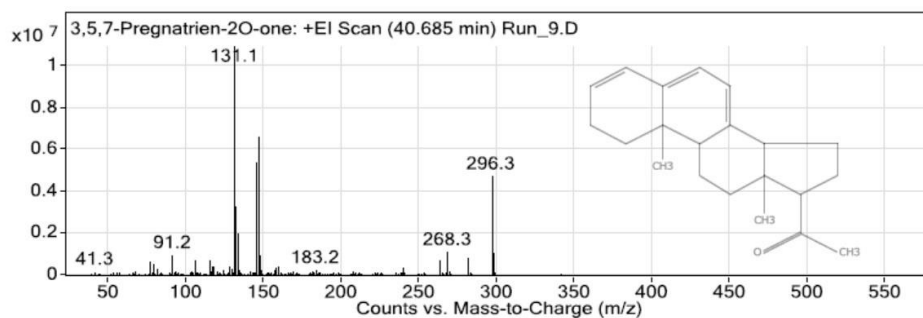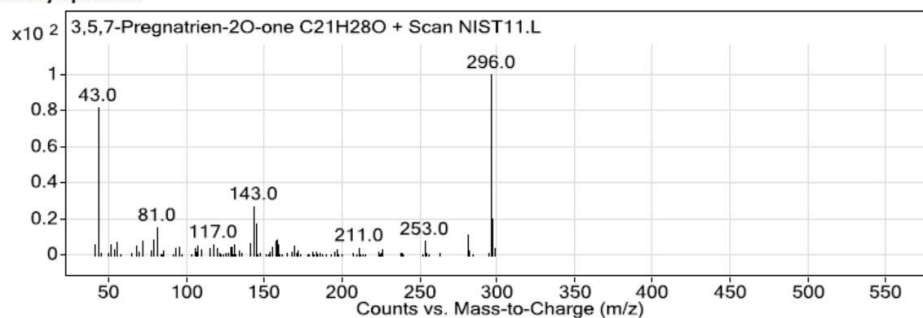
Figure A7 3,5,7-Pregnatrien-2O-one detected by GC-MS compare to library
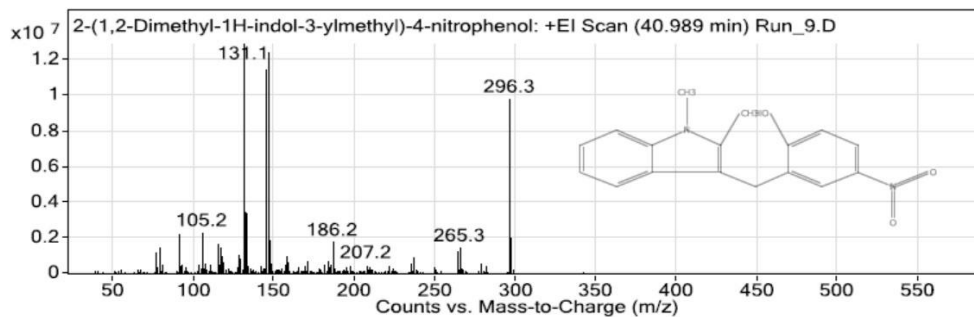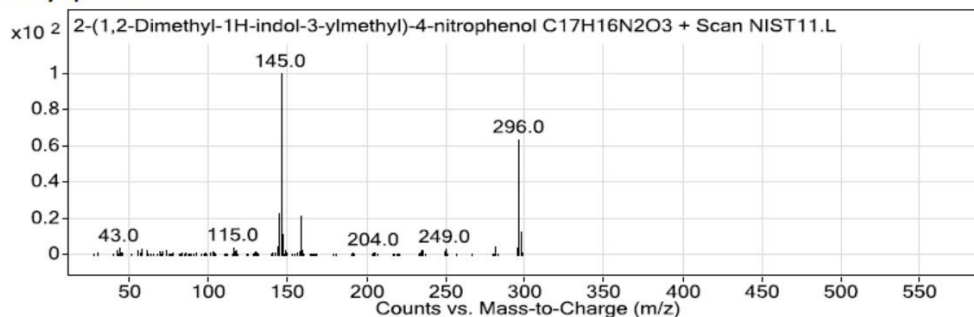
spectrum

Figure A8 2-(1,2-Dimethyl-1H-indol-3-ylmethyl)-4-nitrophenol detected by GC-
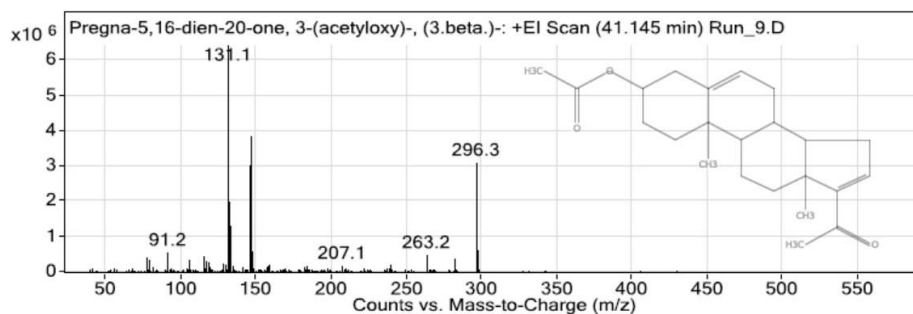
MS compare to library spectrum
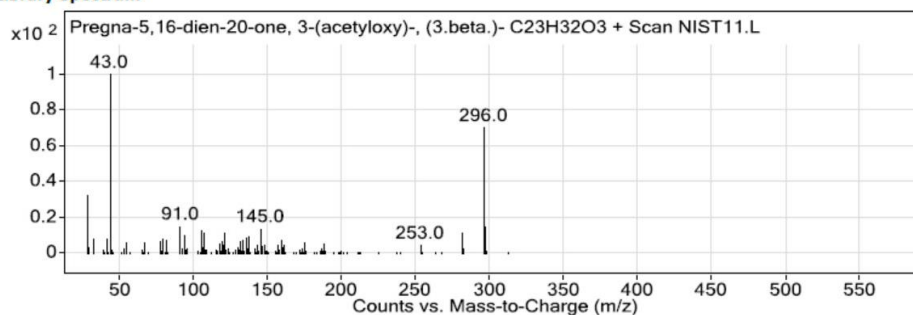
Figure A9 Pregna-5,16-dien-20-one, 3-(acetyloxy)-,(3 beta) detected by GC-MS
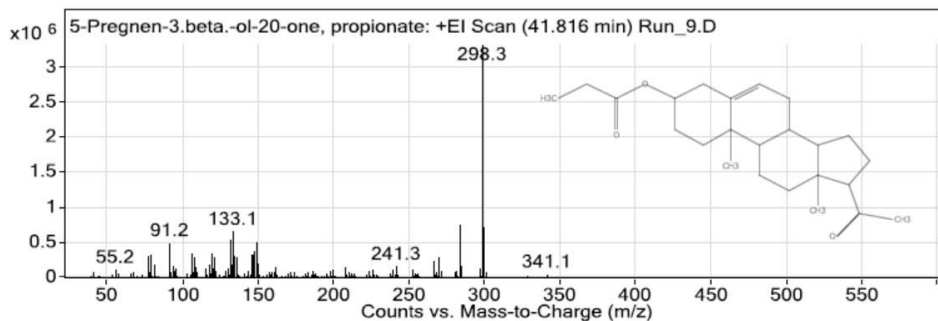
compare to library spectrum.
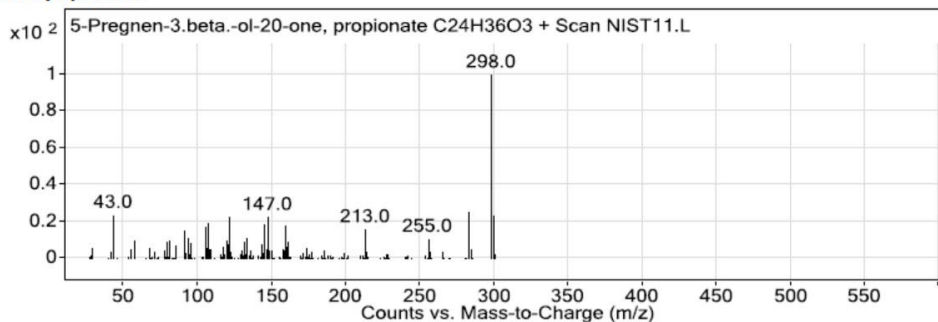
Figure A10 5-Pregnen-3 beta-ol-20-one, propionate detected by GC-MS

compare to library spectrum.

APPENDIX B

CALCULATION OF RESISDENCE TIME IN TUBULAR REACTOR AND

CALIBRATION CURVES FOR BIOFUEL ANALYSIS BY GC

B1. Calculation of residence time in tubular reactor

The calculation of residence time can calculation by the equation as shown in Figure B1

$$\tau = V/v_0 \qquad (1)$$

$$v_0 = \frac{W_{feed}}{\rho_{mixture\ at\ reaction\ condition}} \qquad (2)$$

Figure B1 Equation for calculate the residence time where

τ is the residence time (min)

V is the volume of the reactor (cm^3)

V_0 is volumetric feed flow rate of feed mixture (cm^3/min)

W_{feed} is the flow rate of coffee oil and ethyl acetate mixture (g/min)

ρ is global density of the feed at the reaction condition (g/cm^3)

The global density of the feed mixture was calculated from the study of global density of palm oil and ethyl acetate mixture [62]. The global density of the coffee oil mixture and the residence time in each condition are shown in Table B1 and Table B2.

Table B1 Global density of the coffee oil and ethyl acetate in various temperature

Temperature (°C)	Global density (g/cm^3)
275	0.5411
300	0.4978
325	0.4545
350	0.4112

Table B2 Residence time in tubular reactor in each condition of biofuel production from coffee oil by supercritical ethyl acetate

Feed flow rate (g/min) / Temperature (°C)	2	2.5	3
275	41.5	33.2	27.7
300	38.2	30.6	25.5
325	34.9	27.9	23.3
350	31.6	25.2	21.0

B2 Calibration curve for biofuel product analysis

Ethyl palmitate and ethyl oleate were used as external standards for calculate the amount of FAEE formation in the product. The calibration curves of these standard were shown in Figures B1 and B2. The range of concentration of both standard was 0.625 wt% to 10 wt%.
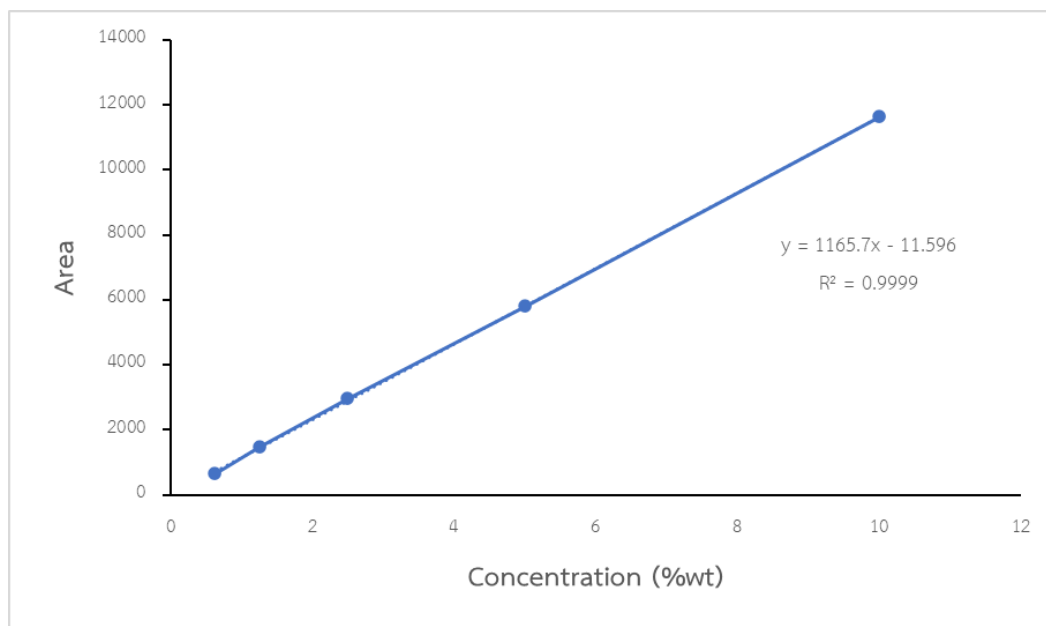
Figure B1 Calibration curve of ethyl palmitate
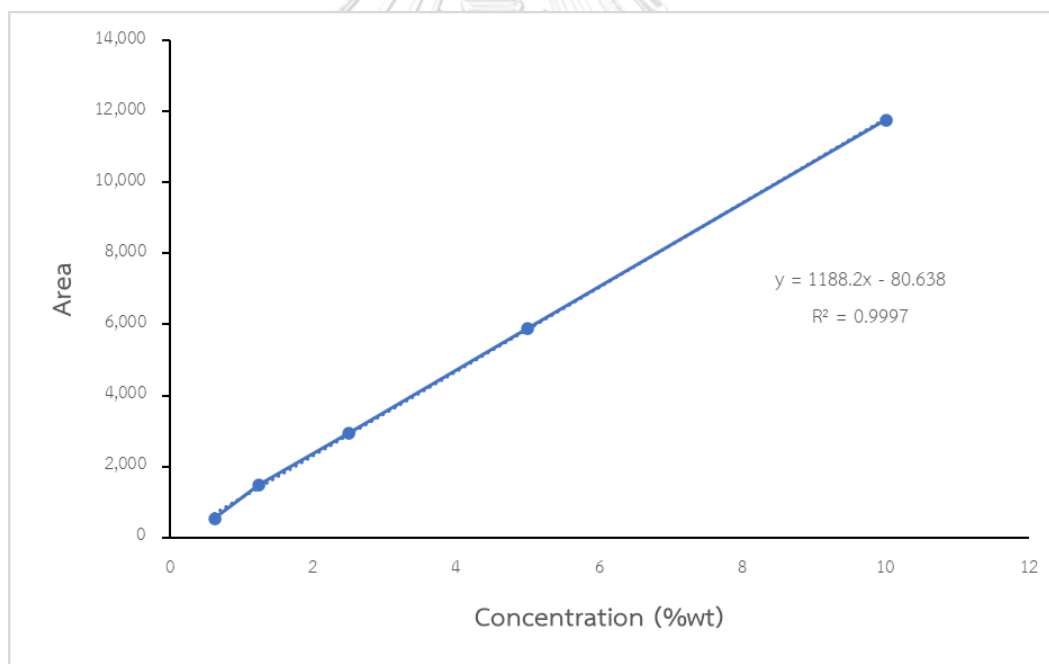
Figure B2 Calibration curve of ethyl oleate

APPENDIX C

THE COMPOSITIONS IN BIOFUEL PRODUCT ANALYZED BY GC-MS
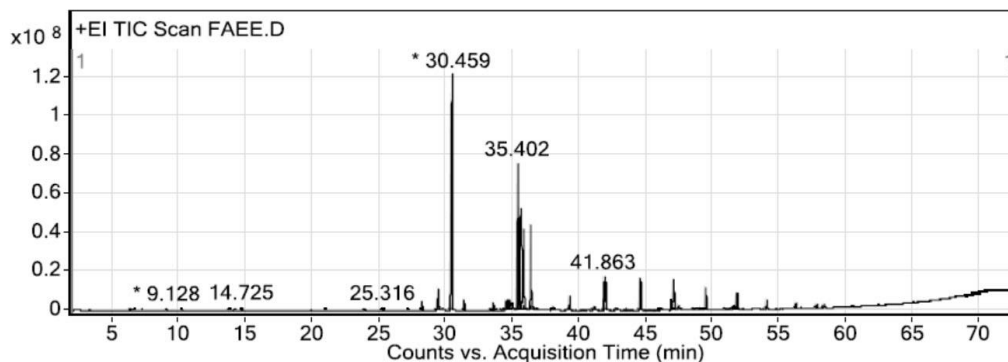
Figure C1 Chromatogram of biofuel product detected by GC-MS

In figure C1 shown the chromatogram of biofuel sample which can detect the compositions in biofuel product as show in this section
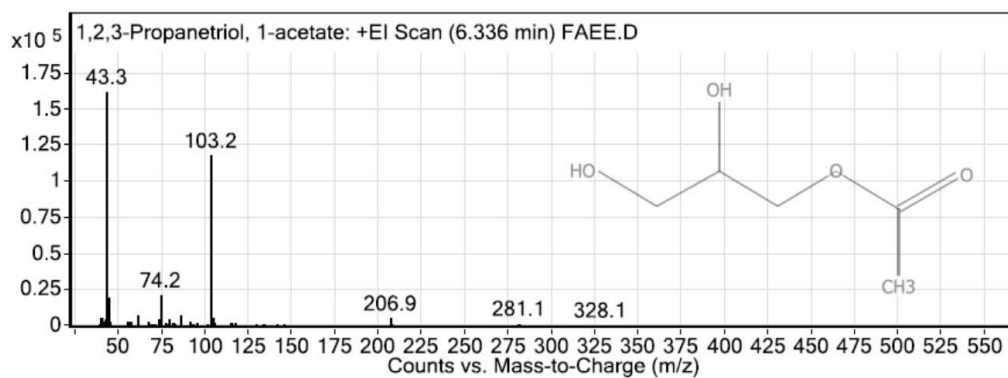
Figure C2 1,2,3-Propanetriol, 1-acetate detected by GC-MS
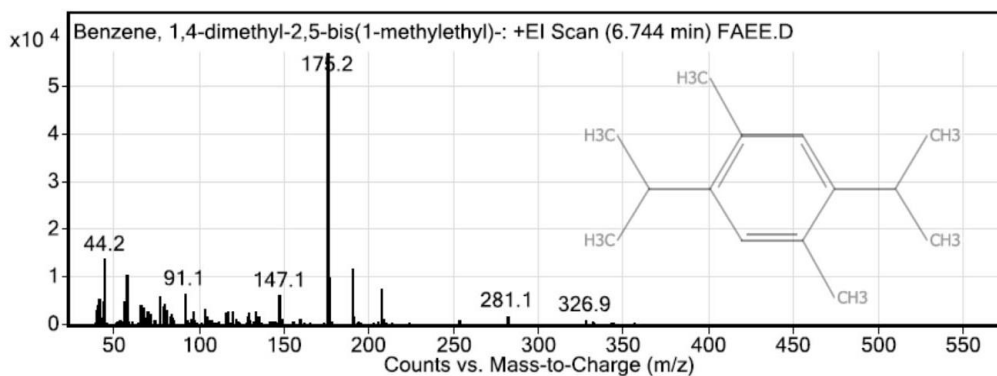
Figure C3 Benzene, 1,4-dimethyl-2,5-bis(1-methylethyl) detected by GC-MS
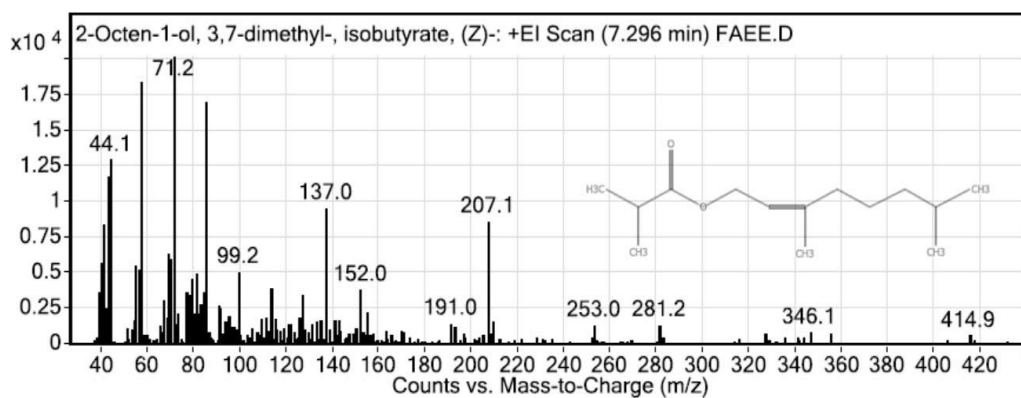
Figure C4 2-Octen-1-ol, 3,7-dimethyl-, isobutyrate, (Z)- detected by GC-MS
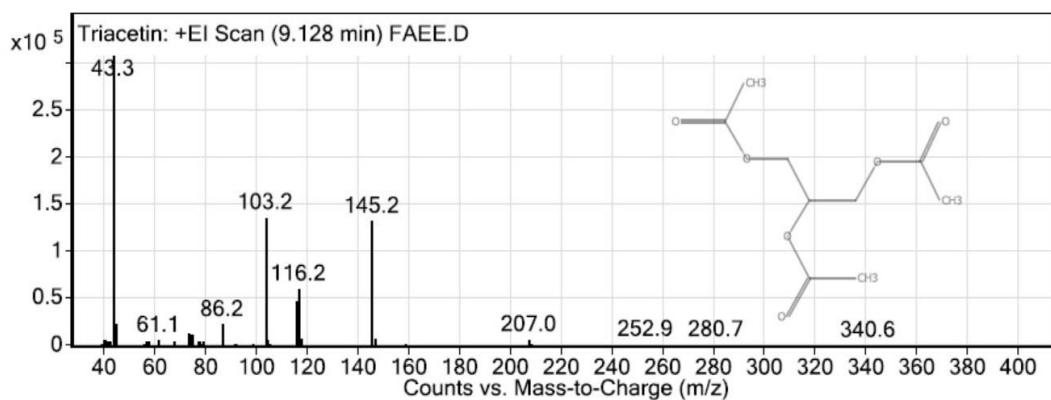
Figure C5 Triacetin detected by GC-MS
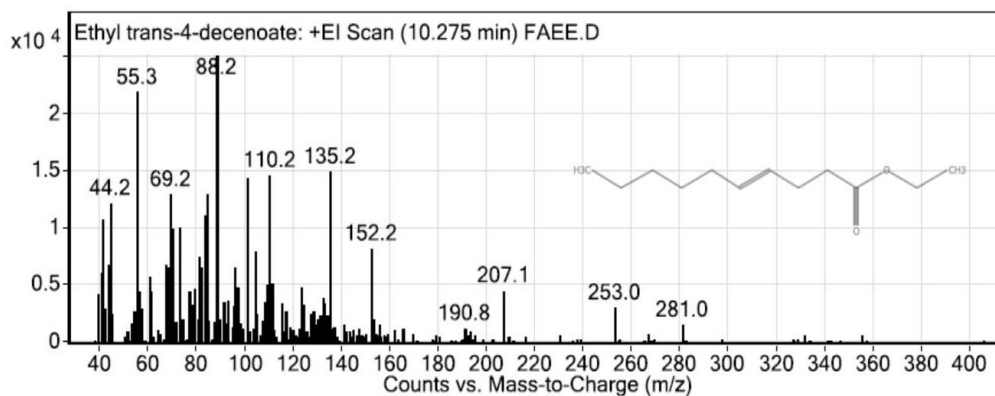
Figure C6 Ethyl trans-4-decenoate detected by GC-MS
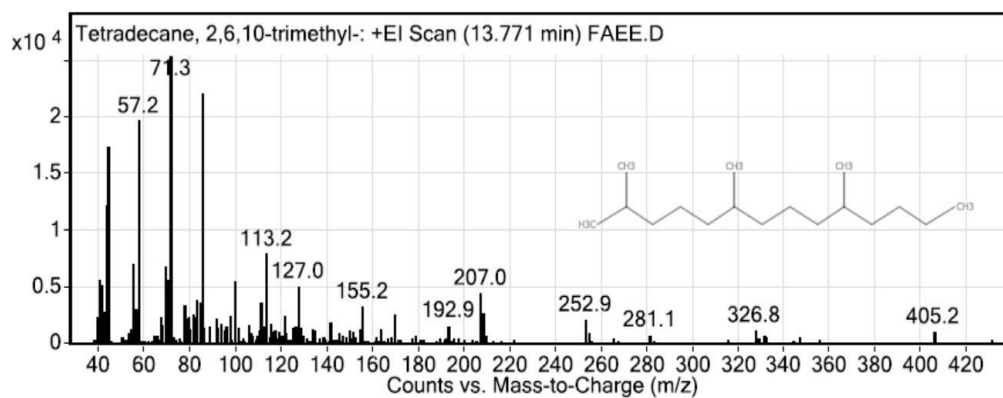
Figure C7 Tetradecane, 2,6,10-trimethyl- detected by GC-MS
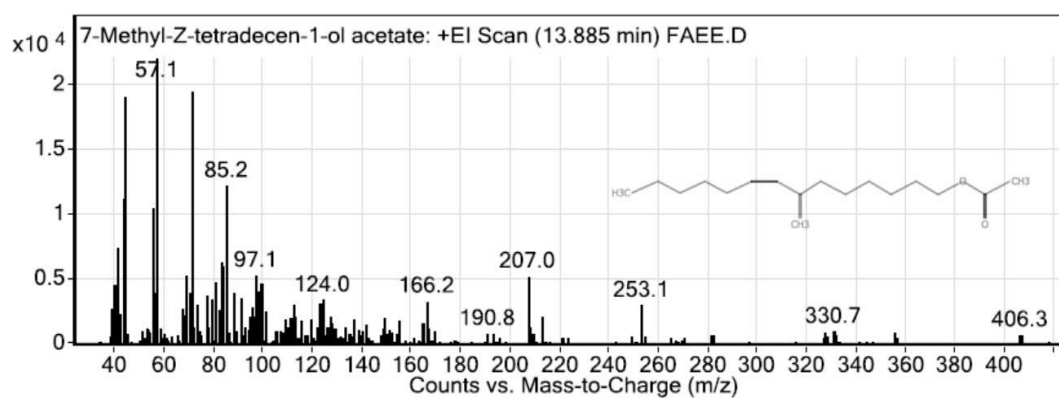
Figure C8 7-Methyl-Z-tetradecen-1-ol acetate detected by GC-MS
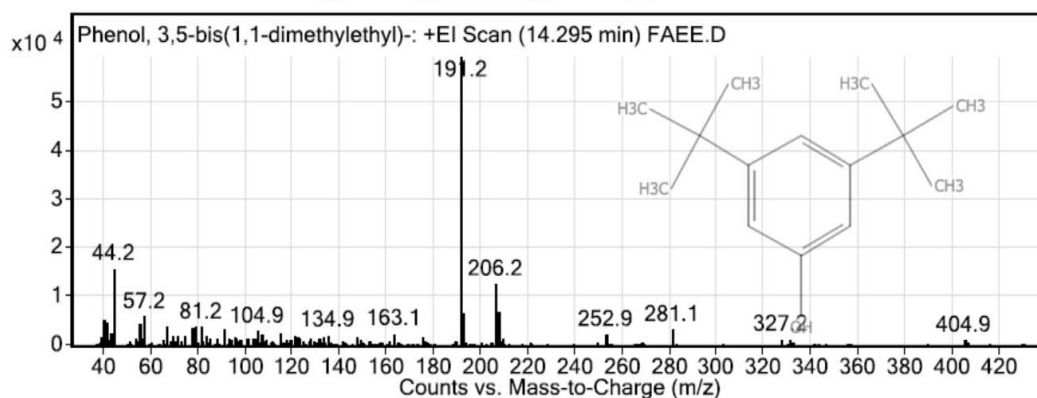
Figure C9 Phenol, 3,5-bis(1,1-dimethylsthyl)- detected by GC-MS
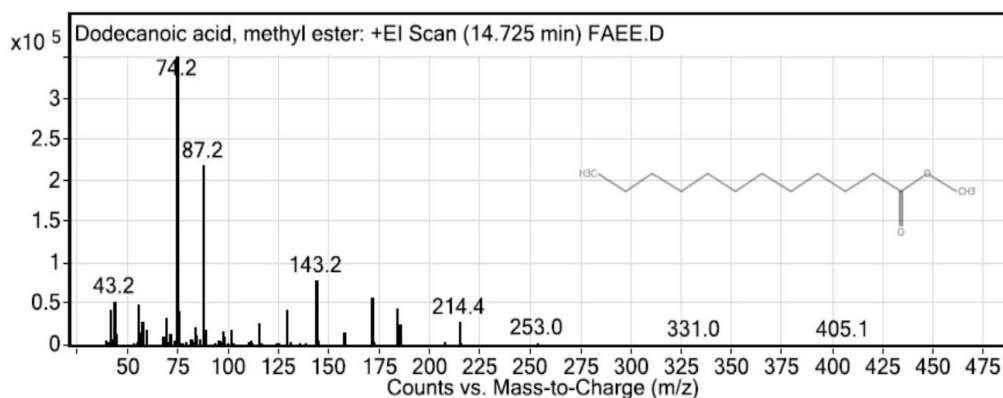
Figure C10 Dodecanoic acid, methyl ester detected by GC-MS
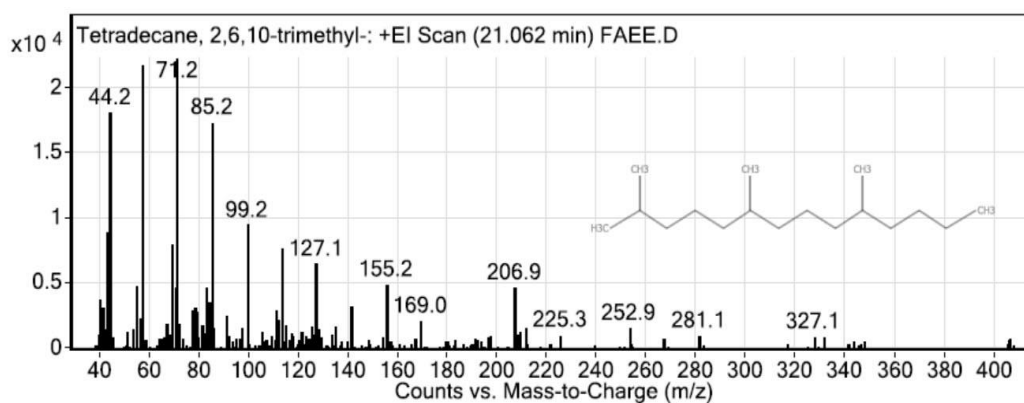
Figure C11 Tetradecane, 2,6,10-trimethyl detected by GC-MS
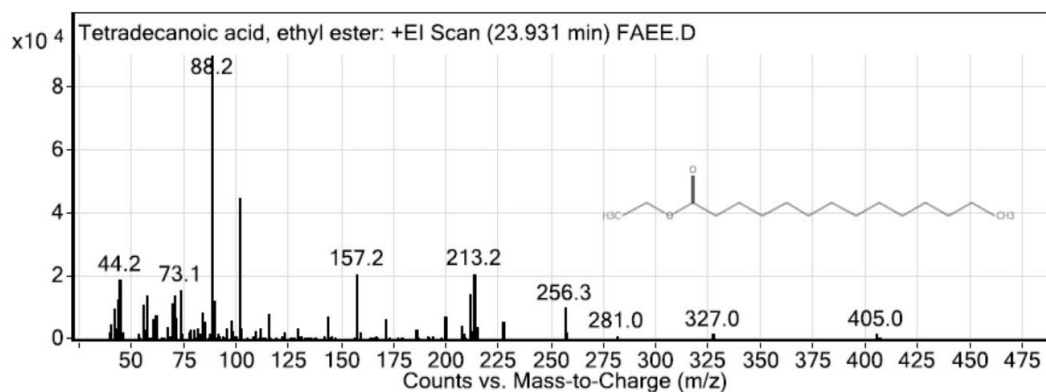
Figure C12 Tetradecanoic acid, ethyl ester detected by GC-MS
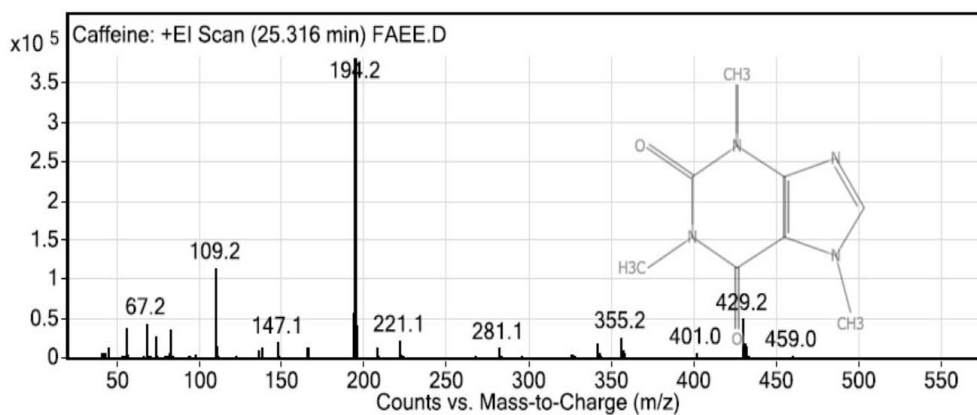
Figure C13 Caffeine detected by GC-MS
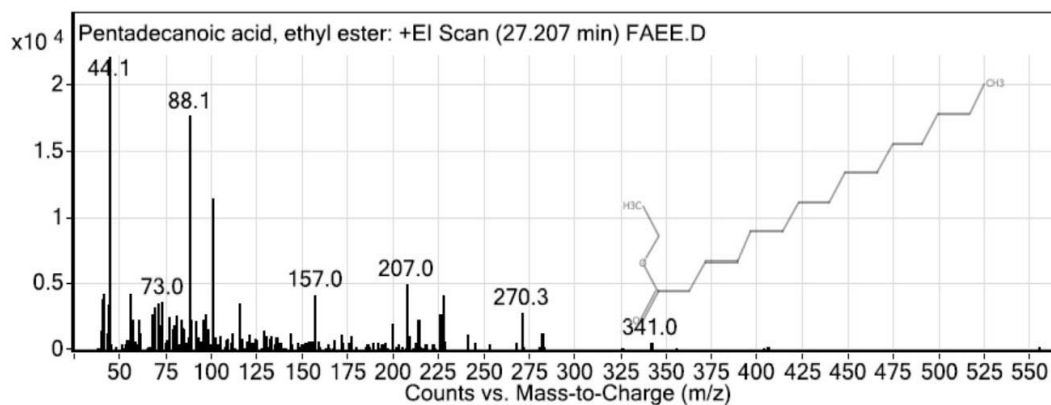
Figure C14 Pentadecanoic acid, ethyl ester detected by GC-MS
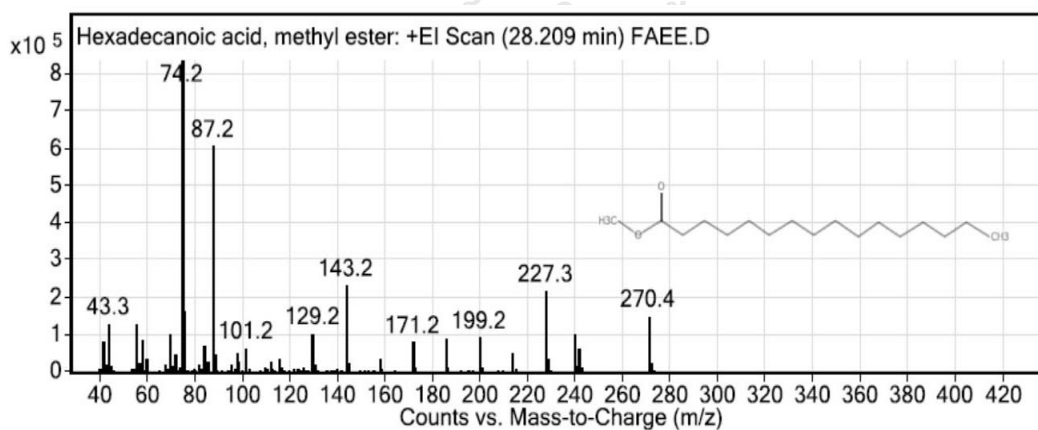
Figure C15 Hexadecanoic acid, methyl ester detected by GC-MS
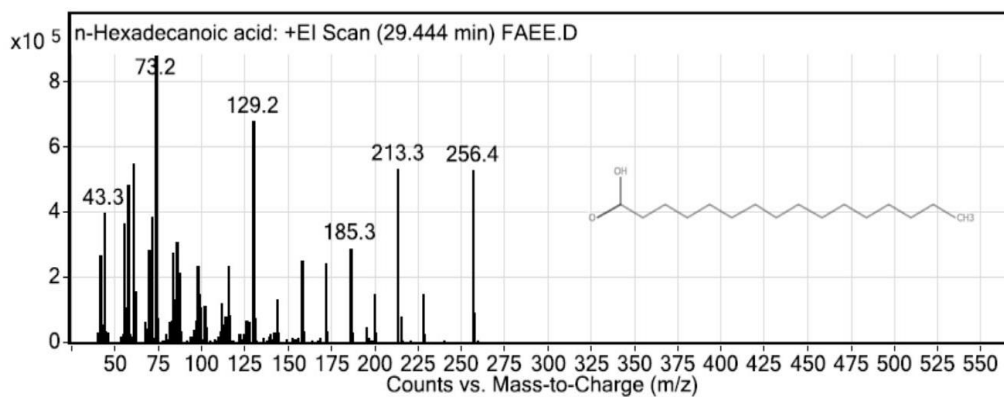
Figure C16 n-Hexadecanoic acid detected by GC-MS
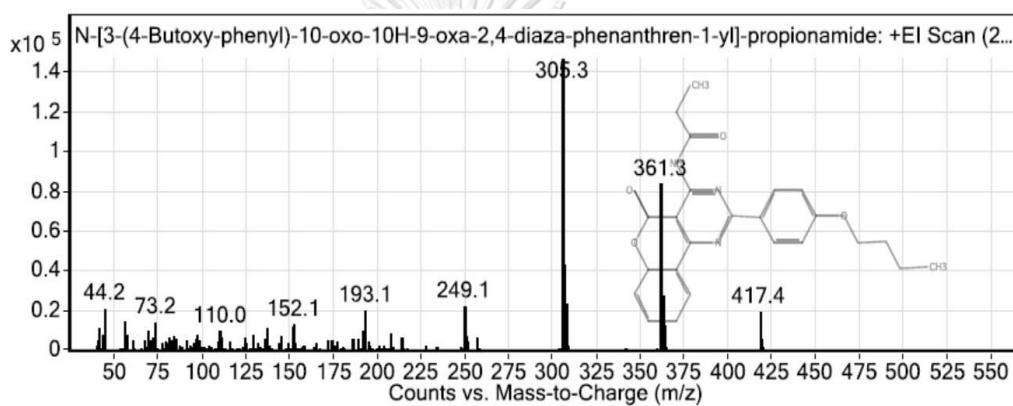
Figure C17 N-[3-(4-Butoxy-phenyl)-10-oxo-10H-9-oxa-2,4-diaza-phenanthren-1-yl]-propionamide detected by GC-MS
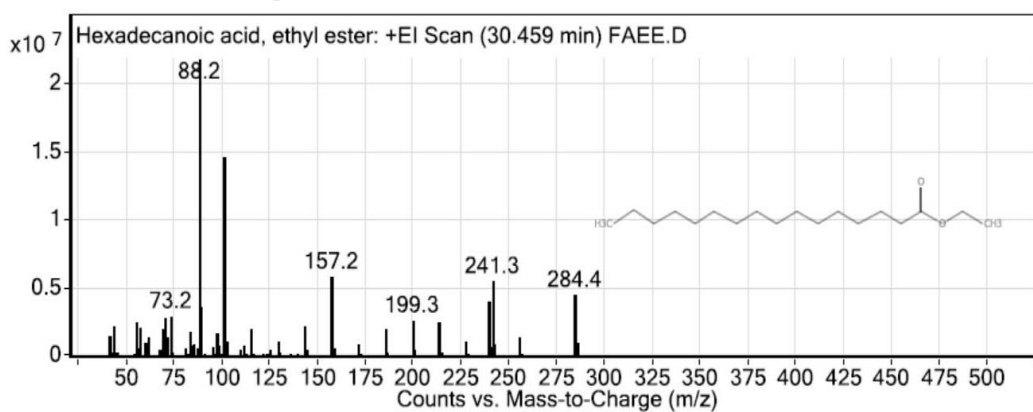
Figure C18 Hexadecanoic acid, ethyl ester detected by GC-MS
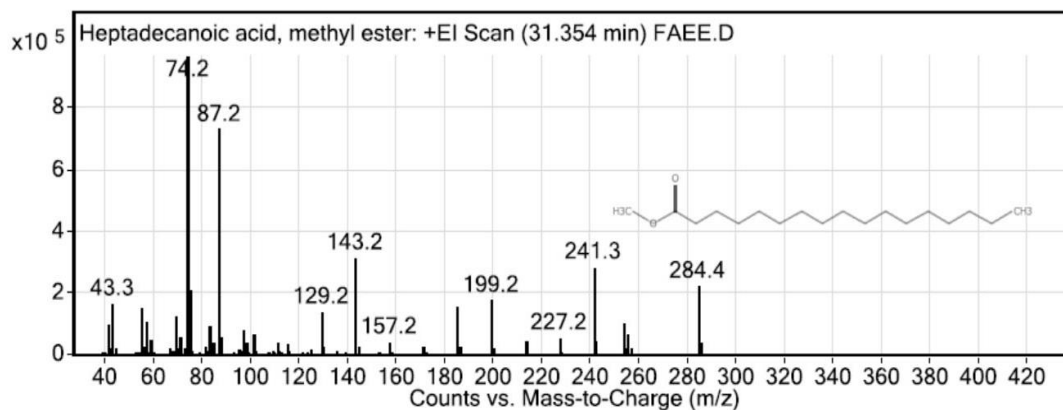
Figure C19 Heptadecanoic acid, methyl ester detected by GC-MS
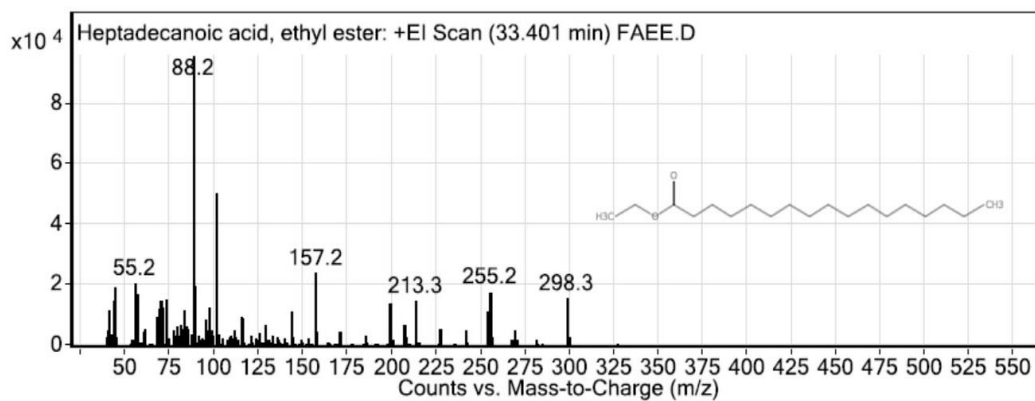
Figure C20 Heptadecanoic acid, ethyl ester detected by GC-MS
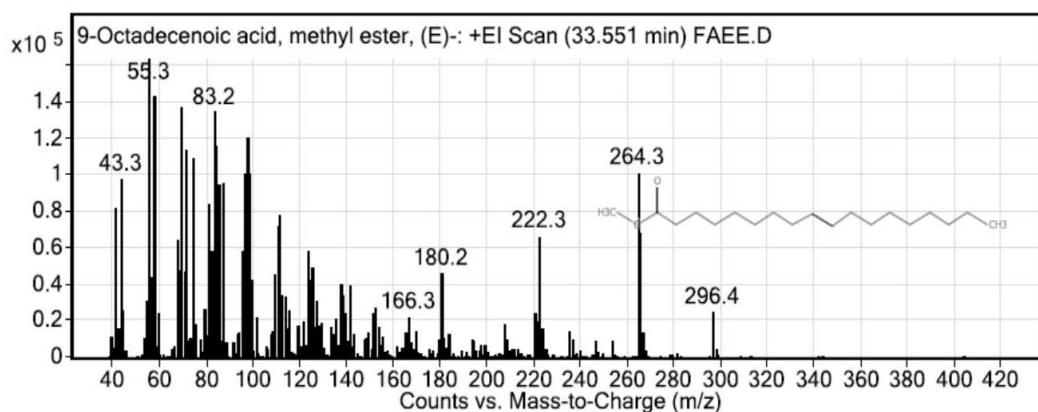
Figure C21 9-Octadecenoic acid, methyl ester detected by GC-MS
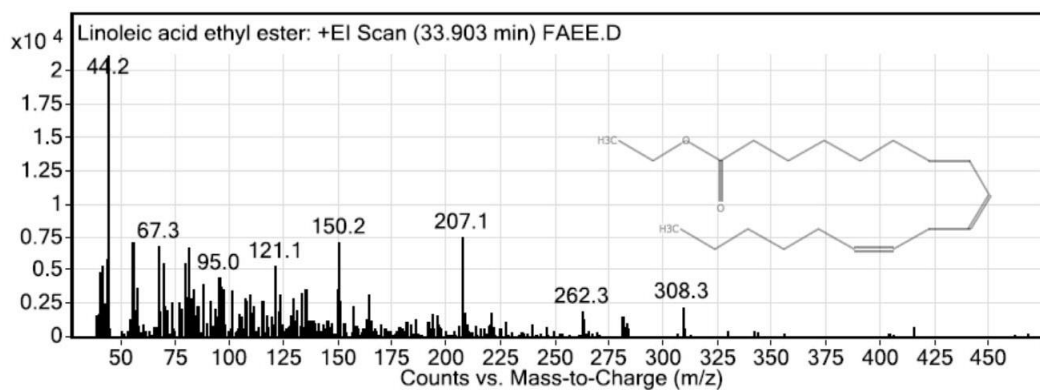
Figure C22 Linoleic acid ethyl ester detected by GC-MS
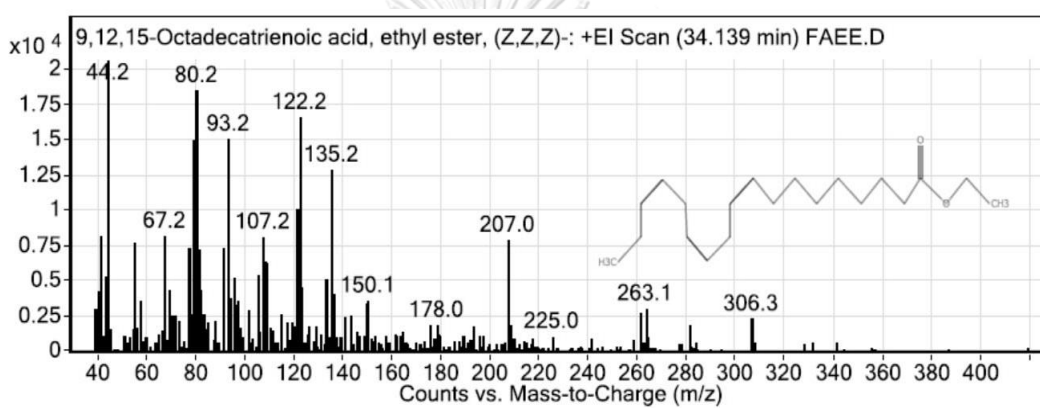
Figure C23 9,12,15-Octadecatrienoic acid ethyl ester, (z, z, z)- detected by GC-MS
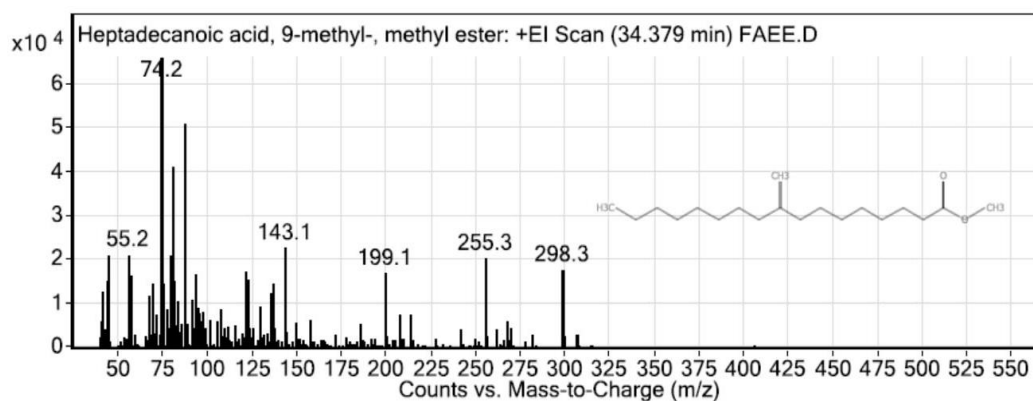
Figure C24 Heptadecanoic acid, 9-methyl-, methyl ester detected by GC-MS
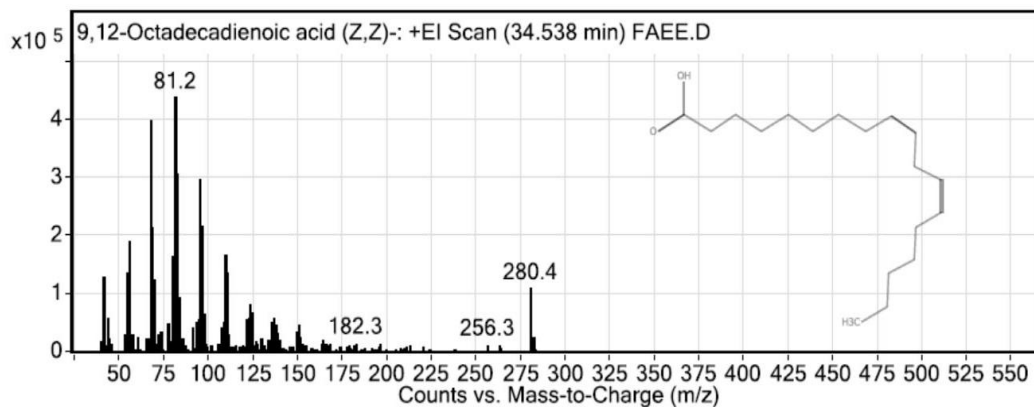
Figure C25 9,12-Octadecadienoic acid (z,z)- detected by GC-MS
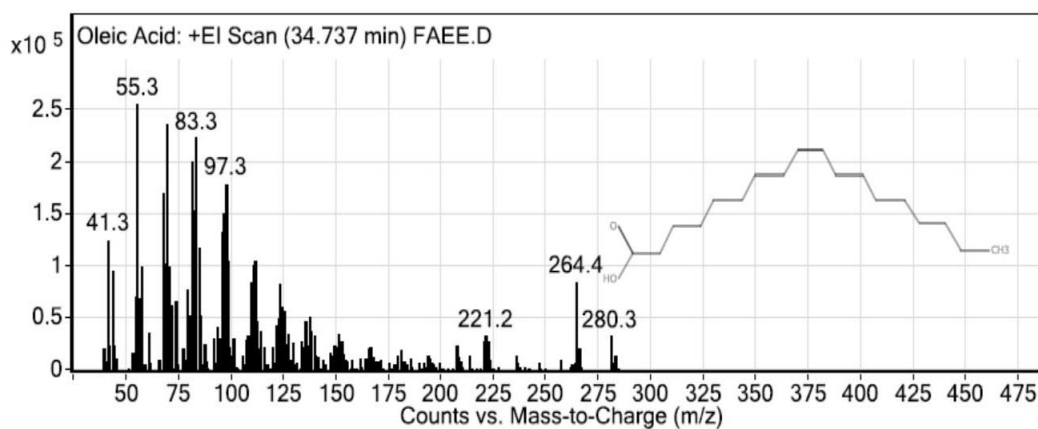
Figure C26 Oleic acid detected by GC-MS
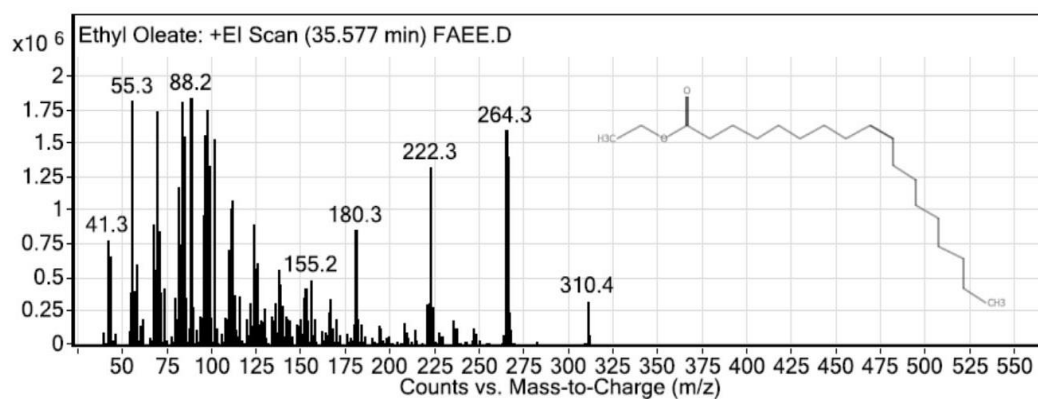
Figure C27 Ethyl Oleate detected by GC-MS
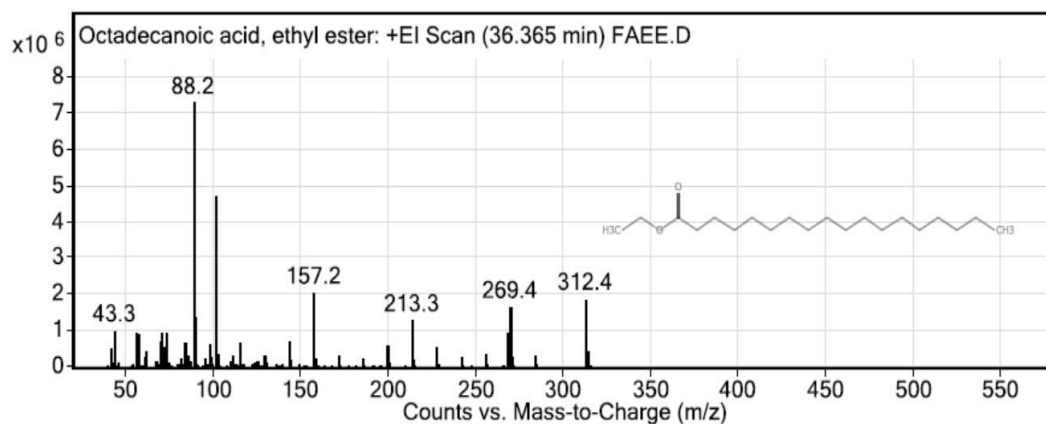
Figure C28 Octadecanoic acid, ethyl ester detected by GC-MS
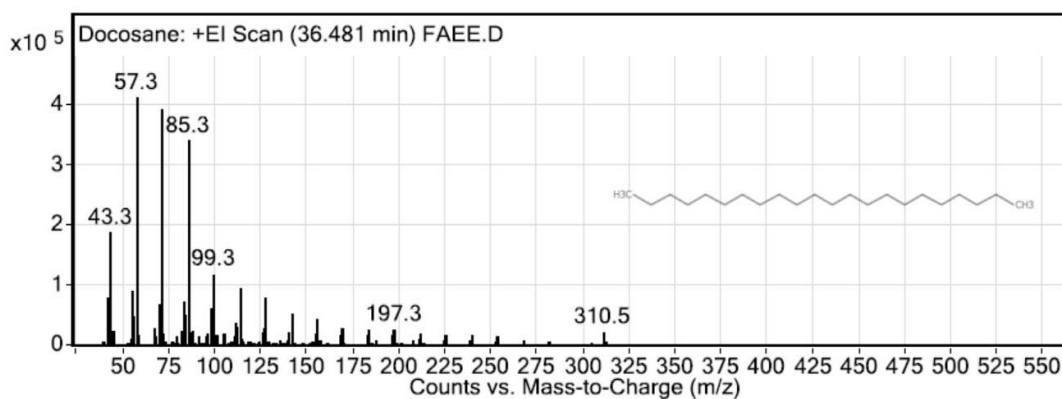
Figure C29 Docosane detected by GC-MS
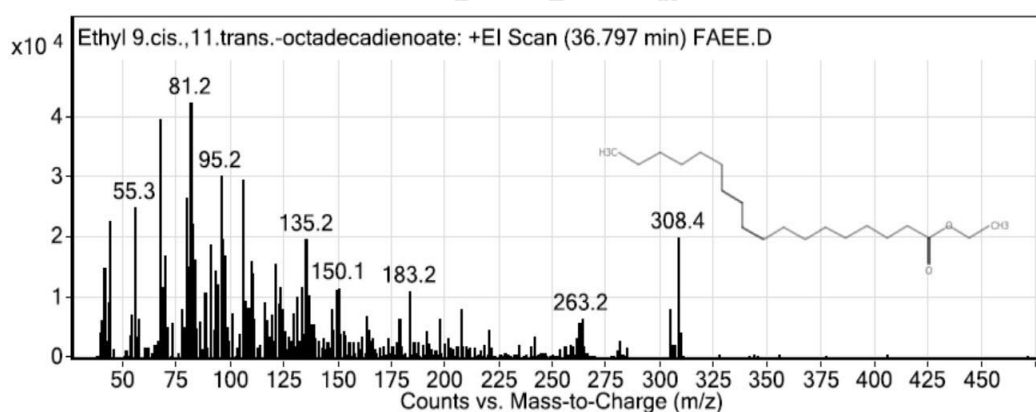
Figure C30 Ethyl 9 cis, 11 trans-octadecadieonate detected by GC-MS
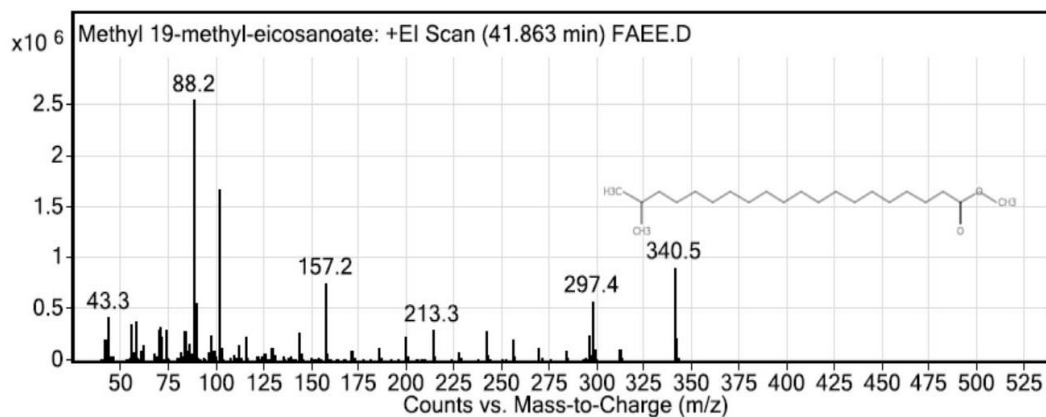
Figure C31 Methyl 19-methyl-eicosanoate detected by GC-MS
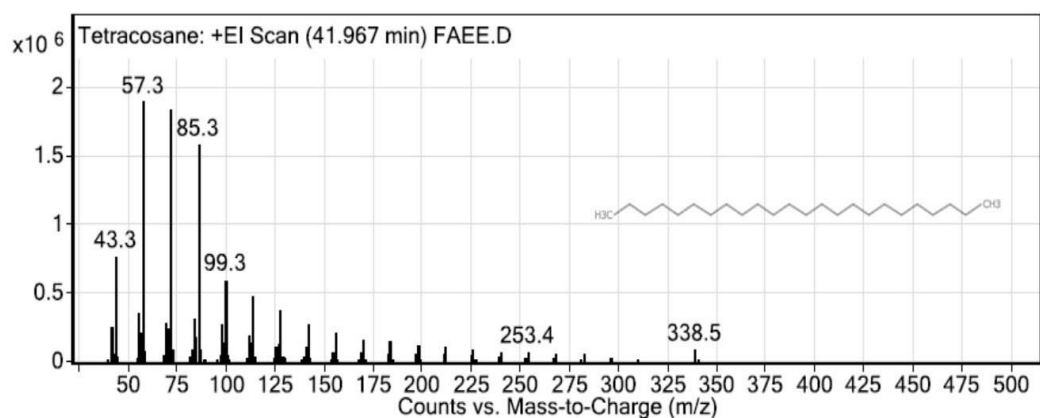
Figure C32 Tetracosane detected by GC-MS
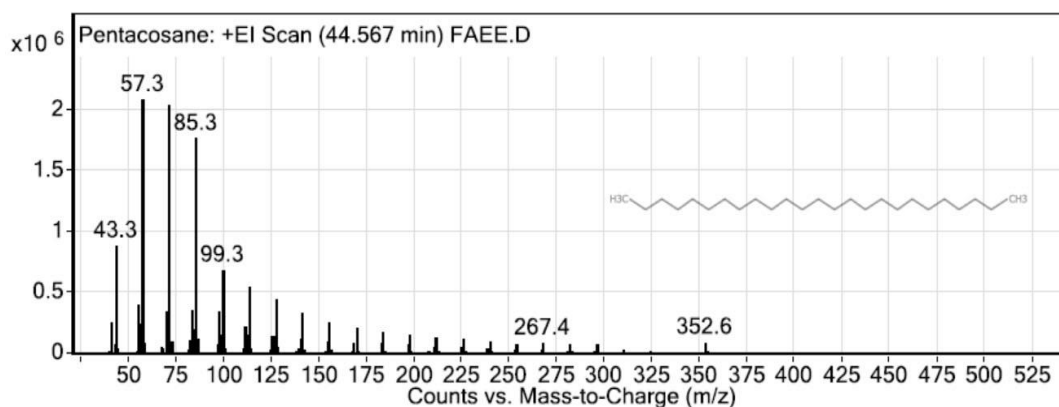
Figure C33 Pentacosane detected by GC-MS
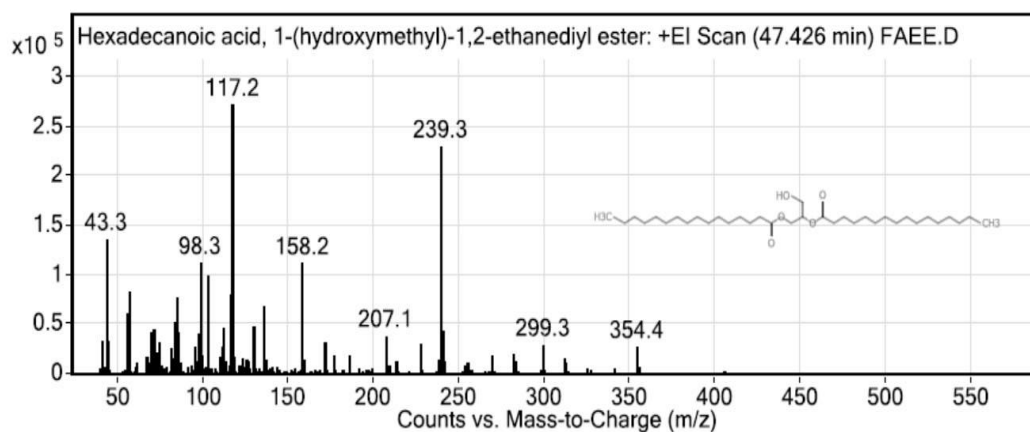
Figure C34 Hexadecanoic acid, 1-(hydroxymethyl)-1,2-ethanediyl ester detected by
GC-MS
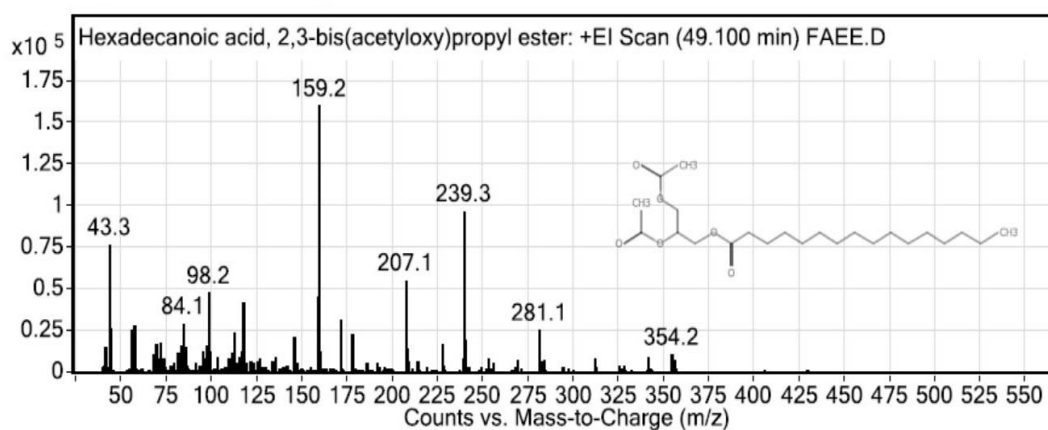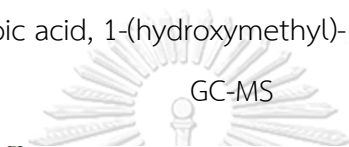
Figure C35 Hexadecanoic acid, 2,3-bis(acetyloxy)propyl ester detected by GC-MS
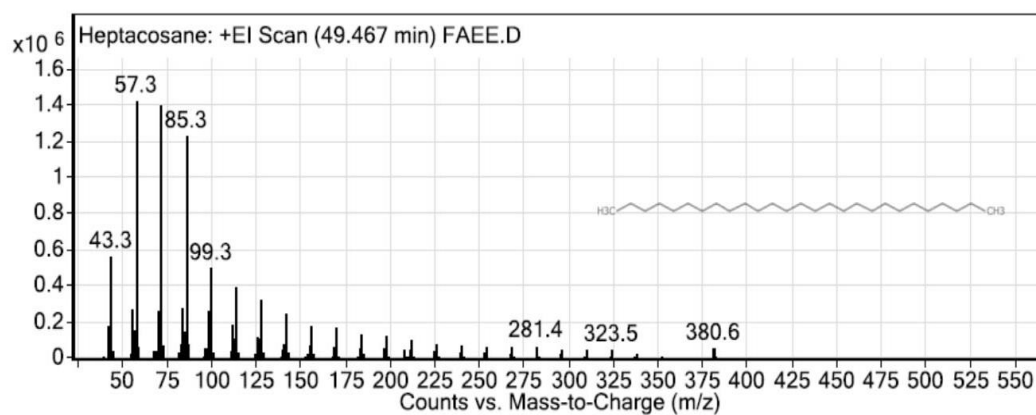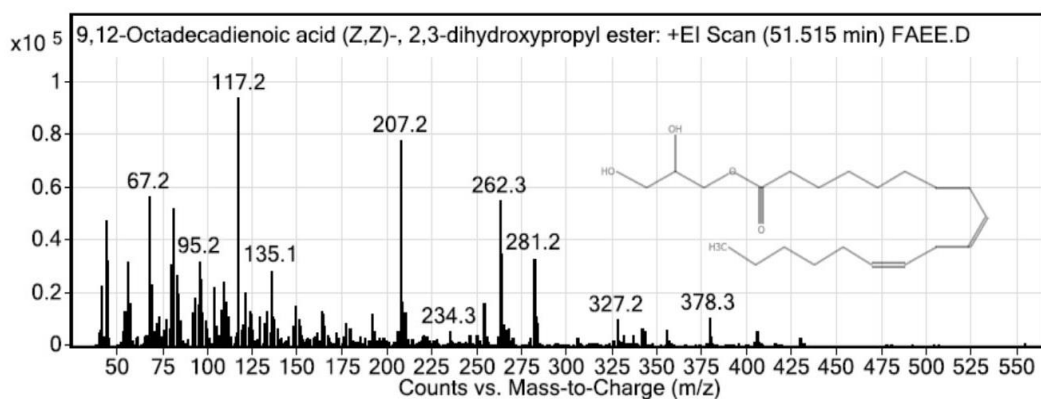

Figure C36 Heptacosane detected by GC-MS

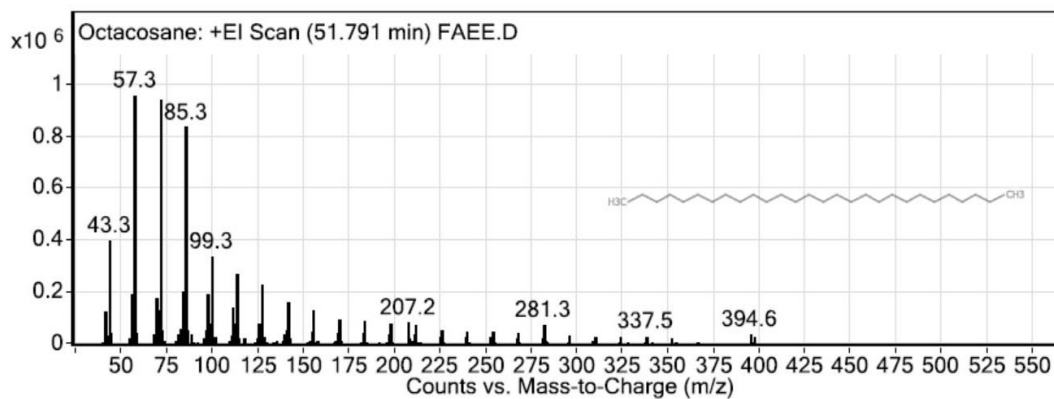**Figure C37** 9,12-Octadecadienoic acid (z,z)-, 2,3-dihydroxypropyl ester detected by

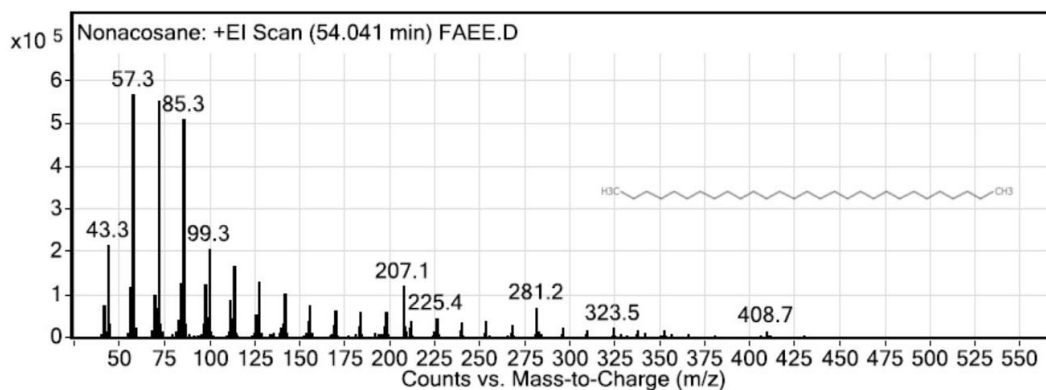GC-MS

Figure C38 Octacosane detected by GC-MS
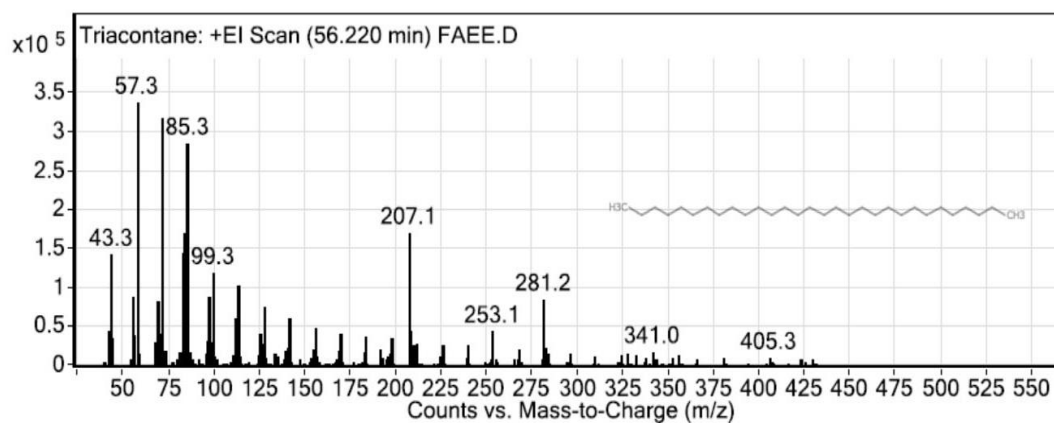

Figure C39 Nonacosane detected by GC-MS

Figure C40 Triacontane detected by GC-MS

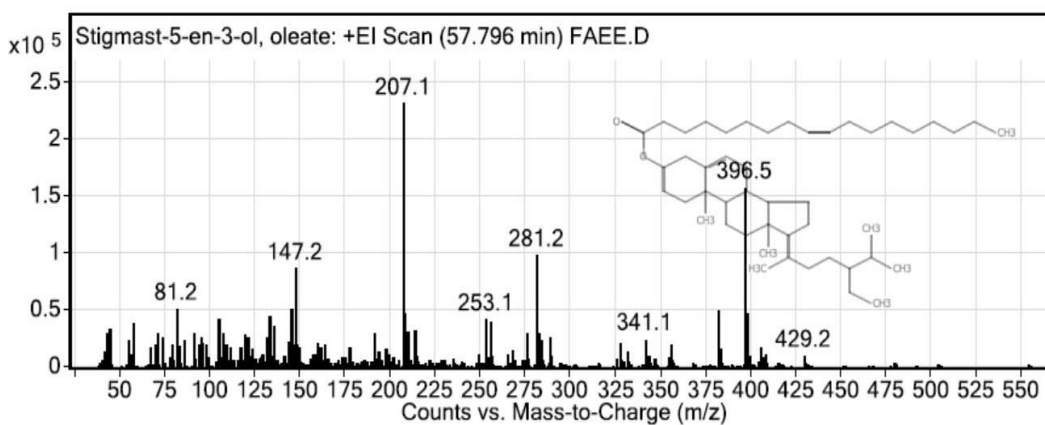**Figure C41** Stigmast-5-en-3-ol, oleate detected by GC-MS

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

VITA

NAME	วิลาสินี ศุภางค์
DATE OF BIRTH	29 มีนาคม 2538
PLACE OF BIRTH	กรุงเทพมหานคร
INSTITUTIONS ATTENDED	มหาวิทยาลัยมหิดล
HOME ADDRESS	725/2 ซอยกิ่งจันทน์ ถนนจันทน์ แขวงบางโคล่ เขตบางคอแหลม กรุงเทพ 10120