Characterization of *Garcinia Mangostana Linn.* Seeds as Potential Feedstocks for Biodiesel Production

L. Nabilah Aminah, S. T. Leong, C. Y. Ho, Y. S. Wong, and C. K. Kairulazam

***Abstract*—Currently, a majority of the world's energy needs are met through the use of fossil fuels, petroleum, coal and natural gas. The depletion of petroleum reserves, rising and extremely volatile crude oil prices, and environmental concerns has led to search for renewable and environmentally friendly fuels - biodiesel. Therefore this study is emphasis on the feasibility of biodiesel preparation from food waste feedstock, *Garcinia Mangostana Linn.* (GML) seed by two-phase solvent extraction (TSE) and two-step transesterification. Nevertheless, the main purposes of this study is to identify the characteristic of GML seed as potential feedstock for biodiesel production by using Fourier transform infraRed spectrometer (FTIR), Thermogravimetry Analyzer (TGA) and Bomb Calorimeter. Hence, a comparison through FTIR analysis was examined between GML seed and GML biodiesel to evaluate the functional group present. The results from the FTIR spectrum indicate that methyl ester of seeds was successfully converted into biodiesel.**

***Index Terms*—Biodiesel, *Garcinia Mangostana Linn.* seeds, two-phase solvent extraction, transesterification.**

I. Introduction

Nowadays, petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, are the majority supplier of the worlds energy needs. All of these sources are dwindling day by day [1]. Each year, Government of Malaysia need to spends US$14 billion for subsidizing gasoline, diesel and gas [2]. Biodiesel seems like a solution for future because of its environmental benefits versus petroleum-based diesel and that is made from renewable resources [3].

Biodiesel oil is derived from vegetable oil or animal fat (triglycerides) react with methanol and a catalyst, yielding fatty acid methyl or ethyl esters (biodiesel) and glycerin as by-product [4]. It is a clean burning fuel produced from vegetable oils and animal grease. Biodiesel is recommended for use as a substitute for petroleum based diesel mainly because it is a non-flammable, biodegradable, non-toxic and favorable combustion-emission profile. It helps to produce much less global warming gas emissions such as carbon monoxide, sulfur dioxide and unburned hydrocarbons compare with petroleum-based diesel [5].

There are three types basic routes that can produce biodiesel form oils and fats, which are base catalyzed transesterification; direct acid catalyzed transesterification; and conversion of the oil and fatty acid then to biodiesel.

Triglyceride converted into fatty acid methyl ester (FAME) reacts with alcohol such as methanol or ethanol, and a catalyst, such as alkali or acid to form esters and glycerol as a by-product is called transesterification process [6]. A successful transesterification process is after certain reaction time has separation of the ester and glycerol [7]. By-product of the process may be sold as it is or it may use in other industries after purified such as pharmaceutical, cosmetics and etc [8].

Prior to transesterification process, two-phase solvent extraction (TSE) method is an advantage to overcome the problem of high free fatty acids contents. Moreover, the addition of acid pretreatment process can reduce the FFA level of *Garcinia Mangostana Linn.* seed oil which suggested by [9]. Besides that, this method also having a lot of advantage including oil leached by hexane, and glusinolate, colloid, free fatty acids colouring matter and other impurities were extracted by a polar solvent phase which was composed of methanol, assistant and water. Furthermore, the quality of product is far better compared with traditional pre-press leaching process [10].

On the other hand, food processing by-product and waste, as well as under-utilized agricultural products have been focused for processing to produce biodiesel. This will reduce the waste disposal problems and can contribute to widen the available resources and thereby various of feedstock for biodiesel production could be utilized [11]. *Garcinia Mangostana Linn.* seeds is one of the food waste from Garcinia Mangostana fruits. It is a one of the most widely recognized tropical fruits, because of its shape, flavor and quality in color. Garcinia Mangostana can possess as anti-inflammatory, antibacterial, astringent, antitumor and antioxidative activities [12].

According to [11], seeds of *Garcinia Mangostana Linn.* showed that they are potential as promising sources of carbohydrate and fat for use as food or feed to bridge the gap of oil deficiency [11]. *Garcinia Mangostana Linn.* seeds oil could be a good edible oil and store with long period without spoilage because of its low level of free fatty acid (4.58 ± 0.16) [11].

Therefore, this study is conducted to determine the characteristics of *Garcinia Mangostana Linn.* seed as potential feedstock for biodiesel production in attempt to reduce the cost of biodiesel production and the problem related to the disposal of seeds. A series of tests will be conducted to investigate the respective characterization properties.

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II. Materials and Methods

A. Materials

Garcinia Mangostana Linn. seeds was obtained from Kelantan, Malaysia. *Garcinia Mangostana Linn.* seeds were removed from the fruits, washed with water and left to air-dry under sun for two days .*Garcinia Mangostana Linn.* Seeds were ground by using mechanical crusher until it become powder form. The powder was then screened by using mesh sample sieve to determine the particle size. Chemicals such as methanol, hexane, sodium hydroxide, acetone, and sulphuric acid were analytical reagent grade and were supplied by A.R. Alatan Sains (K) Sdn. Bhd, Alor Setar.

B. Experimental Procedures

1) Leaching oil process

A Rotary Evaporator (EYELA N-1100S) with maximum 18 mL/min (water) evaporation capacity and a digital water and oil bath (EYELA OSB - 2100) was used for oil leaching process. At the beginning of oil leaching process, 200 ml of methanol, 50ml hexane and 0.2g of sodium dioxide are added into 1L sample flask of rotary vacuum evaporator that equipped with condenser and rotation. The flask is placed in a water bath and heated to 40°C and stirrer is set at 200rpm. 20g ground seed powders were added to flask and the leaching oil process is conducted for 15 minutes. Once the leaching oil process completed, two layers solution were performed: upper layer know as non-polar phase which is contain hexane and seed oil; lower layer know as polar phase which is contain methanol, glucosinolate, desolved FFA and other [9], [10], [13]. Mixture solution in receiving flask is poured into Buchner funnel for separation upper and lower layers of mixture solution. Finally, the upper layer solution was poured into sample flask for next procedure which is synthesizing biodiesel.

2) Acid-catalyzed esterification and alkali-catalyzed transesterification

First, the upper layer solution from leaching process were poured into 1L sample flask and it was immersed in a water bath and heated at temperature of 50°C. The rotary were set at 200rpm to promote a sufficient agitation. Next, a ratio of 4:1 methanol to oil which predissolved sulfuric acid is added into agitated reactor and esterification step was conducted for 15 minutes. After completed those steps, methanol predissolved sodium dioxide is added into agitated reactor again and transesterification step was conducted for certain time. After this, reaction mixture is poured into the funnel to settle for about 2 hours into two layers: the upper layer know as methyl ester phase which is containing commercial hexane, *methyl esters and lower layer know as* glycerol phase which is containing glycerol, methanol, catalyst, and soap [9, 10, 13]. Upper layer need to be washed several times with distilled water at 50°C to remove the residual substances until it become neutral. After the washing process, the methyl ester phase were firstly evaporated to 95°C has removed the hexane by using dried 110°C in an oven to remove its remaining impurities until its weight become constant. The final product was biodiesel.

3) Analytical Methods

Thermogravimetric analysis (TGA) of *Garcinia Mangostana Linn.* seeds was performed using Mettler Toledo TGA-DSC1, the experiments were carried out under continuous nitrogen flow of 20mLmin^{-1}, and the temperature ramp was set at 10 °C min^{-1}. The weight loss was recorded from 25 °C – 850 °C and infrared (IR) spectrums of biodiesel and raw material were obtained using a Fourier Transformed Informed Spectrometer (FTIR) model PerkinElmer Spectrum 400FT-IR/FT-NIR spectrometer. CAL2k calorimeter system with supply oxygen at a pressure of 3.0-3.5MPa within 10 meters was use to analyzed high heating rate (HHR) of raw material.

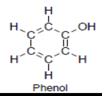
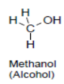
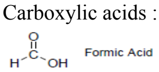
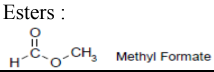
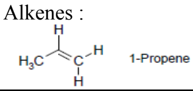
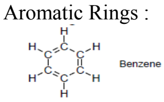
III. Results and Discussions

A. Garcinia Mangostana Linn. seed Characterization

1) Fourier Transform InfraRed Spectrometer (FTIR) Analysis

Fig. 1 shows that the FTIR spectra of *Garcinia Mangostana Linn.* seeds. From the FTIR analysis of GML seed, the functional groups presented are listed in Table I. Spectra show the C=O group of ester at frequency around 1730-1755 cm^{-1} and C-O group of alcohols, carboxylic acids, esters, ethers at frequency around 1000-1320 cm^{-1}. The structure peak is due to the C=O and C-O bonding, which is potential for conversion of ester into methyl ester [14]. Hence, it shows strong evidence that the oil extract from above raw materials may be used as a fuel oil.

TABLE I: FTIR Analysis of *Garcinia Mangostana Linn.* Seed

Functional groups presents	Wave number in cm^{-1}	Type of Vibration
Phenols & alcohols:  	3600 - 3100	Hydrogen-bonded O-H Stretch
Carboxylic acids : 	3400 - 2400	Hydrogen-bonded O-H Stretch
Esters : 	1755 - 1650	C=O Stretch
	1300 - 1000	C-O Stretch
Alkenes : 	1675 - 1600	C-C=C Symmetric Stretch
	1000 - 650	=C-H bend
Aromatic Rings : 	1500 - 1450	C-C=C Asymmetric Stretch

2) Thermogravimetric Analysis (TGA) Analysis

Fig. 2 presents the thermogravimetric curves for *Garcinia Mangostana Linn.* seeds. Through the TGA curve, *Garcinia Mangostana Linn.* seeds in moisture of 1.05%, carbon oxide of 64.95%, and carbon dioxide of 28.02%. From the plot curve, the first region of weight loss obtained at about

80-90°C. This indicates that dehydration of biomass occurred due to the percent loss of water from raw material. It was observed from decomposition of raw material started at 200°C in the second region of weight loss around 200°C. This result attributed to vaporization of organic matter and initial of thermal degradation of raw material at that temperature. The higher thermal stability of the seed is related to its structure typically composed of tryacyglycerol (higher molecular weight) whilst the raw material is composed by a mixture of free esters [15]. This indicates that *Garcinia Mangostana Linn.* seeds have the good potential to produce biodiesel as well. For the third region of weight loss was observed in the range of 360-370°C which attributed to the rapid heating of sample, where most of the thermal decomposition of *Garcinia Mangstana Linn*. seeds occurs [14].

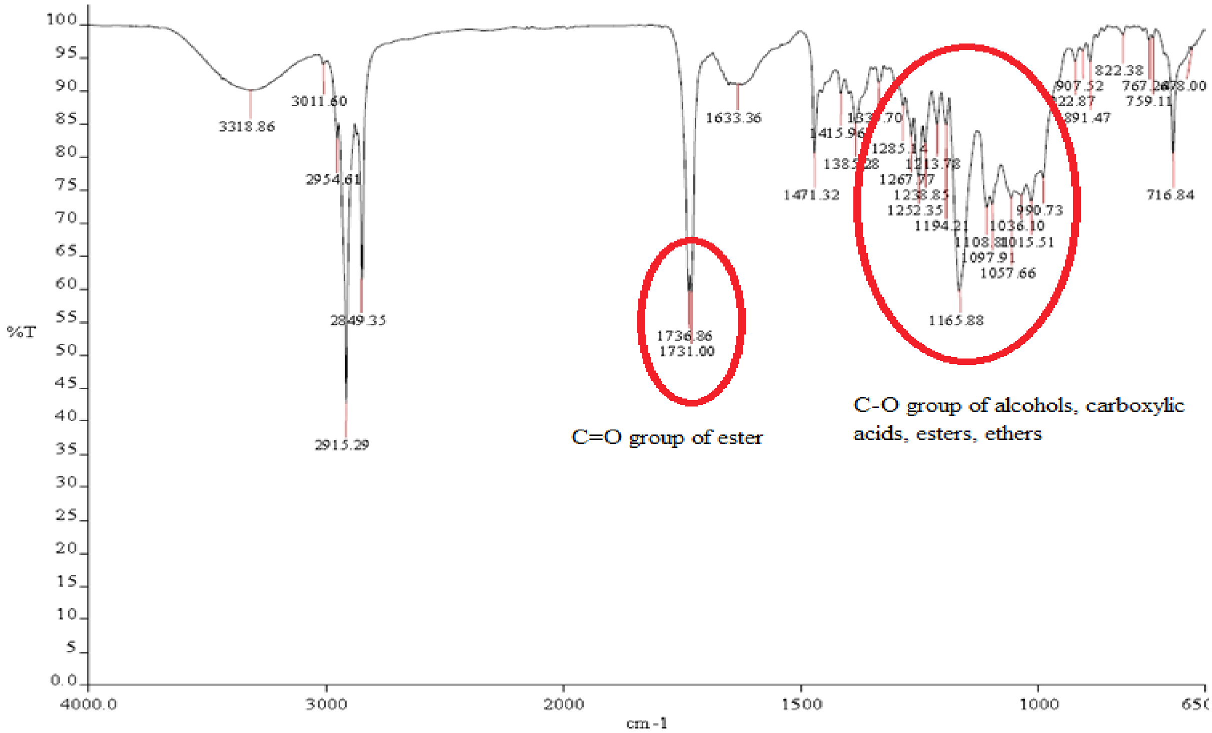


Fig. 1. FTIR spectrum for *Garcinia Mangostana Linn.* Seeds

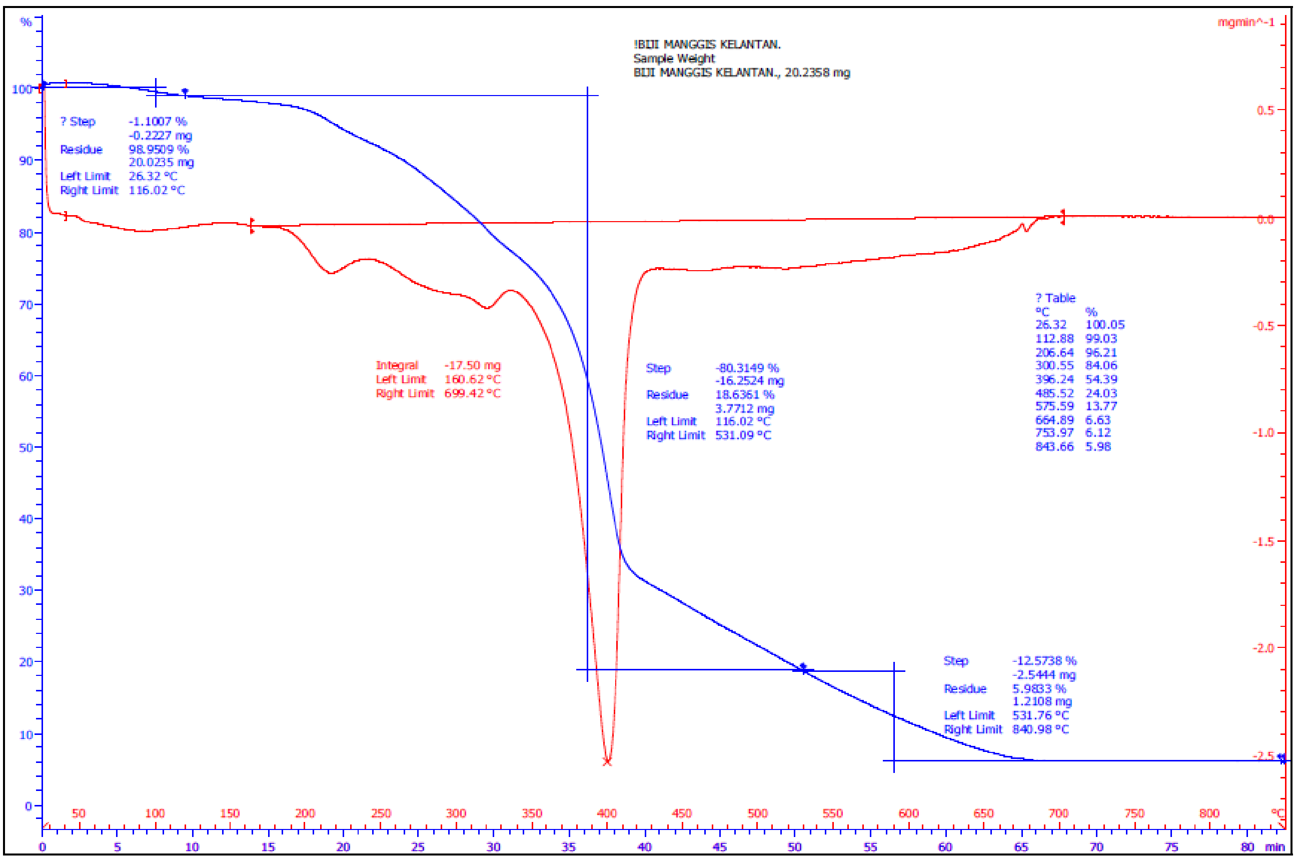


Fig. 2. TGA curve obtained from *Garcinia Mangostana Linn.* Seeds

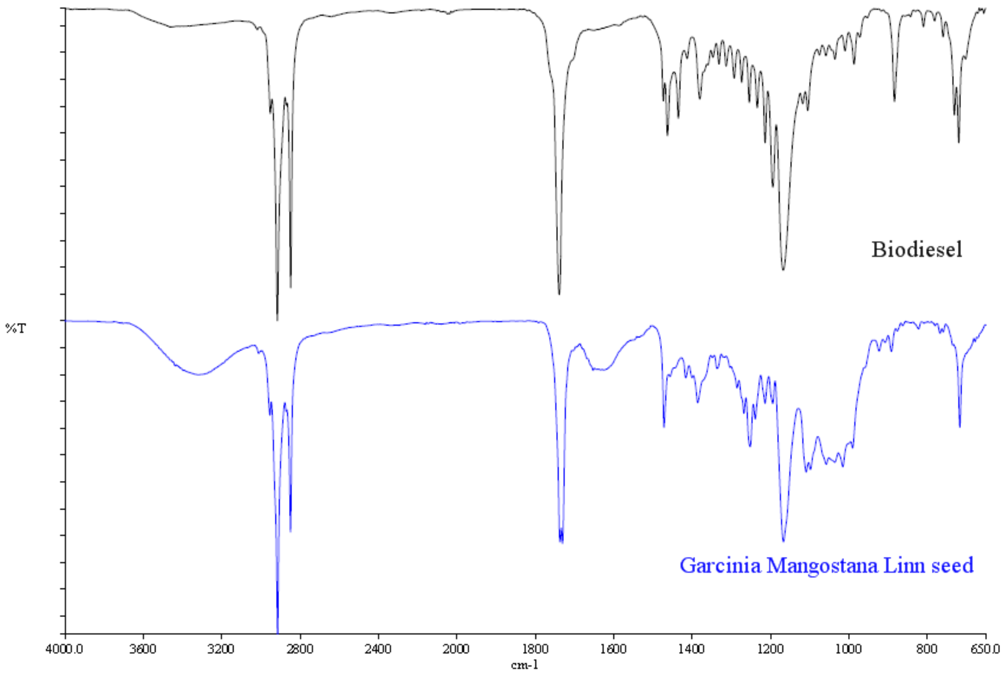


Fig. 3. Comparison FTIR spectrum between G.M.L. seeds and G.M.L. biodiesel

3) High heating rate value (HHV) Analysis

High Heating value (HHV) is an important property of the fuel's characterization. It defines its energy content and thereby its efficiency of fuel as well [16]. Direct domination of heating value of raw material occur when an increasing percentage of the saturated fatty acid from the raw material and a decreasing

acid value of the raw material [17]. Table II shows that high heating rate for *Garcinia Mangostana Linn.* seeds and it indicated *Garcinia Mangostana Linn.* seed was potential for produce biodiesel since heating value for general biodiesel is around 37 KJ/g to 41 KJ/g [16]-[18].

TABLE II: HIGH HEATING VALUE (HHV) FOR *GARCINIA MANGOSTANA LINN.* SEEDS

No.	Weight (g)	Heating rate (KJ)	Heating rate value (KJ/g)
1	0.2149	27.4485	127.73
2	0.2096	25.3562	120.97
		Average	124.35

B. GML Biodiesel Characterization

GML biodiesel characterization was only done using FTIR analysis for the purpose of comparing it with the GML seed (raw) (Fig. 3). It shows that characteristic of FTIR spectrum of G.M.L. seeds is almost similar with G.M.L. biodiesel and in addition, it indicated methyl ester of seeds was successfully converted into biodiesel. The possible structure obtained from FTIR spectrum of methyl esters from both samples including alkyl group (general and long chain substituent), carboxylic acid ester (possible aliphatic), aliphatic ester (possible formate), and carbonyl compound [14].

IV. CONCLUSIONS

This research shows successful characterization of G.M.L. seeds as the potential raw material for biodiesel production using FTIR, TGA and high heating rate analysis by Calorimeter bomb. The FTIR spectrum of GML seed depicts the present of the features of fuel oil/biodiesel base on the functional groups that represent the oil extract from the raw GML seed. In TGA analysis, the higher thermal stability of the seed is related to its structure typically composed of tryacyglycerol (higher molecular weight) whilst the raw material is composed by a mixture of free esters. Besides, high heating rate for G.M.L seeds which is around 124.35 KJ/g indicated G.M.L. seed was potential for making biodiesel. As a conclusion, *Garcinia Mangostana Linn.* seed is a potential feedstock that can reduce the cost of biodiesel production and the problem related to the disposal of seeds.

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