SYNTHESIS, CHARACTERIZATION, AND EVALUATION STUDY ON TRANSESTERIFICATION OF SOLID ACID CATALYSTS DERIVED FROM WASTE BANANA TRUNKS FOR BIODIESEL PRODUCTION

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LIST OF SYMBOLS AND ABBREVIATIONS

NaOH	Sodium hydroxide
KOH	Potassium hydroxide
NaCl	Sodium chloride
$BaCl_2$	Barium chloride
$CaCl_2$	Calcium chloride
K_2CO_3	Potassium carbonate
DCM	Dichloromethane
H_2SO_4	Sulfuric acid
$-SO_3H$	Sulfonic acid
FAME	Fatty acid methyl ester
OA	Oleic acid
MeOH	Methanol
%	Percentage
wt%	weight percent
w/v	weight by volume
ºC	degree Celsius
ºC/min	degree Celsius per minute
mL/min	millilitre per minute
mm	millimetre
um	micrometre
m	metre
mL	millilitre
uL	microlitre

g	gram
rpm	rotations per minute
W	Watt
N	Normality
FTIR	Fourier-Transform Infrared Spectroscopy
TGA	Thermogravimetric analysis
GC-MS	Gas Chromatography-Mass Spectrometry

ABSTRACT

In recent years, with energy resources getting exhausted and worldwide demand for energy rising, it is imperative to discover environmentally friendly sources of energy. Yet, burning fossil fuels releases greenhouse gases that have a negative impact on the environment. As a renewable energy source, biodiesel has several benefits against fossil fuels, including the capacity to be produced from many kinds of feedstocks, reduced emissions of air pollutants, recyclability, and reusability. Biomass feedstock can be utilized for biodiesel production and the waste disposal issue can be eliminated indirectly. Transesterification is employed as it is a cost-effective approach to manufacturing biodiesel under mild reaction conditions. In addition, the implementation of heterogeneous catalysts can significantly enhance biodiesel yield and reduce production costs as it is reusable and recyclable. In this research study, it is aimed to synthesize banana trunks derived sulfonated solid acid catalyst at various temperature which are 200 $^{\circ}$C, 400 $^{\circ}$C, and 600 $^{\circ}$C. Sulfonation reaction was conducted at 80 $^{\circ}$C for 18 hours and the physicochemical properties of the synthesized sulfonated solid acid catalysts were studied and characterized by using different analytical techniques including Fourier-Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), and determination of total acid density. Furthermore, the effects of various temperature of the sulfonated solid acid catalysts will be evaluated through the catalytic activity on transesterification reaction with oleic acid. As a result, sulfonated solid acid catalyst prepared at 400 $^{\circ}$C gave highest biodiesel yield which is 21.05 % under the transesterification conditions of temperature at 85 $^{\circ}$C for 2 hours and with 20:1 MeOH/OA molar ratio and 1 g sulfonated solid acid catalyst. The esterified product was further analyzed by GC-MS to ensure the conversion of OA to FAME and the FAME content in the esterified product.

CHAPTER 1: INTRODUCTION

1.1 General Introduction

Due to a rise in demand for energy brought on by modernization and industrial growth, recent years have experienced a significant energy crisis driven on by excessive fossil fuel consumption (Nazir et al., 2020). Burning fossil fuels emits enormous quantities of carbon dioxide, a greenhouse gas, into the surroundings and leads to environmental issues especially global warming as well as challenges with energy security. These fossil fuels resources are rapidly approaching their maximum capacity and getting exhausted. Therefore, the attempt to search for innovative sources of energy that are technically achievable and environmentally acceptable has been sparked by these concerns. On the other hand, globally, 998,000,000 tons of agricultural wastes are produced annually, and Malaysia disposes about 1,200,000 tons of this agricultural waste into landfills on an annual basis (Fadzil & Othman, 2021). Methane gas, a more potent greenhouse gas than carbon dioxide, would be emitted as a result of Malaysia's poor agricultural waste management practices and eventually lead to environmental issues. Recently, biodiesel has been suggested as a viable renewable source, and production is growing often as a result of its potential to minimize environmental effects, particularly greenhouse gas emissions (Nazir et al., 2020). Nevertheless, it is unlikely that the manufacture of biodiesel would take off due to the high cost of both feedstock and production. The effort to discover a cheap solution has therefore been inspired by this concern. As a result, it was suggested that agricultural waste be utilized as an alternative to conventional fuels as it is widely available and can be used to produce biodiesel.

Furthermore, it was also pointed out that using wastes from agricultural industries is a feasible manner to dispose of wastes and an economical approach to create inexpensive,

ecologically sustainable catalysts (Awogbemi et al., 2021). Catalysts generated from agricultural wastes not only are non-toxic and non-corrosive as they refrain from producing any wastewater, but also are biodegradable and have an excellent rate of conversion. In brief, the application of agricultural wastes to generate catalysts is incredibly beneficial since it offers biodiesel producers an affordable and environmentally appropriate method of disposing of agricultural waste (Awogbemi et al., 2021). Generally, biodiesel is manufactured by chemically reacting triglycerides found in vegetable oils or animal fats and alcohol with an addition of catalyst to form fatty acid alkyl esters (Bashir et al., 2022). Among biofuel, the key benefits for the biodiesel to be recommended as a potential resource as an alternative fuel over fossil fuels are its renewability, biodegradability, lower emissions of air pollutants, and versatility in production from a range of feedstocks (Monika et al., 2023). Although biodiesel's physical and chemical characteristics are strikingly similar to those of petroleum-derived diesel, biodiesel possesses superior qualities to that fuel. Biodiesel not only enhances engine performance since it emits less carbon monoxide and particulates, but also offers lubricating qualities that extend an engine's lifespan. Additionally, since biodiesel has a higher boiling point and is less volatile, it is simple to carry around and store (Monika et al., 2023). The main technique for producing biodiesel at an affordable price and with mild reaction conditions is transesterification (Nazir et al., 2020). Biomass feedstock, which is less harmful, recyclable, renewable, and biodegradable, can be utilized to produce biodiesel. There are many kinds of biomass feedstock available worldwide, including oil crops, lignocellulose materials, agricultural wastes, forestry residues, and many others. Some of the biomass feedstock, such as coffee residue (Battista et al., 2020), sugarcane bagasse (Akinfalabi et al., 2020), rice husk (Li et al., 2014; Zhao et al., 2018, October), corncob (Hussain & Kumar, 2018), and palm kernel shells (Quah et al., 2020), have been extensively studied for manufacturing of biodiesel.

Nevertheless, banana trunks as a biomass feedstock for biodiesel production have received little attention. In fact, in Malaysia, bananas are the second most widely grown fruit. Since banana plants only bear fruit once in their lifespan, the entire plant is thrown away as waste when the fruit is harvested. For every tonne of banana fruit produced, it was projected that about 100 kilograms of waste would be created (Danish et al., 2018). Hence, it is an undeniable fact that it will benefit greatly if this enormous waste can be converted into usable materials such as catalysts. In the study done by Brahma et al. (2023), the peel, trunk, and rhizome of three distinct post-harvest banana plant sections were prepared into calcined materials and subsequently employed as a catalyst for manufacturing biodiesel. In the research outcome of Brahma et al. (2023), the catalyst derived from banana plant parts is capable of producing good quality biodiesel as per international standards and 95.82% of biodiesel yield was achieved. However, in the research study carried out by Brahma et al. (2023), the catalyst was only synthesized and studied at a single temperature which is 550 $^{\circ}$C. As a result, it was proposed in this research study to employ banana trunks as a biomass feedstock for producing catalysts, which would then be utilized for the manufacturing of biodiesel. Also, different catalyst preparation temperatures and their effectiveness in biodiesel production will be examined in this research study.

Apart from that, the catalyst is essential for the production of biodiesel. Catalysts are substances that speed up the rate of a chemical reaction without being consumed by the process (Chemistry LibreTexts, 2023). Generally, there are two types of catalysts which are homogeneous catalysts and heterogeneous catalysts. These two types of catalysts are then further classified into two groups which are acid catalysts (sulfuric acid and hydrochloric acid) and base catalysts (sodium hydroxide and potassium hydroxide). Typically, acid catalysts are frequently employed

to catalyze the esterification reaction as compared to base catalysts due to the reason that base catalysts are able to react with the free fatty acid present in the feedstock during the transesterification reaction and create unwanted products or soap formation through saponification which results in complication product separation, reduce the target product yield and quality, increase in usage of catalyst, and reduce the reactivity of catalyst (Changmai et al., 2020). In contrast, acid catalysts are more effective as catalysts because they are not sensitive to free fatty acids as the acid catalysts are neutral to the free fatty acids, and as a result, they are able to offer more favorable outcomes for the transesterification reactions of vegetable oils or fats that consists of a large quantity of free fatty acids (Changmai et al., 2020).

On the other hand, homogeneous catalysts are those that are present in the same phase either in a gas or a liquid form, whereas heterogeneous catalysts are in a solid form, this means that the catalyst and the reaction mixture are in separate phases (Changmai et al., 2020). In comparison with homogeneous catalysts, heterogeneous catalysts exhibit numerous beneficial properties. The heterogeneous catalysts are recyclable and reusable, very little effluent will be produced throughout the procedure, product can be separated out easily, environmentally friendly, non-toxic, and able to minimize the incidence of corrosion (Changmai et al., 2020). Conversely, homogeneous catalysts which are the liquid catalysts would come into contact with a liquid reactant, making it hard to reuse the spent catalyst. As a result, wastewater would be produced because washing would be needed to remove the catalysts from the final product and thus make the operation to evolve into laborious and costly (Changmai et al., 2020). Based on the aforementioned reasons, it is recommended that heterogeneous solid acid catalysts be employed in this research study for biodiesel production.

In fact, the agricultural waste used as biomass feedstock is subject to an initial phase of being converted into calcined materials, or biochar, before it is transformed into heterogeneous solid acid catalysts. Studies have demonstrated that the excellent morphological qualities, improved thermal sustainability, as well as abundance of functional groups of biochar make it a viable catalyst to promote the development of solid acid catalysts. (Yaashikaa et al., 2020). Furthermore, biochar is employed in biodiesel production due to the reason that biochar is easily accessible, affordable, and beneficial to the environment (Yaashikaa et al., 2020). Moreover, there are plenty of applications for biochar including catalysts (Anto et al., 2021), heavy metal removal (Chen et al., 2022), soil amendment (Burachevskaya et al., 2021), wastewater treatment (Xiang et al., 2020) and so on. Biochar can be utilized to treat and resolve the environmental problems that are currently a concern. This is so because clean and sustainable energy can be created as a byproduct when the biochar is produced and it can be implemented as an alternative for burning fossil fuels, which has worsened global warming through rising greenhouse gas levels.

Generally, biochar can be prepared in various methods. The chemical reactions include pyrolysis, gasification, hydrothermal carbonization, and flash carbonization are frequently employed to produce biochar (Yaashikaa et al., 2020). Among all these techniques, pyrolysis is the most common technique to produce the biochar as it is able to minimize contamination as the organic matter will be burned with minimal to no contamination-causing gasses released (Wang & Wang, 2019). Pyrolysis is a process of combustion of an organic material under oxygen-free conditions. Since there is no oxygen in the pyrolysis process, hence, combustion is unable to take place, instead, the biomass will be thermally breaking down into combustible gasses and biochar. In the pyrolysis process of biomass, there will be three products obtained which are liquid bio-oil,

solid biochar, and syngas (consists of carbon dioxide, hydrogen, and nitric oxide) in gaseous form (Wang & Wang, 2019). Pyrolysis can be classified into two categories which include slow pyrolysis and fast pyrolysis. Fast pyrolysis is characterized by the addition of feedstock to the reactor after the temperature reaches the desired degree and a residence time of several seconds (Wang & Wang, 2019). In contrast, the feedstock for slow pyrolysis is added to the reactor at the beginning of the process and the residence time ranges from half to several hours (Wang & Wang, 2019). Moreover, high heating rates and short residence durations give rise to greater bio-oil proportions in fast pyrolysis (Tomczyk et al., 2020). On the other hand, because of slower heating rates and longer residence durations in slow pyrolysis, it typically produces greater amounts of biochars (Tomczyk et al., 2020). As a result, slow pyrolysis was chosen in this research study due to the fact that biochar can be produced as the major product when this technique is applied. This had been proved by Cai et al. (2020) outlined the major attempts of slow pyrolysis as being biochar (as much as approximately 60 wt%), bio-oil (25-30 wt%), and syngas (the leftover substance). By using this technique, the biomass is pyrolyzed at a temperature ranging between 200 and 700 $^{\circ}$C with a heating rate of 5-7 $^{\circ}$C/min. Furthermore, the secondary reactions are able to continue with the assistance of a favorable environment and a sufficient amount of time delivered by a slower heating rate and a longer vapor residence period (Cai et al., 2020). Ultimately, this results in the production of solid carbonaceous biochar.

Indeed, sulfonation is suggested to be used to generate biochar-based solid acid catalysts as sulfonation is one of the most effective methods to enhance organic matter, generate biodiesel, and synthesize carbon-derived catalysts (Xie et al., 2020). Common sulfonation reagents for transforming sulfonated solid acid catalyst using biochar are oleum, concentrated sulfuric acid,

chlorosulfonic acid, gaseous sulfur trioxide, sulfosalicylic acid, sulfamic acid, and p-toluenesulfonic acid (Xie et al., 2020). The first four compounds are commonly employed in industry as sulfonation reagents, with the first two being utilized more extensively than the rest (Xie et al., 2020). Concentrated sulfuric acid, H_2SO_4 with a purity of 98% to 100% is reactive with a broad range of organic feedstocks and typically exhibits a mild sulfonation reaction with negligible byproducts and side reactions (Xie et al., 2020). Furthermore, concentrated sulfuric acid or its derivatives enable the sulfonic acid group, SO_3H, to be more easily introduced to the surface of biochar. The -SO_3H group is a high-density acidic site that is able to improve biochar's stability and catalytic efficiency, which can facilitate further acidic catalytic processes, particularly esterification reactions (Zhao et al., 2023). Sulfonated biochar has been employed for the production of biodiesel due to their affordability and adaptability (Saidi et al., 2023). Also, the sulfonated biochar is able to produce excellent outcomes for the manufacture of biodiesel (Saidi et al., 2023).

In this research study, it is sought to examine the feasibility of using banana trunks as a biomass feedstock source to generate biochar which then further transforms into sulfonated solid acid catalyst for the transesterification of oleic acid. The effect of various temperatures in the synthesize of biochar was investigated. Various techniques on surface functional groups, thermal stability, and total acid density that enhance the catalytic activity were also examined and discussed in detail.
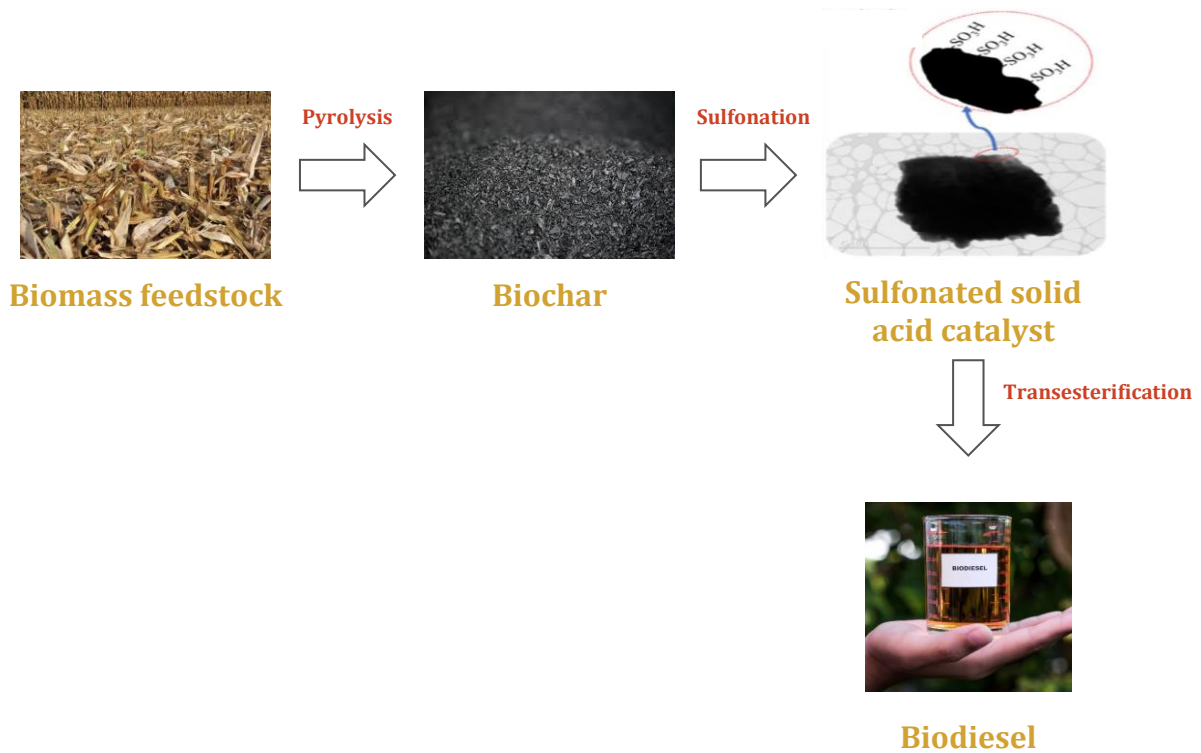
Figure 1: General process for biodiesel production.

1.2 Problem Statements

Recent years have been marked by an alarming increase in global warming and the energy dilemma driven on by an excessive dependency on fossil fuels which are non-renewable sources. This is due to the fact that burning fossil fuels releases large amounts of carbon dioxide, a greenhouse gas, into the surrounding environment. Furthermore, since the beginning of the Industrial Revolution, the quantity of carbon dioxide in the environment has been gradually increasing, and this rise is attributed to the burning of fossil fuels (Soeder, 2020). Global warming is brought about by greenhouse gasses, which retain heat in our surroundings. Additionally, the aforementioned issue contributes to global shortages of food, deteriorating health, and

impoverished circumstances for millions of people. It also leads to environmental degradation, natural resource scarcity, and decline in biodiversity that put all species and their habitats at risk (Wang & Azam, 2024).

On the other hand, individuals worldwide are concerned about the issue of crop residues as it has grown dramatically in recent years and is an important contributor to the world's overall greenhouse gas emissions. Based on the research, agricultural residues are produced nationwide in enormous quantities each year which is more than five billion mega grams (Shinde et al., 2022). Crop residues that rot in landfills will release methane which is an even more destructive greenhouse gas than carbon dioxide to the surroundings. As a result, it is detrimental to human health. Moreover, gathering and managing agricultural residues is not only energy and labor challenging, but it also consumes time, causing subsequent crops to be sown delayed. Therefore, these crop leftovers are burned on the spot in a variety of nations, which pollutes the air, prevents the recycling of nutrients, and negatively impacts soil microbes because of climate change and carbon depletion (Shinde et al., 2022).

In addition, research on the manufacture of biodiesel is currently carried out actively since it has been discovered that biodiesel may tackle both the problem of global warming and the problem of waste disposal. Nevertheless, biodiesel production is unlikely to gain much traction due to the reason that the production costs are high. Although it is occasionally stated that biodiesel is competitive, as it will be if the current developments in feedstock or the product costs are profitable, biodiesel tends to be characterized as being more expensive than traditional diesel fuel (Tabatabaei et al., 2019).

1.3 Objectives of Study

The primary goal of this study is to create the best catalyst attainable for the transesterification reaction for biodiesel production under 200 ºC, 400 ºC, 600 ºC. Therefore, the following are the objectives of this study:

- To generate sulfonated solid acid catalysts with various temperatures.
- To characterize the physicochemical properties of the acid catalyst through Fourier-Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), and determination of total acid density.
- To investigate the effects of various temperatures of the acid catalysts synthesis on the biodiesel yield.

1.4 Scope and Limitations of the Study

The scope that will be covered in this research study is to synthesize the sulfonated solid acid catalyst under various temperatures which are 200 ºC, 400 ºC, 600 ºC. The synthesized sulfonated solid acid catalysts will be utilized in the transesterification reaction for manufacturing of biodiesel. A series of analytical techniques such as FT-IR, TGA, and acid-base back titration for determining total acid density will be conducted in order to examine the performance of each sulfonated solid acid catalyst in terms of catalysis in the biodiesel yield. After all the analyses have been done, the ideal temperature to synthesize solid acid catalyst for application in the transesterification reaction of biodiesel manufacturing can be determined.

The limitations of this study are that the most suitable MeOH/OA molar ratio for the transesterification reaction is not determined and the most effective weight percent of catalyst loading in the biodiesel production is not determined. Furthermore, the most effective reaction temperature for the transesterification reaction is also not determined. These parameters that were employed in this research study were selected based on the journal research. In addition, the most ideal dwelling time for the carbonization of biomass feedstock is not able to be examined due to the limitation of tube furnace in the laboratory. The maximum dwelling time for the tube furnace in the laboratory can only be up to approximately 2 hours.

1.5 Significance of the Study

The significance of this research study has the potential to be advantageous for the community and environment in several ways by enabling the production and implementation of biodiesel in the future. It is an undeniable fact that biodiesel manufacturing is economical, sustainable, and good for the environment. First and foremost, the manufacturing of biodiesel aids society in overcoming energy crisis worries brought on by the excessive consumption of fossil fuels. Furthermore, the waste disposal issue can be substantially resolved by producing biodiesel using biomass feedstock as a primary source. Additionally, the most harmful greenhouse gas, methane gas, will be reduced once the waste disposal problem has been handled. Environmental effects, particularly greenhouse gas emissions that contribute to global warming, can be controlled indirectly. Moreover, as wastes are repurposed as feedstock has been proposed and is capable of being executed in an effortless manner, concerns regarding high feedstock cost and production cost may be disregarded.

CHAPTER 2: LITERATURE REVIEW

2.1 Reasons for Selecting the Biomass Feedstock as a Source for Biodiesel Production

According to da Luz Corrêa et al. (2020), murumuru butter is derived from the partially solid fat extracted from murumuru kernels, which is widely utilized as a drying agent in paint, as well as in the cosmetics sector for the production of creams, soap, and shampoos. The kernel shell, on the other hand, is still a largely undiscovered agro-industrial waste product. There have not been numerous research efforts in the scientific literature on repurposing this agro-industrial waste. Subsequently, da Luz Corrêa et al. (2020) intended to develop an acid catalyst using the murumuru kernel shell while investigating into the sulfonation parameters of the murumuru kernel shells derived biochar in order to make use of them in the esterification reaction to produce biodiesel.

Besides that, according to Zhao et al. (2018, March), China produces roughly three million tonnes of pomelo annually, which makes it one of the nation's most popular fruits. However, 40% of the fruit's weight is wasted in landfills, including its peels, which pose a threat to the environment. Zhao et al. (2018, March) stated that pomelo peels were historically used to generate traditional activated carbons, which are utilized for eliminating organic pollutants from the air, as well as contributing to great anode materials for batteries. Nevertheless, pomelo peel pyrolysis, a carbonaceous material with characteristics resembling activated carbon, has not yet been studied as a catalyst vehicle for generating solid catalysts to produce biodiesel. The fact that biochar has already been researched in the past as an activated carbon precursor, Zhao et al. (2018, March) were very interested in exploring its potential as a carbon derivative to stimulate the transesterification process.

Moreover, the primary reason for Bureros et al. (2019) to select cacao shells in the research is that over 3000 metric tonnes of cacao shells are created every year as an unwanted byproduct of roasting cacao beans for the Philippine chocolate industry. At the moment, the cacao shells are dumped out with common trash. Bureros et al. (2019) believed that if the cacao shells could be transformed into more valuable products, it would not only ultimately beneficial in getting rid of the leftovers, but it would also create a new industry. Consequently, the achievement of zero-waste processes would then be accomplished.

On the other hand, waste orange peel has been chosen in the research of Lathiya et al. (2018) as a carbon source in order to produce solid acid sulfonated carbon catalyst due to the reason that waste orange peel disposal has grown to be a significant issue for a number of food sectors. Yusuff et al. (2022) stated that the eucalyptus trees are widely distributed worldwide, expand rapidly, and produce an abundance of bark that is dumped away as waste materials. In fact, the eucalyptus tree shed bark can be employed as an initial source of material for the manufacture of biochar and has a greater proportion of organic material than other plant-based biomass sources (Yusuff et al., 2022). Next, sugarcane bagasse was selected by Nazir et al. (2020) as the basis of biochar production due to the reason that sugarcane bagasse was globally produced more than 540 million metric tons every year and was disposed of as waste which leads to environmental issues.

To summarize all of the aforementioned information, landfills serve as a place to dispose of waste materials, and this leads to greenhouse gas emissions, which is a major cause for concern. This appears to be an ongoing trend among the research findings. Therefore, the issue of waste disposal can be eliminated through the utilization of these biomass feedstock again. Repurposing

these biomass feedstocks as a resource for biodiesel production additionally makes it possible to implement and employ an easier and more economical technique. As a result, the production of biodiesel can dramatically expand.

Table 1: Summary of the reasons for selecting biomass feedstocks as a source for biodiesel production.

Year	Journal Title	Biomass Feedstock Selected	Reasons
2020	Preparation of sulfonated carbon-based catalysts from murumuru kernel shell and their performance in the esterification reaction	Murumuru kernel shells	Limited research efforts on repurposing this agricultural waste
2018	Biodiesel synthesis over biochar-based catalyst from biomass waste pomelo peel	Pomelo peels	Possess a threat to the environment as 40% of the fruit's peel is wasted in landfills
2019	Cacao shell-derived solid acid catalyst for esterification of oleic acid with methanol	Cacao shells	Appears in large quantities as an unwanted byproduct
2018	Synthesis of sulfonated carbon catalyst from waste orange peel for	Orange peels	Its disposal has grown to be a significant issue for a

			number of food sectors
2022	Sulfonated biochar catalyst derived from eucalyptus tree shed bark: synthesis, characterization and its evaluation in oleic acid esterification	Eucalyptus tree shed barks	An abundance of bark was produced and dumped away as waste materials
2020	Sulfonated Activated Sugarcane Bagasse as Heterogeneous Catalyst for Biodiesel Production from Waste Cooking Oil via Microwave Irradiation	Sugarcane bagasse	Globally produced in an enormous quantity and was disposed of as waste which lead to environmental issues

2.2 Treatments and Parameters for Biodiesel Production

In the research study of da Luz Corrêa et al. (2020), the murumuru kernel shell was first ground and carbonized for 1 hour at 600 $^{\circ}$C in a tubular oven with an 80 mL min^{-1} nitrogen flow. Then, the sulfonation of biochar was conducted in a flask with a flat bottom that was attached to a hot plate and condenser. Various temperatures, times, and solid-acid ratios were used, and the flask was kept constantly agitated. In the research study conducted by da Luz Corrêa et al. (2020), at a temperature of 200 $^{\circ}$C and a 1:10 (w/v) solid-acid ratio, the time parameter was studied for a duration of 1 – 8 hours. The solid-acid ratio was assessed in a variety of 1:10 to 1:30 (w/v), at a temperature of 200 $^{\circ}$C and 4 hours. The impact of the temperature was studied between 120 and 200 $^{\circ}$C, with a sulfonation duration of 4 hours, and a solid-acid ratio of 1:10 (w/v) (da Luz Corrêa et al., 2020). For the collection of the sulfonated solid acid catalyst, the reaction mixture was vacuum filtered following the sulfonation process, and the solids were washed with distilled water to achieve a pH 7, and then dried for 24 hours at 60 $^{\circ}$C in an oven (da Luz Corrêa et al., 2020). After that, by using the resulting sulfonated solid acid catalyst, the esterification reactions between oleic acid and methanol were carried out for the catalytic testing. The catalyst mass percentage (1 to 5%), reaction temperature (60 to 120 $^{\circ}$C), molar ratio of methanol to oleic acid (5:1 to 25:1), and reaction time (0.5 to 2.5 hours) were all evaluated to optimize the esterification parameters (da Luz Corrêa et al., 2020). After esterification, the resulting products were centrifuged to remove the catalyst, transferred to a decantation funnel and washed with 90 $^{\circ}$C distilled water to remove any remaining alcohol and water. The samples were then dried for 24 hours at 80 $^{\circ}$C in an oven.

According to research conducted by Zhao et al. (2018, March), the pomelo peel was first cleaned with distilled water, following an overnight drying at 80 $^{\circ}$C in an oven. For the creation

of pomelo peel biochar, the dried pomelo peel was subsequently pyrolyzed for 2 hours at 600 °C in a nitrogen environment. Generally, 500 ml of 2 M KOH solution was mixed with 2 g of pomelo peel biochar, and the mixture was agitated for 2 hours. Subsequently, the mixture went through filtering, and the resulting biochar encountered numerous washes with distilled water until its pH level reached 7. Ultimately, the resulting biochar was dried overnight at 105 °C in an oven. Next, wet impregnation method was conducted for the preparation of the pomelo peel biochar-supported catalysts by mixing the activated pomelo peel biochar samples with the K_2CO_3 impregnating solution (15 wt.%, 25 wt.% and 35 wt.%) (Zhao et al., 2018, March). The biochar catalysts derived from pomelo peel and methanol were used for the transesterification of palm oil in a three-neck round-bottom flask fitted with a thermometer, condenser, and magnetic heating mantle. The mixture was continuously stirred at 800 rpm while being incubated at 65 °C and at air pressure to complete the transesterification reaction. After the reaction was finished, the mixture was centrifuged to remove the catalyst, and the filtrate was allowed to settle for 24 hours and the evaporation of the upper layer was done by a rotary evaporator at a low pressure to remove the excess of methanol (Zhao et al., 2018, March).

In accordance with the research conducted by Bureros et al. (2019), cacao shells were milled and added into a crucible which then put inside the muffle furnace with a lid on. The furnace was heated to 350 °C at a heating rate of 10 °C/min for an hour. After that, the sulfonation was carried out in a thermal digester using concentrated sulfuric acid at a 1:20 solid-acid ratio and at a rate of 15 °C/min. Sulfonation was performed with various temperatures (80, 100, 120 °C) and sulfonation durations (4, 6 and 8 hours). Afterwards, the digestion tube was allowed to cool in a water bath, the reaction mixture was then diluted and washed with approximately 300 mL hot

distilled water until the pH is neutral (Bureros et al., 2019). The prepared cacao shell-derived solid acid catalyst was filtered and dried in an oven. The cacao shell-derived solid acid catalyst was then used in the esterification reaction of oleic acid with methanol that was conducted in a screw-capped 250 mL flask placed in an incubator shaker. The methanol-to-oil ratio of 7:1, catalyst loading of 5 wt%, temperature of 45 ^{o}C, and reaction time of 4 hours were employed in the esterification reaction (Bureros et al., 2019). After esterification, the reaction mixture was filtered to remove the spent solid acid catalyst and transferred to a separatory funnel. Then, n-hexane was added to dissolve the free fatty acid (FFA) and fatty acid methyl ester (FAME). 5% sodium chloride solution was introduced to the reaction mixture to eliminate leached acid (Bureros et al., 2019). Lastly, the top layer, which is the n-hexane layer that consists of FAME was extracted and concentrated by a rotary evaporator.

Waste orange peel was first carbonized in a teflon-coated autoclave reactor at 180 °C for 6 hours and then processed through sulfonation by adding concentrated sulphuric acid, H_2SO_4 in a teflon-coated autoclave reactor with a 1:20 w/v biochar to H_2SO_4 ratio for 24 hours at 200 °C (Lathiya et al., 2018). After 24 hours, the sulfonated acid catalyst was washed with deionized water for removal of excess sulfuric acid and dried at 110 ^{o}C for 6 hours in an oven. After that, the biodiesel production was carried out by using the traditional reflux method at 65 °C temperature and at a stirring speed of 400 rpm (Lathiya et al., 2018). On the other hand, the sugarcane bagasse was first partially carbonized in a tube furnace for 1 hour at 450 °C under a constant flow of nitrogen gas and followed by a sulfonation reaction with concentrated sulfuric acid at 150 °C for 8 hours and 10 hours with a hot plate and continuous stirring. After sulfonation, the mixture was first washed with 500 mL deionized water, then further washed with hot deionized water (80 ^{o}C)

until the pH became neutral. The sulfonated acid catalyst was filtered and dried in an oven at 105 ºC overnight. The esterification reaction was done in a modified microwave which had a condenser inside at 60 °C, methanol/oil molar ratio of 10:1, and 2 wt% catalyst with a continuous stirring at 400 rpm for 20 minutes (Nazir et al., 2020).

The eucalyptus tree shed barks were first pyrolyzed at 600 °C and ramping rate at 5 °C/min for 1.5 hours in a furnace in the absence of oxygen to produce the biochar (Yusuff et al., 2022). After that, the impregnation technique was used to manufacture the sulfonated biochar catalysts. In the research of Yusuff et al. (2022), p-toluene sulfonic acid monohydrate was introduced in various amounts (2, 4, 6, and 8 g) and gently swirled on a magnetic stirrer at 60 °C for 5 hours. The esterification reaction with oleic acid was conducted by using the reflux technique at a stirring rate of 500 rpm. Also, the effects of temperature (50 - 80 °C), time (1 - 5 hours), methanol/oil molar ratio (4:1 - 12:1), and catalyst loading (1 - 5% wt%) on the esterification process were studied in this research (Yusuff et al., 2022).

The walnut shell was carbonized at 80 °C for 30 hours followed by sulfonation with various proportions of concentrated sulphuric acid (1:10, 1:13, 1:17, and 1:20) with continuous stirring for 30 minutes (Yadav et al., 2023). After that, the reaction mixture was diluted with distilled water and washed multiple times to remove excess sulfate. Then, the solid acid catalyst was filtered and dried in an oven at 80 ºC for 12 hours. In the research of Yadav et al. (2023), the production of biodiesel which is methyl oleate was performed by microwave-assisted esterification as the rate of reaction and product yield can be maximized by employing microwave heating. Various ranges of sulfonated walnut shell catalyst (5 to 11 wt%), oleic acid:methanol molar ratios (1:12 to 1:24),

temperatures (65 to 95 °C), reaction times (60 to 100 minutes) were applied and a 50W microwave power was used (Yadav et al., 2023).

In accordance with the studies mentioned above, transesterification is the most widely employed technique for manufacturing biodiesel as all of the researchers make use of this method. Furthermore, considering that transesterification is a cost-effective and time-saving technology that results in biodiesel with a higher cetane number and enhanced performance, it is strongly recommended to be utilized in the production of biodiesel (Sajjad et al., 2022). Moreover, the researchers used two alternative methods for transesterification which are the conventional reflux method and the microwave irradiation method. These two techniques are capable of providing high biodiesel yields along with excellent performance. In general, the microwave-assisted approach provides a quick and simple path towards this valuable biodiesel with the additional advantages of speeding up the reaction and streamlining the separation procedure (El Sherbiny et al., 2010). Apart from that, various parameters such as molar ratio, reaction temperature, and catalyst loading can be used according to different types of biomass feedstock in order to achieve the highest biodiesel yield. In the majority of instances, researchers will make use of homogeneous alkali catalysts and heterogeneous acid catalysts in their studies. Over homogeneous alkali catalysts, most of the researchers will select heterogeneous acid catalysts. This is due to the reason that heterogeneous acid catalysts have the potential of minimizing the high biodiesel production cost.

Table 2: Summary of treatments and parameters for biodiesel production.

Year	Journal title	Carbonization parameters	Sulfonation parameters	Transesterification parameters
2020	Preparation of sulfonated carbon-based catalysts from murumuru kernel shell and their performance in the esterification reaction	Temperature: 600 ºC Duration: 1 hour In the presence of nitrogen gas with the flow of 80 mL/min	Time: 1 to 8 hours at 200 ºC and solid-acid ratio of 1:10 Temperature: 120 and 200 ºC for 4 hours and solid-acid ratio of 1:10 Solid-acid ratio: 1:10 to 1:30 at 200 ºC for 4 hours	Reaction time: 0.5 to 2.5 hours Catalyst mass percentage: 1 to 5% Methanol-to-oleic acid molar ratio: 5:1 to 25:1 Reaction temperature: 60 to 120 ºC
2018	Biodiesel synthesis over biochar-based catalyst from biomass waste pomelo peel	Temperature: 600 ºC Duration: 2	Wet impregnation method was used	Reaction time: 2.5 hours Catalyst mass

		hours In the presence of constant flow of nitrogen gas	Concentration of K_2CO_3 impregnating solution: 15 wt%, 25 wt%, and 35 wt% Time: 3 hours Temperature: 500 to 700 °C	percentage: 6 wt% Methanol-to-oleic acid molar ratio: 8:1 Reaction temperature: 65 °C
2019	Cacao shell-derived solid acid catalyst for esterification of oleic acid with methanol	Temperature: 350 °C Heating rate: 10 °C/min Duration: 1 hour	Time: 4,6, and 8 hours Temperature: 80, 100, and 120 °C Solid-acid ratio: 1:20	Reaction time: 4 hours Catalyst mass percentage: 5 wt% Methanol-to-oleic acid molar ratio: 7:1 Reaction

				temperature: 45 ºC
2018	Synthesis of sulfonated carbon catalyst from waste orange peel for cost effective biodiesel production	Temperature: 180 ºC Duration: 6 hours	Time: 24 hours Temperature: 200 ºC Solid-acid ratio: 1:20	Reaction time: 274 minutes Catalyst mass percentage: 5 wt% Methanol-to-oleic acid molar ratio: 20:1 Reaction temperature: 65 ºC
2020	Sulfonated Activated Sugarcane Bagasse as Heterogeneous Catalyst for Biodiesel Production From Waste Cooking Oil via Microwave Irradiation	Temperature: 450 ºC Duration: 1 hour In the presence of constant flow of	Time: 8 and 10 hours Temperature: 150 ºC Solid-acid ratio: 1:25	Reaction time: 20 minutes Catalyst mass percentage: 2 wt% Methanol-to-oleic acid molar ratio: 10:1

			nitrogen gas		Reaction temperature: 60 ºC
2022	Sulfonated biochar catalyst derived from eucalyptus tree shed bark: synthesis, characterization and its evaluation in oleic acid esterification	Temperature: 600 ºC Heating rate: 5 ºC/min Duration: 1.5 hours In the presence of constant flow of nitrogen gas	Impregnation method was used Amount of p-toluene sulfonic acid monohydrate: 2, 4, 6, and 8 g Time: 5 hours Temperature: 60 ºC	Reaction time: 1 to 5 hours Catalyst mass percentage: 1 to 5 wt% Methanol-to-oleic acid molar ratio: 4:1 to 12:1 Reaction temperature: 50 to 80 ºC
2023	Microwave-assisted biodiesel production using –SO$_3$H functionalized heterogeneous catalyst	Temperature: 80 ºC Duration: 30	Time: 24 hours Temperature: 80 ºC	Reaction time: 60 to 100 minutes Catalyst mass

	derived from a lignin-rich biomass	hours		percentage: 5 to 11 wt%
			Solid-acid ratio: 1:10, 1:13, 1:17, and 1:20	Methanol-to-oleic acid molar ratio: 12:1 to 24:1
				Reaction temperature: 65 to 95 ºC

2.3 Optimized Conditions for Biodiesel Production

Table 3: Optimized conditions for biodiesel production.

Year	Journal Title	Sulfonation Conditions	Transesterification Conditions	Biodiesel Yield
2020	Preparation of sulfonated carbon-based catalysts from murumuru kernel shell and their performance in the esterification reaction	Time: 4 hours Temperature: 200 °C Solid-acid ratio: 1:10	Reaction time: 1.5 hours Catalyst mass percentage: 5% Methanol-to-oleic acid molar ratio: 10:1 Reaction temperature: 90 °C	97.2 %
2018	Biodiesel synthesis over biochar-based catalyst from biomass waste pomelo peel	Concentration of K_2CO_3 impregnating solution: 25 wt% Time: 3 hours Temperature: 600 °C	Reaction time: 2.5 hours Catalyst mass percentage: 6 wt% Methanol-to-oleic	98.0 %

			acid molar ratio: 8:1 Reaction temperature: 65 ºC	
2019	Cacao shell-derived solid acid catalyst for esterification of oleic acid with methanol	Time: 6 hours Temperature: 120 ºC Solid-acid ratio: 1:20	Reaction time: 4 hours Catalyst mass percentage: 5 wt% Methanol-to-oleic acid molar ratio: 7:1 Reaction temperature: 45 ºC	79.0 %
2018	Synthesis of sulfonated carbon catalyst from waste orange peel for cost effective biodiesel production	Time: 24 hours Temperature: 200 ºC Solid-acid ratio: 1:20	Reaction time: 274 minutes Catalyst mass percentage: 5 wt% Methanol-to-oleic	91.68 %

			acid molar ratio: 20:1 Reaction temperature: 65 ºC	
2020	Sulfonated Activated Sugarcane Bagasse as Heterogeneous Catalyst for Biodiesel Production From Waste Cooking Oil via Microwave Irradiation	Time: 8 hours Temperature: 150 ºC Solid-acid ratio: 1:25	Reaction time: 20 minutes Catalyst mass percentage: 2 wt% Methanol-to-oleic acid molar ratio: 10:1 Reaction temperature: 60 ºC	80.0 %
2022	Sulfonated biochar catalyst derived from eucalyptus tree shed bark: synthesis, characterization and its evaluation in oleic acid esterification	Impregnation method was used Amount of p-toluene sulfonic acid monohydrate: 6 g	Reaction time: 2 hours Catalyst mass percentage: 4 wt% Methanol-to-oleic	97.05 ± 0.28 %

		Time: 5 hours	acid molar ratio: 10:1	
		Temperature: 60 °C	Reaction temperature: 65 °C	
2023	Microwave-assisted biodiesel production using –SO₃H functionalized heterogeneous catalyst derived from a lignin-rich biomass	Time: 24 hours Temperature: 80 °C Solid-acid ratio: 1:20	Reaction time: 60 minutes Catalyst mass percentage: 9 wt% Methanol-to-oleic acid molar ratio: 16:1 Reaction temperature: 85 °C	99.01 ± 0.3 %

In fact, several sulfonation and transesterification conditions are capable of being applied based on the types of biomass feedstock to obtain the maximum biodiesel yield. Generally, for the sulfonation reaction, it is typically conducted at a temperature between 80 and 200 °C for 4 - 24 hours with a solid-acid ratio of 1:10 or 1:20. On the other hand, for the transesterification reaction, it is usually conducted at a temperature between 60 and 90 °C for 1 - 5 hours with 2 - 9 wt% catalyst loading and methanol-to-oleic acid molar ratio of 10:1 or 20:1.

2.4 Reasons for Selecting Oleic Acid in Transesterification Reaction

According to Moradi et al. (2021), the most prevalent free fatty acids (FFAs) in both edible and non-edible oils are palmitic acid, stearic acid, oleic acid and linoleic acid. Nonetheless, a lot of researchers have frequently employed oleic acid for the manufacture of biodiesel. There are multiple reasons for it. First and foremost, the feedstock utilized in the synthesis process determines the characteristics of biodiesel (Moradi et al., 2021). In the research of Kushwaha et al. (2023), it stated that oleic acid was employed as a test substrate in the study due to the reason that oleic acid is an essential component for the majority of feedstocks used in the production of biodiesel. Additionally, as one of the most prevalent free fatty acids in vegetable oils and animal fats, oleic acid was chosen as a model compound in the study carried out by Pan et al. (2016). Furthermore, Moradi et al. (2021) stated that oleic acid is selected as a model oil in the study as it is able to offer the appropriate physical and chemical characteristics, which include density and kinematic viscosity, pour and cloud point, cetane index, high heating value, and so forth.

On the other hand, in accordance with the research conducted by Khethiwe et al. (2020), the ideal vegetable oil used for manufacturing biodiesel should consist of a greater proportion of monounsaturated fatty acids than polyunsaturated fatty acids. This is because oil with a relatively high concentration of polyunsaturated fatty acids typically shows a poor oxidation stability, and it can restrict the fuel properties such as kinematic viscosity and can negatively impact fuel quality. There are two types of unsaturated fatty acids including oleic acid and linoleic acid. The unsaturated fatty acids can be further categorized into two types which are monounsaturated and polyunsaturated. Oleic acid is classified into monounsaturated fatty acid as it only consists of one double bond in the structure while linoleic acid is classified into polyunsaturated fatty acid as it

consists of two double bonds in the structure (Khethiwe et al., 2020). On the contrary, palmitic acid and stearic acid are saturated fatty acids. As a result, they are unlikely to be employed for biodiesel production. Based on the aforementioned reasons, oleic acid is the most suitable vegetable oil to be selected for biodiesel production.

CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 Materials

Cavendish banana (*Musa acuminata*) trunks were obtained from Mr Banana fruit store. Oleic acid and calcium chloride were purchased from R & M Chemicals, Essex, UK. Methanol (Analytical Reagent Grade) and silicone oil were purchased from Chemiz. Concentrated sulfuric acid (98%) was purchased from Fisher Chemical. Barium chloride was purchased from Bendosen Laboratory Chemicals. Sodium chloride was purchased from SYSTERM Chemicals. Dichloromethane (Analytical Reagent Grade) was purchased from ChemSoln, SIME Scientific. Ultra-pure water from Ultrapure Water System (STAKPURE). Sodium hydroxide and phenolphthalein indicator were also used in this research study.

3.2 Instruments and Apparatus

The instruments and apparatus used in this study included tube furnace, centrifuge, Fourier-Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), Gas Chromatography-Mass Spectrometry (GC-MS), 250 mL round bottom flask, 500 mL three-neck round bottom flask, Erlenmeyer flask, reflux condenser, heating magnetic stirrer with digital thermometer, magnetic stirring bar, measuring cylinder, pestle and mortar, volumetric flask, beaker, micropipette, filter paper, vacuum filter, burette, and test tube.

3.3 Catalyst Preparation

3.3.1 Preparation of Biochar

Firstly, the banana trunks were thoroughly rinsed with distilled water in order to remove the sand from it. The banana trunks were then cutted into small pieces approximately 1 cm x 1 cm x 1 cm. After that, the small pieces of banana trunks were dried under sunlight until fully dried. In order to produce biochar, the small pieces of dried banana trunks were pyrolyzed in a tube furnace under no oxygen condition at various temperatures which are 200 °C, 400 °C, and 600 °C with a dwelling time of approximately 2 hours and at a heating rate of 5 °C/min. The pyrolyzed banana trunks were grounded into powdered forms with a pestle and mortar.

3.3.2 Synthesis of Sulfonated Solid Acid Catalysts

The synthesis of sulfonated solid acid catalysts was prepared by modifying the method as stated by Ezebor et al. (2014). 1 g biochar and 10 mL concentrated H_2SO_4 solution (98%) were added into a 500 mL three-neck round bottom flask fitted with a condenser. One of the angled necks was connected to an Erlenmeyer flask with a delivery tube filled with concentrated H_2SO_4 solution as a drying agent while another angled neck was connected to an Erlenmeyer flask with a delivery tube filled with $CaCl_2$ as a drying agent. The 500 mL three-neck round bottom flask was immersed in silicone oil and the mixture was heated on a heating magnetic stirrer with a digital thermometer at 80 °C for 18 hours under nitrogen. After 18 hours, the sulfonated solid acid catalyst was poured into 1500 mL of ultra-pure water and stirred for 10 minutes. After 10 minutes, the mixture was filtered with a vacuum filter and the sulfonated solid acid catalyst was collected. The collected sulfonated solid acid catalyst was then washed three times with 100 mL ultra-pure water preheated to 80 °C. After three times washing, the sulfonated solid acid catalyst was filtered and dried in an

oven at 105 °C for 18 hours. The filtrate of each wash was tested by the addition of drops of $BaCl_2$

solution to ensure that no more sulfate impurities were present.

3.4 Analysis of Sulfonated Solid Acid Catalysts

3.4.1 FTIR Analysis

The surface functional groups of the sulfonated solid acid catalysts were examined by investigating

the FTIR spectra in the wavelength range of 4000 - 650 cm^{-1}.

3.4.2 TGA Analysis

The thermal stability of the sulfonated solid acid catalysts was examined. The analysis was

conducted in a platinum pan and the temperature range used to investigate the thermal stability is

20 - 800 °C with an inert atmosphere of nitrogen gas at a heating rate of 20 °C/min.

3.4.3 Determination of Total Acid Density

The total acid density of the sulfonated solid acid catalysts was determined by using the acid-base

back titration method. In this method, 0.2 g sulfonated solid acid catalyst was stirred with 30 mL

of 1 N NaCl for 4 hours at room temperature. The mixture was then centrifuged, and 25 mL of the

obtained solution was titrated against 0.1 N NaOH solution. Phenolphthalein was used as an

indicator. The titration was triplicated and the volume of NaOH solution used was recorded.

The total acid density of the sulfonated solid acid catalyst was calculated using formula below:

Total acid density $= \frac{C_{NaOH} \cdot V_{NaOH}}{m_{catalyst}}$, where C_{NaOH} is the concentration of NaOH solution, V_{NaOH} is

the volume of NaOH solution used, and $m_{catalyst}$ is the mass of the catalyst.

3.5 Evaluation on Catalytic Activity of Sulfonated Solid Acid Catalysts

3.5.1 Esterification of Oleic Acid

The esterification of OA was conducted by modifying the method as stated by Yusuff et al. (2022).

The conversion of OA to biodiesel via esterification with MeOH in the presence of sulfonated

solid acid catalyst was carried out in a 250 mL round bottom flask attached with a reflux condenser

and a magnetic stirrer. All through the experiments, the 250 mL round bottom flask was immersed

in the silicone oil bath to regulate the temperature. For each experiment, 1 g of sulfonated solid

acid catalyst was suspended in 20 mL of MeOH and allowed to mix for 10 minutes. After 10

minutes, the mixture was poured into the 250 mL round bottom flask and 1 mL of OA was added

to the mixture. The MeOH-to-OA molar ratio is 20:1. Thereafter, the reactants and sulfonated solid

acid catalyst were heated at 85 °C and started continuous stirring immediately for 2 hours. In order

to avoid mass transfer limitation, the stirring rate was fixed at 500 rpm. After the completion of

the esterification reaction, the product mixture was centrifuged at 7500 rpm for 10 minutes to

remove the spent sulfonated solid acid catalyst. The supernatant was then washed with 5 mL

saturated NaCl solution to remove excess MeOH and extract pure biodiesel.

3.5.2 Analysis of Esterified Product

The FAME content in the esterified product was analyzed using GC-MS. A polar column (DB-WAX UI; dimension: 30 m x 0.25 mm x 0.25 um) was used. For each analysis, 20 uL of the esterified product was dissolved in 1.5 mL DCM and 1 uL of the mixture was then injected into the instrument for analysis. The oven was set to operate at 60 °C initially, then raised to 140 °C for 5 minutes. After that, the temperature was continuously raised to 230 °C at a rate of 4 °C/min. Finally, the temperature was set to 230 °C for 20 minutes. The run time for each analysis is 47.5 minutes.

The biodiesel yield was calculated as follows:

$$\text{Biodiesel yield (\%)} = \frac{weight\ of\ FAME\ produced}{weight\ of\ oleic\ acid\ used} \times 100$$

CHAPTER 4: RESULTS AND DISCUSSION
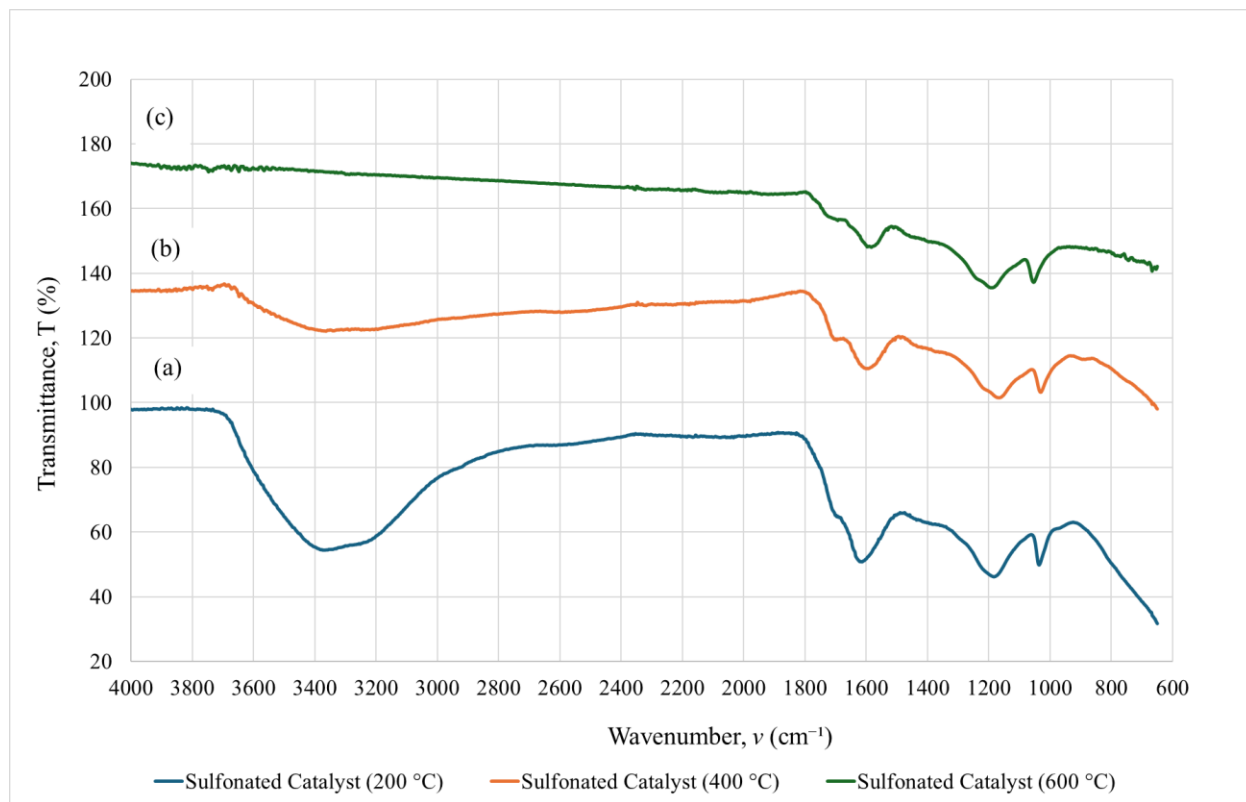
4.1 FTIR Analysis

Figure 2: FTIR spectra of (a) sulfonated solid acid catalyst prepared at 200 $^{\circ}$C, (b) sulfonated solid acid catalyst prepared at 400 $^{\circ}$C, and (c) sulfonated solid acid catalyst prepared at 600 $^{\circ}$C.

From Figure 2 as shown above, the peaks at ~ 1030 cm^{-1} and ~ 1166 cm^{-1} correspond to the symmetric stretching of -SO$_3$H groups and O=S=O bondings, respectively. The peaks are the characteristic absorption bands which demonstrate that the biochar was successfully sulfonated to create a sulfonated solid acid catalyst. Additionally, the peaks showed that the -SO$_3$H Bronsted acid sites had been properly functionalized into the biochars. The purpose of introducing the -SO$_3$H functional group to the surface of the biochar is to improve the effectiveness and capability

of the catalyst during the esterification reaction. The peak at ~ 1030 cm^{-1} follows the intensity order sulfonated solid acid catalyst prepared at 200 ^{o}C > sulfonated solid acid catalyst prepared at 400 ^{o}C > sulfonated solid acid catalyst prepared at 600 ^{o}C, while the intensity order of the peak at ~ 1166 cm^{-1} is sulfonated solid acid catalyst prepared at 200 ^{o}C > sulfonated solid acid catalyst prepared at 400 ^{o}C > sulfonated solid acid catalyst prepared at 600 ^{o}C. This implied that the sulfonated solid acid catalyst which was synthesized at 200 ^{o}C has the maximum sulfur content which is in the form of -SO$_3$H groups and O=S=O bondings.

Besides that, a strong absorption band was obtained at ~ 1594 cm^{-1} for all the samples. This peak represents the C=C stretching in the polyaromatic skeleton (Yadav et al., 2023). Additionally, the peak at ~ 1699 cm^{-1} is associated with the C=O stretching from the -COOH group (Yadav et al., 2023). These results reflect the presence of the acidic groups which are -COOH and -SO$_3$H. In order to covalently bind to the carbon structure, the -SO$_3$H groups replace the hydrogen on the biochar's surface (Yadav et al., 2023). Lastly, the absorption band at ~ 3367 cm^{-1} was observed in the sulfonated solid acid catalyst prepared at 200 ^{o}C and sulfonated solid acid catalyst prepared at 400 ^{o}C. This peak is associated with the -OH group that is present at the surface of the catalysts. Broad band obtained is caused by the existence of a slight quantity of water in the catalysts.

Table 4: Wavenumbers with respective functional groups.

Wavenumber, v (cm^{-1})	Functional groups
~ 3367	O-H stretching
~ 1699	C=O stretching

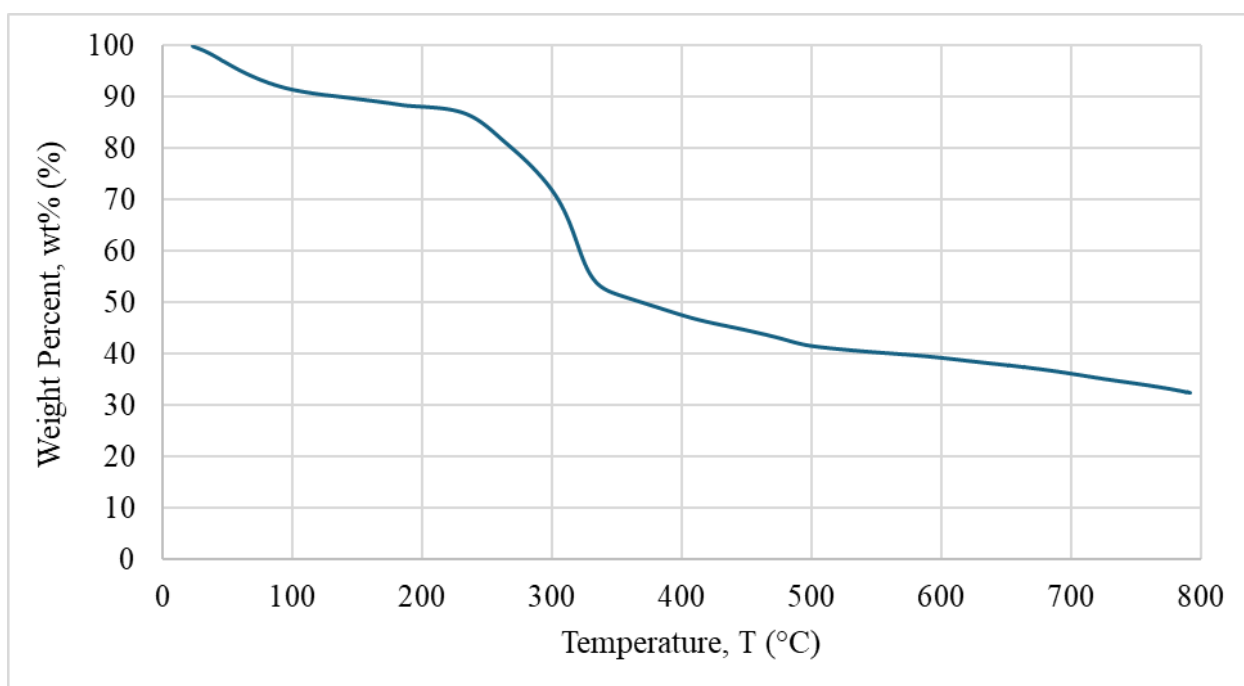| ~ 1594	C=C stretching
~ 1166	O=S=O stretching
~ 1030	-SO₃H stretching

4.2 TGA Analysis

Figure 3: TGA result for raw material (dried banana trunks).

From Figure 3 as shown above, the dried banana trunks as the raw material in this research study exhibited four decomposition stages. There is a slight difference in the percentage of weight loss in the first temperature region which happened at 28.13 °C. One possible explanation for the weight loss of the dried banana trunks can be attributed to the water removal (Kumar et al., 2020).

Furthermore, a notable decrease in weight was observed during the second stage at a temperature of 230.94 °C. This stage had a much steeper slope since the conversion rate and percentage of weight loss changed rapidly as the temperature rises (Kumar et al., 2020). In the second stage, hemicellulose depolymerization and cellulose degradation occurred concurrently (Kumar et al., 2020). Next, the third decomposition stage happened at the temperature of 336.30 °C. At this stage, the curve displayed an inflection point and a less abrupt change in conversion (Kumar et al., 2020). This is prompted by an increase in lignin degradation as well as endothermic or exothermic interactions between different degradation products (Kumar et al., 2020). Lastly, the TGA curve of dried banana trunks remained nearly constant above 501.13 °C, indicating that the decomposition process had come to an end. The residue of dried banana trunks was found to be approximately 32 % which demonstrated that the dried banana trunks had a fairly thermal stability.
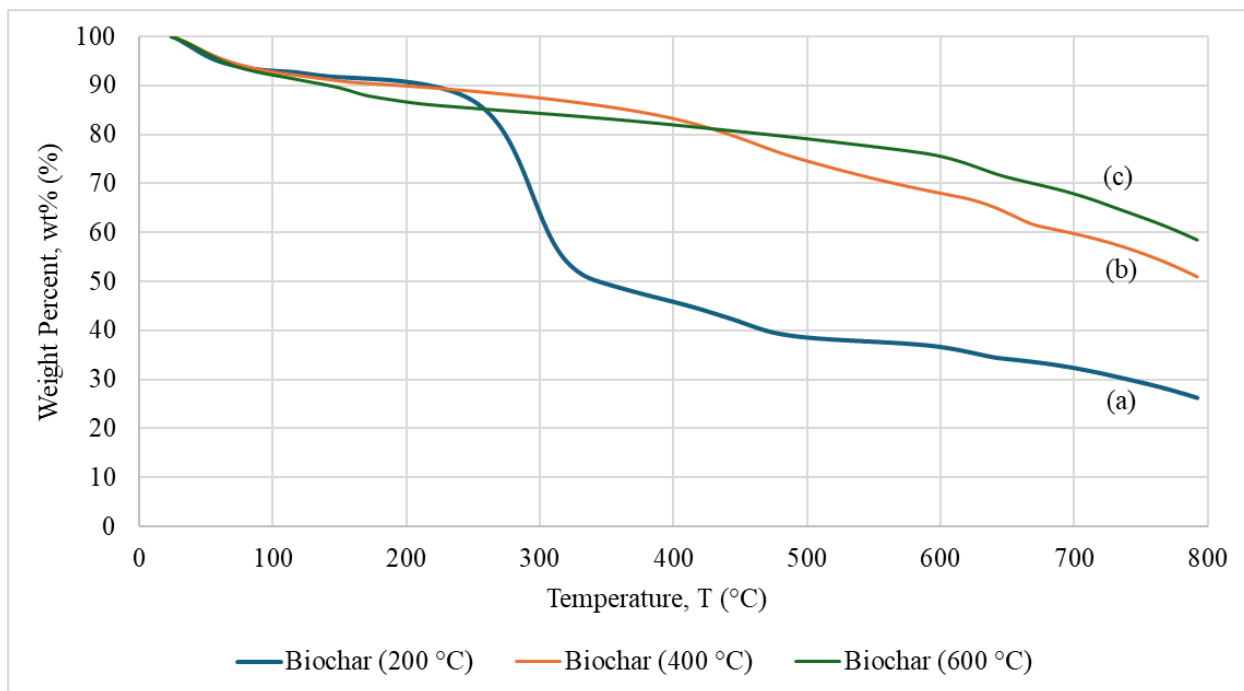

Figure 4: TGA results for (a) biochar prepared at 200 °C, (b) biochar prepared at 400 °C, and (c) biochar prepared at 600 °C.

From Figure 4 as shown above, the biochar prepared at 200 $^{\circ}$C, 400 $^{\circ}$C, and 600 $^{\circ}$C exhibited four decomposition stages. The first stage of decomposition for all three samples were observed at 27.36 $^{\circ}$C which indicated that there is removal of water. Furthermore, the biochar prepared at 200 $^{\circ}$C showed a substantial reduction in weight during the second stage of decomposition, at a temperature of 242.17 $^{\circ}$C. On the other hand, the second stage of decomposition for the biochar prepared at 400 $^{\circ}$C and 600 $^{\circ}$C occurred at 409.05 $^{\circ}$C and 399.05 $^{\circ}$C, respectively. In the second stage, degradation of hemicellulose and cellulose took place (Yusuff et al., 2022).

The biochar prepared at 200 $^{\circ}$C exhibited a significant weight loss as compared to the biochar prepared at 400 $^{\circ}$C and 600 $^{\circ}$C is due to the reason that the biochar prepared at 200 $^{\circ}$C consists of large amounts of hemicellulose and cellulose components. Generally, the pyrolysis temperature for cellulose components is in the range of 300 - 550 $^{\circ}$C (Wang et al., 2020). As a result, the pyrolysis process for dried banana trunks synthesized at 200 $^{\circ}$C in order to transform into biochar was not entirely completed. In contrast, the biochar prepared at 400 $^{\circ}$C and 600 $^{\circ}$C are within the pyrolysis temperature range for cellulose components, hence, the hemicellulose and cellulose components were successfully pyrolyzed during the pyrolysis process. Consequently, there is just a mild change observed in the second stage of decomposition for biochar prepared at 400 $^{\circ}$C and 600 $^{\circ}$C.

Moreover, the third stage of decomposition for the biochar prepared at 200 $^{\circ}$C, 400 $^{\circ}$C, and 600 $^{\circ}$C occurred at 325.58 $^{\circ}$C, 617.96 $^{\circ}$C, and 605.18 $^{\circ}$C, respectively. In this stage, the degradation of lignin will be carried out (Yusuff et al., 2022). Lastly, the fourth stage of decomposition for all

the three samples was nearly uniform above 640 °C, which indicated that the decomposition process had ended. The residue for the biochar prepared at 200 °C, 400 °C, and 600 °C are around 26 %, 50 %, and 59 %, respectively. In general, over 50 % of residues in any sample is considered a significant amount. The residue for biochar prepared at 600 °C is approximately 59 %, this could be ascribed to incomplete degradation of the sample (Gerassimidou et al., 2020). Apart from that, the biochar prepared at 200 °C is the least thermally stable as it consists of the least residue while the biochar prepared at 400 °C is fairly thermally stable as it consists of moderate residue.
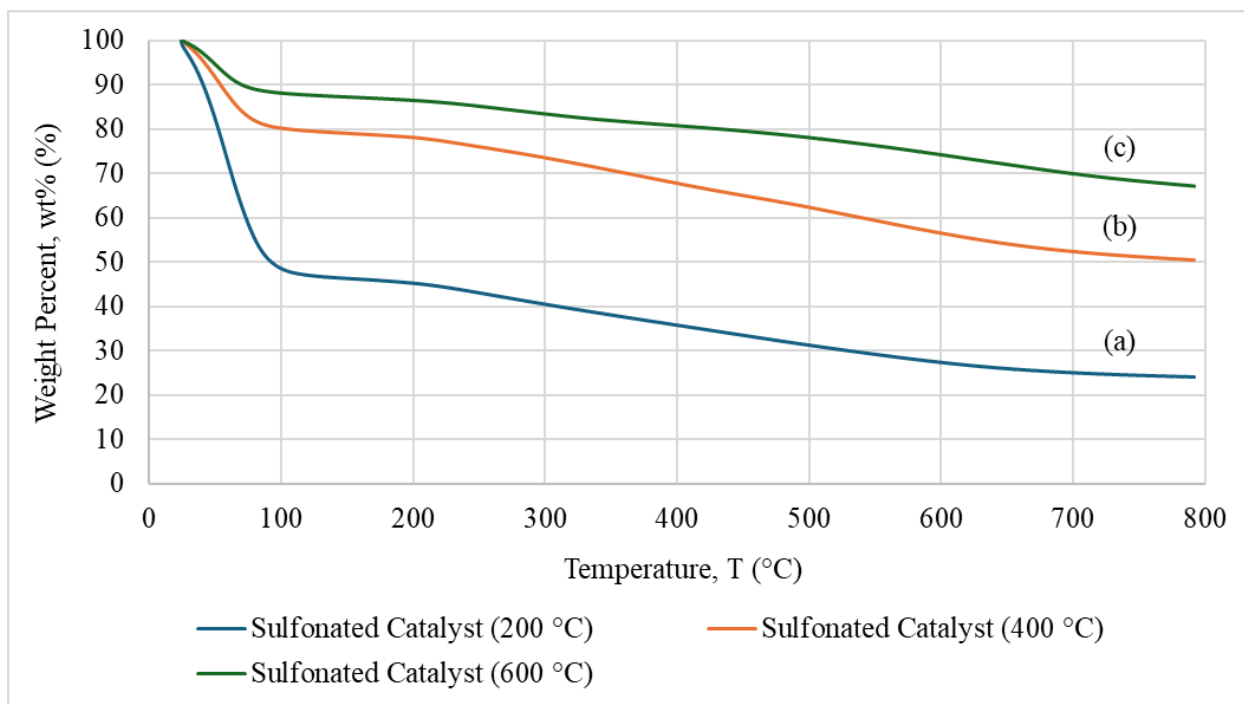

Figure 5: TGA results for (a) sulfonated solid acid catalyst prepared at 200 °C, (b) sulfonated solid acid catalyst prepared at 400 °C, and (c) sulfonated solid acid catalyst prepared at 600 °C.

From Figure 5 as shown above, the sulfonated solid acid catalyst prepared at 200 $^{\circ}$C, 400 $^{\circ}$C, and 600 $^{\circ}$C exhibited three decomposition stages. The first stage of decomposition for all three catalysts occurred at 26.91 $^{\circ}$C, which was attributed to the water removal and the degradation of -SO$_3$H groups (Yusuff et al., 2022). The slope of sulfonated solid acid catalyst prepared at 200 $^{\circ}$C is the steepest followed by sulfonated solid acid catalyst prepared at 400 $^{\circ}$C, and lastly sulfonated solid acid catalyst prepared at 600 $^{\circ}$C. This is due to the reason that the sulfonated solid acid catalyst prepared at 200 $^{\circ}$C consists of a large quantity of the -SO$_3$H group on the surface. This also can be proved by the FTIR result as shown in Figure 2 as the intensity of the -SO$_3$H absorption band is the highest.

The second stage of decomposition for all three sulfonated solid acid catalysts occurred at around 200 $^{\circ}$C. The weight loss of the sulfonated solid acid catalysts is due to the fact that there is the decomposition of lignin as well as the degradation of hemicellulose and cellulose (Yusuff et al., 2022). Last but not least, decomposition for all the three samples was relatively consistent above 600 $^{\circ}$C, suggesting that the decomposition process had come to an end. The residue for the sulfonated solid acid catalyst prepared at 200 $^{\circ}$C, 400 $^{\circ}$C, and 600 $^{\circ}$C are around 24 %, 50 %, and 68 %, respectively. In general, over 50 % of residues in any sample is considered a significant amount. The residue for sulfonated solid acid catalyst prepared at 600 $^{\circ}$C is approximately 68 %, this could be ascribed to incomplete degradation of the sample (Gerassimidou et al., 2020). Apart from that, the sulfonated solid acid catalyst prepared at 200 $^{\circ}$C is the least thermally stable as it consists of the least residue while the sulfonated solid acid catalyst prepared at 400 $^{\circ}$C is fairly thermally stable as it consists of moderate residue.

4.3 Determination of Total Acid Density

Table 5: Results for total acid density of different types of sulfonated solid acid catalysts.

Types of sulfonated solid acid catalyst	Volume of NaOH solution used, mL			Total acid density, mmol/g
	Trial 1	Trial 2	Trial 3	
200 °C	3.0	2.7	3.0	1.45
400 °C	4.5	4.8	4.2	2.25
600 °C	7.2	7.5	7.5	3.70

From Table 5 as shown above, the sulfonated solid acid catalyst prepared at 600 °C had the highest acid density which is 3.7 mmol/g. Nevertheless, high acid density did not correspond to a high FAME yield due to the catalyst's porosity was crucial for the conversion of FAME (Yusuff et al., 2022). In addition, the morphology of the catalyst as a result of thermochemicals such as carbonization and sulfonation treatment can have a significant impact on the catalyst's actual performance and effectiveness (Yusuff et al., 2022). Therefore, it is essential to assess the catalytic activity of the sulfonated solid acid catalyst through actual application, in this research study, the effectiveness of the catalysts was examined in the esterification of oleic acid.

4.4 Biodiesel Yield

Sulfonated solid acid catalyst prepared at 200 $^{\circ}$C:

(0 g / 1 g) x 100 = 0 %

Sulfonated solid acid catalyst prepared at 400 $^{\circ}$C:

(0.2105 g / 1.0000 g) x 100 = 21.05 %

Sulfonated solid acid catalyst prepared at 600 $^{\circ}$C:

(0.0189 g / 1.0000 g) x 100 = 1.89 %

After the sulfonated solid acid catalysts were synthesized, they were used to catalyze the transesterification reaction of OA and their respective biodiesel yields were calculated. Based on the calculation as shown above, the sulfonated solid acid catalyst prepared at 400 $^{\circ}$C is capable of giving the highest biodiesel yield which is 21.05 %. On the other hand, the sulfonated solid acid catalyst prepared at 200 $^{\circ}$C is totally unable to produce any biodiesel while the sulfonated solid acid catalyst prepared at 600 $^{\circ}$C is only able to give 1.89 % biodiesel yield. Since the biodiesel produced from sulfonated solid acid catalysts prepared at 200 $^{\circ}$C and 600 $^{\circ}$C are too little, they were unable to be further analyzed by GC-MS.
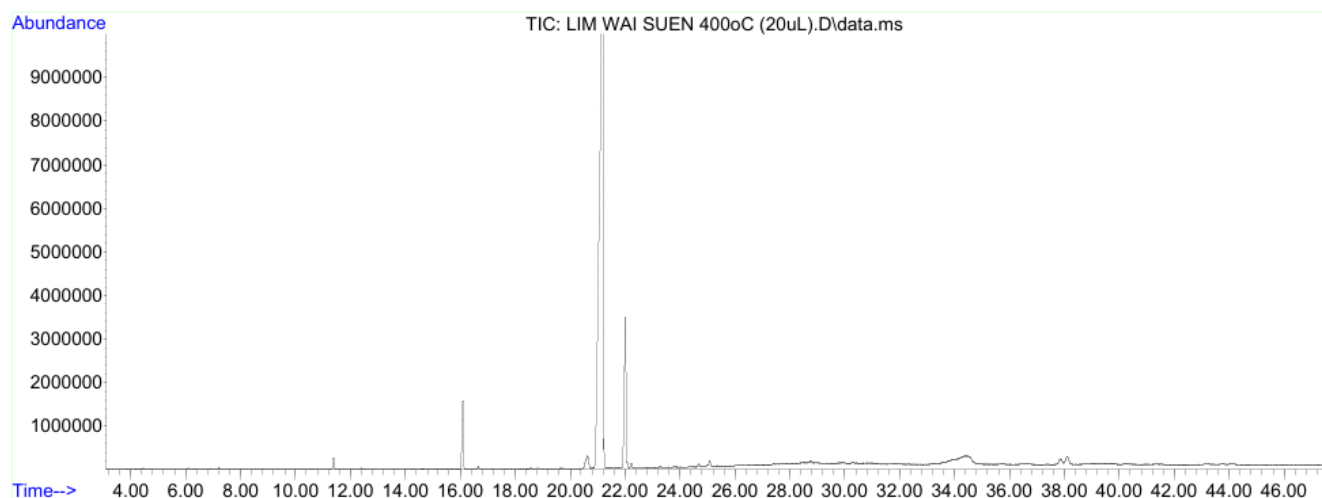
4.5 GC-MS Analysis

Figure 6: GC-MS result for the esterified product catalyzed by sulfonated solid acid catalyst prepared at 400 °C.

GC-MS analysis was conducted in order to ensure the conversion of OA into FAME (biodiesel) is successful and the FAME content in the esterified product. From Figure 6 as shown above, an intense peak was observed at a retention time of 21.181 minutes. From the MS library, it showed the compound name is 9-octadecenoic acid (Z)-, methyl ester which is also known as methyl oleate. Methyl oleate is a methyl ester form for OA and the ester functional group is present in the structure of methyl oleate. As a result, this indicated that the conversion of OA to methyl oleate is successful. The area percent for methyl oleate is 48.622 %.

Figure 7: Structure for conversion of OA to methyl oleate.

On the other hand, other minor byproducts were also found in the GC-MS result. Hexadecanoic acid, methyl ester which is also known as methyl palmitate was found at the retention time of 16.094 minutes with an area percent of 2.647 %. Furthermore, octadecanoic acid, methyl ester which is also known as methyl stearate was found at the retention time of 20.632 minutes with an area percent of 1.149 %. Lastly, 9,11-octadecadienoic acid, methyl ester, (E,E)- which is also known as methyl linoleate was found at the retention time of 22.014 minutes with an area percent of 6.719 %. These byproducts were detected by GC-MS due to some impurities present in the sample.

CHAPTER 5: CONCLUSION

In conclusion, all the objectives of study were successfully achieved. The sulfonated solid acid catalysts with various temperatures which are 200 $^{\circ}$C, 400 $^{\circ}$C, and 600 $^{\circ}$C were successfully synthesized. Characteristic absorption bands (-SO$_3$H and O=S=O stretching) at ~ 1030 cm^{-1} and ~ 1166 cm^{-1} were observed in FT-IR results for all three sulfonated solid acid catalysts which implied the successful sulfonation of the biochars. Furthermore, from the TGA results, the thermal stability of sulfonated solid acid catalyst prepared at 200 $^{\circ}$C is the least as its remaining residue is ~ 24 % while the sulfonated solid acid catalyst prepared at 400 $^{\circ}$C is fairly thermally stable as its remaining residue is ~ 50 %. The remaining residue for sulfonated solid acid catalyst prepared at 600 $^{\circ}$C is too high which is ~ 68 %, suggesting that there is an incomplete degradation of the sample. Moreover, from the determination of total acid density results for all three sulfonated solid acid catalysts, the sulfonated solid acid catalyst prepared at 600 $^{\circ}$C had the highest total acid density which was 3.7 mmol/g. Nevertheless, the effectiveness of the catalyst for the conversion to FAME is largely affected by the porosity and morphology of the catalyst. There was absolutely no assurance of a high FAME production with high acid density. Next, based on the biodiesel yield calculated, sulfonated solid acid catalyst prepared at 400 $^{\circ}$C is the most suitable temperature used for manufacturing catalyst as its biodiesel yield is the highest which is 21.05 %. Last but not least, from the GC-MS result, a maximum FAME content of 48.622 % was obtained by using sulfonated solid acid catalyst prepared at 400 $^{\circ}$C which synthesized at optimum sulfonation conditions which are conducted at heating temperature of 85 $^{\circ}$C for 2 hours with 20:1 MeOH/OA molar ratio and 1 g catalyst loading.

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