BIODIESEL SYNTHESIS VIA HETEROGENEOUS CARBON ACID CATALYSIS FROM DE-OILED JATROPHA CURCAS WASTE

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FACULTY OF ENGINEERING
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BIODIESEL SYNTHESIS VIA HETEROGENEOUS CARBON ACID CATALYSIS FROM DE-OILED JATROPHA CURCAS WASTE

ABSTRACT

In the development of a more efficient and sustainable biodiesel production process, a heterogeneous carbon-based acid catalyst was prepared from the waste seed cake of *Jatropha curcas* (JC) left after de-oiling of the seeds to obtain the crude oil. The de-oiled seed cake was carbonized into carbon form before sulfonated using sulfuric acid (H_2SO_4) to produce the catalyst. The physical and chemical properties of both the carbon precursor and the prepared carbon-based acid catalyst were characterized by a variety of techniques. The catalyst was consequently used to esterify the crude JC oil in order to lower the high free fatty acid content to acceptable levels (<4 mg KOH/g) before conversion into biodiesel can take place. The optimal esterification parameters of 12:1 methanol/oil ratio, 7.5 wt% catalyst, 60 °C, 60 min reaction time at 360 rpm were determined to effectively achieve a maximum conversion yield of 99.13%. The catalytic activity of the catalyst reduced gradually when re-used during multiple esterification cycles but maintained good stability in catalytic activity up to the 4th cycle. The esterified oil was converted into biodiesel by base-catalyzed transesterification under parameters of 1 wt% potassium hydroxide, 6:1 methanol/oil ratio, 60 °C for 60 minutes. The process produced 96% biodiesel yield that met the ASTM D6751 and EN14214 standards. Changes occurred to the properties of the crude JC oil, esterified oil and biodiesel were determined to have improved significantly after utilizing the catalyst in the biodiesel production process. Overall, the prepared carbon-based acid catalyst proved to be an effective and a more sustainable catalyst option to be utilized in the esterification process of JC oil, in producing high yield and quality biodiesel.

Keyword: Carbon-based acid catalyst, *Jatropha curcas*, Seed cake, Parameter, Biodiesel

SINTESIS BIODIESEL MELALUI PEMANGKINAN ASID KARBON HETEROGEN DARIPADA SISA JATROPHA CURCAS

ABSTRAK

Dalam kajian ini, pemangkin asid heterogen berasaskan karbon telah dihasilkan daripada sisa kek benih *Jatropha curcas* (JC) selepas minyak mentah diekstrak keluar dari biji benih tersebut. Kek benih telah dikarbonisasi ke dalam bentuk karbon sebelum disulfonisasi menggunakan asid sulfurik (H_2SO_4) untuk menghasilkan pemangkin tersebut. Sifat-sifat fizikal dan kimia kedua-dua bahan karbon dan pemangkin asid berasaskan karbon itu telah dikaji menggunakan pelbagai teknik. Pemangkin itu seterusnya digunakan dalam pengesterifikasi minyak JC mentah untuk mengurangkan kandungan asid lemak bebas yang tinggi ke tahap yang sesuai (<4 mg KOH / g) sebelum penukaran kepada biodiesel boleh berlaku. Parameter yang optimum iaitu 12:1 nisbah metanol/minyak, 7.5 wt% pemangkin, 60 °C, 60 min tempoh reaksi pada 360 rpm telah dikenalpasti untuk mencapai hasil penukaran maksimum 99.13% dengan berkesan. Aktiviti pemangkin berkurang secara beransur-ansur apabila diguna semula dalam beberapa kitaran esterifikasi namun tetap menunjukkan kestabilan yang baik dalam aktiviti pemangkin sehingga kitaran ke-4. Minyak yang telah diesterifikasi telah diubah menjadi biodiesel melalui transesterifikasi menggunakan parameter 1wt% pemangkin potasium hidroksida, 6: 1 nisbah metanol/minyak, 60 °C selama 60 min. Proses ini menghasilkan 96% biodiesel yang memenuhi piawaian ASTM D6751 dan EN14214. Perubahan berlaku kepada sifat-sifat minyak JC mentah, minyak diesterifikasi dan biodiesel ditentukan telah meningkat dengan ketara selepas menggunakan pemangkin dalam proses pengeluaran biodiesel. Secara keseluruhannya, pemangkin asid berasaskan karbon terbukti menjadi pilihan pemangkin yang lebih efektif dan berkesan untuk digunakan dalam proses pengesterifikasi minyak JC, dalam menghasilkan biodiesel yang tinggi dalam jumlah dan kualiti.

Kata kunci; Pemangkin asid berasaskan karbon, *Jatropha curcas*, Kek benih, Parameter, Biodiesel

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LIST OF SYMBOLS AND ABBREVIATIONS

%	:	Percentage
&	:	and
et al.	:	And others
wt%	:	Percentage by weight
<	:	Less than
>	:	More than
JC	;	*Jatropha curcas*
FFA	:	Free fatty acid
KOH	:	Potassium hydroxide
H_2SO_4	:	Sulfuric acid
HCL	:	Hydrochloric acid
SO_3	:	Sulphate
SO_3H	:	Sulfonic acid
°C	:	Degree celcius (dimension: T)
FAME	:	Fatty acid methyl ester
R	:	Functional groups
-OH	:	Hydroxyl functional group
-O	:	Oxide functional group
NaOH	:	Sodium hydroxide
THF	:	Tetrahydrofuran
DMSO	:	Dimethyl sulfoxide
e. g.	:	For example
ppm	:	Parts per million
Refs.	:	References

$-SO_3H$: Sulfonic acid functional group

-COOH : Carbonic acid functional group

BET : Brunauer-Emmet-Teller

TPD : Temperature Programmed Desorption

GC : Gas chromatography

II : Two

Pa : Pascal, (dimension; $ML^{-1}T^{-2}$)

h : Hour

TGA/SDTA : Thermo Gravimetric Differential Thermal Analyzer

N_2 : Nitrogen gas

mL : Millilitre (dimension; V)

min : Minutes

$SO_4{}^{-2}$: Sulphate ion

L : Litre (dimension; V)

BJH : Barrett-Joyner-Halenda

FESEM : Field Emission Scanning Electron Microscopy

EDX : Energy-Dispersive X-ray Spectrometry

FTIR : Fourier Transform Infrared Spectroscopy

NH_3 : Ammonia gas

H_2 : Hydrogen gas

He : Helium gas

N_2 : Percentage

g : Gram (dimension; M)

M : Mol (dimension; N)

A.V. : Acid value

rpm : Rotations per minute

µm : Micrometre (dimension; L)

@ : at

ASTM : American society for testing and materials

$H_3PW_{12}O_{40}/SiO_2$: Tungstophosphoric Acid/Cs-salt Immobilized-Silica

$Cs_{2.5}H_{0.5}PW_{12}$: Cs-doped heteropolyacid catalyst

CsHPW : Cesium-doped heteropoly tungstate

Ar-SBA-15 : Argon-doped mesoporous Santa Barbara Amorphous-15

MPD-SO_3H-IL : Mesoporous polymeric solid acid

SiO_2-$SiO_3H/COFe_2O$: Magnetic sulfonic acid functionalized silicon co-ferrite solid

$SO_4{}^{-2}/TiO_2$-SiO_2 : Sulphonated titanium silicone dioxide

$Mn_{0.5x}Zr_{0.5y}Al_XO_3$: Alumina supported manganese zirconia

SiO_2-Pr-SO_3H : Sulfonic acid-functionalized silica

WO_3/Zr_2 : Tungstated zirconia

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CHAPTER 1: INTRODUCTION

1.1 Background

In current situations, the extensive use of fossil fuels, especially in the transport sector have led to an alarming degenerative state of the environment and fluctuations in fuel prices. These problems conjoined with the receding fossil fuel supply have been the motivation for the development of alternatives for an energy supply by researchers. Consecutively, biofuels have been extensively researched as the most probable replacement to fossil fuels ("BP statistical review of World Energy," June 2013; Deeba et al., 2012; Panwar et al., 2011).

Biodiesel is a mixture of long-chain alkyl esters produced from organic materials (edible, non-edible, waste frying oil, animal fats and algae biomass) via transesterification reaction in the presence of a catalyst (acidic, basic or enzymatic) (Leung et al., 2010). There are numerous benefits biodiesel has over conventional diesel, which include cleaner production process, engine compatibility, renewability, biodegradability, less toxicity, non-flammable, higher energy return, low exhaust emissions, fumes and odours (Cavalcanti-Oliveira et al., 2011; Sharma et al., 2012).

Currently, most of the feedstock used for biodiesel production is of edible agricultural crops that lead to increased production cost while negatively affect the food supply market (Ahmad et al., 2011). With that, a non-agricultural, non-edible and sustainable feedstock was proposed in order to curb this problem including *Jatropha curcas* (JC) seed oil. Consequently, the high free fatty acid (FFA) content in non-edible oils require for the additional step of an acid catalyzed esterification as a pre-treatment to reduce the FFA value to an acceptable level (<2 wt% equivalent to 4 mg KOH/g) before direct transesterification can be carried out (Ramadhas et al., 2005; Veljković et al., 2006).

Other than the choice of feedstock, the type of catalyst used also play a vital role in producing biodiesel in an efficient and economical way without compromising the biodiesel quality. Therefore much attention is also focused on researching for a suitable catalyst over the years, from the conventional homogeneous catalyst to heterogeneous catalyst, and most recently the development of biomass-based heterogeneous catalyst.

1.2 Problem statement

There are setbacks to biodiesel production that impedes its competition with the conventional diesel. The average price of biodiesel is twice the price of conventional diesel due to the high cost of production incurred (Moser, 2009). With other determinants such as manpower, alcohol, reaction catalyst and purification cost considered, type of feedstock used makes up 80% of the overall production cost incurred (Demirbas, 2007). As a solution, researchers have started to investigate the utilization of non-edible oil as feedstock (Srivastava & Prasad, 2000).

Although direct use of non-edible oil to be converted into biodiesel is attainable, the use of conventional acid catalyst (H_2SO_4) in the esterification process however makes for a more complicated process with additional steps of product separation, washing, and neutralizing with high possibility of product contamination. All of this incure more costs unto the production process. Large amounts of water waste are also generated through these steps that are detrimental to the environment (Meher et al., 2013).

Then, the use of heterogeneous acid catalysts as replacements were introduced in the esterification of high FFA containing oils without requiring any additional steps of product separation or purification. However, past studies have been focused on costly metal-based catalysts that incurred more intensive reaction conditions (Farooq et al., 2013), showed poor reusability and were non-decomposable (López et al., 2005).

For that reason, production of solid acid catalyst from carbon material produced from biomass, glucose or biochar appear as a viable alternative as it is physically and chemically stable, is low in cost, environment friendly, readily available, and deals with waste discarding concerns (Konwar, Boro, et al., 2014; Konwar, Das, et al., 2014; Sharma et al., 2012).

In the present study, *Jatropha curcas* (JC) seed cake was utilized to prepare the carbon-based solid acid catalyst. JC oil contains a high FFA content (25.4 mg KOH/g) subjecting it to a pre-treatment of esterification to lessen the FFA content to a suitable level (<4 mg KOH/g) before biodiesel production can take place. The waste (seed cake) produced from de-oiling the JC seeds is reused by converting it into catalyst, making the overall process more green and cost-efficient. The parameters affecting the progress of esterification were analyzed to determine the optimal conditions needed for maximum catalytic activity of the catalyst. The esterified oil is consequently transesterified into biodiesel and properties of the oil were analyzed throughout the whole experimentation to evaluate the changes incurred and its compatibility with the ASTM D6751 and EN14214 standards.

1.3 Objectives

The aim of this study is to investigate the carbon-based acid catalyst prepared from the de-oiled *Jatropha curcas* waste seed cake. Objectives of study are as follows:

i. To investigate the preparation of carbon-based acid catalyst from *Jatropha curcas* de-oiled seed cake

ii. To analyze the characteristics of the prepared carbon-based acid catalyst

iii. To investigate the effectiveness of the prepared carbon-based acid catalyst in the biodiesel production process

1.4 Scope of study

While there have been several studies conducted on carbon-based acid catalysts before, this study utilized the waste of the oil feedstock to be consequently used in catalyzing the biodiesel production process. A heterogeneous carbon-based acid catalyst was developed from the de-oiled seed cake of *Jatropha curcas* (JC). For catalyst preparation, the suitable carbonization temperature and sulfonation time were determined. The physical structure and chemical content of the prepared catalyst were then analyzed using various techniques. Discussions on the catalysts' build and formation of its catalytic ability was carried out using the data obtained. To determine the catalysts' effectiveness at catalyzing the esterification process, the parameters for optimum conversion yield of FFA in JC oil achieved were studied. The efficiency of the catalyst was verified through the reusability test conducted by re-using the catalyst in multiple esterification cycles and evaluating the change in conversion yield achieved in each cycle. Finally, the esterified oil was transesterified into biodiesel using standard parameters of 1 wt% potassium hydroxide catalyst, 6:1 methanol/oil molar ratio, 60°C, 60 min and 350 rpm (Bala et al., 2012). The overall biodiesel produced from this process was determined with changes occurring to the crude oil, esterified oil and biodiesel analyzed and reported.

1.5 Outline of thesis

Chapter 1 contains background of biodiesel and explains the problems statements and objectives in detail

Chapter 2 explains the use of non-edible oil as biodiesel feedstock as well as contains information on the *Jatropha curcas* seeds and its function as a non-edible feedstock, the process of biodiesel production when using non-edible oil as feedstock, and study of solid acid catalyst from carbon-based material. This chapter also forms a critical review of the information gap and relationship between them

Chapter 3 lists the material and apparatus used and outlines in detail the flow of methodology on how the study was carried out

Chapter 4 presentation and discussion of the data and findings from the study with supportive information from other similar studies

Chapter 5 establishes the cumulative findings of the study and its significant effect in the biodiesel production study

CHAPTER 2: LITERATURE REVIEW

2.1 Biodiesel production from non-edible oil

The biodiesel industry has been using edible oil as feedstock since its first introduction. Described as the first generation biofuel, use of edible oil as feedsctock was enforced upon given its ready availability as raw material and gives high biodiesel yield with alkali catalyst due to its low FFA content (Acevedo et al., 2015). Generally edible vegetable oils (high grade) are easier to be converted into biodiesel due to its purity and low FFA content. The available edible vegetable oils that are utilized as biodiesel feedstock are sunflower oil, soybean oil, cotton oil, palm oil, etc. These oils contain less water content and FFA content <1% which is suitable for homogeneous catalysts (Di Serio et al., 2010).

However, with such large scale utilization of edible oils as source of biodiesel, it puts a big risk to the world, by which even the slightest error in planning, will affect the food supply and economic balance negatively (Gui et al., 2008). Conversion of edible sources into fuels will also compromise the food supply market. The trend in global vegetable oil ending stock shows that, even with sustained or even increased production of edible oils, the ending stock remains at a declining rate as the edible oil-derived biodiesel production is increased by the year (Fox investments, 2006).

Currently, the utilization of non-edible oil is gaining more attention as the future raw material for biodiesel production as it lessens the dependency on edible oils (Verma & Sharma, 2016). Since use of edible oils as biodiesel feedstock arises problems of high cost of production and land consumption (Kumar & Sharma, 2011), non-edible oils are deemed suitable as alternative feedstock as they are not in demand for food, given it is not safe for human consumption due to its toxic components (Shah & Gupta, 2007).

In estimation, the type of feedstock used amounts to almost 70% of the total cost for biodiesel production (Mansir et al., 2017). Comparatively, non-edible oils production costs less compared to edible oils. Except for palm oil, the cost of cultivation per kilogram for non-edible oil is less than of edible oil cultivation (Kumar & Sharma, 2011) making the purchase price for edible oil is more expensive than non-edible oil, especially in developing countries, making the estimated biodiesel production capital using non-edible feedstock to be lower (Balat, 2011). Hence, it is more economical to focus on non-edible resources as a low-cost prospective feedstock for biodiesel production rather than the edible resources (Atabani et al., 2013).

Non-edible oil as feedstock is also favoured due to its sustainability. They can be found in many parts of the world (Azam et al., 2005). Crops of non-edible oils can be cultivated on remote and harsher environments. Systematically, they can also be cultivated on boundaries of agricultural fields, irrigation canals and road sides (Kumar & Sharma, 2011). There is a high availability of the various types of plants which produces non-edible oils suitable to be made into biodiesel. Statistically, 37 out of 75 non-edible oil plant species studied were determined to meet the ASTM standards for biodiesel production, making them viable alternatives for biodiesel feedstock (Azam et al., 2005) (Refer to Appendix A). From this, the most commonly utilized sources include Karanja oil (Paul et al., 2014), Mahua oil (Puhan et al., 2005), Ceiba pentandra (Ong et al., 2014), Calophyllum inophyllum (Atabani & César, 2014) and *Jatropha curcas* (Banković-Ilić et al., 2012).

As feedstock for biodiesel production, non-edible oils has better liquid nature portability, ready availability of resources along with the fuels’ renewability, lower sulfur and aromatic contents and its biodegradability (No, 2011). Non-edible-derived fuel owns good prospects for its ASTM compliant fuel quality with good engine performance and favorable emission characteristics. Through the emergence of new and advanced technologies, the resource will prove to be more efficient and environmentally friendly substitute in improving biofuel characteristics (Atabani et al., 2013).

Generally, the feasibility of non-edible oil as feedstock for biodiesel production largely depends on the composition of fatty acid and free fatty acid (FFA) content. Fatty acids are grouped into two categories, which are saturated and unsaturated fatty acids. The saturated fatty acid group consists of stearic, palmitic and dihydroxystearic acid while unsaturated fatty acid comprises of eloic, linoleic, ricinoleic, plamitoleic, linolenic and eicosenoic acid (Gui et al., 2008).

There are some disadvantages to non-edible oil as feedstock which include higher FFA content in crude oil, higher viscosity, lower volatility and higher percentage of carbon residue in biodiesel produced including reactivity of unsaturated hydrocarbon chains (No, 2011). Non-edible oil also lacks in resource availability in the market and their current demand as industrial bio-lubricants instead (Ashraful et al., 2014).

2.2 *Jatropha curcas* (JC)

The JC plant is found in the wild or semi-cultivated areas in Central and South America, India, Africa and South East Asia. The plant species distribution is documented as shown in **Figure 2.1**.

Figure 2.1: The map shows countries where the species has been planted (WAC, 2013)

It is a drought resistant plant that can grow in arid and semi-arid conditions. Although the plant produces better crop yields in a humid environment, the plant shows high adaptability and can be grown in marginal soils and wastelands (Kumar & Sharma, 2011). Plantation of JC plant is reported to produce seed harvest up to 15 tonnes/ha/year (Ouwens et al., 2007) and the JC oil yields is 1590 kg/ha/year (Ong et al., 2011). However, an updated or detailed data for this plant species plantation industry is still very limited and unclear. The JC seeds contain around 40-60 % of oil which is considerably high (Kumar & Sharma, 2008). The seeds produced are toxic for human consumption (Corro et al., 2010).

2.2.1 *Jatropha curcas* as feedstock for biodiesel production

Cultivation of plants for biodiesel production is usually heavily reliant on the geographical and climate situation of each country. This is why different countries opt for different feedstock choice for their biodiesel production such that sunflower and rapeseed oil are used as the main biodiesel feedstock in Europe, soybean in the United States, canola oil in Canada while palm oil is the feedstock of choice in tropical countries (Cao et al., 2008). Non-edible oils, such as Jatropha and Karanja oil are highly promoted in countries like India (Azam et al., 2005).

Currently JC is deemed as one of most favorable alternative feedstock for biodiesel production in Asia, Europe and Africa. India uses JC oil as its main feedstock of choice for biodiesel production (Karmakar et al., 2010). Given the high availability of the plant in that region, high oil content of JC seeds with no proper care needed, it remains as a good prospective feedstock for biodiesel production (Martín et al., 2010; Rozina et al., 2017)

Over the years, the JC plantation for biodiesel production industry has caught up to Malaysia (Lim et al., 2015). JC plantation is deemed suitable in Malaysia given the JC plant grows well in temperatures of 20-30 °C, wide range of humidity given the seasonal heavy rainfall, varying conditions of soil, pH (Mofijur et al., 2012). JC plantation is seen as sustainable as the produce yields are expected by the second year of establishment, reaches maturity easily under 5 years and the life expectancy is long, up to 50 years (Kumar & Sharma, 2011; Mofijur et al., 2012).

JC is rich in hydrocarbon and has high free fatty acid content (FFA) (41%) (Atabani et al., 2012; Openshaw, 2000). Unlike other Jatropha species, the semi-dry oil of JC contain 37-63% oleic acid as its primary fatty acid, 35% linoleic acid, 14% palmitic and 6% stearic acid (Kumar & Sharma, 2008). Like in other oilseed crops, the fatty acid composition of JC seeds may be altered to concentrate the stearic or oleic acid content by silencing the delta-9 or 12 desaturase genes or interspecific hybridization (Liu et al., 2002). However, quality of JC deteriorates over time as a result of poor handling and storage conditions. Exposure to air may result in increased water content and increased percentage of fatty acid in oil. The altered fatty acid and water content is reported to bear significant effects on the transesterification process (Berchmans & Hirata, 2008; Lu et al., 2009).

Properties of JC oil like acid value, viscosity, oxidation value, etc. is also studied to determine its suitability as feedstock for biodiesel production. **Table 2.1** observes the different properties of JC oil as studied by different researchers. It can be seen that generally the JC oil has the viscosity in the range of 8.72–52.76 mm^2/s, acid value vary within range of 0.92–38.2 mg KOH/g and density is within the range of 892–940 kg m^3. The calorific value is 38.20–42.15 MJ/kg. Considering the high viscosity of JC oil at 28.35 mm^2/s and acid value of 12.73 mg KOH/g, many researchers have stated that the JC oil is not suitable for direct transesterification for biodiesel production as the high FFA content in the oil will react with the base catalyst, forming soap and thus impeding the biodiesel production process. As a result, a two-step process of biodiesel production is suggested comprising of a pre-treatment esterification followed by transesterification (Lu et al., 2009).

Table 2.1: Comparison of crude JC oil properties

Kinematic viscosity (mm^2/s)	Density (kg/m^3)	Flash point (°C)	Calorific value (MJ/kg)	Acid value (mg KOH/g)	Iodine value (g I_2/100 g)	Ref.
34.84	918.6	–	–	–	–	(Silitonga et al., 2011)
35.4	–	237	–	–	101	(Balat, 2011)
49.93	918.6	240	39.774	–	–	(Senthil Kumar et al., 2003)
51	932	242	37.01	–	–	(Jain & Sharma, 2010)
40.06	916	235	39.63	3.71	101.7	(Divakara et al., 2010)
24.5	892	498	38.65	10.5	–	(Deng et al., 2011)
52.76	932.92	210	38.2	–	94	(Pramanik, 2003)
37–54.8	–	210–240	37.83–42.05	0.92–6.16	92–112	(Koh & Mohd. Ghazi, 2011)
49.9	918	240	39.77	–	–	(Chhetri et al., 2008)
24.5	940	225	38.65	28	–	(Parawira, 2010)
35.98	917	229	39.071	–	–	(Agarwal, 2007) and (Y. V. H. Rao et al., 2009)
40.4	917	274	39.86	38.2	112.5	(Ejilah et al., 2010)
29.4	920	225	–	28	–	(Leung et al., 2010)
8.72	912	125	–	–	10.47	(Kywe & Oo, 2009)
24.50–52.76	901–940	180–280	38.20–42.15	–	–	(No, 2011)

2.3 Biodiesel production process

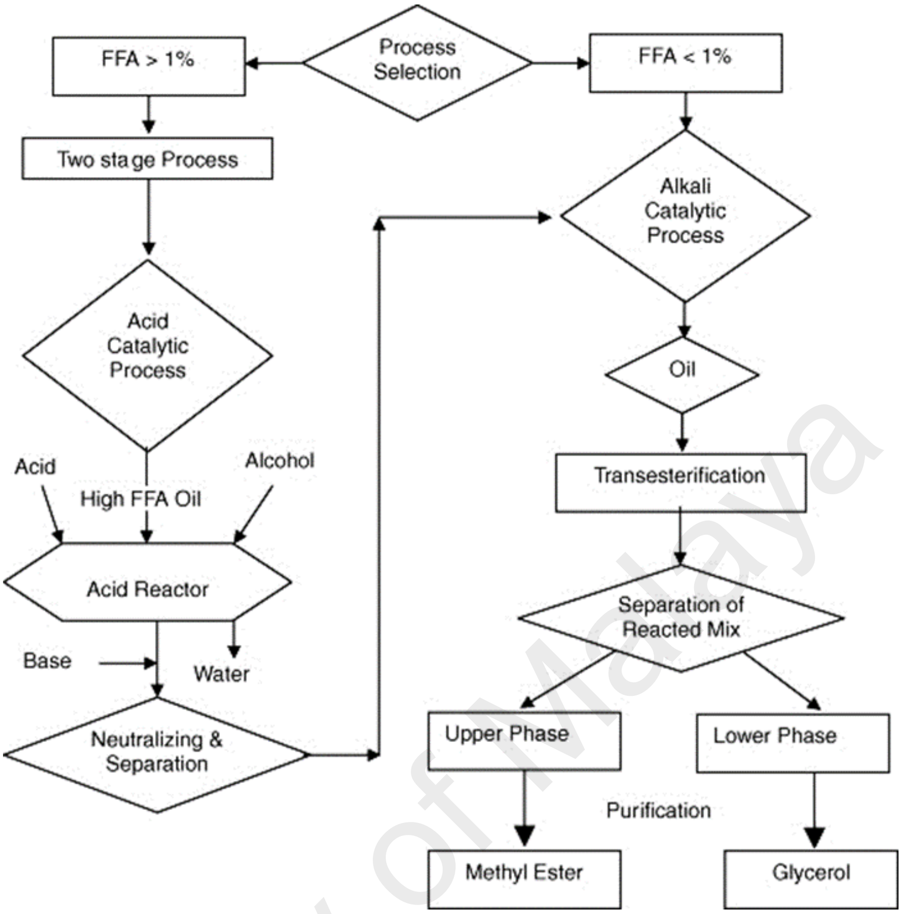


Figure 2.2: Flow chart of conventional biodiesel production (Karmakar et al., 2010; Xue et al., 2011)

As seen in **Figure 2.2**, biodiesel is synthesized mainly by two routes: (i) esterification of long chain fatty acids and (ii) trans-esterification of triglycerides (Ma & Hanna, 1999). Biodiesel production goes through a transesterification process known as "alcoholysis" meaning the breaking down of fats or oil by reaction with an alcohol, forming esters and glycerol (Demirbas, 2008).

Given JC oil is high in FFA count, the FFA is unable to convert into fatty acid methyl ester (FAME), the chemical form for biodiesel, directly due to the high amount of the FFA reacting to the alkali catalyst causing high fuel viscosity, emulsification and forms by-products of soaps and gels which lead to product separation complications, all of which will substantially affect the yield, quality and fuel properties of biodiesel produced (Issariyakul & Dalai, 2014). Soap production also results in increased cost of downstream purification of the biodiesel. Therefore, a pre-treatment of esterification is required to lower the high FFA content in feedstock to a desired level prior to the transesterification process.

In this first step of the biodiesel production process, the crude oil is reacted with alcohol and acid is used as a catalyst to convert FFA into esters. After the FFA level in the feedstock is at the acceptable level, the transesterification step will be conducted employing an alkali catalyst to convert the FFA into FAME (Atabani et al., 2012; Berchmans & Hirata, 2008; Borges & Díaz, 2012; Kumar & Sharma, 2008). The overall reaction of the esterification process is observed as in **Figure 2.3**. To attain the optimal esterification yield, each parameter including the reaction temperature, catalyst loading, reaction duration and molarity of reactants has to be taken into account (Atabani et al., 2012; Hassan & Vinjamur, 2014).

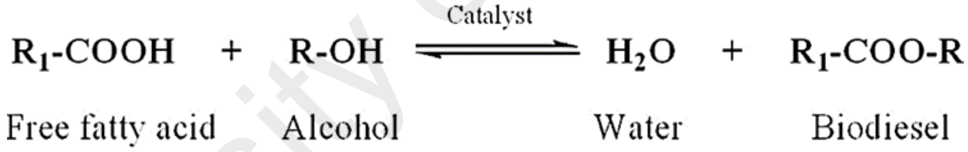


Figure 2.3: Esterification reaction of free fatty acid (Avhad & Marchetti, 2015)

The transesterification process involves the usage of alcohol to break down triglyceride to form fatty acid methyl ester (FAME) which is the desired biodiesel form and glycerol as by-product. An overall view along with the sequential process of the transesterification process is as shown in **Figure 2.4** and **Figure 2.5**, respectively. The transesterification process takes place by a three sequential reaction that is reversible, consisting of triglyceride conversion to diglyceride, diglyceride to mono glyceride and mono glyceride to fatty ester and glycerol (Ma & Hanna, 1999). The study by Sahoo et al. (2009) reported that the conversion rate is highly affected by the amount of alcohol used in the transesterification as alcohol amount in excess is needed in order to push the reaction towards completion. Under parameters of 11:1 methanol to oil molarity, 1.1% (v/v) of potassium hydroxide as catalyst at 66 °C for 120 min., 93% of FAME yield were obtained with improved fuel properties (Sahoo et al., 2009). The base catalysts generally used include sodium hydroxide and potassium hydroxide while alcohol used are mainly methanol and ethanol (Karmakar et al., 2010).

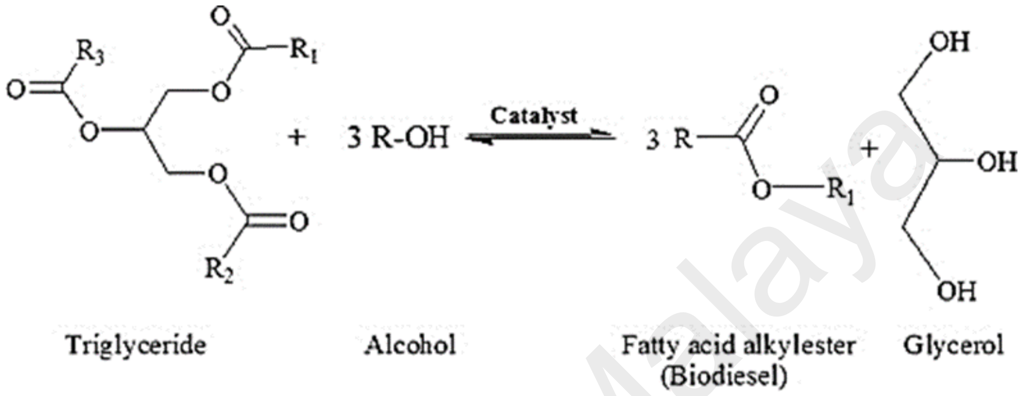


Figure 2.4: Transesterification reaction (Avhad & Marchetti, 2015)

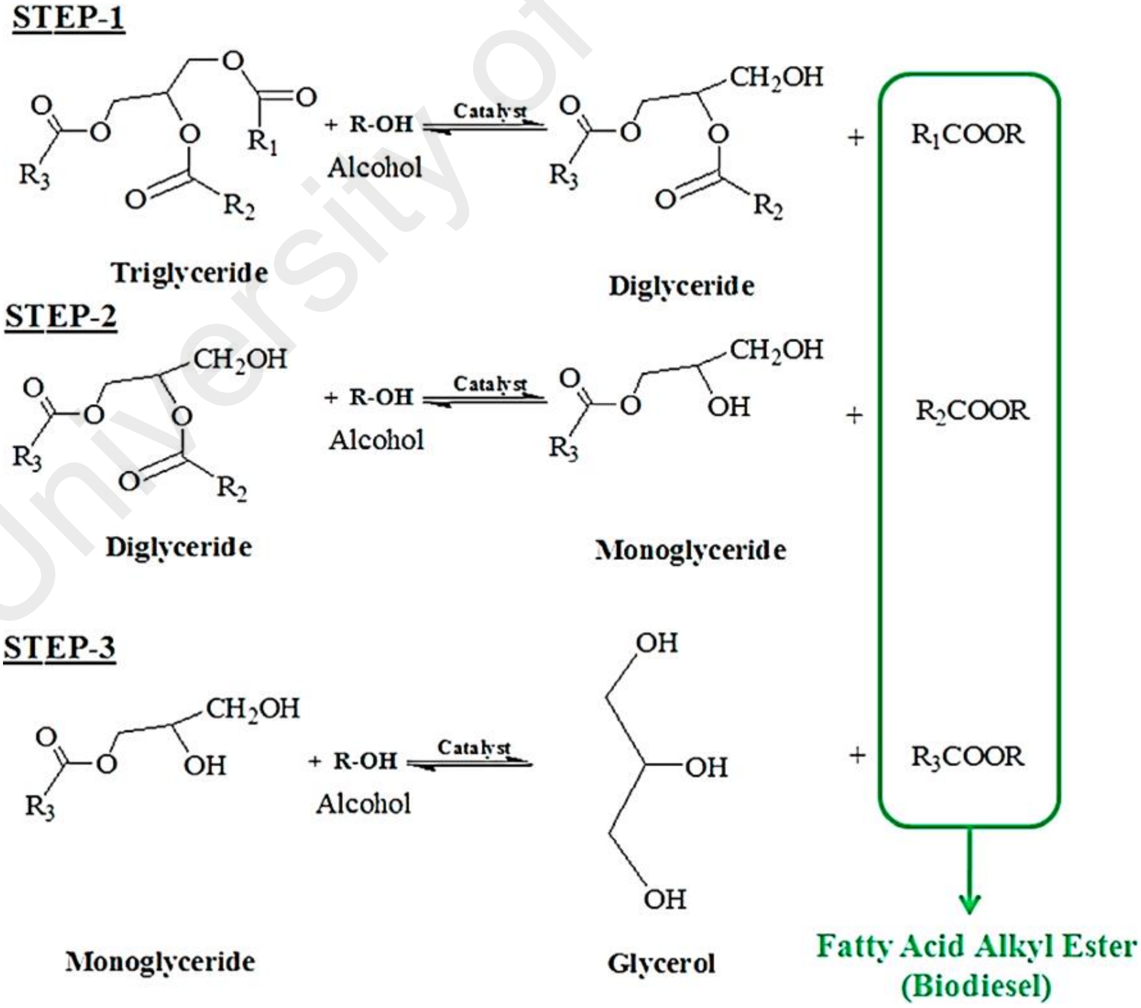


Figure 2.5: Step-wise transesterification reaction (Avhad & Marchetti, 2015)

2.4 Catalyst used in biodiesel production process

In the biodiesel production process, the two most viable factors that highly influence the biodiesel yield and quality is the feedstock and catalyst used. The feedstock used will determine the number of steps and synthesis route of the whole production process while the catalyst hold a vital part in enhancing and facilitating the process (Konwar, Boro, et al., 2014). Given that alcohol is hardly soluble in the oil/fat content of the reactants, the catalyst functions to improve the alcohols' solubility therefore improving the reaction rate of the process (Karmakar et al., 2010).

Generally, the catalyst used in biodiesel production process can be categorized into two groups of homogeneous and heterogeneous catalyst which are further divided into three groups of acid, base and acid-base catalyst (Avhad & Marchetti, 2015). There are various homogeneous and heterogeneous catalysts studied, developed and used to produce biodiesel of ample quality in accordance to the ASTM standards (Gupta et al., 2016). A base-catalyzed process is ensued for feedstock with FFA content lower than 1% whereas acid-catalyzed process is ensued for feedstock containing FFA higher than 1%. With that, the current biodiesel production industry predominantly utilizes the base-catalyzed process (Karmakar et al., 2010).

Conventional base catalysts that are widely used in the biodiesel production industry are usually sodium hydroxide (NaOH) and potassium hydroxide (KOH) (Forson et al., 2004). They are able to generate high biodiesel yield under a short amount of time, almost 400 times faster compared to that of acid catalyst (Fukuda et al., 2001). They are also low in cost and is easily available in the market (Atabani et al., 2013; Avhad & Marchetti, 2015). With that said, the base catalyst is highly sensitive towards moisture and high free fatty acid content in the oil feedstock. The base catalyst face complications of soap formation and catalyst deactivation upon the slightest presence of water. Soap formation not only results in a tedious separation and purification step to be conducted, it also risks contamination of product biodiesel due to emulsion formation upon contact with water during the washing step (Singh et al., 2006). Furthermore, oil feedstocks that are high in FFA is not suitable for direct base-catalyzed tranesterification. These types of oil feedstock will have to go through an acid-catalyzed pre-treatment step to lower the FFA value to a suitable level of 4.0 mg KOH/g before transesterification can take place (Avhad & Marchetti, 2015; Ramadhas et al., 2004).

Acid-catalyzed esterification is conducted to lower the FFA content of the oil feedstock to allow for transesterification. Bronsted acids are usually used as catalyst, preferably sulfuric acid. Other conventional acid catalysts that are used include hydrochloric acid, ferric sulfate and phosphoric acid (Silitonga et al., 2013). Although acid catalysts show a slower reaction rate compared to base catalysts, acid catalysts still produce high yields of biodiesel. The catalytic activity of the acid catalyst is highly influenced by the alcohol to oil molar ratio hence an excess of alcohol is required to push the reaction towards biodiesel production (Atadashi et al., 2013). However, acid catalyst is also highly sensitive to moisture content. The catalytic activity of acid catalysts can be affected by even 0.1 wt% of moisture and even be fully inhibited by moisture content reaching 5 wt%. Conclusively, ensuring the moisture concentration of the reaction to not exceed 0.5 wt% is important in order to obtain an optimal yield (Canakci & Gerpen, 1999).

Nevertheless, researchers noted that if the acid value of feedstock used is too high, a one-step esterification as a pre-treatment may not suffice to lower the FFA content to a suitable level. This is due to the excessive water by-product produced throughout the process. In order to curb this problem, a three-step pre-esterification process is recommended which is the addition of alcohol and acid catalyst mixture into the reaction mixture three times consecutively. Each cycle of esterification generally takes up 2 hours and separation of biodiesel from the water and glycerol by-products needs to be conducted first before the next mixture of acid catalyst and alcohol is added (Leung et al., 2010).

2.4.1 Heterogeneous catalyst

Heterogeneous catalyst acts in a dissimilar form than the reaction mixture, generally in solid form, contrasting to that of homogeneous catalyst which acts in a similar liquid form as the reaction mixture (Borges & Díaz, 2012).

Although homogeneous catalysts have the advantage of using moderate reaction conditions, they require separation and recovery steps for the catalyst used, with meticulous neutralization procedures. Product of the process formed will be in aqueous emulsion form which results in a complicated and costly separation of ester from glycerol. There are various methods of washing practiced in biodiesel production process, including the extensive bubble washing, spray washing, counter current washing and agitation, all of which are deemed too costly and take up too much time. In addition, these washing procedures does not prevent, yet even promote the risk of glycerol contamination that is bound to occur during the separation process (Helwani et al., 2009). Furthermore, the waste water formed as a by-product also require further treatment which in turn also increases the processing costs (Meher et al., 2013).

By using a heterogeneous catalyst, the cost of processing is lowered by the fact that the catalyst is easily recovered and reused, saponification is avoidable thus no separation process is required to obtain the ester with high biodiesel yield up to 98 wt% (Zabeti et al., 2010). There are no by-product of waste water formed from the reaction, making heterogeneous catalyst an environmental friendly process (Meher et al., 2013). It is also reported that the reaction catalyzed by heterogeneous catalyst produce high purity glycerol (above 99%) as by-product that can be sold for revenue. This in turn will benefit the overall economy in the biodiesel production line (Chementator, 2004).

Heterogeneous catalyst also have other advantages such as how it can be engineered to improve its reusability, its selective nature, catalytic capability and longer life span (Gupta et al., 2016). The overall conditions for the biodiesel production process is also less intensive, require less energy intake, corrosion, toxicity although takes up more time for completion of reaction (Leung et al., 2010). Certain heterogeneous catalysts are able to catalyze both the esterification and transesterification simultaneously. This cancels the need for pre-esterification to take place and thus proving that heterogeneous catalyst can be very effective for oils containing high levels of FFA (Leung et al., 2010).

Although heterogeneous catalyst generates a lower reaction rate compared to of homogeneous catalyst, this can be overcome by increasing the reaction conditions or enlarging the reactant volume. Still, the effectiveness and stability of a heterogeneous catalyst is heavily dependent on its composition, active sites, structural morphology, porosity and thermal stability (Avhad & Marchetti, 2015).

In order to prepare a highly effective, sustainable and economical heterogeneous catalyst to be incorporated into the biodiesel production process efficiently, an extensive study is required on these aspects along with an in-depth understanding on the effects of chemical interaction with the catalyst support. Given the already good catalytic activity these catalysts seem to display, more attention can be put into engineering the catalyst to help it withstand deactivation, forming procedures for catalyst regeneration or developing cheaper raw materials as alternatives for catalyst preparation (Atadashi et al., 2013).

A noted disadvantage to using a heterogeneous catalyst is due to the different phases between the catalyst (solid), reactant (oil) and solvent (alcohol). The insolubility brought upon by the difference in phase leads to a diffusion limitation or also known as mass transfer limitation that will negatively impact the overall reaction rate (Mbaraka & Shanks, 2006). This complication can be alleviated by utilizing a co-solvent in the process that could promote the solubility between the reactant (oil) and solvent (methanol). These co-solvents include tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), n-hexane and ethanol. Another option is to incorporate catalyst supports that possess better characteristics such as larger surface area, higher pore density and active site to allow for larger intermediates to for hence reducing the mass transfer limitations (Zabeti et al., 2009). Currently there are not enough research reported being done on the preparation, composition and activity of heterogeneous catalysts (Furuta et al., 2004).

2.4.2 Heterogeneous acid catalyst

Based on past studies, most of heterogeneous catalysts studied thus far are of base or base oxides supported by supports with wide surface area. Base catalysts, either homogeneous or heterogeneous show higher activity compared to acid heterogeneous catalyst (Antunes et al., 2008). However, main drawbacks of using base heterogeneous catalysts are soap formation, leaching of catalytic active sites in reaction medium during reaction, and high sensitivity to moisture and FFA (>1%) content. Its low stability during storage in the presence of water and carbon dioxide is another disadvantage (Sani et al., 2014).

The acid heterogeneous catalyst is widely used in various industrial practices in spite of its inferior activity compared to that of homogenous acid catalyst. This is due to the various acid sites present at varying strengths in the catalyst which are an advantage over the homogeneous acid catalyst. Types of acid site present include Bronsted (e. g. sulphocic acid-containing material) and Lewis (e. g. mixed sulfated oxide) acidity (Singh Chouhan & Sarma, 2011; Helwani et al., 2009). In the case of feedstock used containing high FFA, utilization of an acid heterogeneous catalyst in the pre-treatment step allows the reaction to take place under mild conditions, avoiding the complications that would be otherwise caused by an acid homogeneous catalyst (Meher et al., 2013).

Complications mentioned include higher sulphur content in biodiesel produced, as oppose to the max of 10 ppm, caused by the sulfonation of the high level of FFA in the oil and catalyst residues in the oil (Meher et al., 2013). Use of homogeneous acid catalyst also incurred problems like wearing down of reactors due to harsh acidic nature of catalyst, addition of neutralization step in the process that is time-consuming and costly, as well as production of large amounts of waste water that would damage the ecosystem (Cardoso et al., 2008).

Use of heterogeneous acid catalyst renders environmental benefits and the produced biodiesel attains the required specifications of ASTM standard (Meher et al., 2013). However, the heterogeneous acid catalyst has a weak catalytic activity that require higher reaction temperatures and a longer time to reach the maximum conversion rate (Furuta et al., 2004), hence requiring the catalyst to be thermally stable (Avhad & Marchetti, 2015). It is also important to note that a viable heterogeneous acid catalyst will require to have favourable properties of high concentration of active sites, acidity, hydrophobicity and porosity so as to reduce the mass transfer limitation (Konwar, Boro, et al., 2014).

The heterogeneous acid catalyst can also be used in a one-step transesterification process for biodiesel production. The key feature of the catalyst that allows for the one-step process is its super acid strength of acid sites. However, utilization of such catalyst required for harsh reaction conditions (temperature more than 200 °C) and assistance by methanol vapor pressure (Meher et al., 2013).

Although less focus is given in the direction of study in the heterogeneous acid catalyst in contrast to the base heterogeneous catalyst, there have been a number of different acid heterogeneous catalyst developed and studied by researchers thus far. As in **Table 2.2**, majority of the catalysts studied comprise of heteropoly acids and catalysts that were centered on cation-exchange resins, zeolites and modified inorganic mixed oxides, including silica, sulfated and tungstated zirconia (Avhad & Marchetti, 2015). Nonetheless, the commonly studied catalysts stated showed disadvantageous properties of non-biodegradability, bad reusability require high cost preparation steps and extreme reaction conditions (Soltani et al., 2016). This dictates that several of the proposed solid acid catalysts require more experimentation to enhance their sustainability.

Table 2.2: Solid acid catalysts used in biodiesel production process

Catalyst	**Feedstock**	**Reaction conditions**				**Yield (%)**	**Ref.**
		Temperature (°C)	**Time (h)**	**Catalyst loading (wt%)**	**Methanol/oil molar ratio**		
$H_3PW_{12}O_{40}/SiO_2$	Palm fatty acid distillate (PFAD)	85	15	15	12:2	96.7	(Trakarnpruk et al., 2012)
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Sesame oil	260	1	3	40:1	92	(Shin et al., 2012)
CsHPW	Oleic acid-Soybean mixture	200	10	3	20:1	90.4	(Sheikh et al., 2013)
Ar-SBA-15	Crude palm oil	140	2	6	20:1	90	(Mansir et al., 2017)
MPD-SO_3H-IL	Jatropha oil	160	8	6	50;1	94	(Pan et al., 2016)
SiO_2-$SiO_3H/COFe_2O$	Rambutan oil	65	5	5	20:1	95	(Nguyen et al., 2016)
$SO_4{}^{-2}/TiO_2$-SiO_2	Palm fatty acid distillate (PFAD)	150	3.12	2.67	5.85:1	93.3	(Embong et al., 2016)
$Mn_{0.5x}Zr_{0.5y}Al_XO_3$	Waste cooking palm oil	150	5	2.5	14:1	>93	(Amani et al., 2014)
SiO_2-Pr-SO_3H	Acid oil	100	8	4	15:1	96.78	(Shah et al., 2015)

Table 2.2, Continued

Catalyst	Feedstock	Reaction conditions				Yield (%)	Ref.
		Temperature (°C)	Time (h)	Catalyst loading (wt%)	Methanol/oil molar ratio		
WO_3/Zr_2	microalgal lipids	100	3	15	12:1	94.58	(Guldhe et al., 2017)
Carbon derived catalyst	Calophyllum inophyllum oil	180	5	7.5	30:1	96.6	(Dawodu et al., 2014)

2.5 Carbon-based acid catalyst

Catalysts in the form of carbon is known as activated charcoal or "cabo activates". The catalyst is made of processed amorphous carbon with increased porosity and larger surface area to allow for higher chemical reactions to take place (Demirbaş et al., 2006). The commercial carbon-based catalyst is predominantly produced out of materials with high carbon content like coal, agricultural by-products and lignocellulosic materials (Ahmadpour & Do, 1997) which are highly accessible at a low price making the biodiesel production even more environmentally benign and economical (Konwar, Boro, et al., 2014). **Figure 2.6** exhibits the general overview of the preparation of carbon based catalyst from biomass and its utilization as a catalyst in biodiesel production. This demonstrate that the carbon based catalysts could not only reduce the cost of biodiesel making but also could be used as "green catalyst" (Konwar, Boro, et al., 2014).

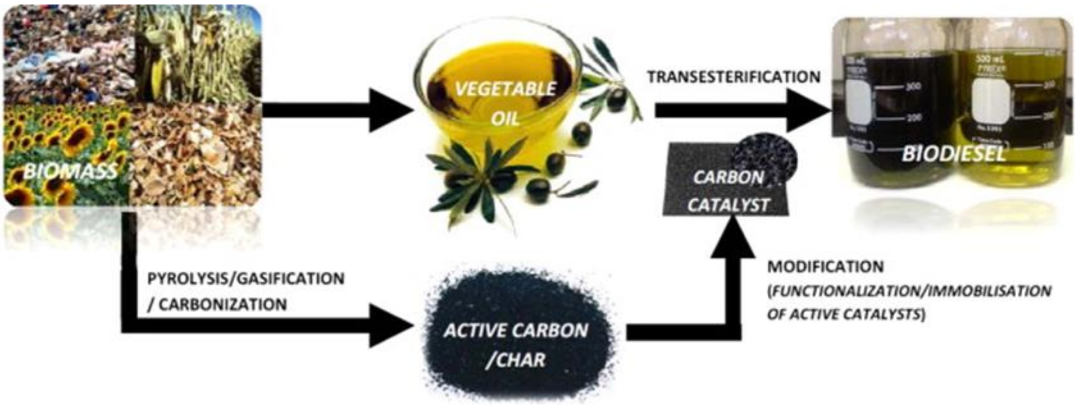


Figure 2.6: Schematic representations for preparation of carbon based catalysts and its utilization for biodiesel production (Konwar, Boro, et al., 2014)

The carbon based catalysts are produced by way of the three step process consisting of dehydration where all water content is removed, followed by carbonization which is the conversion process of the whole organic matter into elemental carbon, and lastly by activation, via removal of tars and developing pore structures (Ahmadpour & Do, 1997). The activation of the catalysts can be conducted either chemically or physically. Through chemical activation, the catalysts are generated via a one-step process using a chemical agent. This method usually utilizes a lower temperature compared to the temperature used in physical activation. Carbon catalysts activated through this method acquire improved pore development and carbon structure with higher carbon yield (Ahmadpour & Do, 1997). Depending on their physical attributes, activated carbons are divided into three groups of powdered activated carbon, granular activated carbon and extruded activated carbon (Konwar et al., 2014).

The general structural build of carbon-based catalysts are estimated to possess a graphite like network consisting of small polycyclic aromatic carbon sheets in a three-dimensional sp 3-bonded structure which can later be modified by way of sulfonation (Konwar, Boro, et al., 2014). The catalysts are described to have an amorphous build that is densely porous with varying pore sizes and show both macro and micro cracks and crevices, even at the molecular phase. This is most probably due to the preparation process (activation) and presence of outside materials that lead to the formation of the catalyst in which they are constructed by carbon-carbon bonds. Yet, the exact atomic build is still unknown. Another probable explanation suggested is that the carbon-based catalyst possess a build that is in relation to fullerenes, which means that it comprises of bent parts enclosing pentagons, hexagons and other non-hexagonal rings which would testify to the micro porosity of the carbon and other attributes mentioned (Harris et al., 2008).

The carbon-based catalyst functions by way of a catalyst support. It has the suitable surface oxides, high surface area, porosity and pore diameter (Ioannidou & Zabaniotou, 2007). The carbon-based catalyst also has a large adsorption capacity, substantial robustness as well as small amount of ash content (Savova et al., 2001). All of the above traits may be improved or altered depending on the processing steps taken. The different pore sizes of the carbon-based catalyst, either microporous, mesoporous or macroporous which greatly reflect the adsorptive capability of the catalyst is determined by the activation temperature and soaking time of the catalyst in the preparation process (Ahmedna et al., 2004; Girgis et al., 2002; Ioannidou & Zabaniotou, 2007), while the total pore volume is directly proportional to the activation temperature used (Tsai et al., 1997). Also, the carbon-based catalysts have other advantageous traits including that they are very stable in either acid or base solutions, very thermally stable even in extreme temperatures, can be designed to have the ascribed physical or chemical traits and also recyclable in the case of any valuable material were used in the catalyst preparation can be retrieved back (Konwar, Boro, et al., 2014). The use of carbon-based catalysts as catalyst support have become popular during the last decade owing to its low material cost and desirable properties like very high surface area: 800–1500 m^2/g and thermal stability (Konwar, Boro, et al., 2014).

The carbon-based catalysts can be grouped into either of the two groups of functionalized catalyst or supported catalyst. The functionalized catalyst have its active parts covalently bonded to catalytic adsorbates. These particular catalysts can further be categorized into acid functionalized catalysts and base functionalized catalysts depending on the functional group covalently attached to the carbon frame (Konwar, Boro, et al., 2014). In terms of the acid functionalized catalysts, an acidic functional group (such as SO_3H) is covalently bonded to the particle surface area upon sulfonation process. A mesoporous catalyst holds an advantage in its large surface area and large acid site density allowing for higher attachment of acidic functional groups, thus resulting in a higher catalytic activity during reaction (Díaz et al., 2000). The complex structure of the carbon catalyst, as well as the nature of hydrophobicity or hydrophilicity can also be manipulated or re-designed through selective functionalization using varying sulfonic acid groups (Avhad & Marchetti, 2015). Studies conducted utilising various carbon-based catalyst have shown yields of 90-98.3 % biodiesel under optimal conditions (Konwar, Boro, et al., 2014).

Toda et al. (2005) have shown the effectiveness of SO_3H-sugar-catalyst in esterifying vegetable oils. The catalyst was prepared by partially pyrolyzing D-glucose into a graphite like material and sulfonating it using H_2SO_4. Following this research, various other materials are extensively studied by researchers to be made into carbon precursor in order to produce a viable carbon-based solid acid catalyst. Dawodu et al. (2014) prepared a carbon catalyst derived from glucose and *Calophyllum inophyllum* seed cake which proved effective in esterifying non-edible oil with high FFA content. Tao et al. (2015) also produced an affective sulfonated carbon catalyst from biomass waste and Shu et al. (2010) utilized vegetable oil asphalt as the carbon catalyst to reduce the high FFA in waste vegetable oil.

2.5.1 *Jatropha curcas* seed cake as feedstock for carbon-based acid catalyst

The oil content of JC seeds generally make up 40% while only 60-80 % of this oil content is successfully extracted from the seed for biodiesel production (Subroto et al., 2015). Given the high yield of JC crude oil required for biodiesel production process, a substantial amount of seed cake waste is generated. Hence, an effective use of the JC seed cake is due in order to expand the value of JC in biodiesel production (Kannoju et al., 2017), also to reduce biomass waste and to facilitate energy security by renewable resources (Vassilev et al., 2015).

Unlike other seed cake wastes produced from industrial processes like sunflower or soy, the JC seed cake waste is limited to be utilized as animal feed since the seed cake contains toxic components including phorbol esters, curcin as well as other anti-nutritional components, including phytate, saponins and trypsin inhibitors (Rakshit et al., 2008). Several methods have been suggested to remove the toxic components from the seed cake either chemically or by irradiation but only limited information is available on the effects of such treatments to the nutritional components of the feed to be given to livestock, thus appears to be a risky solution and economically unfeasible (Kumar & Sharma, 2008; Siddhuraju et al., 2002). Other usage of the JC seed cake include usage as fertilizers or biogas production but those purposes require further processing that consumes high energy and cost. Also, both purposes are still in its early stages of research (Gübitz et al., 1999). After the crude oil is extracted from the JC seeds to be converted into biodiesel, the seed cake residue is stated to consist of the following components as in **Table 2.3**.

Table 2.3: Components of JC seed cake

Components	Percentage (%)	Ref.
Carbohydrates (cellulose, hemicellulose)	40-48	(Pasha et al., 2013; Vassilev et al., 2015)
Protein	25-31	
Fats	0.6	
Fibre	4	
Ash	9	

After complete removal of chemical residue and moisture, the seed cake can function as a low cost feedstock for preparation of carbon support with high surface area via partial carbonization. During carbonization, different mechanism of internal bonding between the components of the seed cake takes place (Hidayat et al., 2014). Structural changes will occur as the hemicellulose, cellulose and lignin of the seed cake decompose to form activated carbon at the temperature range of 250 °C and 300 °C. Different types of seed cake may have differing decomposition temperature points (Madanayake et al., 2016). After carbonization is conducted, the generated carbon is suitable to act as catalyst support for either basic or acid functional group to produce a viable catalyst and can also withstand larger alcohol content. This is possible because of the varying content of functional group on the carbon surface (Konwar, Boro, et al., 2014).

This alternating utilization of the JC seed cake waste as carbon catalyst stands out among others as it not only contributes to the economy of the crop production, it also contributes to the cut down on production cost of biodiesel production, given that commercial solid catalyst such as the Amberlist-15 costs much higher. Furthermore, the production of the carbon catalyst from the JC seed cake require no intensive processing (Vassilev et al., 2015).

With the increased recognition of JC oil as a feasible biodiesel feedstock, a research into the utilization of the resulting seed cake in this direction can be beneficial as it not only allow for maximum utilization of the JC feedstock potential, indirectly it also increases the sustainability of JC as biodiesel feedstock itself. This study is expected to provide further info and details of biomass waste from the biodiesel industry to facilitate the industry itself.

2.6 Preparation of catalyst

The preparation of carbon-based catalysts are generally conducted following the flow of methodology as in **Figure 2.7**. Partial carbonization is first conducted on the biomass material or catalyst feedstock, followed by sulfonation using an acid agent (Abdullah et al., 2017).

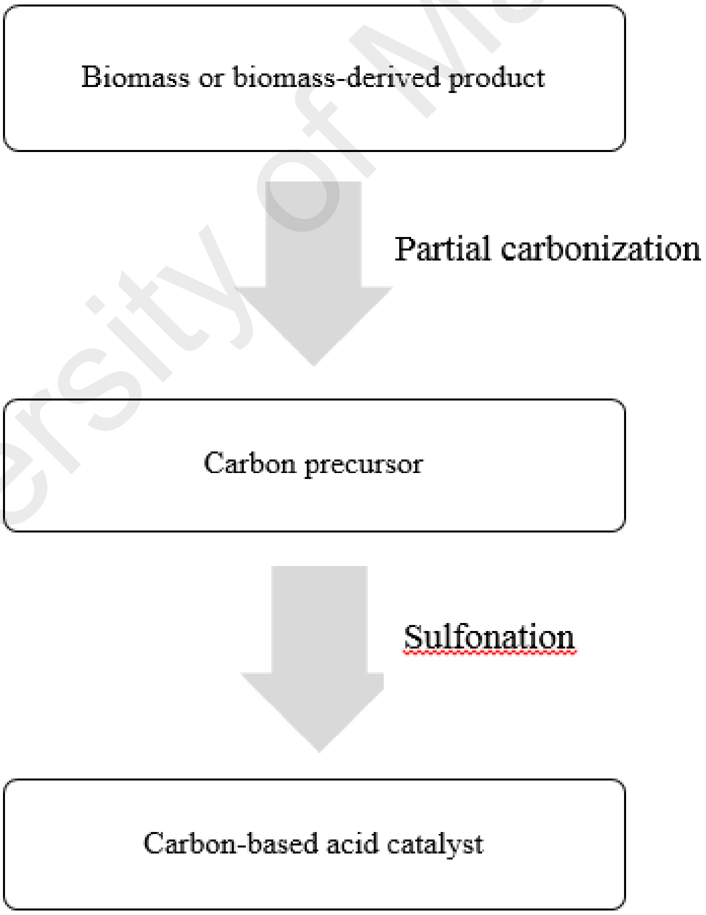


Figure 2.7: General flow chart for the preparation of carbon-based acid catalyst (Abdullah et al., 2017)

2.6.1 Carbonization

Carbonization is also called pyrolysis, a method of energy recapture process that produces char, oi and gas (Pütün et al., 2005). Parameters of the process, that have the largest influence on the products of pyrolysis, are the particle size, temperature and heating rate (Tsai et al., 1997). However, through a previous study, the carbonization temperature was determined to be a bigger influential factor overriding the factor of carbonization duration (Madanayake et al., 2016).

According to literature, the produced carbon is expected to show the properties that are different from the parent biomass material. These differences include the development of the pore density, surface area, pore size (microporosity, mesoporosity and macroporosity) and its physiochemical attributes including its elemental conformation (Haykiri-Acma et al., 2006). It is also stated that due to carbonization, degradation or rearrangement of the biomass material, phenolic and polyaromatic rings are formed in the carbon produced (Toda et al., 2005).

2.6.2 Sulfonation

Majority of the carbon catalysts used in biodiesel production stated in literature thus far are in the form of sulfonated carbon (Konwar, Boro, et al., 2014). Direct sulfonation of carbon is one of the approach that is most extensively studied for attachment of sulfonic acid groups ($-\mathrm{SO_3H}$) onto the supporting carbon base (Toda et al., 2005). Agents of sulfonation include sulfuric acid ($\mathrm{H_2SO_4}$), hydrochloric acid (HCl), sulphate gas ($\mathrm{SO_3}$) and 4-benzenediazoniumsulfonate (Konwar, Boro, et al., 2014).

Sulfonation of a carbohydrate (starch, cellulose, D glucose and sucrose) that is not completely carbonized lead to the formation of a carbon material that consists of polycyclic aromatic carbon sheets (Islam et al., 2014; Islam et al., 2013). Sulfonation of carbon allows the sulfonic acid groups (-$\mathrm{SO_3H}$) to covalently bind to the active site of the carbon which gives the catalyst its acidic nature (Mohan et al., 2005). The catalyst produced is then of high $-\mathrm{SO_3H}$ concentration regardless of the small surface area (Toda et al., 2005). The catalysts are also sturdy in build and stable, with minimal to no leaching of $-SO_3\mathrm{H}$ group upon utilization in the biodiesel production process (Okamura et al., 2006). During the sulfonation process, oxidation of the carbon aromatic rings takes place which lead to formation of graphene carboxylate groups, stabilizing the sulphate (SO_3) amorphous carbon that carries the $-SO_3\mathrm{H}$ groups. Other functional groups attached/formed to the carbon catalyst include hydroxide acid (–OH) and carbonic acid (-COOH) group. These functional groups increases the total acidity of the catalyst and act as binding sites for triglycerides and fatty acids during the esterification process (Hara et al., 2004; Okamura et al., 2006). The hydrophobicity of the catalyst is improved due to the functionalization of the mesoporous carbon bulk with $-\mathrm{SO_3H}$ groups, making the catalyst less waster sensitive and more sustainable as a catalyst (Rao et al., 2011).

Therefore, compared to other solid catalyst, the carbon acid catalyst is able to exhibit great catalytic activity and is a practical alternative to the conventional sulfuric acid catalyst for the esterification of oils containing high levels of FFA (Konwar, Boro, et al., 2014). Nonetheless, very few studies have been conducted on the utilization of a carbon-based acid catalyst prepared by this method.

Summary:

In developing a more efficient and sustainable biodiesel production process, various innovations were studied upon and implemented. The use of non-edible oils as feedstock such as *Jatropha curcas* oil remain as one of the most vastly discussed in the industry due to its easy availability and being low in cost. In regards to this, the biodiesel production process undergoes a two-step reaction process in order to produce biodiesel from high FFA containing non-edible oil feedstock. The additional pre-treatment step of esterification correspondingly require the use of acid catalyst and traditionally a homogeneous acid catalyst is used, causing several complications and increases the production cost.

Another area of prominent enhancement to be made relate to the type of catalysts used in these production processes. With numerous types of catalysts researched and developed, the heterogeneous catalyst has been progressively investigated further with its recent breakthrough of carbon-based catalysts which are produced from the general methodology of carbonization followed by sulfonation.

CHAPTER 3: METHODOLOGY

Methods used in this study include preparation of the carbon-based acid catalyst, characterization of the catalyst prepared and parameter study for optimal conversion yield of FFA in the crude JC oil. To ensure overall success of the production process, the biodiesel yield and its physiochemical properties were also determined. Record of raw material used, apparatus, types of testing and the equipment used are all stated. The flow of steps in the methodology is also shown. A flow chart of the methodology is as shown in **Figure 3.1**.

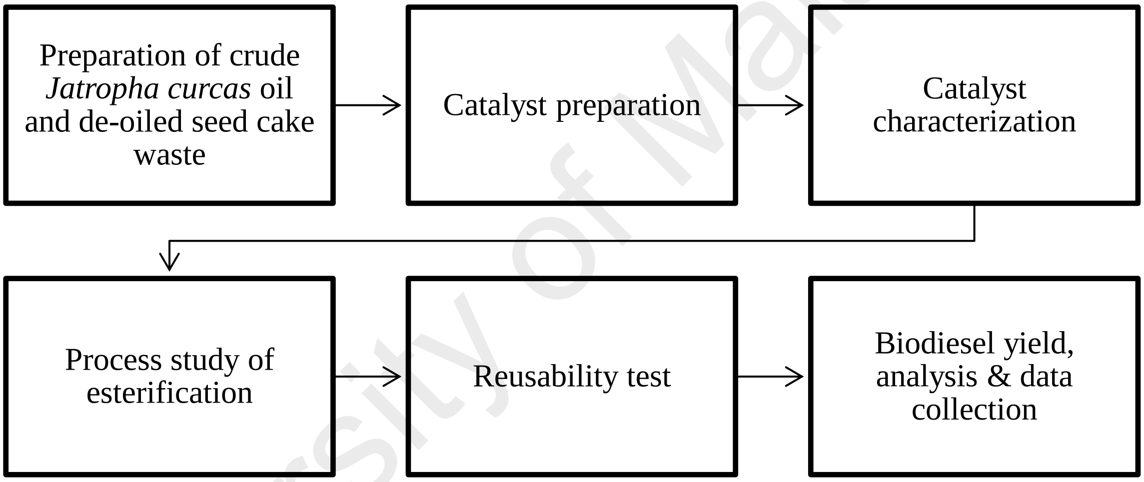


Figure 3.1: Flow chart of methodology

3.1 Raw materials

JC seeds were purchased from Indonesia. Crude *Jatropha curcas* oil was extracted from the seeds using soxhlet extraction method with hexane as solvent. The JC cake is then dried overnight. Other chemicals and solvents including sulfuric acid, methanol and hexane were of analytical grade and purchased from local suppliers in Malaysia.

(a)

(b)

Figure 3.2: (a) JC seeds (b) Thimble extraction of crude JC oil

3.2 Apparatus

List of apparatus used include weighing balance, stirring heating plate, heating mantle, condenser, soxhlet extractor, furnace, rotary evaporator, Tefal blender, magnetic stirrer, separating funnel, vacuum pump, retort stand and clamp, filter funnel, thermometer, measuring cylinder, beakers, spatula, mortar and pestle, forceps.

3.3 Equipment

Table 3.1: List of equipment used and its description

Type of equipment	Description
Biodiesel production experimental rig	To produce biodiesel with varying process parameters
Soxhlet extractor	To extract the crude oil from seed
848 Trinito plus acid value tester and iodine number tester	To measure the acid value and iodine number
Digital bomb calorimeter	To measure the calorific value
LiquiPhysics™ Excellence Density Meter (DM40)	To measure the density
Oxidation stability tester (873) RANCIMAT)	To measure the oxidation stability
Fourier-Transformed Infrared Spectrometry	To measure the chemical bonds and identify the compounds
Thermal Gravimetry Analyzer	To measure the quantity of volatile compounds
BET (Surface Area) Micromeritic	To identify the surface morphology
Temperature Programmed Desorption (TPD)	To measure the acidity of catalyst
Field Emission Scanning Electron Microscopy (FESEM)- EDX JSM 7600-F	To observe the surface morphology of sample
Rotary evaporator	To separate extracted crude oil from hexane solvent. To separate product esterified oil and biodiesel from excess methanol.
Gas Chromatography (GC)	To determine FAME yield of biodiesel
Desiccator	To store carbon sample in a moisture free environment

3.4 Catalyst preparation

De-oiled JC seeds were collected and dried for 24 h to remove all traces of moisture before being crushed into powder form. Weight changes of the carbon precursor was determined by Thermo Gravimetric Differential Thermal Analyzer (TGA/SDTA851^{e}), heated from 30 – 630 °C at a rate of 10 °C/min under a flow of N_2 (flow rate 40 mL/min) to determine the suitable carbonization temperature. The powdered JC seed cake was then carbonized at the designated temperature for 4 h. The product carbon powder was then characterized and analyzed.

The carbon carrier produced was then sulfonated with concentrated sulfuric acid (until fully submerged), heated at 90 °C for a duration of time (5, 10, 15 and 20 h) under constant stirring. The sulphated mixture was then filtered and washed with 2 L distilled water or until no sulphate ion residue ($S0_4{}^{-2}$) can be detected (by $BaSO_4$) (Rao et al., 2011). The catalyst was dried overnight to allow excess chemical to evaporate before being heated again at 110 °C for 3 h to remove any remaining moisture.

Figure 3.3: Carbon precursor

3.5 Catalyst characterization

In order to investigate the physical and chemical properties of the catalyst, the carbon precursor and the prepared catalyst were characterized using a number of varying methods. The structure of the carbon precursor and the prepared carbon-based solid acid catalyst were evaluated and characterized by Surface Area Analysis (BET) via the nitrogen adsorption-desorption instrument, Micrometrics Tristar II 3020 instrument. Prior to analysis, the samples were desorbed in vacuum at 150 °C until static pressure remained less 6.6 × 10 Pa before carrying out the N_2 adsorption at -196 °C. Then, surface area, average pore diameter and pore volume were calculated by Brunauer-

Emmet-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) model respectively (Semwal et al., 2011). The Field Emission Scanning Electron Microscopy (FESEM) was conducted simultaneously with the Energy-Dispersive X-ray Spectrometry (EDX) testing to determine the components of the catalyst using FESEM/EDS system PEGASUS APEX 4 (Ametek/EDAX), Electron Optrics.

The moisture content in both the carbon precursor and catalyst were determined according to the standard method of ASTM D 2867. The sample was taken and put inside a pre-dried tared capsule, making sure that the depth of the sample in te capsule did not exceed 1.25 cm. The capsule was closed with the lid and weighed to the nearest 0.5 mg. The capsules' cover was removed and both the capsule containing the sample and the cover was placed in a pre-heated oven (at 145–155 °C). The oven was closed and the sample was dried to constant weight. The oven was opened and the capsule was immediately closed. The capsule was put in a desiccator to cool to ambient temperature and then weighed. The total moisture content in the sample was calculated using the following formula:

$$\text{Moisture weight, \%} = \left[\frac{(C-D)}{(C-B)}\right] \text{ x } 100 \tag{1}$$

where:

B = weight of capsule with cover, g,

C = weight of capsule with cover plus original sample, g,

D = weight of capsule with cover plus dried sample, g.

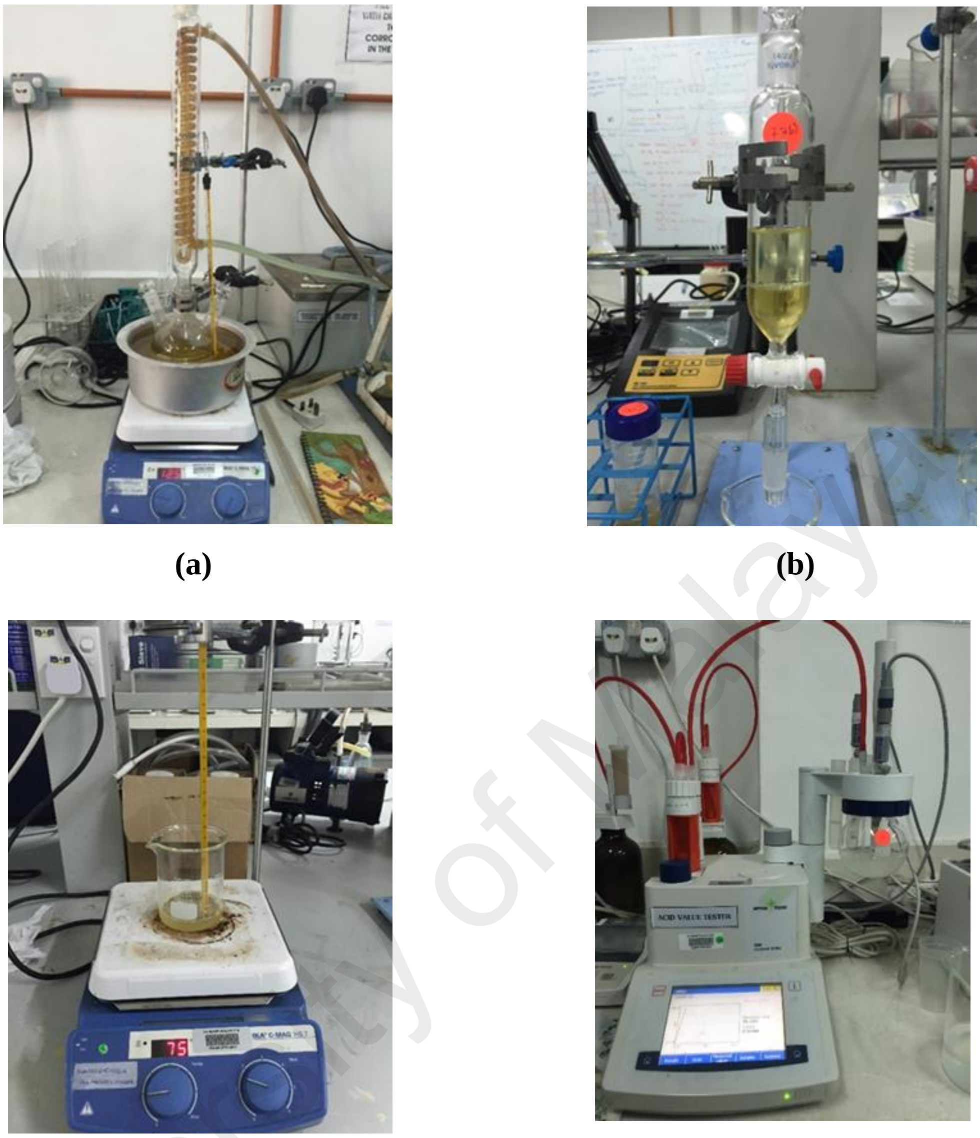
The presence and types of acid sites in the catalyst was determined by observing the catalyst framework vibration through Fourier Transform Infrared Spectroscopy (FTIR) with spectrum of 400-3900 cm^{-1} with resolution of 4 cm^{-1} and 16 scans per spectrum and Temperature Programmed Desorption (TPD-NH_3) respectively using Quantachrome equipment (Model ChemBET 3000, Quantachrome Corporation). The sample was activated at 400 °C in H_2 flow for 2 h (heating rate 10 °C/min. The sample was then cooled to 100 °C in He flow. At this point, 0.1 % NH_3 in N_2 was passed through the sample for 1 h followed by cooling to room temperature in He flow. TPD was carried out from room temperature to 500 °C at a heating rate of 10 °C/min with He flow rate of 35 mL/min.

Total acidity of the catalyst were was determined using the titration method (Chen & Fang, 2011), whereby 0.1 g of sample was added to 20 mL of sodium bicarbonate solution (0.05 M) and stirred for 24 h at room temperature. Subsequently the mixture was filtered and each 5 mL of the filtrate was titrated using hydrochloric acid (0.1 M).

3.6 Process study of esterification

Esterification of JC oil was conducted using a 500 mL three-necked round bottomed flask with attached refluxing condenser, thermometer and a magnetic stirrer. The flask was immersed in an oil bath heated to a stable temperature. The esterification process used 2.5-10 wt% catalyst loading while the methanol to oil molar ratio was varied from 6:1 to 18:1. The reaction time was also monitored from 30-120 min and the reaction is carried out at varying temperature from 45-70 °C. After each reaction, the samples were filtered using a vacuum pump to retrieve the catalyst, the excess methanol was evaporated and the oil product analyzed for acid value (A.V.). The conversion rate was calculated using the following formula (Fadhil et al., 2016):

$$\text{Conversion rate (\%)}: \frac{(\text{Initial A.V.} - \text{Final A.V.})}{\text{Initial A.V.}} \times 100\% \qquad (2)$$



(a) (b)

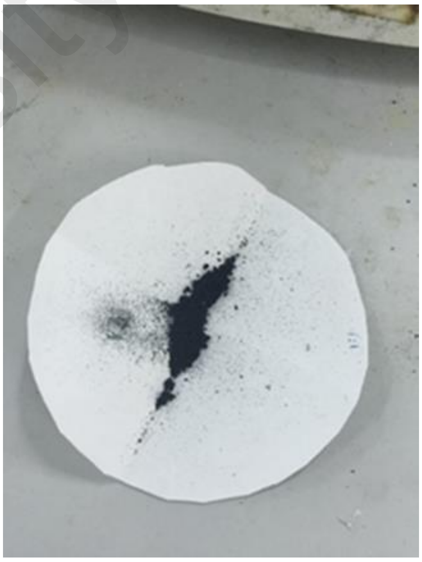
(c) (d)

Figure 3.4: (a) Esterification of crude JC oil, (b) Separation of esterified oil, (c) Manual drying of esterified oil, and (d) Acid value testing of esterified oil

3.7 Reusability test

After esterification, the catalyst was collected and thoroughly washed with hot distilled water (80 °C) and hexane before being dried at 110 °C for 3 h. The catalyst was then re-used to catalyze the esterification process on multiple cycles under the optimum parameters obtained from the study (12:1 methanol/oil ratio, 7.5 wt% catalyst, 60 °C, 60 min, 350 rpm). After each cycle, the esterified oil was tested for acid value and ester conversion yield was calculated to determine the catalyst effectiveness. The filtered methanol was tested for presence of sulphates using barium chloride to determine the presence of leached sulphate ($-SO_3$) groups (Zhou et al., 2016) that might compromise the acid value of the esterified oil. The catalyst was also tested for any changes in the acid capacity after each cycle by the titration method (Chen & Fang, 2011).

(a)



(b)

Figure 3.5: (a) Filtering and washing catalyst and (b) Dried used catalyst

3.8 Biodiesel yield, analysis and data collection

Under the same experimental setup, transesterification of the esterified oil was conducted using 1 wt% KOH as catalyst. The molar ratio of methanol to oil used was 6:1 and the reaction mixture was stirred continuously at 350 rpm at 60 °C for 60 minutes. After completion of reaction, the reaction mixture was poured into a separating funnel and left overnight. The lower layer comprising of glycerol and other impurities were drained off while the remaining upper layer which contain the biodiesel was washed with hot distilled water three times to eliminate any remaining contaminations such as catalyst, soaps or glycerol (Bala et al., 2012).

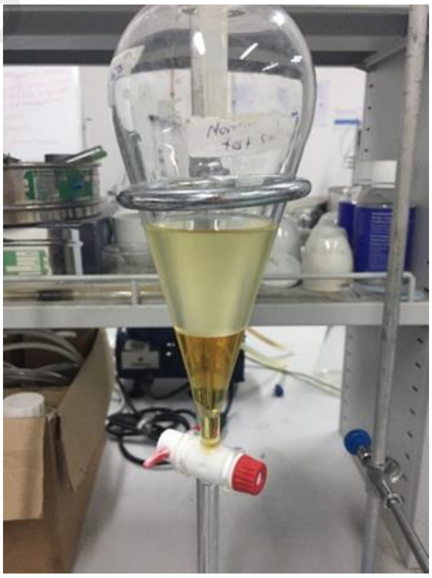
3.8.1 Biodiesel yield

The biodiesel yield was determined by Gas chromatography (GC) analysis. 100 mg of the biodiesel sample was diluted and mixed with 10 ml toluene and 100 mg methyl nonadecanoate (internal standard). A volume of 1 µL of the mixture was injected to GC for analysis. Gas chromatography (Agilent 7890A) equipped with HP-INNOWAX capillary column (30m x 0.320mm x 0.25µm), FID detector, and injector (split and splitless) was used to determine the fatty acid methyl ester (FAME) content. The column temperature was programmed according to EN 14103:2011 standard as follows: 60 °C hold for 2 min, 10°C/min to 200 °C, kept for 0 min, and 5°C/min to 240 °C, hold for 7 min. Both detector and injector were set at 250 °C. Helium was used as the carrier gas with a constant flow rate of 1.5 ml/min. The resulted chromatogram was compared with chromatogram obtained from C8-C24 FAME Mix to determine the methyl ester peaks. FAME yield was obtained by comparing the area of methyl esters peaks with internal standard peak using the following equation:

$$E = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{W_{EI}}{m} \times 100\% \qquad (3)$$

In equation (3), E represents the fatty acid methyl ester content (%), ∑A is the sum of the peak areas of the fatty acid methyl ester content from C8:0 to C24:0, AEI is the peak area of the internal standard, (methyl nonadecanoate), WEI is the weight (milligrams) of internal standard being used, and m is the weight (milligrams) of the biodiesel sample.

(a)



(b)

Figure 3.6: (a) Transesterification and (b) Separation of biodiesel

3.8.2 Property analysis of crude JC oil, esterified oil and biodiesel

The biodiesel properties were determined according to the ASTM 6751 or EN 14214 standard (i.e. kinematic viscosity at 40 °C, density at 15 °C, calorific value, acid value, oxidation stability at 110 °C) were determined and compared with the physicochemical properties of its parent crude oil and esterified oil to observe the changes occurred.

Table 3.2: List of equipment used for property test

Property	**Apparatus**	**Standard method**	**Statistical error**
Kinematic viscosity	NVB classic (Normalab, France), Stabinger Viscometer SVM 3000 (Anton Paar, Austria)	ASTM D445	±0.01 mm^2/s
Density	DM40 LiquiPhysics™ density meter (Mettler Toledo, Switzerland)	ASTM D127	±0.1 kg/m^3
Calorific value	6100 EF Semi auto bomb calorimeter (Perr, USA)	ASTM D240	±0.001 MJ/kg
Acid number	Automation titration rondo 20 (Mettler Toledo, Switzerland)	ASTMD664 and EN 14111	± 0.001 mg KOH/g
Oxidation stability @ 110 °C	873 Rancimat (Metrohm, Switzerland)	EN 14112	±0.01 h
FAME content	Agilent 7890 gas chromatograph (Agilent, USA)	EN14103	±0.008% or 0.0008 min

3.9 Safety precautions

In conducting the dissertation research lab work, protective actions and hazard signs in the laboratory were observed at all times to avoid any possible accidents or injuries. The following precautions are:

- Candidate was in proper attire for lab: covered shoes, lab coat, gloves, and face masks

- The location of all relevant safety equipment in the lab (e.g. first-aid kit, eyewash, fire extinguisher, fire blanket, safety showers) and how to use them was known
- Candidate never work in a laboratory alone or at least without another person within easy call
- Gas chamber was utilized when handling volatile and highly toxic chemicals like sulfuric acid and toluene.
- During heating process of any chemicals (sulfonation, esterification, transesterification), the temperature and water supply to the reflux condenser was regularly monitored
- A time schedule was followed for use of equipment using high voltage power to avoid short circuit when used simultaneously with multiple other equipment
- Testing equipment used were serviced according to schedule to ensure accuracy of results and avoid breakdown
- All chemical and organic waste was discarded into proper designated bins and bottles

CHAPTER 4: RESULTS AND DISCUSSION

This study consists of four parts of investigation. The first determines the vital parameters used in the preparation of the carbon-based acid catalyst such as the carbonization temperature and sulfonation duration in order to attain the production of a highly acidic carbon catalyst that is stable enough to be used in the esterification of crude JC oil. Secondly, the prepared catalyst was characterized to observe its structures, acidic components and to determine the type of acidity that the catalyst has. Third, the parameters for optimal esterification yield of JC oil were consequently determined and its reusability evaluated. Lastly, in order to verify the competency of the whole production process, the biodiesel yield produced from this overall process was determined and its quality measured and evaluated.

4.1 Catalyst preparation

The Thermo Gravimetric Analyzer (TGA) spectra for de-oiled *Jatropha curcas* (JC) seed cake is as shown in **Figure 4.1**. Apart from the loss of weight occurred at 50-150 °C which indicated the loss of adsorbed water in the form of evaporation, the JC seed cake showed dissociation zones at temperature points from 350 °C onwards indicating the start of the functional groups decomposition thus the carbonization temperature during catalyst preparation was selected at 350 °C as the aim is to only partially carbonize the seed cake, while carbonization at higher temperature might lead to excessive breakdown of the macromolecules and removal of organic portions as observed through the mass loss pass 350 °C temperature point (Nisar et al., 2017). Also, usage of lower carbonization temperature will facilitate the consequent sulfonation process by producing a carbon precursor that contains larger amounts of surface functional groups, ensuing the formation of a catalyst with higher catalytic activity (Konwar, Boro, et al., 2014). The TGA result also indicated that the catalyst prepared will be thermally stable below temperature of 350 °C as only a small mass loss occurred before that point. This signifies the feasibility of using this catalyst in the biodiesel production process.

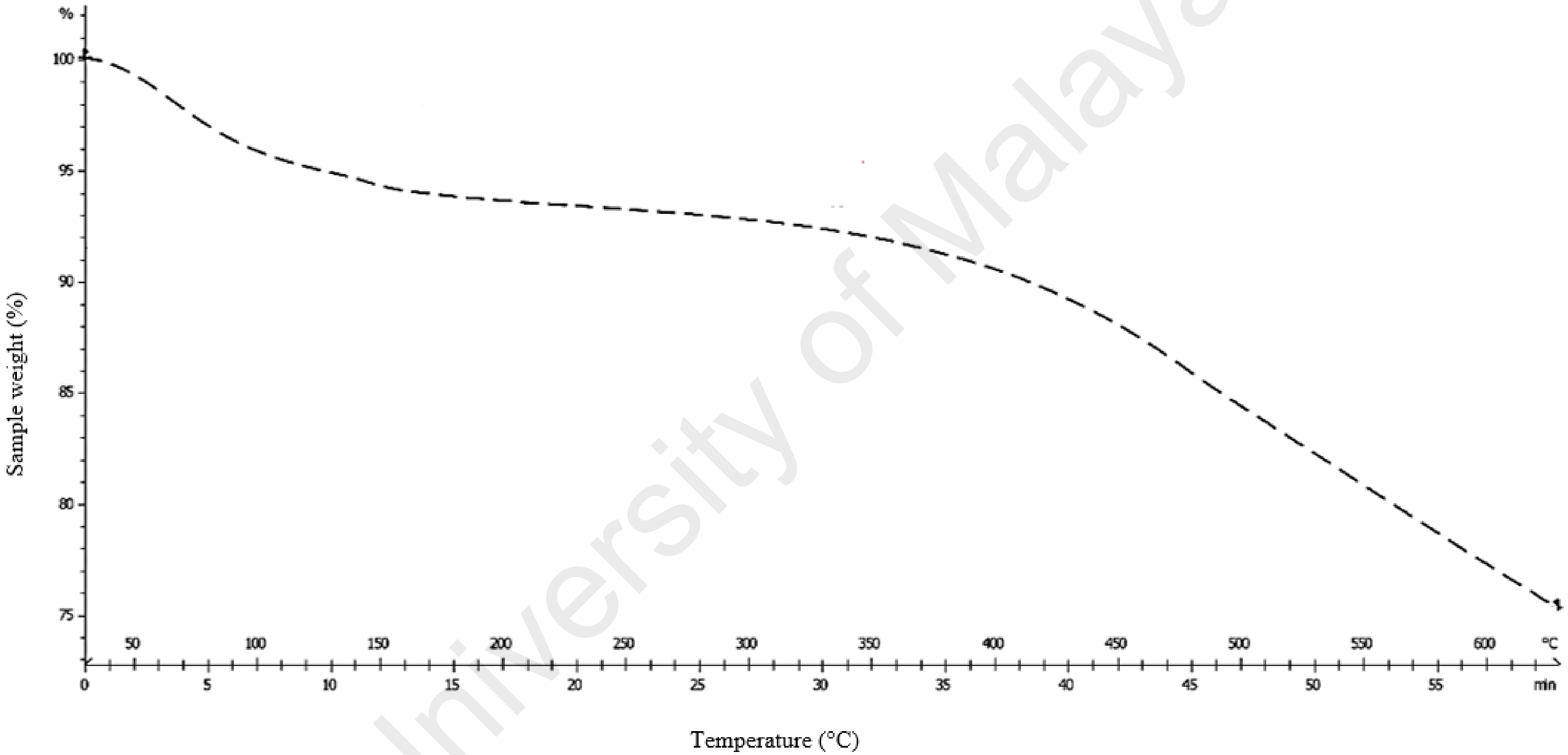


Figure 4.1: TGA spectra of de-oiled *Jatropha curcas* seed cake

The carbon precursor was then sulfonated with concentrated sulfuric acid (80 mL, 99% or until the carbon was fully submerged). The sulfonation was conducted under constant stirring at 90 °C for durations of (5, 10, 15 and 20 h) to achieve maximum attachment of $\mathrm{H_2SO_4}$ molecules to the carbon walls of the catalyst, allowing maximum acid capacity of the catalyst prepared. This is very important as higher acid capacity equals to higher catalytic activity (Tao et al., 2015).

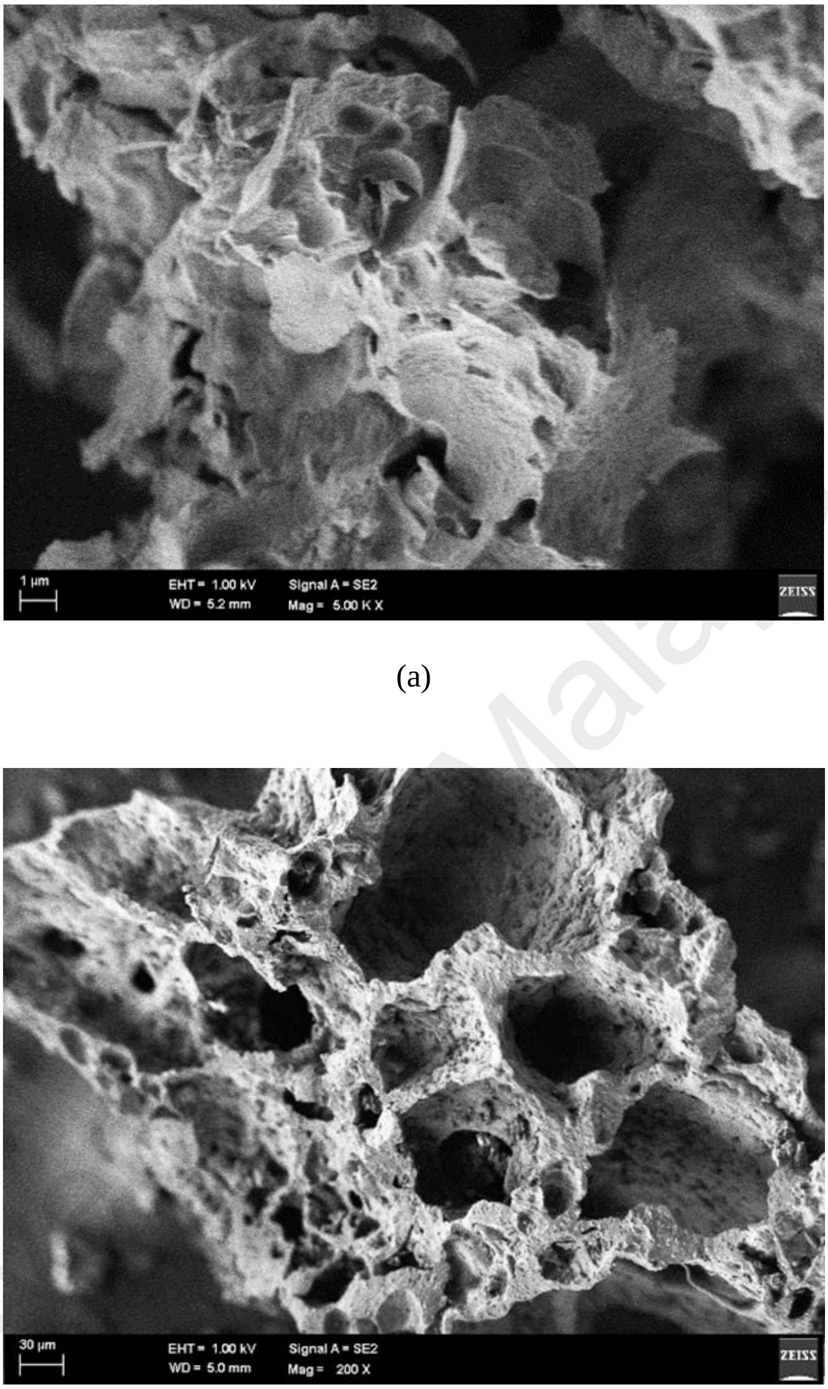
Table 4.1 shows the total acidity of the carbon-based acid catalyst produced by different sulfonation time. It can be inferred that the maximum acidity of 2.24 mmol/g was achieved by 5 h sulfonation time. A sulfonation period exceeding 5 h showed no significant increase in total acidity of the catalyst. Therefore, following carbonization at 350 °C, sulfonation at 90 °C for 5 h under constant stirring is considered as the optimum catalyst preparatory step in this study.

Table 4.1: Effect of sulfonation time on total acidity of catalyst

Sulfonation time (h)	**Total acid content (mmol/g)**
5	2.24
10	2.21
15	1.85
20	2.00

4.2 Characterization of catalyst

According to literature, the catalytic performance is mainly based on the pore structure, total acid density and the surface functional groups contained (Konwar et al., 2014). The morphology of the carbon precursor and the carbon-based acid catalyst is as shown in **Figure 4.2** using the scanning electron microscope (Semwal et al., 2011). The images show that the carbon catalyst possess a rough uneven surface with well-defined mesoporous structure. The pores exhibited were abundant and of different sizes and shape. The number and size of pores appear larger after the carbon precursor was sulfonated by sulfuric acid (H_2SO_4). The external surface of the carbon precursor and the catalyst also has crevices, cracks with grains of various sizes in the pores. Similar morphological features were also observed in a carbon-based catalyst prepared from vegetable asphalt (Shu et al., 2010). Alternatively, depending on the type of catalyst feedstock used, carbon-based catalysts prepared can have differing structures, as in a similar study conducted whereby the catalyst prepared had an irregular compact structure, bigger than 1 µm in size with no pores visible (Nakajima et al., 2007; Okamura et al., 2006) This difference in structure may be due to the difference of carbon source used as it may be deduced that aliphatic straight hydrocarbon polymer form pores easier compared to ring hydrocarbon polymers (Shu et al., 2010).



(a)

(b)

Figure 4.2: SEM images of (a) carbon precursor and (b) carbon-based acid catalyst

Table 4.2 shows the properties of the carbon precursor and the prepared catalyst. The small surface area determined was as expected of a carbon-based catalyst signifying that the catalytic capability of the catalyst is independent of the surface area as a higher surface area might lead to increased leaching of $-\mathrm{SO_3H}$ groups attached to the inside of the catalyst, causing a reduced catalytic activity instead, especially upon reuse of the catalyst (Yu et al., 2011). The total surface area of the carbon precursor slightly decreased from 2.37 to 1.92 $\mathrm{m^2/g}$ in the catalyst after sulfonation indicating structural changes including collapse and degradation of the carbon had occurred to the carbon texture upon sulfonation. The pore volume and pore diameter were also reduced due to the occupation of the pores by functional groups (Wang et al., 2014). The large pore sizes determined in this study provided more active sites for attachment of the $-SO_3\mathrm{H}$ groups (Fadhil & Abdulahad, 2014).

Even after the impregnation of the acid groups, the catalyst still had a feasible pore diameter that can accommodate flow of the reactant intermediate molecules (5.8 nm at the largest for triglyceride) through the catalyst during reaction (Wan Omar & Amin, 2011), whilst a catalyst with a smaller sized pore (<5 nm) would be limited by the internal mass transfer thus decreasing the catalytic activity. Also, considerably small pore sizes tend to get plugged up due to impregnation of acidic groups, more so for preparation of highly acidic catalysts (Granados et al., 2007).

According to the titration method, total acidity of the catalyst was 2.24 mmol/g which was considered high given the low surface area of the catalyst. This may be a result of the high number and large sizes of the catalysts' pores which allowed for high accessibility of sulfuric acid into the catalysts' carbon bulk, leading to more covalent bond formation between the $-SO_3\mathrm{H}$ groups and the carbon surface. A higher concentration of such covalent bonds and acid sites were expected to provide the catalyst with higher acid capacity thus better catalytic ability in the production of biodiesel process (Shu et al., 2010). It also contributes to the increased hydrophilicity of the catalyst which would allow more hydrophilic methanol to enter into the catalyst bulk to react with as many hydrophobic reactants (triglycerides) as possible, both inside and outside of the catalysts' surface (López et al., 2005; Sun et al., 2017).

Table 4.2: Properties of carbon precursor and prepared catalyst

Properties	Carbon	Catalyst
Moisture (wt%)	2.10	5.09
Surface area (m^2/g)	2.37	1.92
Pore diameter (nm)	6.77	6.67
Pore volume (mm^3/g)	3.60	3.20
Acid strength (mmol/g)	-	2.24

As tabulated in **Table 4.3**, the EDX result showed an average of 23.61% sulfur content in the catalyst indicating sulfonic groups have successfully bonded to the carbon support as a result of sulfonation, considering the parent carbon precursor showed no presence of sulfur. Attachment of the sulfonic groups are what gives the catalyst its acidic nature (Prabhavathi Devi et al., 2014). The C content in the carbon precursor decreased slightly from 69.01% to 58.38% after sulfonation, possibly due to breakdown/rearrangement of material by H_2 SO_4 during sulfonation process. This breakdown serves to form bigger and higher number of pores in the catalyst.

Table 4.3: Elemental analysis of carbon precursor and prepared catalyst

Element	**Carbon**		**Catalyst**	
	Mean	**Standard deviation**	**Mean**	**Standard deviation**
%C	69.01	3.84	58.38	5.78
%N	19.49	3.52	13.51	9.26
%O	11.50	0.84	15.00	7.98
%S	-	-	23.61	4.77

FTIR spectra of the catalyst before and after sulfonation are shown in **Figure 4.3** and **Figure 4.4** respectively. Presence of sulphonic group in the catalyst was proven by characteristic peak of stretching mode of $-SO_3H$ groups at 1037 ($-SO_2$symmetrical stretching mode), 1161 ($-SO_2$asymmetrical stretching mode) (Chen & Fang, 2011) in the catalyst spectra which is absent in the carbon precursor spectra. The absorption bands observed at 1772 cm^{-1} is attributed to the (C=O) stretching mode of the COOH group (Cerato & Lutenegger, 2002). The bands at 1616 and 1541 cm^{-1} confirm presence of poly aromatic hydrocarbon in the catalyst (Shu et al., 2010). These bonds that were determined confirm the incorporation of the SO_3H functional groups in the carbon framework of the catalyst (Hara, 2010; Shu et al., 2010).

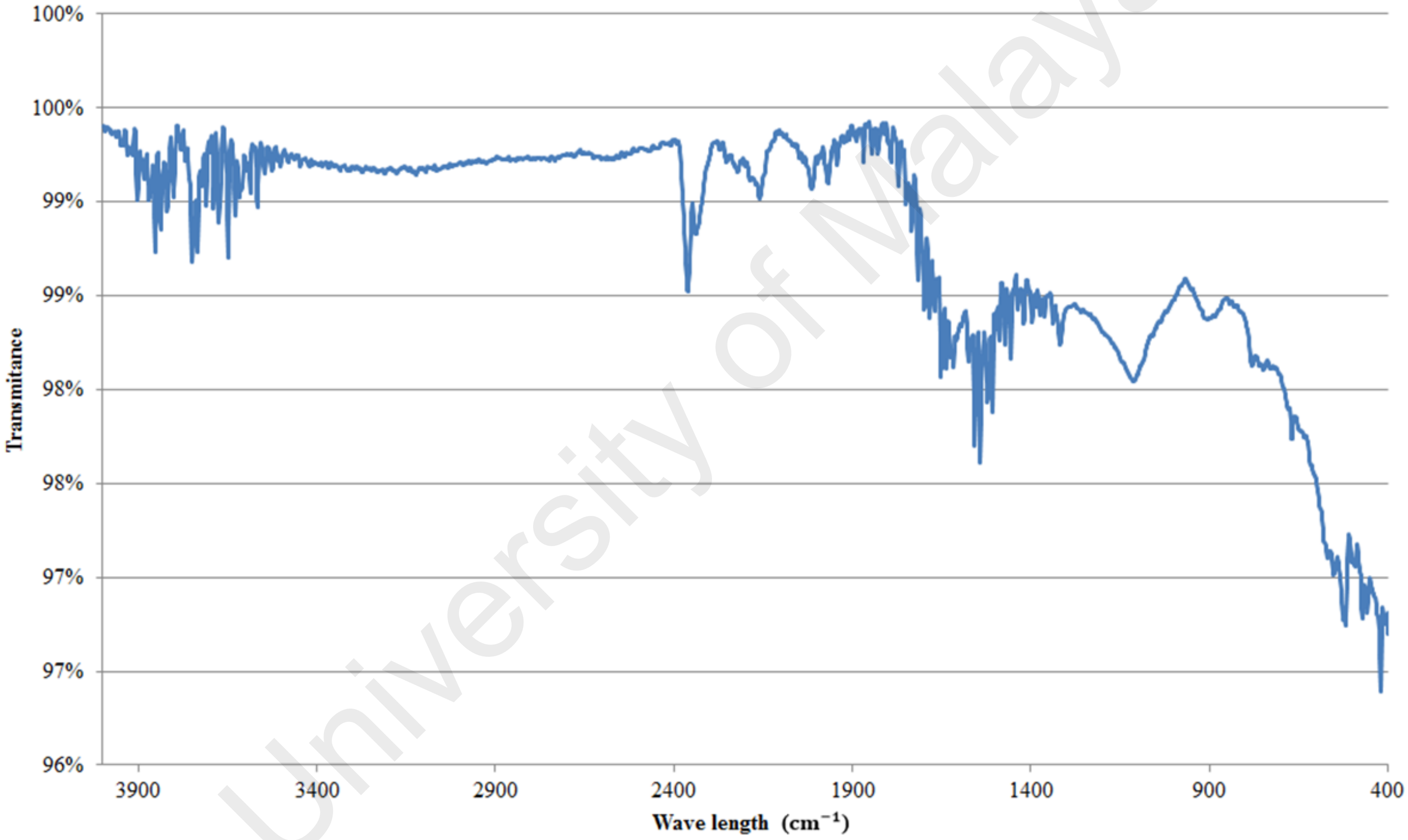


Figure 4.3: FTIR spectra of carbon precursor

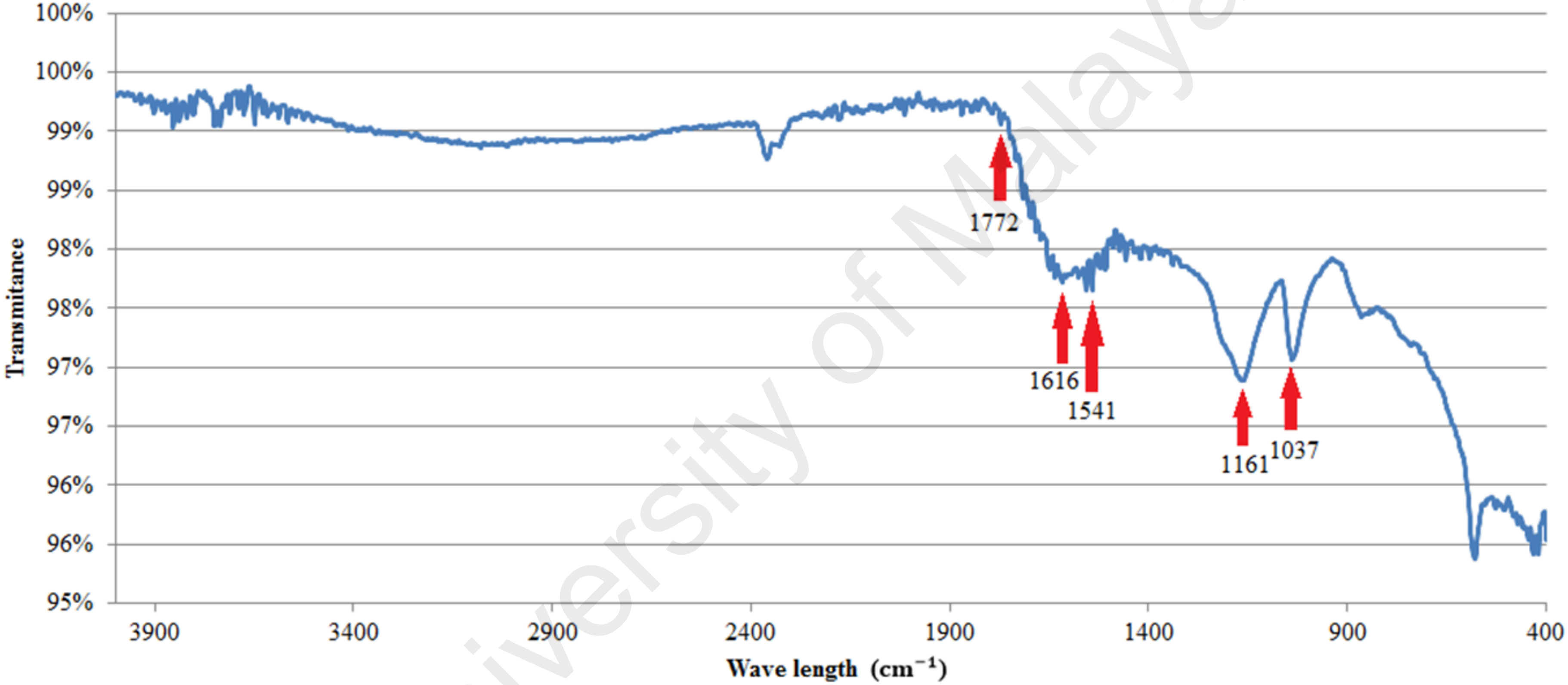
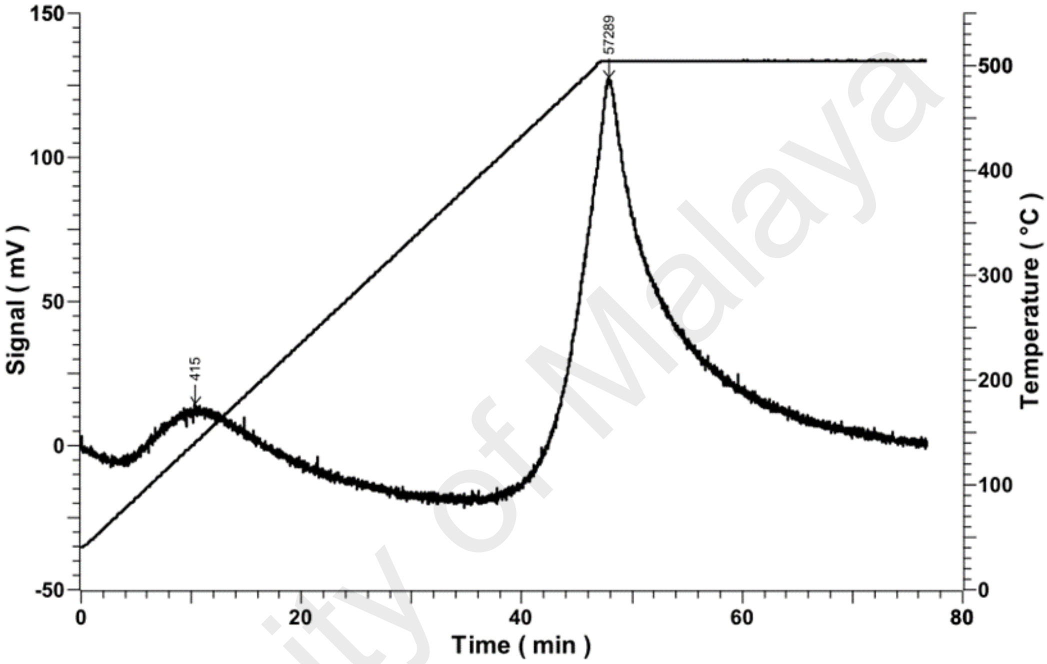


Figure 4.4: FTIR spectra of catalyst

The NH_3-TPD plot of the catalyst in **Figure 4.5** showed that the catalyst had two distinct peaks from 140 to 150 °C and at 504 °C. The low and high temperature peaks refer to weak and strong acid site respectively. Both of these two peaks are categorized as Bronsted acid sites. The form of both strong and weak acid site may be attributed to the difference in pore size of catalyst and distribution of acid site (Liu et al., 2009).



Generally, the strong acid site refers to attachment of $-SO_3H$ groups to the catalyst surface while the weak acid site refers to the attachment of –OH groups instead (Rao et al., 2011).

Figure 4.5: NH_3-TPD plot of catalyst

4.3 Esterification reaction study

The FFA content of the crude JC oil used in the present study was determined at 25.4 mg KOH/g which exceeded the suitable level (<4 mg KOH/g) for direct preparation of biodiesel. Because of this, a pre-treatment step of esterification was required to lower the acid value count in the oil feedstock. Esterification of the crude JC oil was carried out using the carbon-based acid catalyst. Under optimal esterification reaction parameters, the acid value was reduced from 25.4 to 0.22 mg KOH/g. A decrease in the acid value indicated the effectiveness of the catalyst during the esterification process. Parameters affecting the esterification process such as the amount of catalyst loading, reaction time, molar ratio of methanol to oil and reaction temperature was investigated.

4.3.1 Effect of catalyst loading

Since the presence of catalyst in a reaction quickens the rate of reaction by lowering the activation energy for the reaction to progress, an increase in the amount of catalyst used is likely to drive the reaction towards the products' side at a faster rate (Rao et al., 2011). Therefore, the carbon catalyst was used in different loading amounts (2.5, 5, 7.5 and 10 wt%). The other parameters (12:1 methanol/oil molarity, 60 °C, 60 min) were fixed.

The effect of catalyst loading used on conversion efficiency is shown in **Figure 4.6**. The conversion rate of FFA increased as the catalyst loading was increased up until 7.5 wt%. Increment in catalyst loading to 10 wt% showed no substantial increase in conversion yield. This pattern indicated that the rate of FFA conversion was directly proportional to the amount of catalyst loading, until the reaction equilibrium limit was reached at 7.5 wt%. Higher amount of catalyst loading would lead to a decreased conversion rate which could be attributed to the poor mass transfer between the catalyst and the FFA content in the reaction mixture. Also, as more catalyst was used, the esterification rate would progress faster, producing more water by-product at a faster rate that will deactivate the catalyst instead. Although the catalyst was considered water tolerant due to its hydrophobic properties, higher amount of the water by-product (>0.3 wt%) formed would still deactivate the catalyst (Tao et al., 2015). Therefore, it can be concluded that 7.5 wt% is the optimum catalyst loading amount. This correlated with the study by Rao et al. (2011) which found a similar optimum catalyst loading of 7.5 wt%.

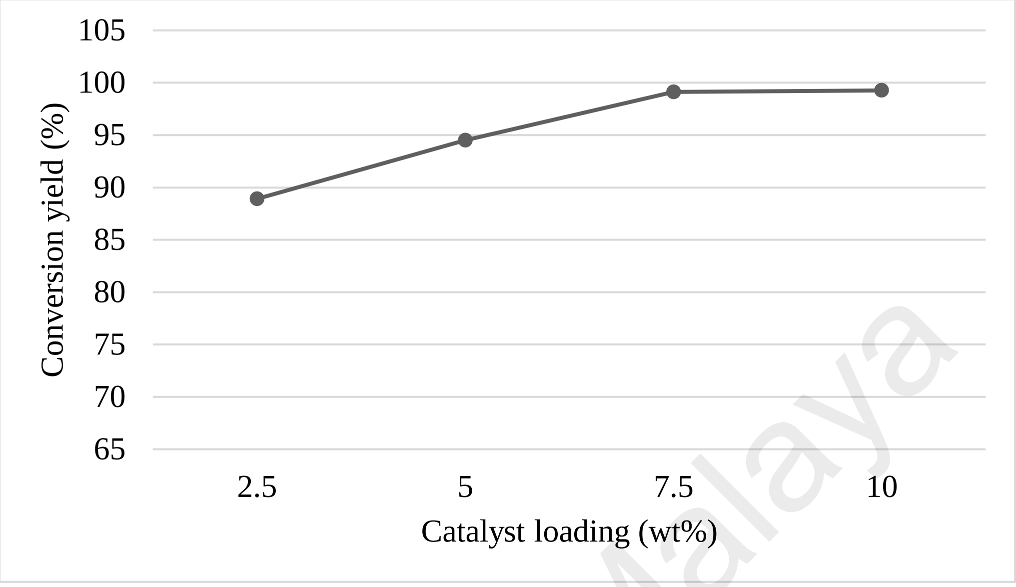


Figure 4.6: Effect of catalyst loading (wt%) on conversion yield (%) of FFA

4.3.2 Effect of methanol/oil molar ratio

Given that the esterification process is an equilibrium reaction, it requires a high methanol/oil molar ratio to push the reaction towards the products side. Use of heterogeneous catalyst and high FFA oils as feedstock particularly require a higher methanol/oil molar ratio (Fadhil et al., 2016). Effect of methanol/oil ratio on the conversion yield of FFA was studied by applying different molar ratios (6:1, 9:1, 12:1, 15:1 and 18:1) to a fixed process parameter (7.5 wt% catalyst loading, 60 °C, 60 min reaction time, 350 rpm).

As observed in **Fig. 4.7**, the conversion yield of FFA in JC oil increased from 69.90% to a maximum 99.13% at 12:1 methanol/oil molar ratio. The conversion yield decreased when higher than 12:1 molar ratio was applied. This can be explained by the over excess methanol content over-flooding the active site of the catalyst, inhibiting the catalytic activity to take place efficiently (Shu et al., 2010). Excess methanol and water by-product formed in the reaction mixture may also hamper the by-product separation step later in the process (Shu et al., 2010). This ultimately will increase the overall cost of biodiesel production (Asri et al., 2013).

Considering the usage of solid catalyst and oil feedstock that has high FFA content in this study, the methanol/oil molar ratio required to push the reaction towards the products' side was expected to be very high such as displayed in other similar studies conducted which required very high methanol/oil molar ratio of 15:1 and 45:1 (Dawodu et al., 2014; Fadhil et al., 2016). This indicated that the catalyst has successfully pushed the esterification to progress more efficiently compared to other heterogeneous catalyst.

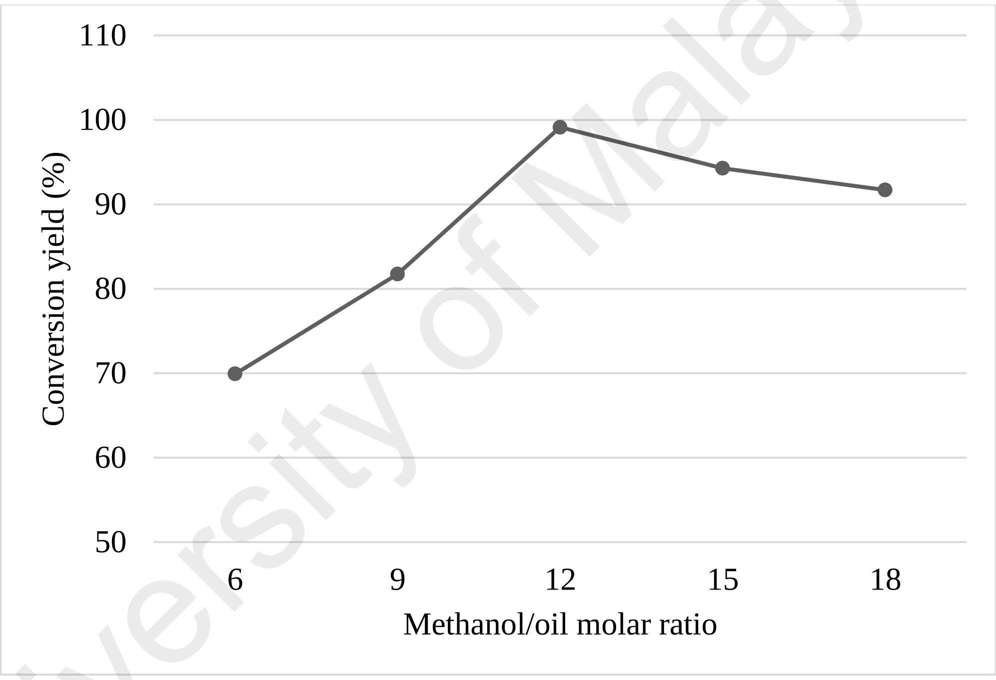


Figure 4.7: Effect of methanol/oil molar ratio on conversion yield (%) of FFA

4.3.3 Effect of temperature

The reaction rate and cost of the overall process is influenced by the reaction temperature. Therefore, varying temperatures (45, 50, 55, 60, 65 and 70 °C) were tested for the esterification process. The study was conducted utilizing methanol/oil molar ratio of 12:1, 7.5 wt% catalyst, for 60 min at 350 rpm. It was observed in **Figure 4.8** that increment of temperature up to 60 °C increased the conversion rate to a maximum of 99.13%. Further increment of temperature above 60 °C showed a decrease in conversion yield. Therefore, it can be deduced that the optimum temperature for esterification using the carbon-based acid catalyst was at 60 °C. This showed that temperature positively influenced the conversion of FFA as esterification is a reversible reaction and temperature higher than the optimum point will result in a back reaction (Tao et al., 2015).

It was also found that the optimum temperature for this study was lower than other studies using similar types of catalyst on high FFA oils. Dawodu et al. (2014) found 180 °C as the optimum temperature to give maximum conversion of *C. inophyllum* oil upon utilizing a solid acid catalyst and Konwar et al. (2014) determined 80 °C as the optimum temperature using a biomass-derived solid acid catalyst.

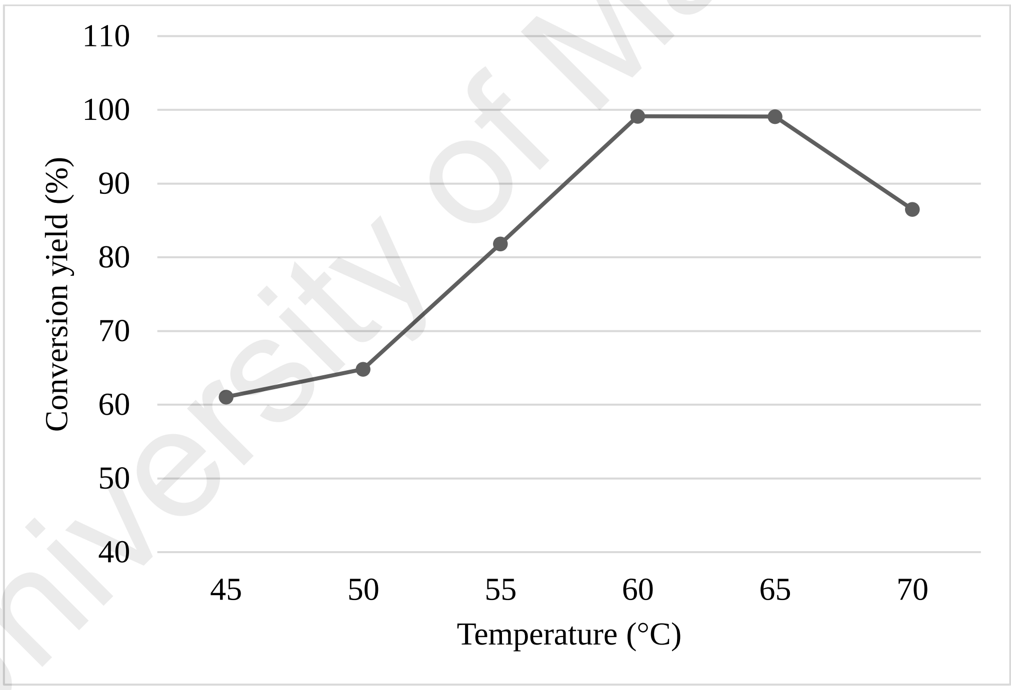


Figure 4.8: Effect of reaction temperature (°C) on conversion yield (%) of FFA

4.3.4 Effect of reaction time

The time needed for completion of the esterification process differ for different catalyst used. The reaction time played an important role in the conversion of FFA in JC oil as shown in **Figure 4.9**. Under fixed reaction parameters (7.5 wt% catalyst, 12:1

methanol/oil molar ratio, 60 °C, 350 rpm), the conversion rate greatly increased to a maximum 99.13% conversion yield from 30 to 60 min reaction time. Further increment in reaction time resulted in a rapid decrease of conversion yield instead. This may be explained as the reaction progressed over time, the FFA concentration dropped considerably reducing the conversion yield that had already reached its maximum point. The accumulation of water by-product over the duration of the reaction would deactivate the catalyst (Zhu et al., 2013). Slow reaction mass transfer may also have occurred over time as a result of adequate stirring of mixture was inhibited by the vicious slurries that formed over time (Rabiah Nizah et al., 2014).

The result obtained showed that the optimum time required for completion of esterification process using the catalyst was shorter than what was required for other similar catalysts studied. A study by Fadhil et al. (2016) and Akinfalabi et al. (2017) required 180 min and 120 min respectively for complete esterification process to take place while Shu et al. (2010) took up 270 min of reaction time. In comparison, it can be deduced that the catalyst prepared showed a substantially high catalytic activity, achieving completion of esterification process under a short amount of time.

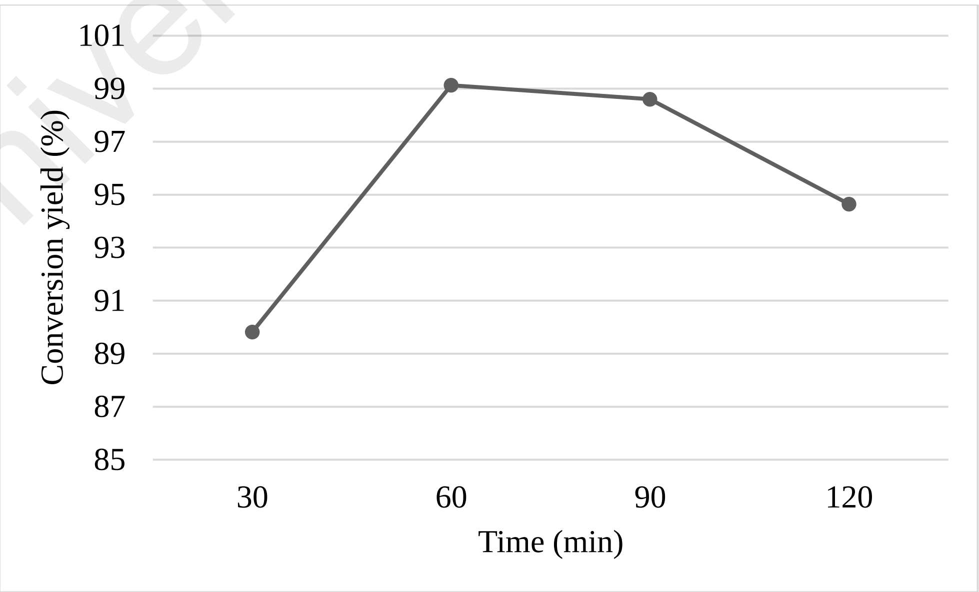


Figure 4.9: Effect of reaction time (min) on conversion yield (%) of FFA

4.3.5 Comparison of carbon-based acid catalyst with conventional sulfuric acid catalyst

Sulfuric acid (H_2SO_4) is one of the most commonly used and effective acid catalyst for esterification. In order to investigate the catalytic capability of the catalyst prepared, esterification was conducted using two different catalyst: the carbon-based acid catalyst and the conventionally used H_2SO_4 catalyst. Under standardized parameters of 12:1 methanol/oil molar ratio, 60 °C and 360 rpm, the reaction was carried out at various duration (30, 60, 90 and 120 min) for complete esterification of the oil feedstock to take place. An optimum conversion yield of 98.97% was achieved using 1 wt% H_2SO_4 at 120 min reaction time while the carbon-based acid catalyst (7.5 wt%) achieved a higher conversion yield of 99.13% at 60 min reaction time. According to **Figure 4.10**, it can be inferred that the carbon catalyst achieved a higher conversion rate of FFA than H_2SO_4 at half the reaction time needed. The strong catalytic performance of the carbon-based acid catalyst could be ascribed to the different hydrophilic functional groups (-COOH, -OH and $-SO_3H$) that are on the surface of the catalyst acting as anchoring sites for attachment of polar substrates such as FFAs and methanol (Fadhil et al., 2016).

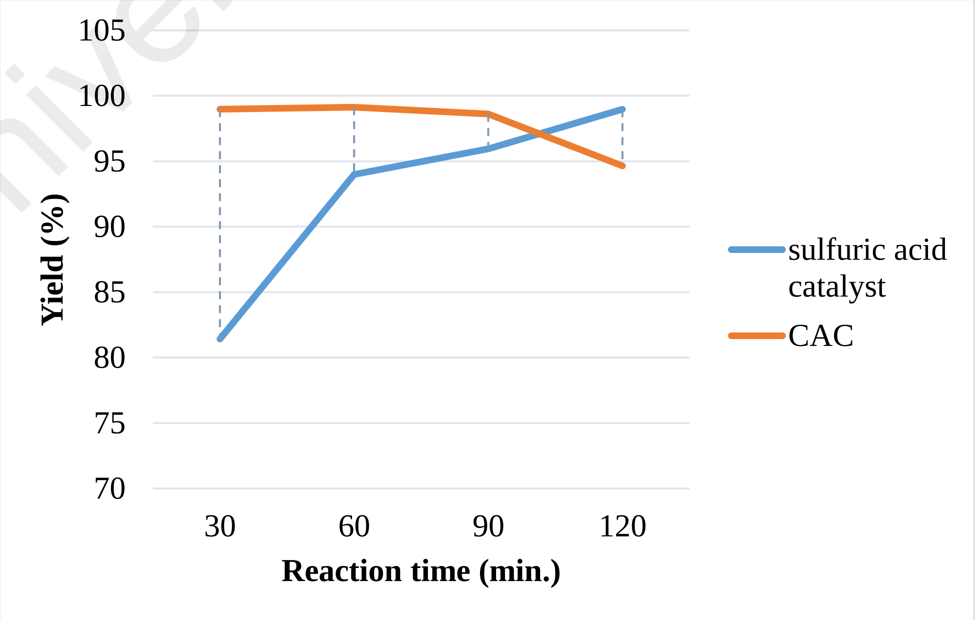


Figure 4.10: Comparison of the two processes (catalyzed by H_2SO_4 and the prepared carbon-based acid catalyst) on the conversion yield of FFA

4.4 Reusability of catalyst

A series of esterification cycles were conducted to evaluate the reusability of the carbon-based acid catalyst using the optimum parameters obtained from the study (12:1 methanol/oil ratio, 7.5wt% catalyst, 60 °C, 60 min, 350 rpm). After each cycle, the catalyst was washed using methanol to eliminate any risk of catalyst contamination due to attached residues of FFAs, FAME, glycerol and oil molecules, followed by drying at 110 °C to eliminate any residual moisture (Zhang et al., 2017). **Figure 4.11** showed sustainable activity of catalyst up until the 4th cycle. A gradual decrease in conversion yield was observed with the highest decrement of 10% occurring by the 4th cycle. Nevertheless, indicating that the catalyst had chemical stability and substantial reusability and can be reused up to 4 cycles without any substantial loss of catalytic activity.

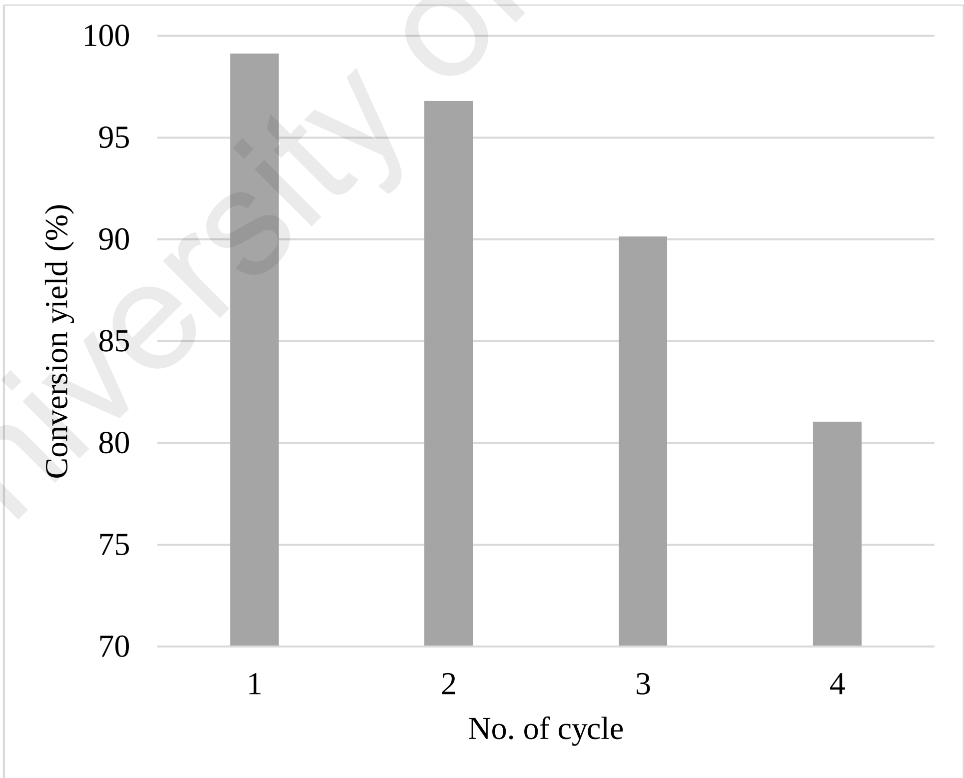


Figure 4.11: Reusability of catalyst

Reduction in the catalytic activity was a result of decreased acid capacity of the catalyst after each cycle due to sulphate leaching from the catalyst during the esterification process as indicated from the reduction of acid capacity in the catalyst in **Table 4.4**. The barium chloride testing of the filtered methanol showed a negative result indicating that the leached $-SO_3$ group was not present in the reaction mixture in the form of sulfuric acid, hence eliminating the possibility of the leached sulphates to mislead the acid value determination of esterified oil to obtain the conversion yield (Abu-Jrai et al., 2017). Other possible explanation for the reduced catalytic activity include the inhibition of triglyceride molecules entering the catalyst through the pores that might be blocked by other large molecules built up through multiple reaction cycle and loss of the active components in the catalyst or even the catalyst itself during washing of the catalyst (Teo et al., 2014).

Although other similar carbon-based catalyst produced showed a higher reusability of catalyst, there are recommendations on the possibility of catalyst regeneration by sulfonation using H_2SO_4, considering that sulfonation is yet the cheapest method of preparing an acid solid catalyst (Chen & Fang, 2011; Mo et al., 2008).

Table 4.4: Effect of reusability on acid capacity of catalyst

Cycle	Conversion Yield (%)	Acid capacity (mmol/g)
1	99.13	2.24
2	96.80	2.20
3	90.14	2.00
4	81.03	1.60

4.5 Biodiesel yield, analysis and data collection

4.5.1 Biodiesel yield

After the pre-treatment of crude JC oil by esterification using the carbon catalyst, the acid value was optimally reduced from 25.4 mg KOH/g to an acceptable value of 0.22 mg KOH/g suitable for transesterification process. The transesterification process was carried out using potassium hydroxide (Forson et al., 2004) as catalyst and parameters of 6:1 methanol/oil molar ratio, 1 wt% potassium hydroxide catalyst, 60°C, 60 min and 350 rpm (Bala et al., 2012). As determined by GC in **Figure 4.12**, the two step process gave a biodiesel yield of 96%.

According to **Table 4.5**, the highest FAME presented in *Jatropha curcas* biodiesel was methyl oleate (C18:1) at 42%, followed by methyl linoleate (C18:2) at 32.51%, methyl palmitate (C16:0) and at 14.08%, methyl octadecanoate (stearic acid) (C18:0) at 6.81%. A higher content of C16:0 and C18 (C18:0, C18:1, and C18:2) is common in non-edible oil derived biodiesel. This difference in fatty acid component may lead to a difference in the engines' combustion and exhaust emission upon using the fuel such that nitrogen oxides emission is lower for C18:0 compared to shorter carbon chain fatty acids but increase with increasing degree of unsaturation (Li et al., 2015).

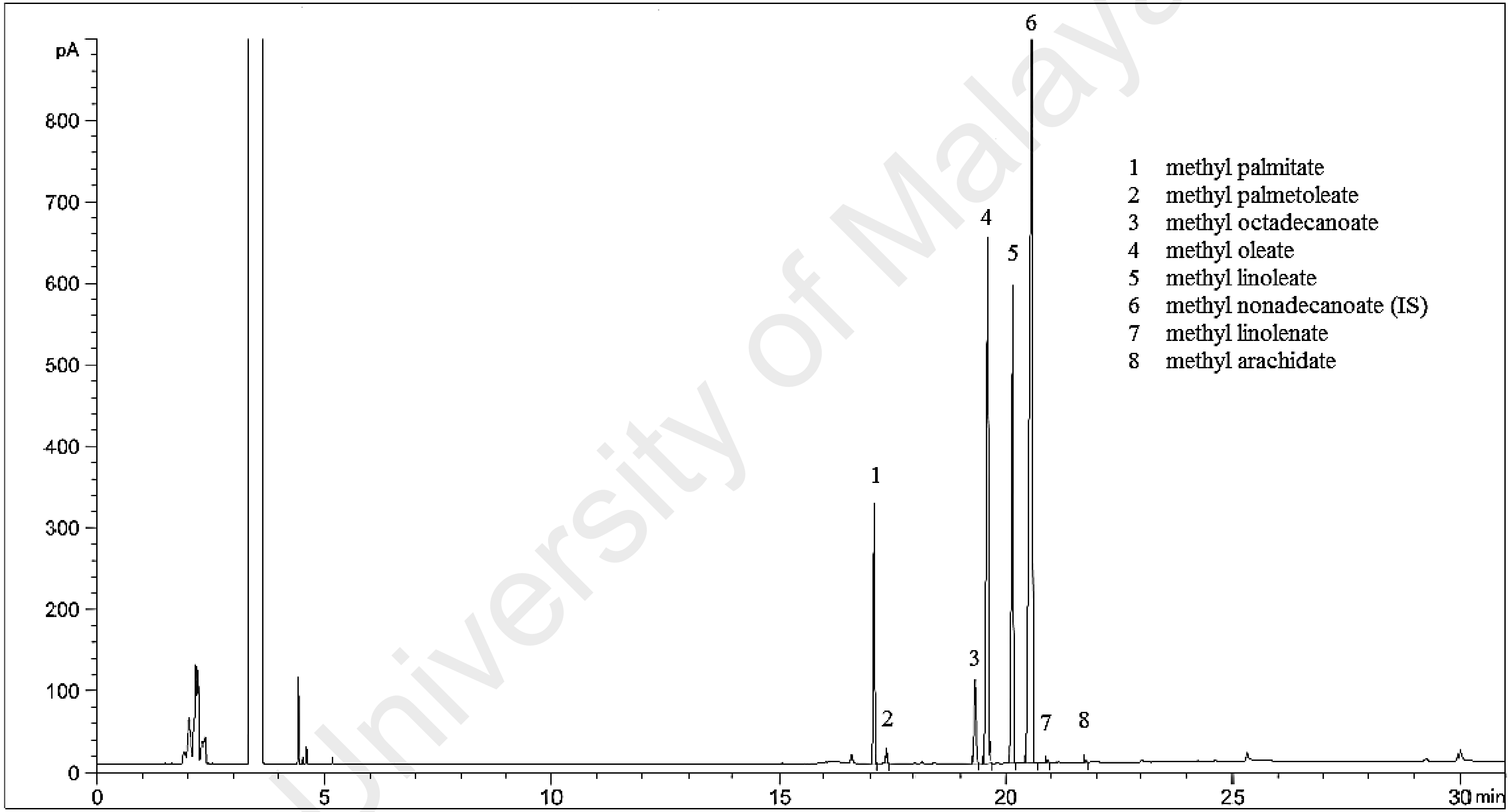


Figure 4.12: Chromatogram of *Jatropha curcas* biodiesel from GC analysis

Table 4.5: Fatty acid composition of final biodiesel

FAME	Carbon	Biodiesel (%)
Methyl palmitate	C16:0	14.0832
Methyl palmitoleate	C16:1	0.7347
Methyl octadecanoate (stearic acid)	C18:0	6.8147
Methyl oleate	C18:1	42.0033
Methyl linoleate	C18:2	32.5096
Methyl linolenate	C18:3	0.2084
Methyl arachidate (eicosanoic acid)	C20:0	0.2357

The biodiesel produced was analyzed by using Fourier transform infrared spectroscopy as in **Figure 4.13**. The wavenumber, functional group, band assignment and absorption intensity of the absorption peaks detected of the biodiesel were tabulated in **Table 4.6**. Results showed that biodiesel was comprised of esters of long-chain fatty acids. Spectra of biodiesel was chemically similar to the parent crude oil. Stretching of C=O has a peak of 1742 cm^{-1} which was located in the range of 1800-1700 cm^{-1} indicating it is of typical esters. This pattern of spectrum is generally found in FAME and refined crude oil (Soares et al., 2008). The main region of spectrum for the biodiesel was in the region range of 1500-900 cm^{-1} which is considered as the “fingerprint” with a peak of 1244 cm^{-1} corresponding to bending vibration of $-\text{CH}_3$ (Rabelo et al., 2015). Additionally, since there were no broad peaks detected in the region of 3100–3500 cm^{-1}, it indicated a very small water content in the biodiesel produced (Nisar et al., 2017).

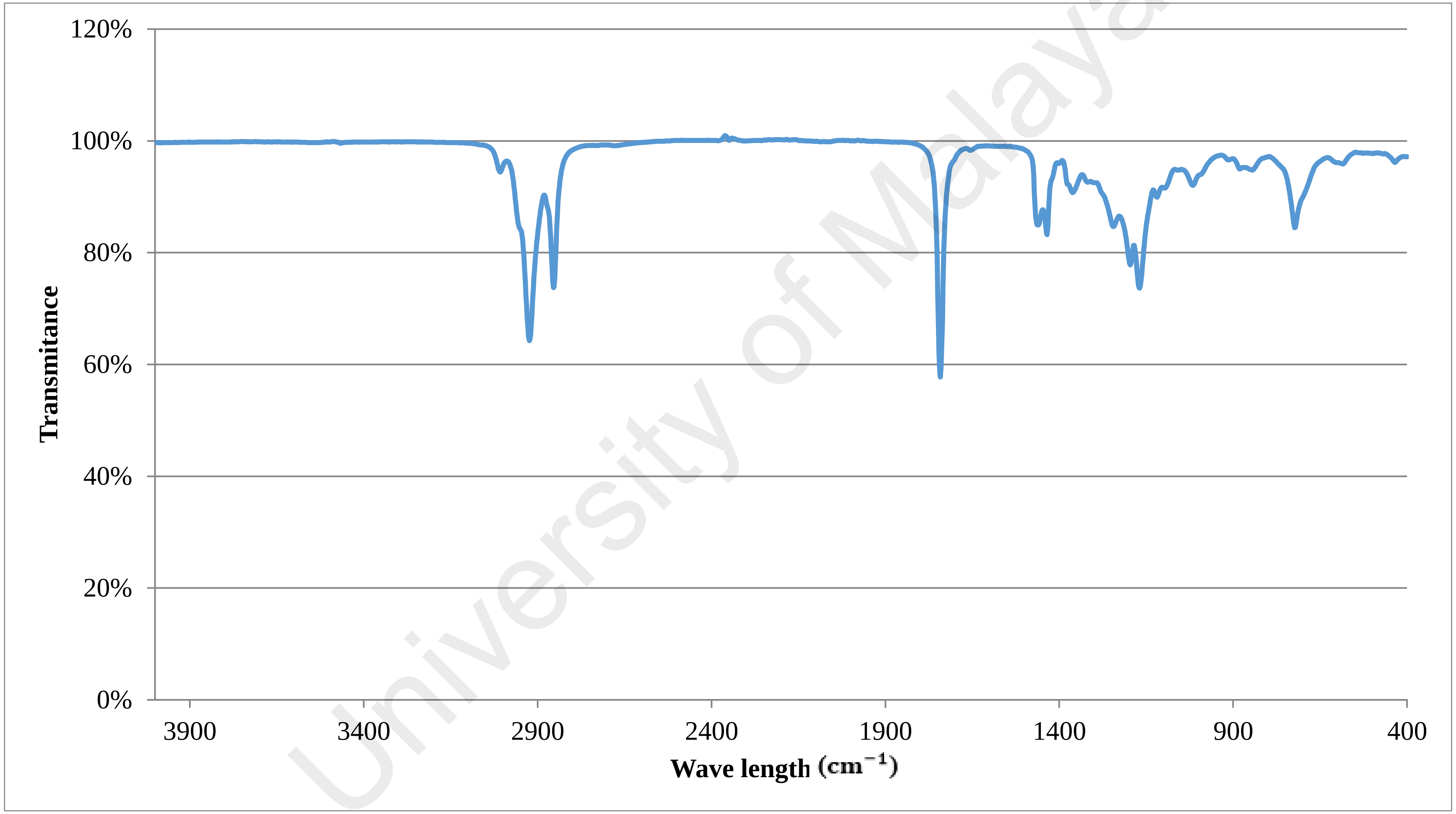


Figure 4.13: Fourier transform infrared spectrum of biodiesel from JC oil using carbon catalyst

Table 4.6: Wavenumber, functional group, band assignment and absorption intensity of the absorption peaks detected in the Fourier transform infrared spectrum of the biodiesel

Wavenumber (cm^{-1})	Group attribution	Vibration type	Absorption intensity
2923	CH	Asymmetric stretching vibration	Strong
2854	CH_2	Symmetric stretching vibration	Strong
1742	CO	Stretching	Strong
1461	CH_2	Sheer type vibration	Weak
1361	CH_3	bending vibration	Middling
1244	CH_3	Bending vibration	Weak
1196	COC	Anti-symmetric stretching vibration	Middling
1169	COC	Anti-symmetric stretching vibration	Middling
1016	COC	Anti-symmetric stretching vibration	Weak
722	CH_2	Plane rocking vibration	Weak

4.5.2 Property analysis of crude JC oil, esterified oil and biodiesel

Several properties of the crude oil, esterified oil and biodiesel produced were evaluated in accordance to the ASTM standards as listed in **Table 4.7**. It can be observed that the acid value of the parent crude oil was reduced to below the acceptable value of 4 mg KOH/g as a result of esterification using the carbon-based acid catalyst, which showed the catalysts' effectiveness in the esterification process. The acid value of the biodiesel produced after transesterification was further reduced to a value compatible to the ASTM and EN standards. Other properties of the JC oil changed drastically after transesterification. Viscosity of the oil decreased from 35.759 mm^2/s of parent crude oil to 4.7097 mm^2/s of biodiesel. The density of biodiesel was also reduced to a lower value (0.8815 g/mL) from the parent crude oil. Oxidation stability of the biodiesel showed an increase to 7.61 h after transesterification from the former 4.09 h of parent crude oil.

Table 4.7: Changes in the physiochemical properties of crude JC oil, esterified oil and biodiesel produced

Property	**Test procedure**	**Crude JC oil**	**Esterified JC oil**	**JC biodiesel**
Acid value (mg KOH/g)	ASTM D664	25.40	0.29	0.18
Kinematic viscosity @ 40°C (mm^2/s)	ASTM 445	35.75	28.88	4.70
Density @ 15.6°C (g/mL)	ASTM D127	0.91	0.89	0.88
Calorific value (MJ/kg)	ASTM D240	40.21	40.05	40.87
Oxidation stability @ 110°C (h)	EN 14112	4.09	6.74	7.61

Also, according to **Table 4.8**, results showed that the process proposed in this study produces biodiesel of high quality that meet the standards of the ASTM D6751 and EN 14214 standards, suitable for its use and commercialization. In comparison with Jatropha biodiesel produced by other researchers using similar type of catalysts indicate that the carbon-based acid catalyst prepared in this study is just as competent in producing high quality biodiesel.

Table 4.8: Biodiesel produced in comparison to ASTM and EN standards

Fuel properties/ fuel standards	**Biodiesel range**				
	ASTM D 6751	EN 14214	Jatropha biodiesel produced	Jatropha biodiesel (Nisar et al., 2017)	Jatropha biodiesel (Mohammed et al., 2016)
Acid value (mg KOH/g)	0.50 max	0.50 max	0.183	0.629	0.066
Kinematic viscosity (mm^2/s)	1.9–6.0	3.5–5.0	4.7	2.45	5.42
Density (g/cm^3)	0.86-0.88	0.86–0.90	0.88	0.86	0.88
Oxidation value	3 h min	8 h min	7.61	-	-

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Most solid acid catalysts studied thus far are comprised of expensive metals that also required harsh reaction conditions. Therefore, increased attention was directed towards the development of a lower-cost, green and sustainable catalyst. This study focused on the preparation of the carbon-based acid catalyst from the de-oiled seed cake of *Jatropha curcas*. Secondly, characterization of the catalyst was studied and reported. Finally, the catalysts' effectiveness in esterifying the Jatropha oil was studied and the optimum reaction conditions required were determined as well as its reusability capability. The produced biodiesel from the overall process and its quality were also determined. Regarding the abovementioned objectives, main findings of this study is as below:

i. A carbon-based acid catalyst was successfully prepared via carbonization at 350 °C, followed by sulfonation using $\mathrm{H_2SO_4}$ at 90°C for an optimal time of 5 h, ensuring the catalyst to possess the highest total acidity value of 2.24 mmol/g.

ii. Through multiple characterization tests conducted, attributes of the prepared catalyst include high porosity, large pore sizes and high amount of covalently bonded $-\mathrm{SO_3H}$ groups in the catalyst which contributed to the high catalytic ability of the catalyst. The catalyst was also determined to carry Bronsted acid sites, due to having both strong and weak acid site considering presence of $-\mathrm{SO_3H}$ groups and –OH groups respectively.

iii. The carbon-based acid catalyst was successfully used to esterify the crude JC oil at an optimum reaction parameter of 12:1 methanol/oil ratio, 7.5 wt% catalyst loading, 60 min reaction time and 60 °C reaction temperature, achieving a 99.13% conversion yield of FFA. The catalyst showed promising catalytic efficiency and stability in esterifying high FFA oil (JC oil) under mild reaction conditions with 4 times reusability. Comparatively, the catalyst outperformed the conventional sulfuric acid catalyst by achieving a higher conversion rate at a shorter reaction time. After the esterified oil was deemed suitable for transesterification, the process was conducted under reaction parameters of 1 wt% KOH, 6:1 methanol/oil ratio, 60 °C for 60 minutes and produced 96% biodiesel yield that were in line with the ASTM D6751 and EN 14214 standards.

The usage of the solid acid catalyst, allowed for easy separation after reaction and eliminated the washing process, making the overall esterification process simpler, more cost-efficient and environment-friendly. The biodiesel produced was also high in yield and of improved and high quality. Therefore, utilization of carbon-based solid acid catalyst produced from JC seed cake is a promising approach in accelerating the development of industrial biodiesel production from feedstocks with high FFA content, replacing the conventional homogeneous catalyst and other expensive metal-based solid catalyst. The lower cost for overall production of biodiesel when using the catalyst allow for reduced government subsidies, making biodiesel more affordable for the public. This is in line with the Malaysia National Energy policy that promotes the use of biodiesel to replace fossil fuel.

5.2 Recommendations

From this study, it is evident that the production of an effective carbon-based acid catalyst from the waste de-oiled seed cake of JC is possible. However, there are still areas for discussions and improvements to be explored as in the following:

- Given the lower reusability count of the catalyst compared to other solid acid catalysts studied by other researchers, the robustness and stability of the catalyst could be enhanced by adding promoters or additives, usually in form of organic compounds during the activation process of catalyst preparation. This is expected to further facilitate the catalyst to maintain its acidic properties under longer periods and harsher conditions.
- It is recommended in order to come up with a more detailed and accurate result, to incorporate optimization methods such as the response surface methodology (RSM) in the parameter study of the esterification process using the catalyst prepared. The system may be useful in effectively determining a more meticulous pattern of effect of each parameter and its combination on the conversion yield of the oil feedstock.
- Establishment of kinetic and thermodynamic parameters of heterogeneous carbon-based catalyst in biodiesel synthesis. This allows better understanding behind the catalytic activity of the catalyst at a molecular and statistical level.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

i. Haziratul Mardhiah, H., Ong, H. C., Masjuki, H. H., Lim, S., Lee, H.V. (2017). A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. [10.1016/j.rser.2016.09.036] Renewable and Sustainable Energy Reviews, (67)1225-1236.
ii. Haziratul Mardhiah, H., Ong, H. C., Masjuki, H. H., Lim S., Pang Y. L. (2017). Investigation of carbon-based solid acid catalyst from *Jatropha curcas* biomass in biodiesel production. [10.1016/j.enconman.2017.04.038] Energy Conversion and Management, (144)10-17.