Nitric Acid-Impregnated Activated Carbon from Palm Kernel Shell as Heterogeneous Catalyst for Biodiesel Production from Waste Cooking Oil

by

Aqilah binti Jazuli

15626

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2015

Universiti Teknologi PETRONAS,
32610 Bandar Seri Iskandar,
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

Nitric Acid-Impregnated Activated Carbon from Palm Kernel Shell as Heterogeneous Catalyst for Biodiesel Production from Waste Cooking Oil

by

Aqilah binti Jazuli

15626

A project dissertation submitted to the
Chemical Engineering Programme
University Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Mohammad Tazli Azizan)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AQILAH BINTI JAZULI

ABSTRACT

The ever-increasing energy demand and gradual depletion of fossil fuels, together with environment concerns, the exploration of alternative source of energy such as biodiesel is gaining considerable attention. However, the high cost of feedstock limits the commercialization of biodiesel compared to conventional diesel. Thus, the utilization of waste cooking oil in the biodiesel production can reduce the total production cost as well solving the disposal problem. In the present work, heterogeneous acid catalysts were studied to develop an effective catalyst for biodiesel production from waste cooking oil of high free fatty acid content with improved catalytic activity and stability. The dried palm kernel shell was calcined in a muffle furnace at 500 ^oC after impregnated with HNO_3 at different concentration. The catalysts then were characterized by various analytical techniques such as N_2 adsorption-desorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and BET surface area and pore size analyzer to explore their physicochemical properties. The catalytic activity of the synthesized catalysts was evaluated in the transesterification reaction of the WCO at the identified reaction conditions. The effect of different acid concentration was studied to evaluate the performance of the catalyst in the biodiesel production. The result shows that the HNO_3 30%/AC gives the higher biodiesel yield (23.45%) in reaction time of 3 h at reaction temperature 70 ^oC, methanol to oil molar ratio of 20:1, and agitation speed of 300 rpm. The physicochemical properties of the biodiesel produced from WCO were further studied and compared with the ASTM and the EN biodiesel specifications.

ACKNOWLEDGEMENT

First and foremost, I am thankful to God for His kind blessings by giving me strong will and determination to complete this Final Year Project (FYP).

I would like to take this opportunity to acknowledge and extent my heartfelt gratitude to my Supervisors, Dr. Mohammad Tazli Azizan of the Chemical Engineering Department UTP and Dr. Anita Ramli of the Fundamental and Applied Science Department (FASD) UTP for their invaluable patience, ideas and guidance. This research would have not been possible without the assistance of Dr. Farooq from FASD for the helps received in completing the work. I also want to thank to all lecturers of the Chemical Engineering Department for their direct and indirect contributions toward this work as well as the coordinators of FYP I and FYP II, Dr. Sintayehu and Dr. Nurul Ekmi for their efforts in guiding us throughout the semesters.

Lastly, I want to express my profound gratitude to my mother, Salma Hashim, my family and friends for the encouragement and support through thick and thin of time. It is the unfailing support from them that has enabled me to complete this FYP course.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATION

AC	Activated carbon
HNO_3 5%/AC	Activated carbon impregnated with 5% nitric acid
HNO_3 15%/AC	Activated carbon impregnated with 15% nitric acid
HNO_3 30%/AC	Activated carbon impregnated with 30% nitric acid
BET	Brunauer-Emmet-Teller theory
FFA	Free fatty acid
FAME	Fatty acid methyl ester
FT-IR	Fourier transforms infrared spectroscopy
H_2SO_4	Sulphuric acid
HNO_3	Nitric acid
KOH	Potassium hydroxide
PKS	Palm kernel shell
SEM	Scanning Electron Micrograph
TGA	Thermogravimetric analysis
WCO	Waste cooking oil

CHAPTER 1

INTRODUCTION

1.0 Background of Study

The ever-increasing energy demand and gradual depletion of fossil fuels, together with environment concerns, the exploration of alternative source of energy is gaining considerable attention. In this alarming situation, biodiesel could be a promising alternative toward the replacement of conventional petro-diesel [1] due to its renewable resources, lower greenhouse gas emission, clean combustion, biodegradability and good engine performance. Moreover, biodiesel has energy content and physicochemical properties that almost similar to conventional diesel. Therefore, it can be used on its own or blended with conventional diesel in the existing engines without any major modifications. Generally, biodiesel is produced through catalytic transesterification of vegetable oils and animal fats with alcohol in the presence of catalyst to obtain a mixture of fatty acid alkyl esters (biodiesel) and glycerin.

Conventionally, homogeneous base or acid catalysts are used in commercial biodiesel production via transesterification process due to its high catalytic activity. However, the use of homogeneous catalysts leads to several problems including soap production, difficulty in recovering the catalyst and the production of large amounts of waste water. Many researches now are oriented towards the production of heterogeneous catalyst in biodiesel production from waste cooking oil. Heterogeneous catalyst can overcome the limitations related to the use of homogeneous catalysts through easy separation, fewer disposal problem and catalysts reusability [1] without any major loss in their catalytic activity.

1.1 Problem Statement

Despite several advantages offered by biodiesel, it has currently not yet been commercialized all over the world as compared to conventional diesel fuel. The major drawback is the high cost of raw materials used for biodiesel production [2] which greatly prohibits its commercialization. It has been reported that approximately 70-95% of the total biodiesel production cost is associated to the cost of raw materials [3]. In this context, synthesis of biodiesel from waste cooking oil (WCO) can effectively use biomass waste and reduce the cost of war material to 60-70%. Almost all of the waste cooking oil will be disposed of down the sinks or drain, eventually causing clogging of pipes and pollution of water source. This will lead to the significant impact to environment and aquatic life forms, as well as the increase of drainage maintenance costs. Hence, the utilization of waste cooking oil for biodiesel production will solve the problems associated with WCO disposal.

Generally, homogeneous base or acid catalysts are used in commercial biodiesel production via transesterification process due to its high catalytic activity. However, the use of homogeneous catalysts lead to several problems including soap production, reactor corrosion, difficulty in recovering the catalyst and the production of large amounts of waste water, thus raising the overall biodiesel production cost [3]. Heterogeneous catalyst can overcome the limitations related to the use of homogeneous catalysts through easy separation, fewer disposal problems and catalysts reusability [1] without any major loss in their catalytic activity.

Palm kernel shell (PKS) is the most widely available agricultural waste material in Malaysia with nearly 4.3 million tons of PKS is produced annually. Large portion of the waste is burned in open air or dumped scattered in areas around the oil palm mill [4]. The problems associated with the burning of these solid fuels are the emissions of dark smoke and excess carbon dioxide. Therefore, the utilization of PKS as activated carbon catalyst in transesterification reaction in biodiesel production gives a chance to eradicate disposal and environmental problems associated to the unutilized PKS at the palm plantation.

1.2 Objectives

The main objectives of this project are:

- To prepare activated carbons from palm kernel shell by using nitric acid, HNO_3 impregnation method.
- To characterize the physicochemical properties of the modified activated carbon from PKS.
- To study the performance of the catalyst in the transesterification of WCO to biodiesel production.

1.3 Scope of Study

1.3.1 Modification of Activated Carbon with Nitric acid

The student will conduct an experiment to synthesize the new modified activated carbon from palm kernel shell (PKS) for transesterification of biodiesel from waste cooking oil (WCO). Activated carbons are impregnated with HNO_3 with different concentration from 5-30 wt%.

1.3.2 Characterization of Catalyst

The physicochemical properties of the synthesized catalysts are studied by various characterization techniques as illustrated in Table 1.1.

Table 1.1 Characterization methods to study physicochemcial properties of synthesized catalysts

Techniques	Function
N2 adsorption-desorption	To measure specific surface area, total volume pore, mean pore diameter.
X-ray diffraction (XRD)	To determine catalysts crystallinity, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering.
Temperature program desorption (TPD)	To provide information on the binding energies of atomic and molecular species adsorbed on the catalysts surface.
Fourier Transform Infrared Spectroscopy (FTIR)	To analyze the surface functional groups of the synthesized catalysts to obtain peaks at different wavelengths.
Scanning Electron Micrograph (SEM)	To study the surface morphology, size distribution and porosity of the catalyst

1.3.3 Characterization of WCO

The key physical and chemical characteristics of WCO, such as acid value, saponification value, flash point, specific gravity, iodine value, viscosity and calorific value are determined experimentally following standard test methods.

1.3.4 Catalytic Activity on Transesterification of WCO

The catalytic activity of the synthesized catalysts is evaluated in the transesterification reaction of the WCO at the identified reaction conditions. The performance of catalyst at different HNO_3 concentration in activated carbon the biodiesel production is studied in this research.

1.3.5 Characterization of Synthesized Biodiesel

Important physicochemical properties of the biodiesel produced from WCO, such as viscosity, density, acid value, flash point, moisture content, calorific value and methyl ester content are determined following the well-established methods. Moreover, the biodiesel are further characterized by various analytical techniques such as FTIR, TGA, Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and gas chromatography (GC) equipped with a flame ionization detector.

CHAPTER 2

LITERATURE REVIEW

2.0 Summary

This chapter gives a detail review on pertinent literature on the activated carbon as heterogeneous catalyst, characterization and its utilization, besides discussing the used of palm kernel shell as the precursor for activated carbon production in previous studies. Moreover, various physicochemical properties that signify the development of microporous structure and the methodology adopted are portrayed. It also demonstrates the overall parameters of activated carbon in the esterification and transesterification reaction in biodiesel production.

2.1 Activated carbon

Activated carbon (AC) is an amorphous carbonaceous materials that exhibits a high degree of porosity and an extended interparticulate surface area [5].

2.1.1 Porous Structure of Activated Carbon

Activated carbons that have high adsorptive capacities are due to the well-developed porous structure in which related to surface area, pore volume, and pore size distribution [6]. The porous structure of AC formed during the carbonization process and was developed further during activation, when the spaces between the elementary crystallites are cleared of tar and other carbonaceous material [5]. The activation process enhances the volume and enlarges the diameters of the pores. The structure of pores and pore size distribution largely depend on the nature of the raw material and activation process route. A conventional classification of pores according to their average width, which represents the distance between the walls of slit shaped pore or the radius of a cylindrical pore, proposed by Dubinin et al., (1960) and officially adopted by the International Union of Pure and Applied Chemistry (IUPAC) is summarized in Table 2.1.

Table 2.1 Classification of pores according to their width (IUPAC, 1972)

Types of pores	**Width**
Micropores	< 2 nm (20Å)
Mesopores	2 – 50 nm (20 – 500 Å)
Macropores	>50 nm (> 500 Å)

Each of these groups of pores lays a specific role in the adsorption process. The micropores constitute a large surface area and volume; therefore, determining the adsorption capacity of given activated carbons. Mesopores, on the other hand, act as conduits which lead the adsorbate molecule to the micropores network. The macropores enable adsorbate molecules to pass rapidly to smaller pore situated deeper within the particles of activated carbons. The typical pore size distribution of activated carbon can be observed in Figure 2.1.

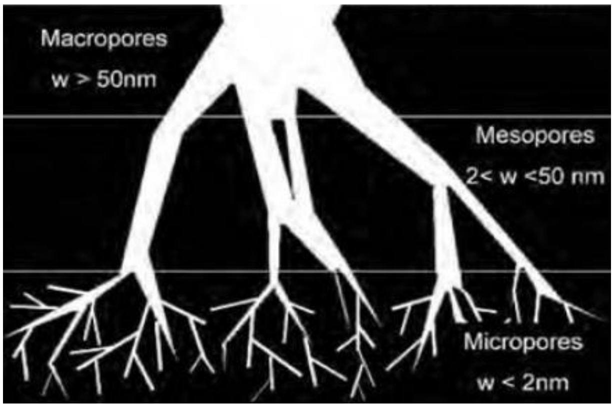

Figure 2.1 Graphical presentation of pore structure in activated carbon.

2.1.2 Preparation of Activated Carbon

Preparation method of activated carbon is vital in determining the textural and surface chemical properties of the end product. There are two basic activation methods of preparing activated carbon which are generally classified as either physical activation or chemical activation. Generally most of the precursors used for the preparation of activated carbon are rich in carbon such as palm kernel shell [4, 7-10], coconut husk [11], flamboyant pods [1] and rice husk [12].

2.1.2.1 Physical Activation

In physical activation, also referred to as thermal activation process, the raw materials are carbonized in a furnace a high temperature under an inert atmosphere such as pure nitrogen. Typical temperatures for the carbonization of palm kernel shell step ranges from 170^{o}C and is nearly completed at 600 ^{o}C [13]. The carbonization stage is subsequently followed by the gasification of char, carried out at 800-1000 ^{o}C with carbon dioxide, steam or mixture of both [14].

A research conducted by Lua et al. (2006) to study the pore development of palm kernel shell activated carbons, pyrolysis of the raw material is chosen as the method of production. Based on the results obtained, the optimum condition that yielded the highest specific surface area and pore volume are at a temperature of 600 ^{o}C for 2 hours hold time with nitrogen flow rate of 150 cm^{3}/min.

2.1.2.2 Chemical Activation

On the other hand, chemical activation method uses an acidic or basic solution as activating agent, such as H_3PO_4, $ZnCl_2$, KOH or K_2CO_3 to decompose the precursors pyrolytically as mentioned by Rodriguez-Reinoso and Molina-Sabio (1992). In this method, the precursor is carbonized after the addition of the activating agent to increase the yield of activated carbons. Several recent researches have been using microwave irradiation rather than conventional heating technique because it requires less activation time, provides volumetric and internal heating [7], thus optimizing the energy and chemical usage [10].

2.2 Biodiesel production

Biodiesel is a mono alkyl ester of fatty acid which is produced by either transesterification of triglycerides with alcohol to fatty acid alkyl ester (biodiesel) and glycerol (byproduct), or esterification of fatty acid (FA) with alcohol to fatty acid alkyl ester (biodiesel) and water (byproduct)[15], in the presence of catalyst. Both transesterification and esterification reactions are illustrated in Figure 2.2.

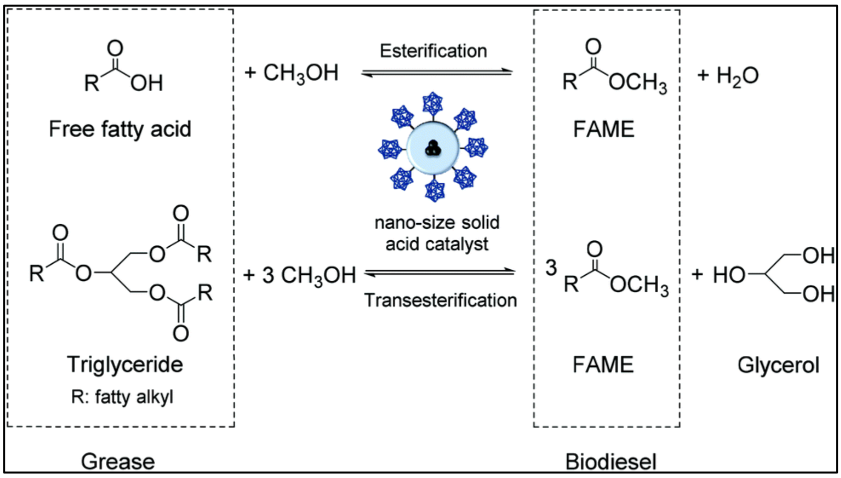

Figure 2.2 Esterification and transesterification reaction in to produce biodiesel

Currently, biodiesel is produced from natural and renewable sources such as vegetable oils like soybean, pal, sunflower, canola, rapeseed and cotton seed [16]. However, due to the high cost of the raw materials used for its production, biodiesel has currently not yet been commercialized all over the world, thus prohibiting its widespread application. A source of biodiesel should have low production costs and large production scale [16], making the low quality feedstock such as waste cooking oil as an attractive feedstock substitute for biodiesel production.

2.2.1 Biodiesel Production from WCO

Waste cooking oil (WCO) refers to the vegetable oil which has been used for food preparation and which is not viable for its intended use. Considerable quantity of used cooking oil is available all over the world. These are generated locally whenever food is cooked or fried in oil. The use of WCO in biodiesel production brings substantial environmental benefits as it provides an alternative for the final disposal of the oil previously discharged off in the environment. Some of the WCO are used in soap preparation, but major quantity is illegally dumped into landfills and rivers, creating pollution of land and water resources. The cost of waste frying oil is estimated to be about half the price of virgin oil. The use of these wastes as a reactant for biodiesel synthesis not only helps in the disposal but also reduces the cost of production. The use of WCO as a biodiesel source has a potential to reduce CO2, particulate matter and other greenhouse gases as the carbon contained in biomass-derived fuel is largely biogenic and renewable. The review done by Yakob et al. (2013) suggests that WCO is a promising feedstock in biodiesel production.

Generally, cooking oils that are used for frying are disposed of after several time of use. The presence of heat and water accelerates the hydrolysis of triglyerides, increasing the content of free fatty acids in the oil which has been considered as negative effects upon the transesterification reaction [15]. This is proven by feedstock characterization done by Farooq et al. (2013) to obtain the physicochemical properties of the selected WCO as shown in Table 2.2. The acid content in the WCO found to be 3.27 mg KOH/g which is relatively high. Besides that, it can be seen that the oil viscosity increases considerably due to the formation of dimers and polymers in the used cooking oil. The mean molecular mass and the iodine value decrease, while the saponification value and oil density increase.

Table 2.2 Physicochemical properties of WCO

Property	**Unit**	**Value**	**Test method**
Acid Value	mg KOH/g	3.27	EN 1404
Calorific value	J/g	38462	ASTM D240
Kinematic viscosity at 40 ^oC	cSt	41.17	ASTM D-445
Specific gravity at 30 ^oC	-	0.903	ASTM D-7042
Saponification value	mg KOH/g	186.12	AOCS Cd 3a-94
Flash point	^oC	274	ASTM D93
Moisture content	%	0.102	ASTM D6304
Mean molecular mass	g/mol	920.42	GB 5530-85

2.2.2 Methods for Biodiesel Production from WCO

In biodiesel production, the transesterification reaction is carried out in the presence of suitable catalyst in order to obtain reasonable conversion of feedstock to biodiesel. In the current scenario of biodiesel production, wide ranges of catalysts are used such as homogeneous acid catalysts, homogeneous base catalyst, heterogeneous acid catalyst, and heterogeneous base catalyst.

2.2.2.1 Homogeneous Acid/Base Catalysis

Commercially biodiesel is produced by transesterification reacting using methanol and homogeneous catalyst such as sodium hydroxide (base catalyst) and sulfuric acid (acid catalyst) in which the reaction is in homogeneous stage where all reagents being in liquid stage [17]. Generally, homogeneous acid or base catalysts show a very good catalytic activity in biodiesel production (Sharm et al., 2008) for a reaction time within 1 hour and the reaction takes place in mild reaction condition with less energy consumption. However, excessive soap formation during the process decreases biodiesel conversion rate and yield resulting in large amount of waste water in product purification process [17, 18].

2.2.2.2 Heterogeneous Acid/Base Catalysis

The utilization of heterogeneous catalyst can overcome the problems associated with the conventional homogeneous catalysts in biodiesel technology. Heterogeneous catalysts are non-corrosive and environmental friendly, can be easily separated, reusable and simplify the biodiesel production process [3]. Many researchers reported that the reusability of heterogeneous catalyst is 4-13 cycles without significant loss in catalyst activity with biodiesel yield 89.3-97.7% at reaction temperature 60-65 ^{o}C. Nevertheless, problems associated with heterogeneous base catalyst are their ability to tolerate the high free fatty acids (FFAs) contents in feedstock that will cause excessive soap formation if FFA more than 2 wt% [17]. On the contrary, it is reported that heterogeneous acid catalysts are suitable for conversion of low grade oil feedstock that contain high FFA, but the water generated during the conversion results in leaching and deactivation. A survey on the literature related to the use heterogeneous solid catalyst for biodiesel production from waste cooking oil is given in Table 2.3.

Table 2.3 Survey on heterogeneous catalytic transesterification of waste cooking oil to produce biodiesel

References	**Feedstock (oil:alcohol molar ratio)**	**Catalyst (wt% to oil mass)**	**Operating Conditions**		**Biodiesel yield**	**Catalyst reusability without significant activity loss**	**Findings**	**Research Gaps**
			Reaction Temperature (°C)	**Reaction time, Agitation speed**				
[19]	WCO, methanol (1:8)	CZO (12)	55	50 min	97.71%	5 times	Presence of metal oxides in nanocomposite possesses more active sites, results in high yield. Good reusability (5 times)	- Metal oxide catalysts only possess basic sites. - Soap formation
[1]	Hevea brasiliensis oil, methanol (1:15)	KOH-AC from flamboyant pods (3.5)	60	1 h, 750rpm	89.3%	7 times	High carbon yield of the catalyst Carbon supported catalyst reveals better reusability (7 times)	- Soap formation - Synthesized catalyst is for feedstock with low content of FFA
[18]	WCO, methanol (1:15)	Chicken bones (5)	65	4 h	89.33%	4 times	Surface area increases as calcination T is increased. Strong	- Synthesized catalyst is for feedstock with low content of

							active basic sites on catalyst surface, which exhibit better transesterification reaction performance.	FFA
[12]	WCO, methanol (1:20) constant	Rice husk-SO_3H solid acid catalyst (5)	110	3 h (FFA conversion) 15 h (FAME yield)	FFA conversion (98.2%) FAME yield (87.6%)	5 times	Catalyst has a favorable thermal stability. Good catalyst for high FFA contents. High conversion and yield.	- Solid acid catalyst require long reaction time and require high reaction temperature, high molar ratio methanol to oil
[3]	WCO, methanol (1:27)	Mo-Mn/γ-Al_2O_3 (15)	100	4 h, 500rpm	91.4	8 times	Both active acidic and basic sites improve catalytic activity. No soap formation. Mixed metal support > high catalyst reusability and chemical stability (8 times)	- Require high molar ratio methanol to oil, long reaction time. - Conventional catalyst requires higher cost

2.2.3 Activated Carbon from PKS as Catalyst Support for Biodiesel Production

2.2.3.1 Palm kernel shell

Palm oil or its scientific name *Elaeis guineesis* is a major source of edible oil in which the kernel of the fruit and its surrounding fibre (mesocarp) are used for oil extraction (Salleh, 2010). In oil palm industry, Malaysia is the second largest producer of palm oil with 17.7 million tonnes or 41% of the total world supply [20] with the current planted area is expanding to around 4.5 million hectare. In line with the growth of palm oil production in Malaysia, the amount of wastes generated from the industry also increased tremendously [20]. These biomass residue, especially palm kernel shell have become one of the most attractive renewable energy fuel in South East Asia.

Palm kernel shells (PKS) are the fibrous shell fractions left after the nut has been removed after the oil extraction. Compared to other wastes from the industry, palm kernel shell is preferable due to its low moisture content, uniform size distribution, easy handling, low ash contents and high carbon contents [8]. Lua, Lau and Guo also reported on the use of palm kernel shells as precursors to produce activated carbons for the removal of gaseous pollutants. In addition, the high concentration of volatiles in the palm kernel shells is ideal for creating highly porous structures within the activated carbon matrix [8].

The structural and elemental compositions of palm kernel shell are given in Table 5 [4].

Table 2.4 Structural and elemental compositions of PKS

Structural composition Percentage (%)	
Lignin	52
Cellulose	7
Hemicellulose	26
Moisture	6
Ash	9

Elemental percentage (%)

Carbon	50
Hydrogen	5.6
Nitrogen	0.72
Oxygen	35

2.2.3.2 Study on literature related to the use of activated carbons from PKS in biodiesel production

In recent years, scientists focused on the preparation of activated carbon catalysts from various waste materials as this technology not only solves the problem of waste disposal, but also converts a potential waste to a valuable product. Transesterification of biodiesel using activated carbons has various advantages over other catalysts. Activated carbon can meet the desirable properties of green catalysts as it is highly effective as catalyst support in liquid and vapor phase reactions [21]. The appreciable microporous surface of activated carbon makes it suitable to be used as catalyst support in transesterification reaction [1]. Therefore, acid or base catalyst like H_3PO_4 and KOH can easily be dispersed onto the surface of activated carbo resulting high surface area and low ash content subsequently enhances the reaction.

Very few researchers have worked on activated carbon from PKS as catalyst support in biodiesel production. Several researchers used carbon–based solid acid catalyst in the preparation of biodiesel from vegetable oils with large amounts of free fatty acids (FFAs) and obtained 80.5-90.4% of yield at reaction temperature 220 ^{o}C, 16.8M ratio of methanol to oil, 0.2 wt% catalyst loading and reaction time of 4.5 hours [2]. These researches highlighted that process requires high reaction time and very high reaction temperature as compared to activated carbons catalysts. When Dhawane et al. (2015) used flamboyant pods derived steam activated carbon in the transesterification of Hevea *brasiliensis* oil to biodiesel, it is reported that maximum yield of 89.3% is obtained at reaction temperature 60 ^{o}C, reaction time 1 hour, methanol to oil ratio 15:1 and catalyst loading 3.5 wt%.

Among various carbonaceous supports, palm kernel shells have been chosen as precursor in this work to develop catalyst support due to its high availability, zero cost, high carbon contents, low ash contents and uniform size distribution. A research made by Baroutian et al. (2010), potassium hydroxide catalyst supported on palm shell activated carbons is developed for transesterification of palm oil to biodiesel. The highest yield is obtained at 64.1 ^{o}C reaction temperature, 1 hour reaction time, 30.3 wt% catalysts loading and 24:1 methanol to oil molar ratio. In addition, it is found that potassium hydroxide species is highly distributed upon the surface of the support (as shown in Figure 2.3), therefore increases its catalytic activity and efficiency. It is reported that the physicochemical properties of the produced biodiesel under the optimum conditions meets the standard specifications. Thus, this study proves that activated carbon supported catalysts is effective for transesterification reaction in biodiesel production.

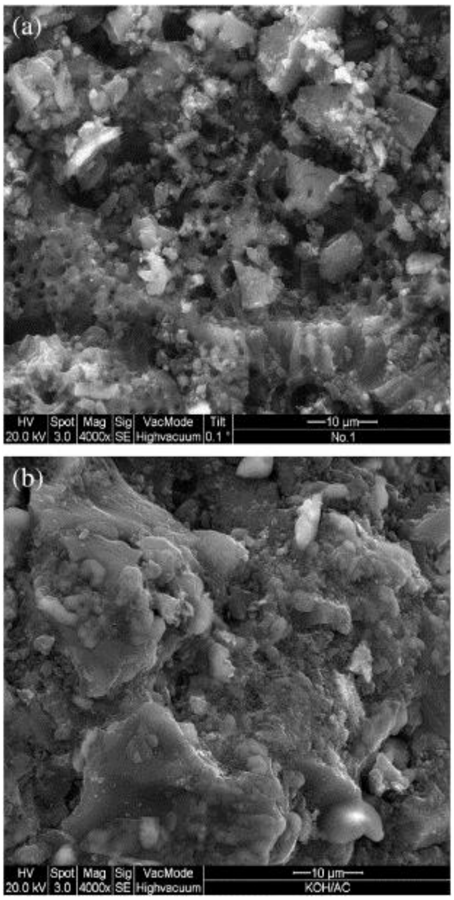

Figure 2.3 Scanning electron micrographs (SEM) of (a) palm shell activated carbon (b) KOH/AC catalyst

CHAPTER 3

METHODOLOGY

3.1 Project flowchart

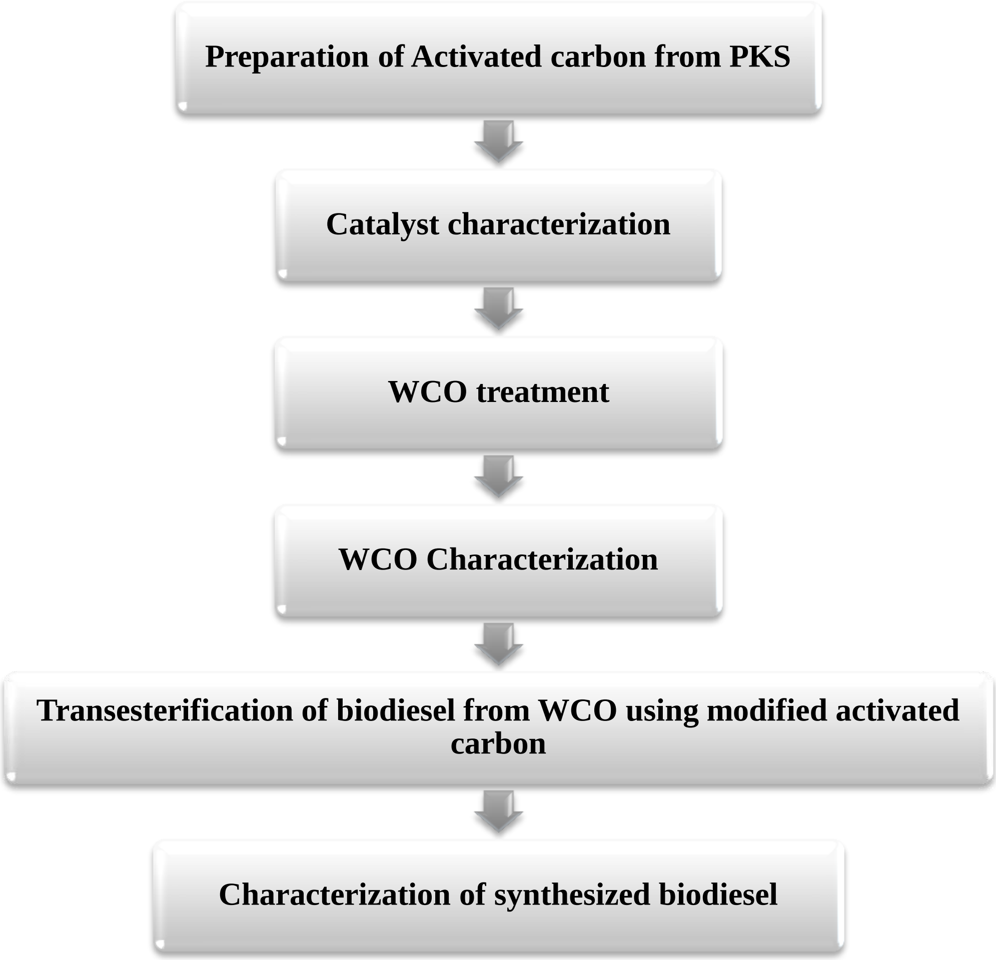

Figure 3.1 Flowchart of the research project

3.2 Materials

- Palm kernel shell (PKS)
- Nitric acid, HNO_3
- Methanol
- Waste cooking oil
- Distilled water
- Silica gel

3.3 Experiment Methodology

3.3.1 Preparation of Activated Carbon

1) PKS samples are obtained from nearest palm plantation in Seri Iskandar. They are washed with distilled water to remove dust and dirt and then dried in an oven at 105 ^{o}C for 24 hours.
2) The dried sample is crushed and passed through a set of sieves. Particles ranging 700 µm - 1.18 mm are collected in this research.
3) 20g of PKS are mixed with nitri acid, HNO_3 with different concentration (5, 15, and 30 %) and impregnation ratio (acid:PKS) of 2 for six hours with constant stirring at 300 rpm at 100 ^{o}C.
4) The slurry is then dried in a vacuum oven at 100 ^{o}C for 24 hours to remove the water.
5) The impregnated PKS are calcined at 500 ^{o}C in the presence of air in the muffle furnace for 5 hours.

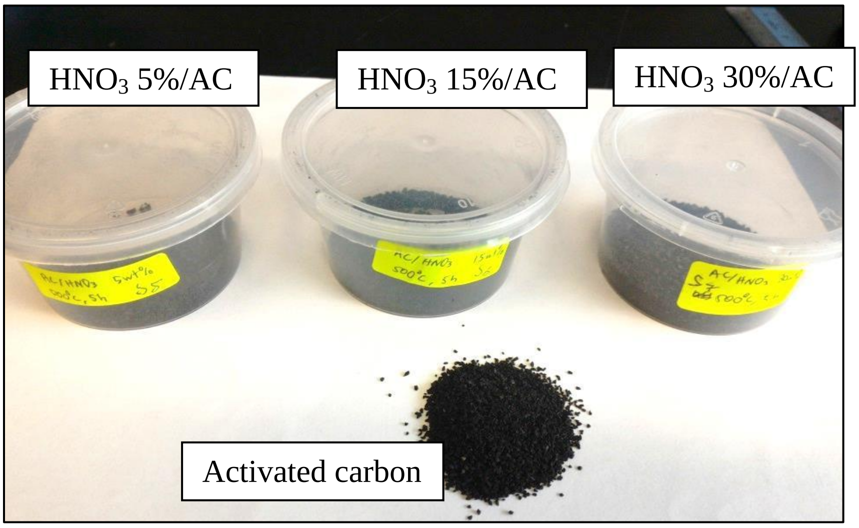

Figure 3.2 The synthesized activated carbon.

3.3.2 Characterization Method

The physical and chemical characterizations of the activated carbons and the modified activated carbons are studied by various characterization methods.

1) N_2 adsorption-desorption isotherms is used to measure the specific surface area, total volume pore and mean pore diameter.
2) CO_2 and NH_3 adsorption-desorption
3) X-ray diffraction (XRD) is used to determine the catalysts crystallinity.
4) Temperature programmed reduction (TPR) is used to utilize the basic properties of the prepared catalysts.
5) CO_2 temperature programmed desorption (TPD) is used to study the basic properties of the prepared catalyst.
6) Fourier Transform Infrared Spectroscopy (FTIR) is used to analyze the surface functional groups of the prepared activated carbons to obtain peaks at different wavelengths.

3.3.3 Feedstock Treatment

Figure 3.3 WCO before and after treatment

1) Waste cooking oil (WCO) collected is filtered using fine cloth to remove all the insoluble impurities and washed repeatedly with hot distilled water to remove salt and other soluble materials.
2) 10wt% silica gel is added to the washed WCO and stirred for 3 hours to remove the water used during washing.
3) Vacuum filtration using Whatman filter paper is used for the removal of silica gel.
4) The oil is then dried at 100 ^{o}C for 24 hours in an oven.

3.3.4 Characterization of Feedstock

The important physicochemical properties of the WCO are determined experimentally by using standard methods as shown in Table 3.1.

Table 3.1 Test methods for characterization of WCO

Property	Test method
Acid value	EN 1404
Calorific Value	ASTM D240
Kinematic viscosity at 40 ^{o}C	ASTM D-445
Specific gravity at 30 ^{o}C	ASTM D-7042
Saponification value	AOCS Cd 3a-94
Flash point	ASTM D93
Moisture content	ASTM D6304
Mena molecular mass	GB 5530-85

3.3.5 Reaction Procedure

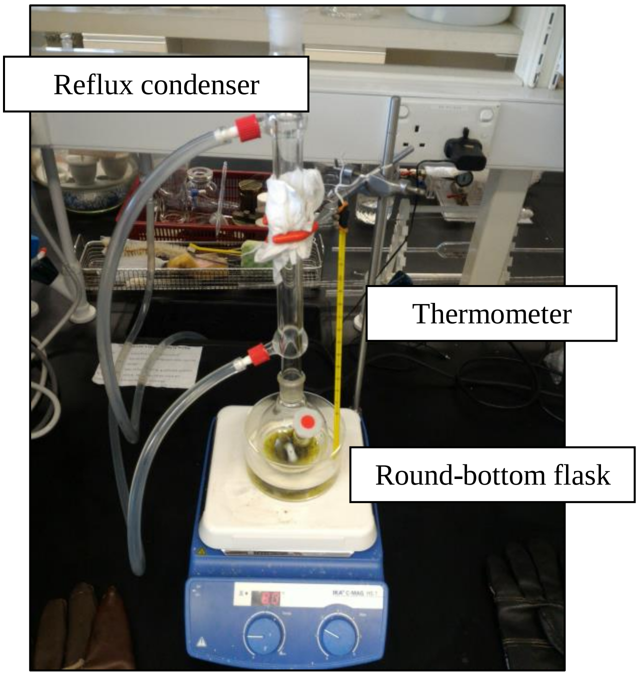

Figure 3.4 Transesterification reaction

1. The transesterification reaction of WCO is performed in a two-necked 250 mL round-bottom flask fitted with a water-cooled condenser and thermometer as shown in Figure 3.4.
2. The catalyst is first activated by dispersing it in methanol at 40^{o}C with constant stirring for 40 minutes using magnetic bar.

3. After the catalyst activation, required amount of WCO (heated at 100 ^{o}C for 1 h prior to the reaction) is added to the reactor and the reaction is carried out under the identified reaction conditions.
4. After reaction completion, the reaction mixture was filtered through a filter paper and then centrifuged to separate the catalyst.
5. The mixture is then transferred to a separating funnel and allowed to stand for 24 hours. Biodiesel is obtained as the top layer while glycerol at the bottom. The biodiesel yield is calculated using Eq. (1) (Berla et. al., 2012; Knothe, 2006).

$$Biodiesel\ yield\ (\%) = \frac{W_{FAME} \times M_{oil}}{3 \times W_{oil} \times M_{FAME}} \times 100 \quad (1)$$

3.3.6 Physicochemical Properties of Synthesized Biodiesel

By using well established methods, important properties of the biodiesel produced from WCO such as viscosity, density, acid value, flash point, moisture content, calorific value and mean molecular mass can be determined. Besides that, the synthesized biodiesel is further characterized by various analytical techniques such as Fourier-transform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and Gas chromatography (GC) equipped with a flame ionization detector.

3.4 Gantt Chart and Key Milestones

Table 3.1 Ganttchart and project key milestones

	2015																2016	
Task	**May**		**Jun**		**July**		**Aug**		**Sept**		**Oct**		**Nov**		**Dec**		**Jan**	
Selection of Project Title	🟨																	
Literature study	🟨	🟨	🟨	🟨														
Submission of Extended Proposal					🟩													
Proposal Defence						🟨												
Catalyst Synthesis							🟨	🟨	🟨	🟨								
Interim Report Submission								🟩										
Catalyst Characterization									🟨	🟨	🟨	🟨						
Submission of Progress Report											🟩							
Catalytic activity testing and optimization												🟨	🟨	🟨	🟨	🟨		
Characterization of Synthesized biodiesel															🟨	🟨		
Submission of Dissertation (soft bound)																	🟩	
Submission of Technical Paper																	🟩	
Viva																		🟨
Submission of Project Dissertation (Hard Bound)																		🟩

🟨 **Process**	🟩 **Key milestone**

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of catalyst

4.1.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was conducted to investigate the thermal degradation behavior of the precursor PKS and to determine the minimum calcination temperature for the preparation of activated carbon. The profile of thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) regarding the decomposition of PKS in air atmosphere is shown in Figure 4.1.

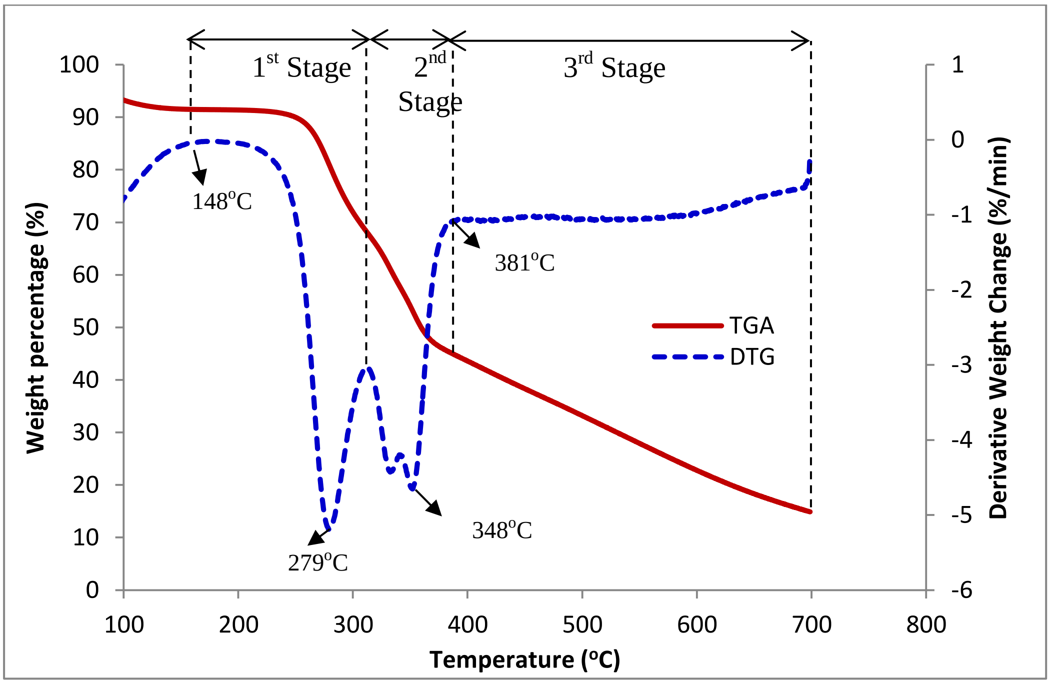

Figure 4.1 TG/DTG curves of PKS degradation under air atmosphere

The results indicate that the thermal degradation took place within range of 100-700 ^oC, in which three distinct mass loss stages are observed: 148-314 ^oC, 314-381 ^oC and 381-700 ^oC. The two significant mass loss peaks as shown in DTG curve indicate a fast degradation of the first two stages while the third stage was a slow degradation stage. The structural composition of PKS is mainly composed of hemicellulose, cellulose and lignin. Comparing the individual degradation trend of cellulose, hemicellulose and lignin reported by Ma et al. [22], the weight loss (32.1 mass%) at 148-314 ^oC was mainly attributed to the degradation of the hemicellulose (185-325 ^oC).

Second stage of degradation process (314-381 ^oC) shows a simultaneous degradation of cellulose (290-380 ^oC) with mass loss of 23.1 mass%. Thermal stability of cellulose was found to be higher than the hemicellulose because cellulose is a high-molecular compound with long linear chain composed of D-glucosyl [23]. Besides that, a part of cellulose has crystalline structure made of ordered microfibrils, thus resulting thermal degradation more difficulty than hemicellulose [24]. Finally, the slow degradation in third stage (381-700 ^oC) was likely due to lignin degradation based on the analysis done by Ma et al. [22] in which the main product from this degradation is char. Based on the TGA analysis, the minimum calcination temperature of PKS was selected as 500 ^oC.

4.1.2 Scanning Electron Micrograph (SEM) Analysis

The scanning electron microscope (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the catalyst. It has been useful to determine the particle shape, porosity and size distribution of the activated carbon. Scanning electron micrographs of the samples are presented in Figure 4.2(a) - 4.2(d).

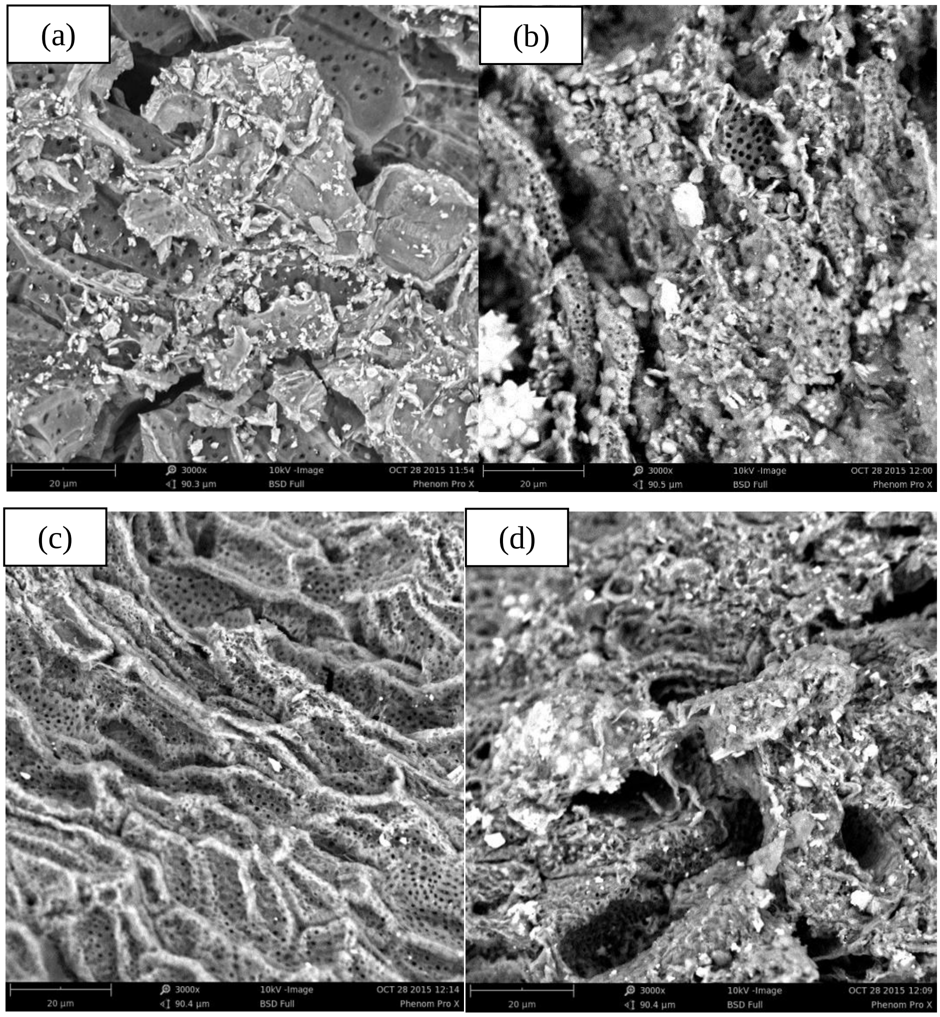

Figure 4.2 SEM images of (a) raw carbon (b) HNO_3 5wt%/AC (c) HNO_3 15wt%/AC (d) HNO_3 30wt%/AC

It is found that in the most of the previous studies on nitric acid impregnation of activated carbon, formation of oxygen groups at the entrances and the walls of pores cause the tightening of micropores; thus reducing the total pore volume and total surface area [25]. Moreover, it is reported that HNO_3 modification has a corrosive effect on the surface of activated carbon in which the surface area substantially decreased with increasing of HNO_3 concentration [26]. In contrast, some other researchers have observed higher surface area in activated carbon after nitric acid impregnation through acid-ash dissolving and opening of some blocked pores [27].

In this study, it is revealed that HNO_3 as activating agent is appreciably capable of modifying the surface structure of PKS. The activation process was effective in developing micropores on the AC surface to produce high surface area desirable for good catalyst. HNO_3 5%/AC and HNO_3 15%/AC show significant dispersion of HNO_3 onto the surface of the AC confirmed by the blockage of the pores as compared to raw carbon as shown in Figure 4.1(a). The average pore size for the three catalysts was 30Å - 40Å, demonstrating the existence of some mesopores which are favorable to macromolecules such as oleic acid, triolein , and methyl oleate, diffusing in and out the interior of the catalyst [2] thus improving catalytic activity.

4.1.3 BET Surface Area and Pore Size

The BET surface area and pore size were measured by the multipoint N_2 adsorption-desorption method at liquid nitrogen temperature ($-195.8^{o}C$). The average pore size of HNO_3/AC impregnated at concentration of 5%, 15% and 30% was found to be 33.85 Å, 48.01 Å, and 35.43 Å, allowing reactant to diffuse easily into the interior of the activated carbon catalyst due to the combination on micropores and mesopores structure. The results show that acidic surface modification has a strong effect on the textural properties of the AC sample. Table 4.1 shows that S_{BET} and V_t increase when the concentration of nitric acid is increased from 5wt% to 30wt% under N_2 gasification. At lower concentration, the active site carbons partially react with HNO_3 to form new small micropores. Increasing the concentration of HNO_3 should enhance the activation process and thus improve the porosity.

The nitrogen adsorption-desorption isotherms of the ACs prepared using different concentration are shown in Figure 4.3. This plot shows that the nitrogen adsorption isotherm of the N2-activated samples are type I for HNO_3 5%/AC and HNO_3 15%/AC, exhibit microporous structure while in the case of HNO_3 30%/AC, which has a type IV isotherm, indicating microporosity and mesoporosity.

Table 4.1 Textural properties; BET surface area (S_{BET}), total pore volume (V_t), and average pore size (D_p) of different heterogeneous catalyst

Catalyst	**S_{BET} (m^2/g)**	**V_t (cm^3/g)**	**D_p (Å)**
HNO_3 5%/AC	163.67	0.0938	33.848
HNO_3 15%/AC	272.07	0.1230	48.014
HNO_3 30%/AC	381.35	0.1521	35.429

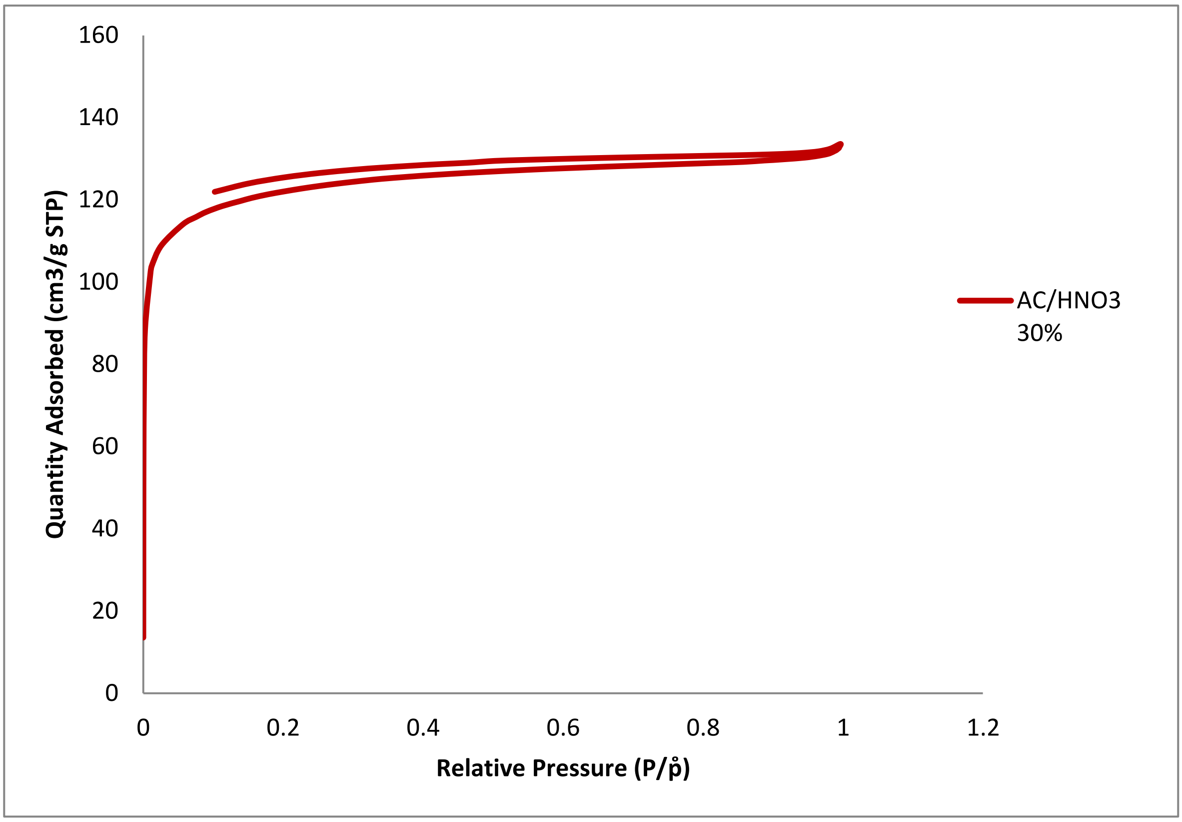

Figure 4.3 N_2 adsorption-desorption isotherms of ACs prepared at different concentration of HNO_3

4.1.4 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

FTIR spectrum of the raw carbon and activated carbon impregnated with nitric acid at different concentration is shown in Figure 4.4. The broad adsorption band of 3200–3600 cm^{-1} with the peak around 3450 cm^{-1} is ascribed to the hydroxyl, O-H stretching vibration in hydrogen bonds which enlarged after the modification along with the increase of HNO_3 concentration. The band around 1618 cm^{-1} is corresponding to the stretching vibration of the carbonyl (C=O) groups and C=C groups. The FTIR spectra of the ACs in the range of 1500–1900 cm^{-1} where significant differences in the surface functional groups, made during the acidic treatment, can be obviously recognized.

The peak at 1745 cm^{-1} in the ACs spectrum is said to be the specific peak for stretching vibrations of C=O bond in carboxylic acid functional group [25]. The new peak appeared at 1550 cm^{-1} after nitric acid modification in AC/HNO_3 5% indicates the presence of asymmetric NO_2 stretch vibration. Symmetric NO_2 stretch vibration also presents in the spectrum of AC/HNO_3 15% and AC/HNO_3 30% at range 1519-1548 cm^{-1} as a new peak. Existence of NO_2 groups on the surface means that HNO_3 oxidation promotes to addition of nitrogen containing groups on the surface and supports increase in nitrogen content. The presence of very weak bands at about 2360 cm^{-1} at raw carbon and nitric acid treated activated carbon may represent ketone groups. The broad peaks within the range of 1000-1300 cm^{-1} emerged after the HNO_3 impregnation can be assigned to various C-O bonds. The FTIR results demonstrate that the nitric acid treatment has greatly modified the AC surfaces through increasing the amount of oxygen-containing functionalities, which might provide more chemical sorption sites to improve the electrochemical capacitivity.

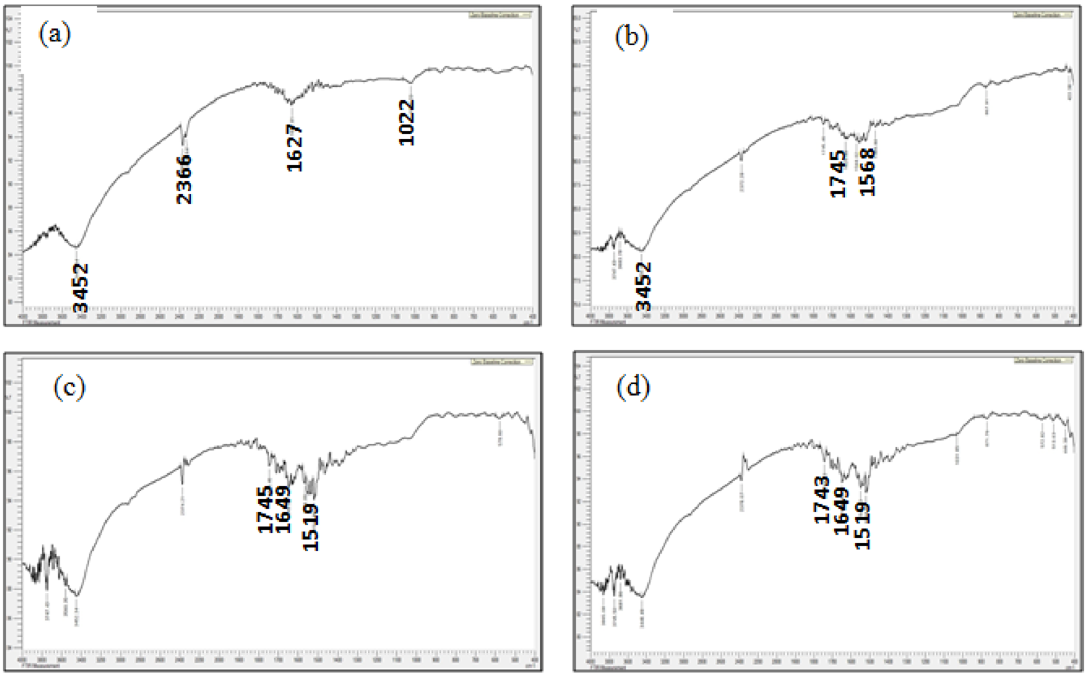

Figure 4.4 Fourier transforms infrared spectra of (a) raw carbon (b) HNO_3 5%/AC (c) HNO_3 15%/AC and (d) HNO_3 30%/AC.

4.2 Waste Cooking Oil Characterization

The key physicochemical properties of treated WCO were determined experimentally following standard test methods as shown in Table 4.2.

Table 4.2 Physicochemical properties of treated WCO

Property	Unit	Value	Test method
Acid value	mg KOH/g	5.77	EN 1404
FFA content	wt%	2.64	-
Kinematic viscosity at 40 ^{o}C	cSt	39.76	ASTM D-445
Specific gravity at 30 ^{o}C	-	0.903	ASTM D-7042
Saponification value	mg KOH/g	197.95	AOCS Cd 3a-94
Moisture content	%	0.106	ASTM D6304
Mean molecular mass	g/mol	860.69	GB 5530-85

4.3 Catalytic Activity Testing

The catalytic activity of the synthesized catalysts was evaluated in the transesterification reaction of the WCO at the following identified reaction conditions.

- Reaction temperature: 70 ^{o}C
- Reaction time: 3 hours
- Methanol to oil molar ratio: 20:1
- Agitation speed: 300rpm
- Catalyst loading: 5wt%

The results of the transesterification reaction for all the catalyst are shown in Figure 4.5. Among different catalyst tested, HNO_3 30%/AC shows the best catalytic activity in the transesterification reaction and provides the maximum yield of 23.45%. The improved catalytic activity of the catalyst compared to other catalyst with lower concentration of HNO_3 could be due to the presence of higher strength of the active acidic sites on the surface of the catalyst. This suggests that the activated carbon with nitric acid has potential for transesterification reaction to produce biodiesel from WCO with high FFA.

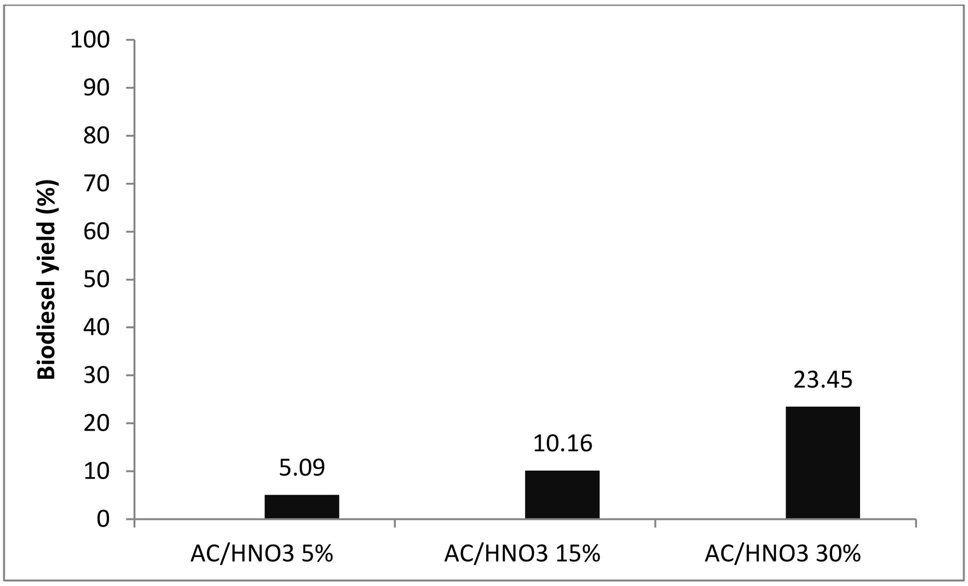

Figure 4.5 Biodiesel yield percentage of different catalyst

However, when compared to few studies of different heterogeneous acid catalyst such as sulphuric and sulfonated acid, the synthesized catalyst proved to be less efficient because it gives maximum biodiesel yield less than 30% whereas other catalysts could reach more than 80% yield of biodiesel [28]. The other reason of the low yield could be due to the presence of water in WCO that is not well heated prior to the reaction. It is known than the acid catalyzed reactions are more susceptible to water content and Canakci et al. [29] reported that the presence of more than 0.5% water in the oil will decrease the ester conversion to below 90%. According to Siakpas et al., the greater affinity of water will lead to the acid catalyst prefentially interacting with water rather than alcohol with the consequent deactivation of the catalyst.

The higher acid site concentration was the major factor that contributed to higher catalytic activities of the catalyst. In the present study, Temperature Programmed Desorption (TPD) was not able to be performed due to equipment limitation; hence the amount of catalyst acidity was not determined. However, the low yield of biodiesel might be related to the low active site concentrations of the catalyst that inhibits the adsorption and desorption process of FFAs. Consequently, this could lead to a lower reaction rates than those yielded from the higher acidity catalysts and hence, loss in activity.

Pore size of catalyst plays an important role towards the reaction rate. Few researchers reported that even though catalyst mesopores provide higher percentage sites on the catalyst, it is the macropores that minimize mass transfer hindrances by breaking up the mesopore domain size [30]. In this study, the characterization results show that all the synthesized activated carbon prepared were ranged between 30 Å to 50 Å which indicates the dominating microporosity and some mesoporosity. The smaller the pore size, the lower accessibility of the FFAs to the acid sites of the catalysts thus limits the mass transfer of reacting species. The dominant variable that plays significant role in reducing mass transfer limitation is particle size. Catalysts with smaller particle sizes provide higher dispersion which leads to the greater exposure of the catalytic sites and increased catalytic activity [30].

Moreover, the reaction parameters were not further optimized using different reaction conditions to identify the real maximum biodiesel yield as well as during catalyst preparation; thus the result obtained could be further improved. For instance, the catalytic activity processes may be increased by the use of larger amounts of catalyst typically ranged between 1 and 5 wt% as mentioned by Freedman et al. (1986). Canakci et al. [29] used different amounts of acid (1, 3 and 5 wt%) in the transesterification reaction and found that the ester yield went from 72.7 to 95.0% as the catalyst concentration was increased. The dependence of reaction rate on catalyst concentration has been further verified by other studies.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

The heterogeneous acid catalysts were successfully prepared by using wet impregnation method with nitric acid. The results show that acidic surface modification has a strong effect on the textural properties of the heterogeneous catalyst. The N_2 adsorption isotherm shows a type IV isotherm indicating microporosity and mesoporosity of the ACs with average pore size of 30Å - 40Å. It is revealed that the S_{BET} and V_t increased when the concentration of nitric acid was increased. HNO_3 30%/AC shows the highest surface area of 381.35 m^2/g and total pore volume of 0.152 cm^3/g thus allowing the diffusion of molecules during the reaction.

The catalytic activity of the nitric acid activated carbon support shows that the HNO_3 30%/AC gives the higher biodiesel yield compared to other catalyst tested. However, the maximum biodiesel yield (23.45%) is very low indicating that the nitric acid as the activating agent is not as efficient as other acid reported in few studies for the transesterification reaction of WCO with methanol. Despite the low conversion, it is revealed that the catalyst has the potential to produce low cost biodiesel from low cost feedstock for sustainable energy production.

Therefore, it is suggested in future work to improve the catalytic activity of the catalyst AC/HNO_3 30% by further modification of physicochemical properties of the activated carbon. The catalyst can be further treated with strong acid such as H_2SO_4 to increase the acid site densities of the catalyst in order to achieve sufficient strength of active acidic sites for complete reaction.

Apart from that, future studies are recommended to studies the optimization of the transesterification reaction parameters such as reaction temperature, reaction time, methanol to oil molar ratio, agitation speed and catalyst loading. This study is important in order to identify the best operating condition to give the maximum biodiesel yield and showing improved catalytic activity.

REFERENCES

[1] S. H. Dhawane, T. Kumar, and G. Halder, "Central composite design approach towards optimization of flamboyant pods derived steam activated carbon for its use as heterogeneous catalyst in transesterification of Hevea brasiliensis oil," *Energy Conversion and Management,* vol. 100, pp. 277-287, 2015.

[2] Q. Shu, J. Gao, Z. Nawaz, Y. Liao, D. Wang, and J. Wang, "Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst," *Applied Energy,* vol. 87, pp. 2589-2596, 2010.

[3] M. Farooq, A. Ramli, and D. Subbarao, "Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts," *Journal of Cleaner Production,* vol. 59, pp. 131-140, 2013.

[4] M. A. A. Zaini, T. W. Meng, M. J. Kamaruddin, S. H. M. Setapar, and M. A. C. Yunus, "Microwave-Induced Zinc Chloride Activated Palm Kernel Shell for Dye Removal," *Sains Malaysiana,* vol. 43, pp. 1421-1428, 2014.

[5] R. C. Bansal and M. Goyal, *Activated Carbon Adsorption*. Boca Raton: Taylor & Francis Group, 2005.

[6] R. Gottipati, "Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium(VI) from Aqueous Phase," Doctor of Philosophy in Chemical Engineering, Department of Chemical Engineering, National Institute of Technology Rourkela, Odisha, 2012.

[7] R. Hoseinzadeh Hesas, A. Arami-Niya, W. M. A. Wan Daud, and J. N. Sahu, "Microwave-assisted production of activated carbons from oil palm shell in the presence of CO2 or N2 for CO2 adsorption," *Journal of Industrial and Engineering Chemistry,* vol. 24, pp. 196-205, 2015.

[8] A. C. Lua, F. Y. Lau, and J. Guo, "Influence of pyrolysis conditions on pore development of oil-palm-shell activated carbons," *Journal of Analytical and Applied Pyrolysis,* vol. 76, pp. 96-102, 2006.

[9] E. C. Okoroigwe, A. C. Ofomatah, N. F. Oparaku, and G. O. Unachuku, "Production and evaluation of activated carbon from palm kernel shells

(PKS) for economic and environmental sustainability," *International Journal of Physical Sciences,* vol. 8, pp. 1036-1041, 2013.

[10] A. Kundu, B. Sen Gupta, M. A. Hashim, and G. Redzwan, "Taguchi optimization approach for production of activated carbon from phosphoric acid impregnated palm kernel shell by microwave heating," *Journal of Cleaner Production,* 2014.

[11] K. Y. Foo and B. H. Hameed, "Coconut husk derived activated carbon via microwave induced activation: Effects of activation agents, preparation parameters and adsorption performance," *Chemical Engineering Journal,* vol. 184, pp. 57-65, 2012.

[12] M. Li, Y. Zheng, Y. Chen, and X. Zhu, "Biodiesel production from waste cooking oil using a heterogeneous catalyst from pyrolyzed rice husk," *Bioresource Technology,* vol. 154, pp. 345-348, 2014.

[13] B. E. Meteku, "Production of Activated Carbon from Palm Kernel Shell for Gold Adsorption using Leachates from Cocoa Husk Ash (Crude Potash) As Activating Agent," Master of Science in Chemical Enginering, Department of Chemical Engineering, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana, 2013.

[14] H. Marsh and F. Rodriguez-Reinoso, *Activated Carbon*. United Kingdom: Elsevier Ltd, 2006.

[15] C. D. Mandolesi de Araújo, C. C. de Andrade, E. de Souza e Silva, and F. A. Dupas, "Biodiesel production from used cooking oil: A review," *Renewable and Sustainable Energy Reviews,* vol. 27, pp. 445-452, 2013.

[16] S. E. Mahesh, A. Ramanathan, K. M. M. S. Begum, and A. Narayanan, "Biodiesel production from waste cooking oil using KBr impregnated CaO as catalyst," *Energy Conversion and Management,* vol. 91, pp. 442-450, 2015.

[17] Y. H. Tan, M. O. Abdullah, and C. Nolasco-Hipolito, "The potential of waste cooking oil-based biodiesel using heterogeneous catalyst derived from various calcined eggshells coupled with an emulsification technique: A review on the emission reduction and engine performance," *Renewable and Sustainable Energy Reviews,* vol. 47, pp. 589-603, 2015.

[18] M. Farooq, A. Ramli, and A. Naeem, "Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones," *Renewable Energy,* vol. 76, pp. 362-368, 2015.

[19] B. Gurunathan and A. Ravi, "Biodiesel production from waste cooking oil using copper doped zinc oxide nanocomposite as heterogeneous catalyst," *Bioresource Technology,* vol. 188, pp. 124-127, 2015.

[20] M. L. Palmetti, *Palm Oil: Nutrition, Uses and Impacts*: Nova Science Publisher, 2011.

[21] S. Baroutian, M. K. Aroua, A. A. A. Raman, and N. M. N. Sulaiman, "Potassium hydroxide catalyst supported on palm shell activated carbon for transesterification of palm oil," *Fuel Processing Technology,* vol. 91, pp. 1378-1385, 2010.

[22] Z. Ma, D. Chen, J. Gu, B. Bao, and Q. Zhang, "Determination of pyrolysis characteristics and kinetics of palm kernel shell using TGA–FTIR and model-free integral methods," *Energy Conversion and Management,* vol. 89, pp. 251-259, 2015.

[23] M. A. Lopez-Velazquez, V. Santes, J. Balmaseda, and E. Torres-Garcia, "Pyrolysis of orange waste: A thermo-kinetic study," *Journal of Analytical and Applied Pyrolysis,* vol. 99, pp. 170-177, 2013.

[24] H. Yang, R. Yan, T. Chin, D. T. Liang, H. Chen, and C. Zheng, "Thermogravimetric Analysis−Fourier Transform Infrared Analysis of Palm Oil Waste Pyrolysis," *Energy & Fuels,* vol. 18, pp. 1814-1821, 2004.

[25] H. ShamsiJazeyi and T. Kaghazchi, "Investigation of nitric acid treatment of activated carbon for enhanced aqueous mercury removal," *Journal of Industrial and Engineering Chemistry,* vol. 16, pp. 852-858, 2010.

[26] Y. Gokce and Z. Aktas, "Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol," *Applied Surface Science,* vol. 313, pp. 352-359, 2014.

[27] J. Jaramillo, V. Gómez-Serrano, and P. M. Álvarez, "Enhanced adsorption of metal ions onto functionalized granular activated carbons prepared from cherry stones," *Journal of Hazardous Materials,* vol. 161, pp. 670-676, 2009.

[28] P. M. Ejikeme, I. D. Anyaogu, C. L. Ejikeme, N. P. Nwafor, C. A. C. Egbuonu, K. Ukogu, *et al.,* "Catalysis in Biodiesel Production by

Transesterification Processes - An Insight," *E-Journal of Chemistry*, vol. 7, pp. 1120-1132, 2009.

[29] M. Canakci and J. V. Gerpen, "Biodiesel Production from Oils and Fats with High Free Fatty Acids," *American Society of Agricultural Engineers*, vol. 44, pp. 11429-1436, 2001.

[30] Y. M. Sani, W. M. A. W. Daud, and A. R. Abdul Aziz, "Activity of solid acid catalysts for biodiesel production: A critical review," *Applied Catalysis A: General*, vol. 470, pp. 140-161, 2014.