ONE STEP ACTIVATION USING POTASSIUM HYDROXIDE ON PREPARED ACTIVATED CARBON FOR BASE TRANSESTERIFICATION REACTION

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A dissertation submitted in partial fulfillment of the
requirements for the awards of degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

MARCH 2015

For my beloved family & friends……

To my beloved family and friends that never stopped giving of themselves in countless ways, both direct and indirect. I was going to start listing them all, but realized they are just too many to do that justice - so please accept the fact that you are all mentioned in my daily prayer of thanks to a loving ALLAH s.w.t. who will convey that thanks in His own way back to you all.

ACKNOWLEDGEMENT

All praise be to ALMIGHTY ALLAH, the omnipotent, the omnipresent, the most merciful and the most compassionate who blessed me with tolerant attitude, realistic thinking, family supporting, talented supervisor and enable me to complete this dissertation. This dissertation is the result of effort on my part, along with assistance of many others. Nevertheless, with the help of others, this work has finally come to fruition.

Upon completion of this project, I would like to express my gratitude to many parties. My special thanks and appreciation go to my supervisor, Prof. Dr. Abdul Rahim Yacob for his technical help, valuable suggestions and encouragement throughout my studies. This work would not have been completed without his keen interest. Beside that, I would also approach to thank to all the lecturers in Department of Chemistry and staff, especially to Physical Chemistry Lab II for the diligent advices, suggestions and solutions right the way through this study.

Finally, heartful thanks are extended to my family, friends who always give me their helpful efforts. Their cooperation was appreciated and most thankful. Thank you all for your cooperation.

ABSTRACT

Palm kernel shell is an abundant solid waste from palm oil processing mills in tropical countries like Malaysia and Indonesia. The utilization of these agricultural wastes in production of activated carbon will greatly help overcoming environmental issue economically. In this study, activated carbon from palm kernel shell via one-step activation with potassium (AC/KOH) was successfully prepared. The activated carbon has been prepared using different percentage concentrations of KOH and carbonized at 600^{o}C for 2 h. All the prepared AC/KOHs were characterized using Fourier Transformed Infrared (FTIR), Nitrogen Adsorption Analysis, Field Emission Scanning Electron Microscope (FESEM), X-ray Powder Diffraction (XRD) and X-ray Fluorescence (XRF). The soluble basicity and the basic strength of the prepared AC/KOHs were determined using back titration and Carbon Dioxide Temperature Program Desorption (CO_2-TPD). FTIR analysis of the raw palm kernel shell showed the presence of various functional groups. However, after the activation and carbonization, most of the functional groups were eliminated. A high BET surface area of 1054 m^2/g was obtained from 10% AC/KOH, while the BET surface area for 15%, 20% and 25% AC/KOH decreased probably due to KOH residue or the collapse of the pore walls, which blocked the pores. From the basicity analysis, when the percentage of KOH concentrations increases, the basicity of the AC/KOH was also increased. The prepared AC/KOH was then used as a heterogeneous base catalyst for transesterification of palm oil and dimethyl carbonate (DMC). Dimethyl carbonate was selected to replace alcohol to prevent the leaching of KOH into the biodiesel. Besides that, the used of DMC in transesterification produced glycerol free-fatty acid methyl ester (FAME). Analysis and determination of biodiesel production were performed using Gas Chromatography–Flame Ionization Detector (GC-FID) and Gas Chromatography-Mass Spectrometer (GC-MS). Increased percentage concentrations of potassium in AC/KOH made a significant impact on the conversion of palm oil to biodiesel. The percentage conversion of biodiesel for 10% AC/KOH, 15% AC/KOH, 20% AC/KOH and 25% AC/KOH calculated about 35%, 45%, 63% and 67%, respectively. Thus, it can be concluded that the AC/KOH can be used as a catalyst in biodiesel production.

ABSTRAK

Tempurung kelapa sawit adalah sisa pepejal yang banyak didapati di kilang kelapa sawit di negara-negara tropikal seperti Malaysia dan Indonesia. Pengunaan sisa pertanian ini dalam penghasilan karbon teraktifkan sangat membantu untuk mengatasi isu-isu alam sekitar secara ekonomi. Dalam kajian ini, karbon teraktifkan daripada tempurung kelapa sawit melalui pengaktifan satu langkah dengan menggunakan kalium hidroksida (AC/KOH) telah berjaya disediakan. Karbon teraktifkan telah disediakan menggunakan peratus kepekatan KOH yang berbeza dan dikarbonisasi pada suhu 600^oC selama 2 jam. Kesemua AC/KOH yang telah disediakan dianalisis mengunakan teknik Inframerah Transformasi Fourier (FTIR), Analysis Penjerapan Nitrogen, Mikroskopi Medan Pancaran Imbasan Elektron (FESEM), Pembelauan sinar-X (XRD) dan sinar–X pendarflour (XRF). Kelarutan bes dan kekuatan bes AC/KOH yang telah disediakan ditentukan melalui pentitratan kembali dan Program Suhu Penyahjerapan-Karbon Dioksida (CO_2-TPD). Analisis FTIR tempurung kelapa sawit mentah menunjukkan kehadiran pelbagai kumpulan berfungsi. Walaubagaimanapun, selepas pengaktifan dan karbonisasi, kebanyakan kumpulan berfungsi ini telah disingkirkan. Luas permukaan BET yang tinggi iaitu 1054 m^2/g telah diperolehi daripada 10% AC/KOH, manakala luas permukaan BET untuk 15%, 20% dan 25% AC/KOH menurun mungkin disebabkan oleh sisa KOH atau keruntuhan dinding liang yang menghalang liang. Daripada analisis kebesan, apabila peratus kepekatan KOH meningkat, kebesan AC/KOH juga turut meningkat. AC/KOH yang telah disediakan ini digunakan sebagai pemangkin bes heterogen untuk transesterifikasi minyak kelapa sawit dan dimetil karbonat (DMC). Dimetil karbonat telah dipilih menggantikan alkohol untuk mencegah larut lesap KOH ke dalam biodiesel. Selain itu, pengunaan DMC dalam transesterifikasi menghasilkan asid lemak metil ester (FAME) bebas gliserol. Analisis dan penentuan pengeluaran biodiesel telah dilakukan dengan menggunakan GC-FID dan GC-MS. Peningkatan peratus kepekatan kalium ke dalam AC/KOH memberikan impak yang besar kepada penukaran minyak kelapa sawit kepada biodiesel. Peratus penukaran biodiesel untuk 10% AC/KOH, 15% AC/KOH, 20% AC/KOH dan 25% AC/KOH masing-masing dikira sebanyak 35%, 45%, 63% dan 67%. Oleh itu, dapat disimpulkan bahawa AC/KOH boleh digunakan sebagai pemangkin dalam pengeluaran biodiesel.

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ABBREVIATIONS

AC/KOH	-	Potassium hydroxide activated carbon
BET	-	Brunauer–Emmett-Teller
CO_2-TPD	-	Carbon dioxide- Temperature Program Desorption
DMC	-	Dimethyl carbonate
FTIR	-	Fourier Transform Infrared
FID	-	Flame Ionization Detector
FAME	-	Fatty acid methyl ester
FAGs	-	Fatty acid glycerol carbonate
FESEM	-	Field Emission Scanning Electron Microscope
GC-FID	-	Gas Chromatography-Flame Ionize Detector
GC-MS	-	Gas Chromatography Mass Spectrometer
KOH	-	Potassium hydroxide
PKS	-	Palm kernel shell
TGA	-	Thermo-Gravimetric Analyzer
XRD	-	X-ray Powder Diffraction
XRF	-	X-ray Fluorescence

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Activated carbons (ACs) also known as activated charcoal or activated coal is a carbonaceous material, which is predominantly amorphous in nature with a large internal surface area and highly developed porosity resulting from several processes and treatment (Abechi *et al*., 2013). Productions of the activated carbon depend mostly on the raw material and method used. ACs can be produced from different type of raw material, including coal, lignite peat and woods (Gua and Lua, 2001). Moreover, it is the most cost effective and environmentally conscious to produce ACs from agricultural by-product such as coconut shell (yang *et al*., 2010; Hu and Srinivasan, 1999) pistachio nut shell (Lua and Yang, 2004), sugar cane Bagasse (Kalderis *et al*., 2008) olive stones (Reinoso *et al*., 1995) macadamia nut-shell (Ahmadpour and Do, 1997) and etc.

Palm kernel shell (PKS) is the agricultural waste generated from the palm oil industries in Malaysia which is the biggest producer of palm oil. It is estimated that for every one million tonnes of palm oil produces 0.8 million tonnes of palm kernel shell is created. Based on the total oil production of 7.4 million tonnes in 1993, the amount of palm shell generated in that year alone was about 6 million tonnes (Yacob *et al*., 2008; Daud *et al*., 2000). This indicates that a huge volume of kernel shell is being generated without consideration to their significant disposal problem. Therefore, in this study palm kernel shell was used as a raw material in the production of activated carbon, hence their utilization in the production activated carbon is a feasible solution to this environmental issue.

Activated carbons are important material, which have been widely used in various industrial applications, which include separation/purification of liquid and gas and removal of heavy metal. In the preparation of heterogeneous catalyst, activated carbon has proved to be highly effective as catalyst support. Its large surface area allows the active phase to disperse over it effectively and show inertness in acidic and basic media. ACs are an ideal carrier or supported for catalytic metal or indeed as a catalyst in its own right (Auer *et al*., 1998). Besides, there are various other reactions employing ACs as catalyst or catalyst support. One of the areas that employ carbon based catalyst is the production of biodiesel. In biodiesel production, catalyst plays an important role. Preparation of carbon based catalyst from agricultural waste and its utilization as heterogeneous catalyst not only reduces cost of biodiesel production but also could be used as “green catalyst”.

Due to environmental concerns, biodiesel has received many attentions as a replacement fuel since it has unique advantage such as being biodegradable, non-toxic and suitable for domestic production. Biodiesel is defined as a mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat, other sources that can be used to produce biodiesel is from algae and waste cooking oil (Marchetti *et al*., 2007). There are several different methods can be used to produce biodiesel, but transesterification is the most favoured process in biodiesel industrial because of its simple process and low cost (Khalid and Khalid, 2011).

Conventionally, in the transesterification, triglyceride reacts with an alcohol, usually methanol and ethanol, to produce fatty acid alkyl esters and glycerol with the present of acid or base catalyst. The general reaction of this reaction is shown in Figure 1.1 (Ejikeme *et al.*, 2010).

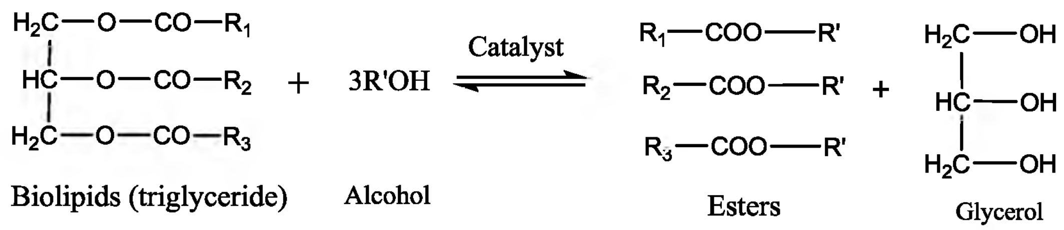

Figure 1.1: Transesterification of triglyceride with alcohol (Ejikeme *et al.*, 2011)

In particular, FAME is produced together with glycerol as undesired by-product in transesterification reaction. This glycerol needs to be separated and refined for further used which are costly and technically difficult. To overcome the problem Dimethyl Carbonate (DMC) is used in this reaction as an alternative to alcohols, which produce free glycerol FAMEs. DMC could be used as a reagent for the transesterification reaction process because of its advantageous physical properties such as environmental inertness chemical reactivity and do not produce glycerol as by-product (Pandiangan and Simanjuntak, 2013; Fabbri *et al.*, 2007).

Therefore, in this study, activated carbon from palm kernel shell was produced through one-step activation using potassium hydroxide (KOH) as activating agent and this potassium hydroxide activated carbon (AC/KOH) was tested as a potential heterogeneous base catalyst in production of biodiesel from palm oil. In addition, by taking into account the advantages offered by DMC, it was chosen as a reagent and reactant in this reaction replacing alcohol, which is reputed to be models of green reagents for its health and environmental inertness. The general reaction for transesterification of triglycerides and DMC is shown in Figure 1.2 as reported by Fabbri *et al.*, (2007) and Zhang *et al.*, (2010). The reaction of triglyceride (TG) with DMC produces mixtures of FAME and fatty acid glycerol carbonates (FAGCs).

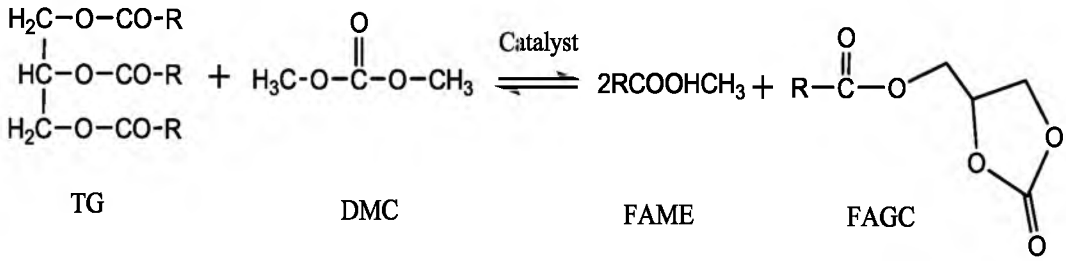

Figure 1.2: Transesterification of triglyceride with DMC (Fabbri *et al.*, 2007)

1.2 Problem statement

Palm kernel shell is an abundant solid waste from oil processing mills in tropical countries like Malaysia, Thailand and Indonesia. Some of these wastes are either used as fuel, whereas a large portion of them burnt in the open air or dumped in the area adjacent to the mill, which will increase the area need for their landfill and create many environmental problems. The utilization of these agricultural by product as a prospective starting material for the production of the activated carbon will greatly help with environmental issues as an effective discharge of this waste material, which can reduce the area need for their landfill disposal.

In this study, palm kernel shell activated carbon was produced by means of chemical activation with KOH. Chemical activation is more preferred in production of activated carbon and offer several advantages over physical activation, however, the main drawback in chemical activation arises after the process, activating agent is left as impurities and this incorporation of impurities sometimes may affect the chemical properties of activated carbon. Therefore, washing step is required, which is costly, time consuming and sometimes can cause an environmental issue. Hence, in this study instead of washing the activating agent, the impurities left on the activated carbon will use as a base catalyst and will be testing in biodiesel production.

Generally, in transesterification reaction, triglycerides react with alcohol, mostly methanol produce biodiesel or fatty acid methyl ester (FAME) with glycerol as undesired by-product. This glycerol needs to be separated and refined for further used which is costly and technically difficult. In this study, dimethyl carbonate (DMC) is used to perform the transesterification reaction with palm oil replacing methanol, which can overcome the problem. DMC is a green reagent because it is non-toxic, non-irritating, biodegradable, stable and easy to handle. With DMC, the reaction is free from the production of glycerol and can yield high purity biodiesel. Moreover, with DMC, alkali catalysed acted as a solid catalyst, which will not dissolve or leach out and therefore separation can be easily done through centrifugation or filtration (Dawodu *et al.*, 2014).

1.3 Significance of study

To prepare and characterize a new environmental friendly heterogeneous catalyst from cheap and renewable source. Palm kernel shell as mentioned before, one of the most abundant agricultural waste in our country. The utilization of this agricultural waste will help to overcome the environmental issue. Furthermore, the used of activated carbon as catalyst or as catalyst support in biodiesel industries reduce the cost of production because this raw material is cheap, abundant and easy to prepare. Next, the potassium hydroxide activated carbon (AC/KOH) is used as catalyst in the base transesterification of palm oil and DMC, which produced glycerol-free FAME and avoid the leaching of catalyst into biodiesel. The process is cost saving since the step for removing the glycerol and purification steps is not required.

1.4 Objective of the study

The objectives of this study are:

1. To prepare potassium hydroxide activated carbon catalyst (AC/KOH) via one-step activation using different percentage concentrations of potassium hydroxide on palm kernel shell and characterize the prepared AC/KOH.

2. To test the prepared AC/KOH as base heterogeneous catalyst in the transesterification of palm oil with dimethyl carbonate (DMC) towards production of biodiesel.

3. To analyze and characterize the composition of biodiesel produce from transesterification reaction.

1.5 Scope of the study

The scope of the study can be divided into 3 major aspects. The first aspect is to prepare activated carbon with KOH via one step activation by impregnate different percentage concentrations of 10%, 15%, 20% and 25% potassium hydroxide into the palm kernel shell and carbonized at 600°C for 2 h.

The second aspect is to characterize prepared potassium hydroxide activated carbon catalyst. The Thermogravimetry analysis (TGA) for raw palm kernel shell will be applied in order to determine the optimum activation temperature to produce high surface area activated carbon. Then the prepared AC/KOH catalyst will be characterized via Fourier Transform Infrared (FTIR), X-ray Powder Diffraction (XRD), X-ray Fluorescence (XRF) and Nitrogen Adsorption Analysis. While Field

Emission Scanning Electron Microscope (FESEM) will analyze their surface morphology and the basicity and basic strength of the catalyst will be carried out by back titration method and via Temperature Programmed Desorption (CO2-TPD) for conformation. The possibility of catalyst leaching into biodiesel will be analysed by X-ray Fluorescence (XRF)

The third scope of this study is to apply the prepared AC/KOH catalyst in the transesterification of palm oil with DMC, which is environmentally friendly to produce biodiesel without production of glycerol. The analysis and determination of biodiesel will be performed by Gas Chromatography-Flame Ionization Detector (GC-FID) and the confirmation of the methyl esters will be performed by Gas Chromatography Mass Spectrometer (GCMS).

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