BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING CALCIUM OXIDE/NANOCRYSTAL CELLULOSE/POLYVINYL ALCOHOL CATALYST IN A PACKED BED REACTOR

BY

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ABSTRACT

Environmental problems and a shortage of conventional fossil fuel caused by the global consumption of fossil fuel have promoted the production of biodiesel from renewable resources. Biodiesel is produced from a chemical process of vegetable oil or animal fats and alcohol in the presence of a catalyst. Use of homogeneous catalyst indirectly produces a high amount of wastewater in order to purify the complex product from the reaction, and the catalyst is not reusable thus it is economically inviable. In the current work, biodiesel was synthesized from a reaction of waste cooking oil (WCO) and methanol in the presence of a catalyst which was derived from chicken bone and coconut residue in a packed bed reactor. Calcium oxide (CaO) was extracted from calcined chicken bone and nano-crystal cellulose (NCC) was isolated from coconut residue by acid hydrolyzed. CaO and NCC were supported by polyvinyl alcohol (PVA). The catalyst was analyzed using Fourier transform infrared (FTIR), Field emission scanning electron microscopy (FESEM), Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) to study its elemental composition and surface morphology. The parameters used for the reaction were optimized by Design of Experiment (DOE) using Central Composite Design (CCD) of Response Surface Methodology (RSM) to produce maximum biodiesel yield. The maximum yield of 98.40 % was obtained at optimum temperature, methanol: oil and catalyst loading of 65 ºC, 6:1 and 0.5 wt% respectively. Evaluation of catalyst reusability indicated that it was reusable for four times while maintaining over 90 % of biodiesel yield. Investigation on the kinetic characteristics of the reaction specified that the reaction followed pseudo-first-order reaction with k-value ranged from 0.0092 min^{-1} to 0.0151 min-1 and the model was attested by Thiele modulus less than 2. The activation energy Ea observed for the transesterification reaction was 45.72 kJ/mol. Therefore, utilizing waste for biodiesel production of biodiesel can lower the production cost as well as help to save and clean the environment.

خلاصة البحث

المشاكل البيئية ونقص الوقود الأحفوري التقليدي الذي سببه الأستهلاك العالمي للوقود الأحفوري عززت الحاجة إلى إنتاج وقود الديزل الحيوي من موارد متجددة. يتم إنتاج وقود الديزل الحيوي من الموارد المتجددة في عملية كيميائية من زيت الخضروات أو الدهون الحيوانية والكحول في وجود محفز. وثبت أن استخدام المحفز المتجانس ينتج بشكل غير مباشر كمية كبيرة من مياه الصرف من أجل تنقية المنتج المعقد الناجم من التفاعل كما أن المحفز غير قابل لإعادة الاستخدم وبالتالي فهو غير قابل مجد اقتصادياً. في الدراسة الحالية تم تصنيع وقود الديزل الحيوي من تفاعل متبقي زيت الطهي (النفايات) (WCO) والميثانول في وجود محفز مشتق من عظام الدجاج وبقايا جوز الهند في مفاعل العامودي المحشي. تم استخلاص أوكسيد الكالسيوم (CaO) من عظام الدجاج المكلسة وعزل السليولوز النانوي البلوري (NCC) من بقايا جوز الهند بواسطة التحلل الحمضي. تم دعم CaO و NCC باستخدام كحول البولي فينيل (PVA). ثم تم تحليل المحفز باستخدام مطياف الأشعة تحت الحمراء (FTIR) وحقل المسح الضوئي والمسح المجهري الالكتروني (FESEM) والتحليل الحراري (TGA) وانكسار الأشعة السينية (XRD) لدراسة المكونات العنصرية والخواص الشكلية للسطح. تم تحسين العوامل المتغيرة المستخدمة للتفاعل من خلال تصميم التجربة (DOE) بأستخدام التصميم المركب المركزي (CCD) لمنهجية استجابة السطح (RSM) لتحقيق أقصى عائد من وقود الديزل الحيوي. وتم الحصول على أقصى قدرة من المحصول بنسبة 98.40% عند درجة الحرارة المثلى (65 درجة مئوية) وكانت نسبة الميثانول:الزيت (1:6) وتحميل المحفز 0.5% بالوزن. تبين من خلال تقييم إعادة استخدام المحفز أنه يمكن إعادة استخدامه اربع مرات مع الحفاظ على أكثر من 95%من إنتاج الديزل الحيوي. أظهرت دراسة الخصائص الحركية للتفاعل أنه شبيه تفاعل من الدرجة الأولى مع قيمة K تراوحت من 0.0092 الى 0.0151 لكل دقيقة. وشهد النموذج بواسطة معامل ثيل أقل من 2. وتلاحظ أن طاقة التنشيط لتفاعل تقنية الأسترة (transesterification) 45.72 كيلو جول/مول. لذلك فإن استخدام المتبقي من زيوت الطهي أي النفايات في إنتاج وقود الديزل الحيوي كمادة وسيطة ومحفزة يمكن أن يقلل من تكلفة الإنتاج وكذالك يساعد علي توفير بيئة نظيفة.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Biotechnology Engineering).

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as whole for any others degrees at IIUM or other institutions.

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Signature ……..…….. Date ……

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Signature Date

This thesis is dedicated to my parents Zik bin Muda and Zainab binti Salleh and my family.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BC	Bacterial cellulose
CCD	Central composite design
CNC	Cellulose nano-crystal
CNF	Cellulose nano-fibrils
DOE	Design of experiment
Ea	Activation energy
EPA	Environmental Protection Agency
EU	European Union
FAME	Fatty acid methyl ester
FESEM	Field emission scanning electron microscopy
FFA	Free fatty acid
FTIR	Fourier Transform Infrared
GCMS	Gas chromatography mass spectrometry
k	Rate constant
Kpa	Kilopascal
MFC	Micro-fibrillated cellulose
NCC	Nano-crystal cellulose
NFC	Nano-fibrillated cellulose
OPEC	Organization of the Petroleum Exporting Countries
PBR	Packed bed reactor
PVA	Polyvinyl alcohol
RSM	Response surface methodology
TGA	Thermogravimetric analysis
WCO	Waste cooking oil
XRD	X-ray diffraction

LIST OF SYMBOLS

%	Percent
° C	Degree Celsius
μm	Micro Meter
h	Hour
g	Gram
pH	Potential Hydrogen
V	Volume
M	Molarity of Standard NaOH (M)
W	Mass of Sample
TG	Triglycerides
t	Time
X_{ME}	Methyl ester
r	Ratio of reactant size
Y	Biodiesel yield
ø	Thield modulus
Ea	Activation energy
k	Rate of reaction

CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION

In recent years, the environmental issues associated with the emission of the greenhouse gases such as NO_x, SO_x, CO, CO_2 and shortage in the conventional fossil fuel sources were caused by the global consumption of fossil fuel (Alsharifi et al., 2017). Moreover, the consumption of fossil fuel keeps rising and cannot be sustained. This is because, energy is considered as the most important element for the growth and development of an economy (Hashmi et al., 2016).Therefore, in order to overcome this problem, an alternative measurement has to be taken.

Biodiesel is a source of energy that can be renewed and has the potential to replace fossil fuels thus it can be defined as a biofuel (Hashmi et al., 2016). Normally, biodiesel can be produced from transesterification reaction which is a chemical reaction from vegetable oil or animal fat that react with alcohol in the presence of a catalyst to produce methyl esters (biodiesel) and glycerin (soap, side product) (Hua et al., 2015). The example of vegetable oils are soybean oil, palm oil and corn oil which are edible oils. Besides, waste cooking oil (WCO) also can be used in biodiesel production. European Union (EU) produces about 700,000 to 1,000,000 tonnes of WCO annually and it was estimated approximately 40,000 tonnes of WCO produced per year in Asian countries including Malaysia (Hanisah et al., 2013).

In addition, to have a high yield of biodiesel, the type of catalyst used and the parameters for the transesterification process play as an important role in biodiesel production. This is because, the catalyst is used to enhance the reaction rate and

increase the yield of a reaction (Hua et al., 2015). There are several types of catalysts that can be used in biodiesel production such as homogeneous, heterogeneous and enzymatic catalyst. However, catalyst must be separated at the end of the reaction therefore, by using heterogeneous catalyst, it can be separated easily and reusable and resulted in lower production cost (Hua et al., 2015; Suwannasom et al., 2016). Besides, the heterogeneous catalyst also has a low sensitivity towards free fatty acid (FFA) which can result in saponification, exhibit high catalytic activity during the reaction, shows reusability, prevent equipment corrosion and also reduce wastewater production (Hashmi et al., 2016; Ma et al., 2017; Suwannasom et al., 2016).

Furthermore, in order to increase the biodiesel production, nano-cellulose catalyst was also used in this study which is the most abundant, inexpensive and readily available carbohydrate polymer in the world, traditionally extracted from plants or their waste are the superiority of cellulose (Esa et al., 2014). It has to undergo a chemical process with alkali and acid treatment to obtain the pure product because this type of polymer normally branches with hemicellulose and lignin. Moreover, cellulose is widely distributed in nature and it exhibits biocompatibility to biological molecules, easy modification with usual ligands, and has a suitable porosity for high adsorption capacity (Zhang et al., 2015). In this study, the nano-cellulose was produced from coconut residue.

In Malaysia, coconut also is an important industrial crop after palm oil, rubber, and paddy in terms of total planted area (Sivapragasam, 2008). In 2017, Berita Harian had reported that the total crop area for coconut tree in Malaysia is 95,000 hectare. However, most of the coconut supply was imported from Indonesia was about 90,000,000 in 2017. This scenario causes the increased of coconut waste in Malaysia. For instance, Malaysia produces annually approximately 168 million tons of biomass

production including coconut waste (Ozturk et al., 2017). Therefore, in this study, nano-cellulose was extracted from coconut residue in order to reduce the total of biomass in Malaysia yet enhance the production of biodiesel yield.

Upon that, to support the nano-catalyst, polyvinyl alcohol (PVA) was used in this study. PVA is a semi-crystalline synthetic polymer, which is soluble in water, slightly soluble in ethanol and insoluble in other organic solvents, tasteless, odourless, has a good mechanical properties (tensile strength), has a high ability to form films and also a good compatibility and biodegradability in human tissues and fluids (Marin et al., 2014). PVA has been applied in many applications such as in the production of composites reinforced with polyester or cellulose to give mechanical strength to carbon nanotubes, medical field, etc. (Marin et al., 2014).

In addition, in this study, the packed-bed reactor has its own advantages which was used for the continuous process due to its simple and easy to operate, good mixing performance and high production efficiency. Thus, it became the most attractive reactor due to its advantages (Chueluecha et al., 2016). Besides, it is also reported that a packed-bed reactor is considered as one of the most promising reactors for continuous biodiesel synthesis. During transesterification reaction, the catalyst use was easily damaged due to continuous stirring in the slurry reactor and in order to minimize catalyst mechanical damage, a packed-bed catalytic reactor configuration can be useful (Borges et al., 2013). In this study, methanol and WCO was used as a source of alcohol and triglyceride to undergo transesterification reaction with the presence of nano-catalyst, CaO/ nano-cellulose which was supported on PVA to enhance the production of biodiesel.

1.2 PROBLEM STATEMENT

The rises of global consumption on diesel fuel has resulted in environmental problems in relation to the emission of greenhouse gases and a shortage of conventional fossil fuel sources. In addition, the disposal of WCO through irrigation system caused the clogging of drainage system and also increasing the breeding of pests which can affect human health. In biodiesel production, WCO can be used in transesterification reaction with methanol in the presence of catalyst to reduce the cost of the production instead of using edible vegetable oil as it could match up with food.

However, in the process of producing biodiesel, the type of catalyst that is widely used in the industry is the homogenous base catalyst which is sodium hydroxide (NaOH) or potassium hydroxide (KOH). After the transesterification reaction by using these type of catalyst, the products of the reaction have to be washed and purified in order to collect the FAME (biodiesel) that is soluble with the catalyst (homogeneous catalyst). This caused a high production of waste water during the purification process that could affect the environment. Thus, by using a heterogeneous base catalyst in biodiesel production the catalyst can be separated easily from the byproducts and indirectly reduces the production time.

Heterogeneous base catalyst is a solid catalyst that can be used in biodiesel production. Most of the heterogeneous catalysts that is used in biodiesel production are derived from non-renewable resources and is highly expensive with low stability. However, it can be controlled by the amount and strength of the active basic site. In order to increase the active site of this type of catalyst, a small-sized catalyst which is the nano-sized catalyst can increase the surface area and the active site of the catalyst. The nano-catalyst was supported with PVA to enhance the yield of biodiesel.

In addition, by using a solid catalyst, the mechanical damage of catalyst can occur due to continuous mechanical stirring during the transesterification process. However, this issue can be solved by using a packed bed reactor (PBR) for when the catalyst stays confined in the PBR, the products can be easily separated while achieving a mechanical stability of catalyst particles.

In this study, NCC/CaO/PVA nanocatalyst was used as heterogeneous catalyst in producing biodiesel where NCC/CaO was derived from waste. Furthermore, WCO, methanol and the prepared nano-catalyst reaction produced biodiesel by transesterification reaction.

1.3 RESEARCH OBJECTIVES

1. To investigate and characterize nano-catalyst CaO / nano-crystal cellulose from chicken bones and coconut residue supported by polyvinyl alcohol (PVA) for biodiesel production.
2. To investigate the kinetics of transesterification in a packed bed reactor for the production of biodiesel production using nano-catalyst CaO / nano-crystal cellulose supported on polyvinyl alcohol (NCC/CaO/PVA).
3. To optimize the reaction conditions of transesterification such as methanol to oil ratio, temperature, and catalyst amount in a packed bed reactor.

1.4 SIGNIFICANCE OF STUDY

In this study, biodiesel was produced from the transesterification reaction between WCO and methanol in the presence nano-sized of NCC/CaO supported by PVA. This study is an alternative to substitute the commercial diesel fuel with biodiesel with a

high yield of production. This is because, the consumption of diesel fuel has resulted in the environmental problem associated with the emission of greenhouse gases and the shortage of the conventional diesel fuel sources which are expected to be run out in 2050 as the fuel is consumed 10^5 faster than its natural production. This natural fuelcannot be sustained yet the consumption keeps rising. However, these issues can be overcome by replacing diesel fuel with biodiesel. Biodiesel is a renewable source of energy and environmental friendly. Besides, it is also biodegradable, non-toxic, free from sulfur and aromatics as well as contains oxygen in its structure. In addition, by using biodiesel, it does not only overcome the issues which caused by diesel fuel, but it also provides a good lubricity which can enhance the durability of the engine

In addition, the WCO that normally discarded trough drainage system which resulted in pollution and clogging of the system, was collected from the night market and used for the production of biodiesel. Besides, in order to have a high yield of biodiesel, the catalyst was synthesized from chicken bone (CaO) and coconut residue (NCC) which is a waste that abundantly available in restaurants, night markets, shops and etc. Chicken bone was boiled, washed, dried, calcined, and used as a catalyst while NCC was extracted from coconut residue by bleaching, alkaline treatment and hydrolysis process. The methanol to oil ratio, temperature, and catalyst loading were varied in order to optimize its conditions in a transesterification reaction to have a high yield of biodiesel. Then, the produced biodiesel was analyzed and study its kinetics of the reaction in the production of biodiesel.

1.5 SCOPE OF STUDY

Calcium oxide (CaO) was synthesized from chicken bone and was dried in an oven at 55 °C for 48 hours before it was crushed and blended to a fine powder. Then, the fine powder of chicken bone was calcined at temperature 700, 800 and 900 °C with 4, 5 and 6 h for every different temperature. Meanwhile, nano-crystal cellulose (NCC) was extracted from coconut residue which has been dried in an oven for 24 hours before bleached with hydrogen peroxide (H_2O_2) and acid hydrolyzed with sulfuric acid (H_2SO_4).

The produced nano-catalysts were characterized by Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA) and X-ray Diffraction (XRD) respectively. The CaO was mixed with the same amount of NCC based on the result of the screening and supported by polyvinyl alcohol (PVA) before transesterification reaction took place.

The transesterification reaction was carried out in a packed bed column which was connected to three-neck round bottom flask equipped with a condenser, a mechanical stirrer and a temperature controller. The transesterification reaction in this study was a reaction between waste cooking oil (WCO) and methanol was pumped into packed bed column in the presence of nano-sized of NCC/CaO supported by PVA for 4 hours with a temperature between 55 to 65 °C and was stirred at 600 rpm.

In addition, the kinetic study was performed in three separate experiments at 55, 60 and 65 °C. For each experiment set up, the methanol: oil molar ratio and catalyst loading in weight percent were kept constant. The yield of biodiesel was measure in 5, 10, 15, 30, 60, 90, 120, 180, and 240 minutes.