SYNTHESIS OF BIODIESEL IN CONTINUOUS FLOW PACKED WITH ION EXCHANGE KENAF FIBER

By

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Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for Degree of Master of Science

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Chair: Luqman Chuah Abdullah, PhD
Institute: Tropical Forestry and Forest Products

Biodiesel has become increasingly attractive to be explore further for its environmental benefits such as renewable, bio-degradable, non-flammable, non-toxic, and sulfur-free. The most common biodiesel technologies employ homogenous catalysts to induce the reaction between alcohol and the triglycerides during transesterification. Although the transesterification reaction of triglycerides with alcohols using homogeneous catalyst is well known and practiced on a commercial scale, there is plenty of scope to improve this process. There is an approach that involves the use of heterogeneous catalysts that could be packed in a packed-bed reactor, and this would enable a continuous process to be developed. Recent progresses in the development of heterogeneous catalysts have been the generation of ion exchanger to improve transesterification. Previous studies have reported the application of anion exchange catalyst that derived from synthetic materials for production of biodiesel. However, removal of spent catalyst is a problem as it falls under the category of non-biodegradable wastes. The discovery of a novel low cost and environment friendly catalyst is an attractive option for their utilization and safe disposal.

This study aims to investigate the use of kenaf fiber in the preparation of anion exchange catalyst used in transesterification. The fabrication of an anion exchange kenaf catalyst involved three steps: delignification of kenaf fiber, pre-irradiation induced emulsion graft polymerization of kenaf fiber and quaternary amination. The objective of this work was to develop a continuous system using an anion exchange kenaf catalyst and to evaluate the performance of this plant-based catalyst to produce biodiesel in a packed bed reactor. The transesterification of refined palm oil with ethanol in the presence of a ananion exchange kenaf catalyst was carried out. A single tubular flow reactors system in the concurrent up-flow configuration was built in the laboratory scale.The effect of the process parameters such as molar ratio ethanol to refined palm oil, packed bed height and volumetric flow rate on the triglycerides conversion and FAEE (fatty acid ethyl ester) yields were investigated.

Screening design using full factorial were conducted to find the important factors and to identify the optimum range of the yield. The optimum range was between 95 - 97% conversion within a reaction ethanol to oil ratio 40:1 - 60:1, packed bed height of 4 cm – 12 cm and volumetric flow rate of 0.3 - 0.5 mL min^{-1}. The response surface methodology (RSM) based on the central composite design (CCD) was used to optimize the process. The optimization were conducted around the optimum range established by the full factorial design. The optimum conditions for transesterification of refined palm oil to fatty acid ethyl ester were obtained at 9.81 cm packed bed height, 50:1 ethanol to oil molar ratio and volumetric flow rate of 0.38 ml min^{-1}. At these optimum conditions, the FAEE yield was 96.74 %, which is well within the yield of 97.29 % as predicted by the model. Although it was shown that high conversions can be achieved over extended time on stream, it was clear that the catalyst was losing its activity. Measurements also showed that during a regeneration experiment, kenaf fiber was dissolved in the solvent and leaching of the catalyst active sites which resulted in poor catalyst reusability. Based on the results obtained, anion exchange kenaf catalyst exhibited good performance for the transesterification of refined palm oil with ethanol to produce FAEEs in packed bed reactors.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS BIODIESEL DALAM ALIRAN BERTERUSAN DIMANTAPKAN DENGAN PERTUKARAN ION DARI GENTIAN KENAF

Oleh

NUR HARYANI BINTI ZABARUDDIN

Mei 2020

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Biodiesel telah menjadi topik yang semakin menarik untuk diterokai dengan lebih mendalam atas faedah-faedahnya terhadap alam sekitar seperti boleh diperbaharu, biodegradabel, tidak mudah terbakar, tidak toksik, dan bebas sulfur. Teknologi biodiesel kebiasaanya menggunakan pemangkin homogen untuk mendorong tindak balas antara alkohol dan trigliserida semasa proses transesterifikasi. Walaupun tindak balas transesterifikasi trigliserida dengan alkohol menggunakan pemangkin homogen yang telah digunakan secara komersial, mempunyai banyak perkara yang harus memperbaiki dalam proses ini. Terdapat satu pendekatan yang melibatkan penggunaan pemangkin heterogen dalam reaktor turus terpadat untuk mengantikan pengunaan pemangkin homogen. Kemajuan terkini dalam penghasilan pemangkin heterogen adalah penjanaan penukar ion untuk memperbaiki proses transesterifikasi. Kajian sebelum ini telah melaporkan aplikasi pemangkin pertukaran anion yang diperbuat daripada bahan sintetik untuk penghasilan biodiesel. Walaubagaimanapun, pengasingan pemangkin yang telah digunakan menjadi masalah kerana ia berada di bawah kategori sisa bukan biodegradabel. Penemuan pemangkin kos rendah dan mesra alam adalah pilihan yang menarik bagi penggunaan dan pelupusan yang selamat.

Kajian ini akan mengkaji penggunaan gentian serat pokok kenaf untuk penyediaan pemangkin pertukaran anion untuk digunakan dalam proses transesterifikasi. Penghasilan pertukaran anion kenaf melibatkan tiga langkah iaitu pendeligninan serat kenaf, pempolimeran emulsi serat kenaf yang telah di pra-irradiasi cas teraruh dan kuaterner pengaminaan. Objektif kajian ini adalah untuk membangunkan sistem berterusan mengandungi pemangkin kenaf pra-irradiasi cas teraruh dan menilai prestasi pemangkin tersebut berdasarkan kemampuaan menghasilkan biodiesel di dalam reaktor turus terpadat. Transesterifikasi minyak sawit dan etanol dengan kehadiran pemangkin kenaf telah dijalankan. Satu sistem reaktor aliran tunggal yang berkonfigurasi aliran keatas dibina dalam skala makmal. Kesan parameter proses seperti nisbah molar etanol kepada minyak sawit, ketinggian reaktor turus terpadat dan kadar aliran volumetrik terhadap penukaran trigliserida ke asid lemak etil ester telah dikaji.

Ujian saringan menggunakan reka bentuk pemfaktoran penuh telah dilakukan untuk mengenal pasti faktor penting dan julat optimum hasil. Julat optimum adalah antara 95 - 97% dalam keadaan nisbah etanol kepada minyak dari 40:1 hingga 60:1, ketinggian reaktor turus terpadat sebanyak 4 cm ke 12 cm dan kadar aliran volumetrik 0.3 hingga 0.5 mL min^{-1}. Kaedah Gerak Balas Permukaan berdasarkan reka bentuk komposit pusat (CCD) digunakan untuk mengoptimumkan proses tersebut. Kajian mengoptimumkan dilakukan di sekitar julat optimum yang ditetapkan oleh reka bentuk pemfaktoran penuh. Keadaan optimum untuk transesterifikasi minyak sawit ke asid lemak etil ester diperolehi pada ketinggian reaktor turus terpadat 9.81 cm, 50:1 nisbah molar etanol kepada minyak dan kadar aliran volumetrik pada 0.4 mL min^{-1}. Pada keadaan optimum ini, hasil biodiesel yang dicatatkan adalah 96.87%, sedikit berbeza dari hasil 97.29% seperti yang diramalkan oleh model. Walaupun penghasilan biodiesel yang tinggi boleh dicapai dengan masa proses yang lama, namun jelas terlihat bahawa pemangkin yang dihasilkan kehilangan aktivitinya jika lebih dari sekali penggunaan. Semasa eksperimen penggunaan semula pemangkin, serat kenaf telah larut di dalam pelarut dan menyebabkan kemerosotan aktiviti pemangkin. Secara keseluruhan, pemangkin kenaf memperlihatkan prestasi yang baik untuk transesterifikasi minyak kelapa sawit bersama etanol di dalam reaktor turus terpadat.

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LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared spectroscopy
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
BET	Brunauer, Emmet and Teller
CCD	Central composite-design
DAG	Diglyceride
EDX	Electron Dispersive X-ray Spectroscopy
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FESEM	Field Emission Scanning Electron Microscopy
GCMS	Gas Chromatograph-Mass Spectrometer
GC-FID	Gas chromatography flame ionization detector
HPLC	High Performance Liquid chromatography
KOH	Potassium hydroxide
MAG	Monoglycerides
NaOH	Sodium hydroxide
PEG	Polyethylene Glycol
PBR	Packed-bed reactor
PTFE	Polytetrafluoroethylene
RSM	Response surface methodology
TMA	Trimethylamine
TAG	Triglycerides
TGA	Thermo Gravimetric Analysis
UV	Ultraviolet
HPLC	High performance liquid chromatography
VBC	Vinyl benzyl chloride
XRD	X- Ray Diffraction Technique

CHAPTER 1

INTRODUCTION

1.1 Background

Energy is essential in human everyday activities including transportation, agriculture telecommunication, and industrial that influence economic development. Figure 1.1 shows that the transportation sector accounted for the highest consumption of energy in Malaysia which is transportation (43%), followed by industrial (26%), residential (15%), and agriculture (2%).

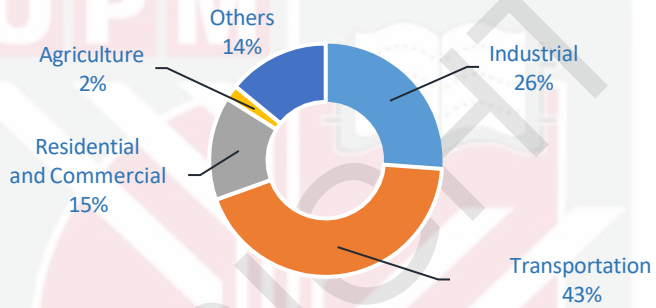

Figure 1.1: Malaysia Final Energy Consumption by Sector in 2013. (Source: Tenaga, 2015)

The percentage of the industrial sector, transportation sectors, and domestic sectors (commercial, residential, and agriculture sector) were accounted for approximately one-third of end-use energy consumption in Malaysia in 2013. Figure 1.2 shows that in the past 15 years of trends in the consumption of energy resources. It is noted that the renewables consumption percentage displays a surprisingly high growth in terms of the new size, investment, and high growth rates in developing countries that have transformed the landscape for the energy sector. It was predicted that, the upsurge in global energy consumption in 2040 by 48%, with an increase of 1.4% annually. On top of that, renewable energy demand increases by an average 2.6% per year likely to gradually replacing consumption of non-renewable energy. Renewables energy is now established as one of the world's sources of energy, and counter contributes almost half of the world's new power generation capacity. According to Agency (2015), the coverage of mandatory green energy efficiency regulation worldwide expanded to more than a quarter of global consumption.

Figure 1.2 The past 15 years trends in the consumption of energy resources. (Sources: Council, 2016)

Renewable energy is also known as Sustainable Energy or Green energy is an energy that naturally occurring, and replenished fast by environment over quite short period of time (John & Anthony, 2006). In 2005, the Unites States, and the European Union announced the policies, and intensives to support the increased usage of biofuels. Biodiesel has become increasingly attractive to be explored further for its environmental benefits over fossil fuel, as it is renewable, non-toxic, portable, readily available, biodegradable, and sustainable. Masjuki and Abul (2013) reported that biodiesel can be used directly in standard diesel engines without major modification. The utilization of biofuels in vehicle engines helps reduce greenhouse gas (GHG) emission because the carbon dioxide released from combustion is offset by the carbon dioxide sequestered while growing the energy feedstock. It also reduces the emission of unburned hydrocarbon, carbon dioxide, sulphates, nitrated polyacrylic aromatic carbon, and particulate matter to the atmosphere. Several studies showed that biodiesel blend could last longer in conventional compression-ignition engines which need no major modification. At 20% blend biodiesel with petro-diesel would eliminate the hazardous soot emitted during acceleration. Besides, the blending of biodiesel with diesel fuel is another alternative to lessen the high price of 100% biodiesel for combustion fuel. Commercially, these blends are designated as Bxx either B10, B20, or B100 to represents the volume percentage of biodiesel composition blend with diesel fuel (Zabeti *et al.*, 2009). Nowadays, many countries have explored and commercially produce a biodiesel blend for vehicles, and public transport. The global potential volume of biodiesel production is 51 billion liters each year and the biggest contributor countries to biodiesel production including United States, Brazil, Argentina, Indonesia, and Malaysia account for over 80% of the total production (refer Table 1.1 in Chapter 2).

Driven by the need to reduce greenhouse gas emissions, the development, and production of biodiesel fuel around the world continue to grow. The conventional method, pyrolysis has been investigated for over 100 years as a route to synthesize petroleum, however, catalytic transesterification of triglycerides to fatty acid alkyl esters using short-chain alcohol is by far, the most efficient, and simplest method which required no major modification in diesel engine for combustion fuel use. Any mineral acid can also be used to catalyze the transesterification process (Marchetti & Errazu, 2008a; Shu *et al.*, 2010).

Even though acid catalyst shows better adaptability to FFAs than base catalyst the biodiesel yield is high using acid catalyst, it is seldom used on large scale industrial production as it gives many disadvantageous in the process such as easily corrode the equipment, required extreme reaction condition such as high temperature, pressure, and slow reaction rate (Semwal *et al.*, 2011). Among various catalytic methods available for producing biodiesel, the alkali-catalyzed transesterification of vegetable oils, and animal fats is the most adopted method. A base catalyst such as potassium hydroxide (KOH), and sodium hydroxide (NaOH) offers several advantages such as cheap, high yield at shorter reaction time, and mild operating conditions. However, enormous biodiesel quality problems related to the application of homogeneous base-catalyzed transesterification were encountered, and it was the main hindrance for bulk production of biodiesel. A homogenous base catalyst is overly sensitive to the presence of free fatty acids (FFA), and water, which easily generate a by-product such as soap, water, and glycerol. It is difficult to produce biodiesel from crude vegetable oils with base catalyst due to these undesirable components. Free fatty acid will react with base catalysts to form soaps, whereas present excess water in feedstock oil leads to the saponification of esters (Thangaraj *et al.*, 2018). Hence, crude vegetable oils need to be refined prior to use, in a series of process stages such as degumming, neutralizing and, bleaching as n is suitable only for biodiesel production from a feedstock containing low levels of free fatty acid less than 1%. It is possible to directly use of crude vegetable oil without go through a refining process. Cho *et al.* (2012) conducted studies of biodiesel production from palm fatty acid distillate by means of the noncatalytic esterification method.

Several studies have proven that solid basic catalysts are more active than solid acid catalysts, and results in comparable high biodiesel yield to the homogeneous catalyst (Shibasaki-Kitakawa *et al.*, 2007). Heterogeneous basic catalysts tolerate a high amount of free fatty acid, and water. The utilization of abundant, and inexpensive natural resources to produce heterogeneous catalysts help to minimize the overall cost of biodiesel production. For instance, about 168 million tons of biomass production was produced in Malaysia annually including kenaf crop plants (Ozturk *et al.*, 2017). Thus, this research will be focusing on the development of anion exchange catalyst from low cost, and environmentally-safe kenaf fiber to reduce the total of biomass in Malaysia yet improve the production of biodiesel yield. In addition, a continuous flow transesterification system using a packed-bed reactor is considered as one of the promising reactors for the production of biodiesel due to its advantages which is simple, and easy to operate, good mixing performance, and high production efficiency (Chueluecha *et al.*, 2017). Packed bed reactor can minimize catalyst mechanical damage which obviously found in the slurry reactor. In this study, ethanol, and refined palm oil were used as a source of alcohol, and triglycerides to undergo a continuous transesterification reaction with the presence of anion exchange kenaf catalyst to accelerate the biodiesel production.

1.2 Problem Statement

The depletion of fossil fuel is a critical issue that needs to be solved, and many efforts have been put on finding alternative renewable fuels. Concerning environmental protection, biodiesel has become increasingly attractive to be explored further for its environmental-friendly benefits as a replacement to fossil fuel. As reported by IEA (2015), biodiesel production that adapted current technologies produced by the Organization for Economic Co-operation, and Development (OECD) member countries are more pricey than the price of petro-diesel. Also, various review on the economic feasibility studies in 2019 shows that biodiesel (B100) cost over $3.72 per gallon compared to $3.05 per gallon for petro-diesel. The price of biodiesel is 1.5 to 3 times higher than the petro-diesel cost in developing countries (environmental, 2020). This statistic shows that the current production of biodiesel is not yet economically feasible and required more research, and technological development for future benefits. Thus, the selection of the best catalyst, type of feedstocks and technology used is vital to ensure low biodiesel costs. Some countries including Malaysia, focus on utilization of bio-based feedstocks, such as palm oil and jatropha curcas oil, for producing alternative energy. In the production of biodiesel, the wide availability of vegetable oil and continuity of supply makes it a good choice of raw material. Palm oil is a major source of sustainable, and renewable raw material for the biodiesel industry in the world, but even so, the biodiesel production in Malaysia is still underdeveloped (Mohammadi et al., 2016).

Commonly, biodiesel technologies employ homogenous catalysts to accelerate the reaction between alcohol and triglycerides during transesterification. Although batch transesterification reaction system using homogeneous catalysts such as sodium hydroxide and potassium hydroxide is well known and practiced on a commercial scale, this process is tedious, slow, labour-intensive, and not well adapted to automation (Peterson *et al.*, 2002). Meanwhile, the homogeneous catalysts have a problem with the separation of catalysts from the product and the formation of stable emulsion and a large number of by-products such as water and a low grade of glycerol (Watcharathamrongkul *et al.*, 2010). In comparison to homogeneous catalysts, heterogeneous catalyzed production of biodiesel has arisen as a preferred way as it is environmentally benign, less sensitive to FFAs and water content, needs no water washing and easy product separation. Ion exchanger is one of the remarkable heterogeneous catalysts for biodiesel production due to its advantages such as high catalytic activity, no soap formation, easy and regeneration, and reusability. The growing development of ion-exchange catalysts has increased the demand for robust assessment practices to identify promising candidates for biodiesel production. The early batch mode experimental of conversions refined sunflower to methyl ester has been studied by Vicente *et al.* (1998) using various types of ion exchange resin compare to homogenous catalysts. Unfortunately, all type of ion exchange resin in this study; Amberlyst A26 functionalized with $-N^{+}(CH_3)_3OH^{-}$, Amberlyst A27 functionalized with $-N^{+}(CH_3)_3HCl^{-}$ and Amberlyst 15 with the active site $-SO_3H$ appeared to have a poor biodiesel conversion compared to homogeneous sodium hydroxide catalyst. In contrast with Shibasaki-Kitakawa *et al.* (2007)'s work where the anionic exchange resin functionalized with $-N^{+}(CH_3)_3Cl^{-}$ (PA306s) obtained high conversion close to 80% and reasonably comparable to those of alkaline homogenous catalyst. More recently, Ueki *et al.* (2011) developed an anionic exchange in fibrous form by radiation-induced grafting technique for biodiesel production. It found that the excellent conversion of biodiesel was three times greater than commercial anion

exchange resins. This is believed due to small in fiber diameter (10-20 μm) as compared to the spherical resins. Nevertheless, most of the heterogeneous catalysts used in biodiesel production were derived from synthetic material and expensive. There are only a few studies reported the production of biodiesel using bio-based heterogeneous catalysts.

In addition, anion exchanger has a potential commercial application in the continuous production of biodiesel due to the faster reaction, easy handling, and proven to act as both catalyst and absorbent. Packed-bed reactor (PBR) is considered as one of the promising reactors for continuous biodiesel production as it can minimize mechanical destruction of the catalyst caused by harsh continuous mechanical stirring during the transesterification process in a slurry batch reactor. The heterogeneous catalyst remains confined in the PBR, likewise, the mechanical stability of the catalyst particles is achieved. Moreover, the final products can be easily separated from the spent catalyst at the end of the process with less purification step needed, therefore, indirectly reduces the production time. This study will be conducted to replace the existing batch biodiesel production process by developing a packed-bed continuous flow reactor loaded with a heterogeneous catalyst from renewable plant-based resources; Kenaf fiber.

1.3 Objective of the Study

1. To examine and characterize the ion exchange kenaf fiber catalyst via physical and chemical characterization methods.
2. To optimize the reaction conditions of transesterification such as packed bed height, ethanol to oil ratio and volumetric flow rate in a packed bed reactor using Response Surface Methodology (RSM).
3. To investigate the catalyst regeneration on biodiesel conversion in the continuous flow reactor at optimum conditions.

1.4 Scope of the study

The scope of the study can be expressed as follows:

a) Synthesis of anion exchange kenaf catalyst using radiation-induced graft polymerization techniques for continuous transesterification of refined palm oil.
b) Characterization of fabricated anion exchange kenaf catalyst. The characterization of the catalyst was done using Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR), Field Emission Scanning Electron Microscope (FESEM- DX), Thermogravimetric analysis (TGA) X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET).
c) The continuous transesterification reaction was carried out in a bench scale packed bed reactor packed with the fabricated anion exchange kenaf catalyst. The experimental set up for the continuous transesterification system was concurrent up-flow configuration. The ethanol and refined palm oil were mixed in feedstock tank and supplied to the bottom of the column at room temperature and a constant flow rate using a peristaltic pump.
d) The individual effect including the packed bed height, volumetric flow rate, and oil to ethanol molar ratio on the biodiesel conversion will be investigated. The interaction effects among these reaction variables will be investigated using response surface methodology (RSM) based on Central composite design and the optimum conditions within the optimum range of significant variables will be estimated as well.
e) The reusability of the catalyst was tested.

1.5 Significance of the study

The global oil industry has driven the search for a new source of fuel from renewable energy sources owing to the spike market price due to high world demand production and a negative impact on the environment. As demand increases, the development of a continuous flow system using column techniques is important to overcome this major holdback facing by the biodiesel industry. It is a modern production of the biodiesel process. The combination of radiation-induced catalytic fibers and the continuous flow system is expected to enhance the biodiesel output and to reduce the production cost. Biodiesel is a better option because of its environmental-friendly advantage while function well in the standard diesel engine without a complex modification. Moreover, the plenty of availability on feedstock promises a continuous biodiesel production. However, it depends on the type of feedstock used. Palm oil has a far better advantage and potential as a feedstock for biodiesel production compared to other types of feedstocks because it is a perennial crop that produces at highest yield and continuously for several years. This study aims to develop and utilize a bio-based heterogeneous catalyst derived from kenaf fiber for transesterification of refined palm oil biodiesel in a packed-bed reactor. A bio-based heterogeneous catalyst can be considered as a good substitute for its potential to help in reducing the shortcoming and risks associated with the usage of homogeneous catalysts. In addition, the analysis of the operating parameters and its effect using design of experiment (DOE) will enhance in-depth knowledge of continuous transesterification process.

1.6 Structure of the thesis

This thesis is divided into five chapters, and it is organized in the following manner:

Chapter 1: Introduction

This chapter will introduce the research title and discusses the background study which includes the problem statement, objectives, and scope of the research study.

Chapter 2: Literature Review

This chapter is a compilation of a comprehensive summary of previous research on this topic. It provides knowledge on the scientific strategies and deficiencies encountered by other researchers. The comparison between previous studies will also be discussed in this chapter.

Chapter 3: Material and Methodology

This chapter presents a detail of the approaches taken to achieve research goals and objectives. The details on materials, catalyst characterization, continuous transesterification experimental set-up, and analytical techniques used for the experimental work are justified in this chapter. Moreover, the methods and strategies used for the optimization of continuous transesterification using the design of experiments (DOE), data collection, and evaluation of results were explained.

Chapter 4: **Characterization Heterogeneous Catalyst**

This chapter represents the characterization result of the catalyst which is been carried out on the fabricated catalyst for biodiesel production. The physical and chemical properties characterization was performed using a Field Emission Scanning Electron Microscopy (FE-SEM) equipped with Energy-Dispersive X-ray Spectrometry (EDX), Fourier transform-infrared spectroscopy (ATR-FTIR), Elemental analysis, thermo-gravimetric analysis (TGA) and X-Ray Diffraction analysis (XRD), surface area, pore-volume, average pore diameter, and sodium capacity determination. The summary of all the physical and chemical characterization for kenaf catalyst was stated at end of this chapter.

Chapter 5: **Continuous Transesterification of Palm Oil-Based Biodiesel**

This chapter provides a detail of the experimental findings and the analysis of the results. The results from preliminary study and screening design were verified against the developed model for validation and reliability. This section presented the statistical and optimization study results. Experiments were carried out using the response surface methodology based on central composite design.

Chapter 6: **Regeneration Study**

In this chapter, the reproducibility of fabricated catalysts for the continuous transesterification experiments was evaluated.

Chapter 7: **Conclusion and Recommendations**

Conclusions that wrap up the overall research work and recommendations for future work are presented in this chapter.

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