UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF SULFONATED BIO-BASED CATALYSTS FOR THE ESTERIFICATION OF PALM FATTY ACID DISTILLATE

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By

SHEHU IBRAHIM AKINFALABI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

November 2019

DEDICATION

My gorgeous wife; Shukura Oluwaseun Ibrahim

My two beautiful Angels; Fauziyyah and Najwa Ibrahim

And my amazing Father, HRM Oba Dauda Ajolola Adebimpe Akinfalabi

For your patience, support and understanding.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

SYNTHESIS OF SULFONATED BIO-BASED CATALYSTS FOR THE ESTERIFICATION OF PALM FATTY ACID DISTILLATE

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November 2019

Chairman : Umer Rashid, PhD
Institute : Advanced Technology

The synthesis of sulfonated of bio-based catalysts from palm seed cake (PSC), sugarcane bagasse (SCB) and kenaf seed cake (KSC), for the esterification of palm fatty acid distillate (PFAD), have been demonstrated in this work. The derived biomass materials were subjected to different levels of pretreatment that is triggered by the chemical activation period over ortho-phosphoric acid. The pretreated biobased materials were calcined at different temperatures in a nitrogen controlled atmosphere for about 2 to 5 h at 400 ^{O}C. The average SULFONATION time and temperature were between 5 to 12 h and 230 ºC. Whereas, the volume of the sulfonating agents used were between 100 – 250 mL in concentrated form.

The synthesized biobased catalysts were further characterized in terms of their active acid sites using the ammonia-temperature programmed desorption (NH_3-TPD), field emission scanning electron microscopy (FESEM) to confirm the morphology, the Brunauer, Emmett and Teller (BET) analysis to ascertain the surface area definition. To ensure the attachment of the functional group (–SO_3H) attachment, the fourier transform infrared (FTIR) analysis was carried out, while the thermal stability of the catalyst was checked using the thermogravinometric analysis (TGA) and X-ray dispersion (XRD) to validate the amorphous nature of the catalysts.

These catalysts; sulfonated - soaked palm seed cake (SPSC-SO_3H), kenaf seed cake (SO_3H-KSC) and sugarcane bagasse (SCB-SO_3H), showed enhanced catalytic properties. The SPSC-SO_3H had an acid density of 12.08 mmol/g and a specific surface area of 483.07 m^2/g while the SO_3H-KSC had an acid density of 14.32 mmol/g, specific surface area of 365.63 m^2/g and the SCB-SO_3H recorded an acid density of 5.63 mmol/g and specific surface area of 298.34 m^2/g and this is as a result of the pretreatment processes, highlighting the novelty of this work. The palm waste biochar

was further used for the appraisal of sulfonation processes, where three corresponding catalysts were appraised; ammonium sulphate – palm waste biochar (PWB-$(NH_4)_2SO_4$) catalyst, chlorosulfonic–palm waste biochar (PWB-$ClSO_3H$) catalyst and sulfuric – palm waste biochar (PWB - H_2SO_4) catalyst.

The optimized esterification reaction conditions for SPSC-SO_3H were 60 ^oC reaction temperature, 2 h reaction time, 9:1 methanol:PFAD molar ratio and 2.5 wt % catalysts weight, with a- free fatty acid (FFA) conversion of 98.2 % and fatty acid methyl ester (FAME) yield of 97.8 %. Whereas, for SO_3H-KSC catalyst, at optimum esterification conditions–reaction time 90 mins, temperature of 338 K, methanol:PFAD molar ratio of 10:1 and catalyst concentration of 2 wt.%—an FFA conversion of 98.7% and FAME yield of 97.9% was achieved. For the SCB-SO_3H, at optimum reaction conditions of; reaction time 1.5 h, reaction temperature 60 °C, catalyst loading 2 wt.% and methanol:PFAD molar ratio 10:1; a FAME yield of 98.6% was achieved. The SCB-SO_3H was used for six reaction cycles.

The fuel properties of produced biodiesel where appraised and compared with biodiesel EN 14214 and ASTM D-6751 standard limits. The PFAD methyl ester was further blended with petro-diesel from B0, B3, B5, B10, B20 and B100, on volumetric basis. The blends were characterized by TGA, DTG and FTIR. With acid value of 0.42 (mg KOH/g), iodine value of 63 (g.I_2/100g), kinematic viscosity of 4.31 (mm^2/s), the PFAD methyl ester has shown good fuel potential, as all of its' fuel properties were within the permissible international standards for biodiesel.

Overall, the synthesized biobased catalysts have shown impressive thermal stability, high specific surface area, improved pore diameter and pore volume, high yield and conversions and ability to run multiple reaction cycles. Sulfuric acid have also been proven to be a good sulfonating agent and the palm biomass showed better properties as a precursor than kenaf and sugarcane bagasse. These catalysts have also demonstrated a great potential to catalyze high FFA feedstock such as PFAD for the production of biodiesel while also maintaining good reusability. The success of the biobased catalysts is attributed to the attachment of sulfonic group (-SO_3H) on the surface of the biobased materials. The fuel properties of the synthesized biodiesel also showed great positive outcome as the blends show similar fuel properties as compared to the petroleum fuel.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS PEMANGKIN BERBASIS BIO BULAN UNTUK PERTEMUAN DARIPADA BAHAN ASID LEMAK SAWIT SULINGAN

Oleh

SHEHU IBRAHIM AKINFALABI

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Sintesis sulfonasi pemangkin berasaskan bio dari kek biji sawit (PSC), bagas tebu (SCB) dan kek biji kenaf (KSC), untuk pengesterilan asid lemak kelapa sawit (PFAD) ditunjukkan dalam kajian ini. Bahan-bahan biomas yang terhasil adalah bergantung kepada tahap yang berbeza yang telah dicetuskan oleh tempoh pengaktifan kimia ke atas asid ortofosforik. Bahan biobased pretreated telah dikalsinasi pada suhu yang berbeza dalam suasana dikawal nitrogen selama 2 hingga 5 jam pada suhu 400 ^{o}C. Sementara itu masa dan suhu sulfonasi adalah antara 5 hingga 12 jam pada suhu 230 ^{o}C. Selain itu, jumlah agen sulfonat berbentuk pekat yang digunakan adalah di antara 100 - 250 mL.

Pemangkin biobased yang tersintesis dicirikan lagi dari segi tapak asid aktif mereka menggunakan desorpsi diprogram suhu ammonia (NH_3-TPD), menggunakan mikroskop elektron pengimbasan pelepasan medan (FESEM) untuk mengesahkan morfologi, menggunakan analisis Brunauer, Emmett dan Teller (BET) untuk menentukan kawasan permukaan. Bagi memastikan lampiran kumpulan fungsional (-SO_3H), analisis empatier transform inframerah (FTIR) dijalankan, sementara itu kestabilan haba pemangkin telah diperiksa menggunakan analisis termogravinometrik (TGA) dan penyebaran sinar-X (XRD) untuk mengesahkan sifat pemangkin amorfus. Pemangkin ini, kekacang - biji sawit direndam (SPSC-SO_3H), kek biji kenaf (SO_3H-KSC) dan bagas tebu (SCB-SO_3H), menunjukkan sifat pemangkin yang dipertingkatkan. SPSC-SO_3H mempunyai ketumpatan asid 12.08 mmol/g dan luas permukaan spesifik 483.07 m^2/g manakala SO_3H-KSC mempunyai kepadatan asid 14.32 mmol/g, luas permukaan spesifik 365.63 m^2/g dan SCB- SO_3H mencatatkan kepadatan asid 5.63 mmol/g dan luas permukaan spesifik sebanyak 298.34 m^2/g dan ini disebabkan oleh proses prapreatment, menonjolkan kebaharuan kerja ini. Biochar sisa sawit digunakan lagi untuk penilaian proses sulfonasi, di mana tiga pemangkin yang sepadan telah dinilai; ammonium sulphate-biochar sisa sawit (PWB-$(NH_4)_2SO_4$)

pemangkin, pemangkin biochar sisa buangan chlorosulfonic - sawit biochar (PWB-$ClSO_3H$) dan pemangkin biochar sisa sawit sulfat (PWB-H_2SO_4).

Keadaan tindak balas esterifikasi yang telah dioptimumkan untuk SPSC-SO_3H ialah pada suhu 60 ^oC, masa tindak balas 2 h, 9:1 metanol: nisbah molar PFAD dan berat pemangkin 2.5 wt %, dengan penukaran asid lemak bebas (FFA) sebanyak 98.2% dan lemak asid metil ester (FAME) sebanyak 97.8%. Sementara itu, untuk pemangkin SO_3H-KSC, pada keadaan esterifikasi optimum-masa tindak balas 90 minit, suhu 338 K, metanol: nisbah molar PFAD 10:1 dan kepekatan pemangkin 2 wt % - penukaran FFA sebanyak 98.7% dan hasil FAME daripada 97.9% telah dicapai. Untuk SCB-SO_3H, eadaan tindak balas optimum; masa tindak balas 1.5 jam, suhu tindak balas 60 °C, pemangkin pemangkin 2% dan % methanol: nisbah molar PFAD 10:1; Hasil FAME sebanyak 98.6% telah dicapai. SCB-SO_3H digunakan untuk enam kitaran tindak balas.

Sifat bahan bakar biodiesel yang dihasilkan di mana dinilai dan dibandingkan dengan had standard biodiesel EN 14214 dan ASTM D-6751. Methyl ester PFAD selanjutnya dicampur dengan petro-diesel dari B0, B3, B5, B10, B20 dan B100, secara volumetrik. Campuran dicirikan oleh TGA, DTG dan FTIR. Dengan nilai asid 0.42 (mg KOH/g), nilai iodin 63 (g.I_2/100g), kelikatan kinematik sebanyak 4.31 (mm^2/s), metil ester PFAD telah menunjukkan potensi bahan bakar yang baik, kerana semua bahan ' piawaian antarabangsa untuk biodiesel.

Secara keseluruhannya, pemangkin biobased yang disintesis telah menunjukkan kestabilan haba yang mengagumkan, kawasan permukaan spesifik yang tinggi, diameter liang yang lebih baik dan jumlah, hasil yang tinggi dan penukaran dan keupayaan untuk menjalankan pelbagai kitaran tindak balas. Asid sulfurik juga telah terbukti menjadi agen sulfonat yang baik dan biomas sawit menunjukkan ciri-ciri yang lebih baik sebagai prekursor daripada kenaf dan bagasse tebu. Pemangkin ini juga telah menunjukkan potensi yang besar untuk memangkinkan bahan makanan FFA yang tinggi seperti PFAD untuk pengeluaran biodiesel sambil mengekalkan kebolehgunaan semula yang baik. Kejayaan pemangkin biobased adalah disebabkan oleh lampiran kumpulan sulfonik (-SO_3H) pada permukaan bahan biobased. Sifat-sifat bahan bakar biodiesel yang disintesis juga menunjukkan hasil positif yang baik apabila campuran menunjukkan ciri-ciri bahan api yang sama berbanding bahan api petroleum.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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AC-KSC	Activated Carbon Kenaf Seed Cake
ANOVA	Analysis of Variance
AOCS	American Oil Chemist's Society
ASTM	American Standard Testing Method
BET	Brunauer Emmett Teller
CCD	Central Composite Design
CCR	Canradson Carbon Residue
CCRD	Central Composite Rotatable Design
CFPP	Cold Filter Plugging Point
CHNS	Carbon Hydrogen Nitrogen Sulfur
CPO	Crude Palm Oil
DF	Diesel Fuel
DIN	Deutsches Institut für Normung (The German Institute for Standardization)
DG	Diglycerides
EDX	Energy Dispersive X-ray
EN	Euro Norm
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FESEM	Field Emission Scanning Electron Microscope
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
GC-FID	Gas Chromatography-Flame Ionization Detector

ITMA	Institute of Advanced Technology
KSC	Kenaf Seed Cake
MG	Monoglyceride
MPOB	Malaysian Palm Oil Board
MT	Metric Tons
MWCNTs	Multi-Walled Carbon Nanotubes
PFAD	Palm Fatty Acid Distillate
Nm	Nanometer
PFADME	Palm Fatty Acid Distillate Methyl Ester/Biodiesel
PME	Palm Methyl Ester
PH	Pseudo-Homogeneous
PSC	Palm Seed Cake
PSC-AC	Palm Seed Cake – Activated Carbon
PWB	Palm Waste Biochar
PWB – Soaked	Palm Waste Biochar – Soaked
PWB-H_2SO_4	Palm Waste Biochar – Sulfuric
PWB-$ClSO_3H$	Palm Waste Biochar – Chlorosulfonic acid
PWB- $(NH_4)_2SO_4$	Palm Waste Biochar – Ammonium Sulfate acid
RDB	Refined, Bleached Deodorized
RSM-CCRD	Response Surface Methodology- Central Composite Rotatable Design
SCB	Sugarcane Bagasse
SCB-Biochar	Sugarcane Bagasse Biochar
SCB – SO_3H	sulfonated – Sugarcane Bagasse
-SO_3H	sulfonated / Sulfonic Group
SPSC	Soaked Palm Seed Cake

SPSC-SO_3H	sulfonated – Soaked Palm Seed Cake
SPSC-AC	Soaked Palm Seed Cake – Activated Carbon
SO_3H-KSC	sulfonated Kenaf Seed Cake
TAG	Triglycerides
TGA	Thermogravimetric Analyzer
TPD-NH3	Temperature Programmed Desorption-Ammonia
USA	United States of America
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Renewable energy

The existence of humans is essentially depended on energy, how and where it is sourced. Presently, fossil fuel has been the major contributor to the global energy requirement and demand and the depletion of this fossil fuel is imminent in the near future (Borges and Díaz, 2012). Human's ever-increasing population has led to an energy crisis, where the energy demand is rapidly increasing and the fossil fuel reserve is quickly drying up. (Agarwal, 2007). Economically, the movement of materials, goods and services, have been greatly driven by energy (Jothiramalingam and Wang, 2009; Sarkar *et al.*, 2012). The transportation industry is hugely influenced by petroleum energy, sourced from fossil fuel. The transportation industry uses about 96 % of fossil fuels and on a yearly basis, global fuel consumption rises up to 62 % (Piriou *et al.*, 2013). Similarly, hydroelectricity, natural gas, coal and nuclear energy have all been exploited as viable energy sources. (Sani *et al.*, 2014).

In addition to the constant fluctuation in petroleum fuels' prices, is the environmental concern it raises. The continuous exploitation of fossil resources has led to severe environmental degradation to the ecosystem. The combustion and flaring of gas to produce petroleum products as fuel, generates carbon dioxide gas which is deposited into the atmosphere thereby contributing to the increase in global temperature. As a result, the greenhouse gases have also dramatically increased, leading to drastic climate changes. (Fauzi and Amin, 2013). Consequently, the need for alternative fuel source becomes imperative.

In recent years, biofuels have gained traction as a viable alternative to fossil resources as they are derived from multiple biomass sources. Biofuels, by their nature, are environmentally benign, economically feasible and are readily available (Avhad and Marchetti, 2016).

1.2 Biodiesel

Math *et al* (2010), defines biodiesel as the mono-alkyl esters having long chains of fatty acid derived from fats and oils such as animal fats and vegetable oils. In the past twenty years, biofuel has attracted a lot of interest as a promising alternative to fossil fuel diesel, mainly because of its non-toxicity to the environment, ability to degrade easily and the potential for renewability (Li *et al.*, 2010; Marchetti, 2013). Additionally, fuel produced from biomass resources (biodiesel) does not add to the total atmospheric carbon dioxide (CO_2), chlorofluorocarbons (CFCs) and methane. During biodiesel combustion, most CO_2 emitted can be recycled by simple steps of photosynthesis of the plant where the biodiesel is derived from. This therefore shows that emissions from biodiesel processes are greatly minimized (Peterson and Hustrulid, 1998). In biodiesel production, the most popular methods are transesterification and esterification, where feedstocks with high free fatty acids (FFA) are converted to fatty acid methyl esters (FAME) with the aid of catalysts in the presence of excess alcohol. Biodiesel contains about 10 % oxygen, and as a result, speeds up combustion rate and lowers environmental pollutants such as polycyclic aromatic compounds (PACs), particulate matters (PMs) and carbon monoxide (CO) (Agarwal, 2007). Lower sulfur content, better cetane number, higher flash point and increased lubrication are some of the other advantages of biodiesel usage as contrast to petroleum diesel (Knothe, 2009; Marchetti, 2012). These biodiesel properties have increased the chances of it to be a better alternative to petroleum diesel, as it is currently being used as blends around the world in diesel engines.

1.2.1 Feedstocks selection in biodiesel production

Availability and geographical location plays an important role in the feedstock selection for the production of biodiesel mostly when the production is large scale. In countries like the United States, where soybean oil is mostly used (about 9,431 million pounds in 2015) and in Europe, where rapeseed oil is abundant (about 6.17 million tons, which makes 55% of total production in 2014), it is easy for these feedstocks to be used. In Asia, of the total of 59 million tons of palm oil produced globally in 2014, Malaysia, being the second largest global producer and exporter of palm oil, produced 19.4 million tons of palm oil, which is approximately 33% of global production (Kapor *et al.*, 2017; MPOB, 2016). Therefore, it becomes plausible for the production of biodiesel from palm waste and other biomass sources. Non-edible fats/oils, refined vegetable oils and some crude wastes are other sources of biodiesel production. The fuel properties of biodiesel is largely dependent of the type of feedstock used for the biodiesel production. Some of these properties are viscosity, oxidation stability, cetane number, heating value, density and low temperature properties (Ferrero *et al.*, 2016; Ruhul *et al.*, 2016). Some of the edible vegetable oils used for the synthesis of biodiesel are oil palm, coconut, canola and sunflower oil. (Demirbas, 2007). However, the debate of food versus fuel will not allow these vegetable oils to be sued as they are major sources of food and this will lead to high price of combustible vegetable oil against petroleum diesel (Choudhury *et al.*, 2013; Talebian-Kiakalaieh *et al.*, 2013a).

A viable solution would be to opt for non-edible or waste oils such as palm fatty acid distillate (PFAD), waste cooking oils, Jatropha and rubber seed. In all of these, intensive research have carried out on PFAD as best alternative to serve as a feedstock for biodiesel production. (Al-Jaberi *et al.*, 2017; Cho *et al.*, 2012; Chongkhong *et al.*, 2007; Lokman *et al.*, 2016; Yujaroen *et al.*, 2009). PFAD is a by-product derived from oil palm refinery during the stripping and deodorization in the production of palm oil. It contains a large amount of free fatty acid (FFA) and has a production capacity of about 649,459 tons. For every one ton of crude palm oil produced in Malaysia, PFAD makes about 3.25 % (Kapor *et al.*, 2017).

1.3 Catalysts

Catalysts play an essential role in the transesterification and esterification of biodiesel. It speeds up the reaction and increases the conversion and yield of FAME or FAEE. These catalysts are categorized as acid, alkali and enzyme catalysts (Nelson *et al.*, 1996; Shimada *et al.*, 1999) and are either homogeneous or heterogeneous catalysts especially the alkali and acid. Generally, heterogeneous catalysts are solids, in a different phase with the reaction while homogeneous catalysts are liquids, similar phase with the reaction (Borges and Díaz, 2012; Phan *et al.*, 2006). These homogenous catalysts (alkali or acid), have some drawbacks which will lead to the generation of waste water because of the washing of biodiesel with a large amount of water in order to separate the catalysts from the biodiesel and can also lead to biodiesel loss as well as the corrosion of the equipment. Consequently, heterogeneous catalysts emerged to proffer solutions to these problems since they can easily be removed from the reaction and be reused for several reaction runs (Sharma *et al.*, 2011). Of all the heterogeneous catalysts, base catalysts have been successful used to provide high yield of biodiesel. Nevertheless, when feedstocks with high FFA are used, especially PFAD, base catalysts' performance are affected. Hence, heterogeneous acid catalysts have provided an alternative and a solution because of their non-hydrophobicity nature and do not lead to soap formation. They can also simultaneously undergo bi-functional esterification and transesterification reactions.

Besides the reusability and ease of separation, heterogeneous acid catalysts do not cause equipment corrosion as can be seen in some homogeneous acid catalysts such as sulphuric acid. Some of the reported heterogeneous catalysts for biodiesel production are sulphated tin oxide (SO_4^{2}-/SnO_2) (Furuta *et al.*, 2004), sulphated zirconium oxide (SO_4^{2}-ZrO_2) (Park *et al.*, 2008), sulfonated carbonized catalyst (Deshmane *et al.*, 2013) and heteropoly acids (Zhang *et al.*, 2009). Some disadvantages of these heterogeneous catalysts are long reaction time, expensive materials, high reaction temperature and leaching. This, can however, be minimized, by paying attention to the process of the catalyst preparation. To overcome these prevailing problems, bio-based heterogeneous catalysts with a functionalized acidic group (–SO_3H) have emerged and have been reported to be thermally stable; they enhance mass transfer, are cheap and easily accessible, and their continuous usage can solve some problems surrounding solid waste management (Konwar *et al.*, 2014; Akinfalabi *et al.*, 2017).

Bio-based solid catalysts have recently been exploited from hardwood biochar (Dehkhoda *et al.*, 2010), rice husk (Li *et al.*, 2014), and numerous palm parts (palm frond, palm spikelets, palm empty fruit bunch, and palm trunk) (Konwar *et al.*, 2014.; Sani *et al.*, 2015). Biomass sources from palm cake waste biochar (PCWB), sugarcane bagasse and kenaf seed cake are yet to be fully exploited, and these forms the basis for this work. About 7.3 m tons of palm waste biochar was processed in 2016, as at March of the same year, 162,519 tons were produced; 256,747 tons were in stock; and 77,005 tons were exported (Index Mundi., 2017). Also, the Malaysian sugar industry produces a huge amount of sugarcane bagasse and it is estimated that one metric ton of sugarcane yields about 280 kg of bagasse as by product (Cheah *et al.,* 2010). Economically, kenaf seed is generally regarded as a crop that can easily replace tobacco, because it is well adapted to arid regions, and is seen as Malaysia's next industrial crop because of its industrial potential (Tahery *et al.,* 2011).

1.4 Problem statement and hypothesis

Energy has become a major issue of concern for humans, which has led to a global crisis. This crisis is mainly surrounded by the availability of power produced naturally (*i.e.,* natural gases, fossil fuels and coal) and how they are depleting steadily. The petrochemical sources of energy have in the past decades provided the much needed energy, for human consumption. However, the depletion of these sources of energy have raised serious concerns to seek for alternatives for energy sources. The continuous interest by scientists and researchers on biodiesel is a good indicator that biodiesel could be the best alternative to petrol-based diesel. However, the routes to biodiesel production carries a huge cost burden due to expensive edible feedstocks. This has hindered the progress of biodiesel production with regards to usage and commercialization as compared to petro-diesel fuel. The cost of edible oil takes up to 75 % of the total production cost and thus making the biodiesel production cost almost 1.5 times higher than petroleum diesel. The use of non-edible waste material can help in cutting down the cost of production of biodiesel. PFAD, a non-edible and cheap feedstock has been used in this work as a feedstock for biodiesel production. It is theorized that PFAD will greatly reduce the cost of production of biodiesel and help in the management of waste from palm oil refinery.

Catalysts synthesis plays a major role in the production of biodiesel, to improve the efficiency of the conversion. Although, the major cost of production comes from fatty acid feedstock materials, but other costs arises from the use of costly catalytic synthetic routes. Catalysts are extensively used for organic synthesis, especially for the esterification reaction to produce biodiesel. Sodium hydroxide (NaOH), potassium hydroxide (KOH) and sulfuric acid (H_2SO_4) are conventionally used as basic and acidic homogeneous liquid catalysts. However, homogeneous basic and acidic catalysts have encountered numerous shortcomings such as soap formation, difficulties with catalyst recovery, equipment corrosion, and waste-water generation, consequently leading to environmental pollution. However, to overcome these prevailing problems, we have synthesized bio-based heterogeneous catalysts with a functionalized sulfonic acidic group ($–SO_3H$). They are thermally stable; they enhance mass transfer, are cheap and easily accessible, and their continuous usage can solve some problems surrounding solid waste management (Akinfalabi *et al.,* 2017).

Previously, the synthesis of carbonized materials as catalysts takes about 15 hours for calcination and up to 12 hours for SULFONATION with sulfonic agents (Lokman *et al.,* 2015) this shows a high use of energy consumption. Therefore, it becomes necessary to reduce the calcination and SULFONATION time. In this study, we have developed our catalysts with shorter calcination time of 2-3 hours and SULFONATION time of 5 - 10 hours in a modified SULFONATION and calcination method. Furthermore, biodiesel blends (petro-biodiesel mixture) have been demonstrated as a viable solution that can greatly reduce the cost of fuels, while also reducing the hazardous environmental impacts of petroleum fuel (Ali *et al.,* 2016). We have blended our synthesized biodiesel with petroleum diesel in an attempt to increase the chances of biodiesel to be readily available and affordable.

1.5 Objectives

The objectives of this study are:

1. To synthesize and evaluate the characteristics of biobased acid catalysts from biomass wastes (palm seed cake, kenaf seed cake and sugarcane bagasse).
2. To optimize the catalysts synthesis variables (*i.e.* SULFONATION time, volume of sulfonating agent, weight of catalyst and sulfonating temperature) to produce sulfonated biobased catalysts.
3. To produce biodiesel from PFAD using synthesized biobased catalysts and to assess the influence of different reaction parameters for esterification such as methanol: PFAD molar ratio, reaction temperature, reaction time, catalyst concentration and reusability.
4. To investigate the characteristics and fuel properties of the produced biodiesel and to evaluate the fuel blend properties with TGA and FTIR.

1.6 Scope of the research

The scope of this research work covers the synthesis, optimization and application of sulfonated biobased catalysts using palm seed cake, kenaf seed cake and sugarcane bagasse. A chemical impregnation period was introduced to help increase the porous properties of the biobased materials before calcination. The calcination time was optimized to achieve shorter calcination time. Furthermore, the synthesized catalysts were optimized based on the SULFONATION time, volume of sulfonating agent, SULFONATION temperature and the weight of the catalyst. The synthesized biobased catalysts were subjected to a detailed characterization in order to assess the catalytic properties of the catalysts produced. This is done to understand the physicochemical behavior of the catalysts during and after the esterification reaction. Finally, the biobased catalysts were applied via the reflux batch reactor for the esterification reaction. The esterification reaction process variables namely; reaction time, reaction temperature, catalyst concentration and molar ratio of methanol to PFAD were fully optimized. The fuel properties of the PFAD derived biodiesel were also investigated and the produced fatty acid methyl esters (FAME) were blended with petroleum diesel from B0, B3, B5, B10, B20 to B100 and characterized with TGA and FTIR.

1.7 Thesis outline

The overall thesis follows the paper format and therefore is presented as what has been published or submitted for publication. The thesis is divided into eight chapters. Chapter one is the introductory chapter, it discusses the background of the subject matter, highlights the current problems by focusing on the significance of the synthesis of biobased catalysts as it can efficiently aid the biodiesel production as an alternative energy source and also defines the objectives of the study. Chapter two is the presentation of the review of literature, which gives a wider range on the various subjects exclusive to the current research. It discusses a larger biobased catalysts synthesis overview, characterization, optimization and analysis as presented by previous authors. It further highlights the application in the production of biodiesel and the properties of the produced biodiesel.

Chapter three is the presentation of the results from the synthesis of biodiesel from palm fatty acid distillate using sulfonated palm seed cake catalyst. The chapter established the plausibility of palm waste biochar utilized as catalysts with results and detailed discussions and analysis of the results. Chapter four presents the appraisal of different SULFONATION processes to synthesize palm waste biochar catalysts for the esterification of palm fatty acid distillate (PFAD). It highlights the major SULFONATION process to derive the best SULFONATION method with sulfuric acid. The fifth chapter discusses sulfonated kenaf seed cake catalyst synthesis for efficient biodiesel production while using sulfuric acid as the sulfonating agent. Chapter six shows the biobased catalyst characterization and optimization via enhanced SULFONATION method for optimum FAME production. Sugarcane bagasse was used as the catalyst precursor. The seventh chapter highlights the utilization of response surface methodology (RSM) for the characterization and process optimization of FAME blends from biorefinery by-products - PFAD. It discusses the use of palm waste biochar as our best synthesized catalysts to produce biodiesel from PFAD while using RSM-CCRD as the optimization tool. It also highlights the fuel properties of biodiesel blends with petroleum diesel. It also shows the characterization of the biodiesel with FTIR and TGA. Lastly, chapter eight stands for general conclusion of the research and recommendation for future research work.

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LIST OF PUBLICATIONS

Akinfalabi, S. I., Rashid, U., Yunus, R., & Taufiq-Yap, Y. H. (2017). Synthesis of biodiesel from palm fatty acid distillate using sulfonated palm seed cake catalyst. *Renewable energy*, *111*, 611-619.

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