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DEVELOPMENT OF SULFONATED CARBON-BASED CATALYSTS DERIVED FROM PALM KERNEL SHELL FOR ACETYLATION OF GLYCEROL

NDA-UMAR USMAN IDRIS

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By

NDA-UMAR USMAN IDRIS

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

December 2020

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DEDICATION

To
my loving wife, Layla,
for her love, sacrifice, and understanding,
and
to our children,
Asmau, Idris, Khadijah, and Khalid.
To inspire them to know that destiny is about a functioning mind and not a matter of chance.

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

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December 2020

Chairman : Associate Professor Irmawati bt Ramli, PhD
Faculty : Science

The production and utilization of biodiesel have led to a significant increase in its by-product, glycerol, leading to a glut and value depreciation. Catalytic conversion of glycerol to acetin, a versatile industrial chemical, is one of the routes to improve its utilization. Currently, the homogeneous catalysts deployed are associated with many negative effects, while some of the existing heterogeneous catalysts exhibits low selectivity to triacetin, which is the most valued product. Carbon-based material, palm kernel shell (PKS), was processed and carbonized using direct, chemical, and template methods under CO_2 environment and subsequently functionalized using inorganic, organic, and hybrid of organic-inorganic sulfonating agents. The catalysts were characterized using proximate analysis, acid-base titration, CHNS analyzer, X-ray diffraction (XRD), Fourier transform infra-red (FTIR) spectroscopy, temperature programmed desorption of ammonia (TPD-NH_3), N_2 physiosorption analysis (BET), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), thermogravimetric-differential thermogravimetric analysis (TGA-DTG), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and solid state Nuclear Magnetic Resonance (NMR) spectroscopy, respectively. The carbon-based catalysts were deployed in glycerol acetylation and the product was analyzed using gas chromatography coupled with mass spectrometer (GC-MS), gas chromatograph equipped with flame ionization detector (GC-FID), FTIR and NMR. The catalyst obtained via template carbonization method at 800℃ exhibited excellent glycerol conversion (GC) with the highest triacetin selectivity. On optimization using RSM based on two-level, three-factor, face-centred central composite design (2^3 CCD), 97% GC and selectivity of 4.9, 27.8, and 66.5% monoacetin (MA), diacetin (DA), and triacetin (TA) were achieved under the optimum conditions of temperature 126±2℃, glycerol-to-acetic acid mole ratio (G/AA) 1:10.4, and catalyst load (CL) 0.45 g in 3 h reaction time. Amongst the organosulfonic acid functionalized catalysts, the ethanesulfonic acid (ESA) catalyst exhibited the highest TA selectivity and on optimization using RSM, 99.03% GC and selectivity of 6.91, 54.86, and 37.71% MA, DA, and TA were achieved at the optimum conditions of temperature 120±2℃, G/AA mole ratio 1:8, CL of 0.69 g and 3 h reaction time. Furthermore, the carbon-based catalyst obtained from the functionalization using the hybrid mixture of concentrated ethanesulfonic acid and sulfuric acid (1:9) exhibited excellent results after optimization. 99.8% GC and selectivity of 1.48, 24.64, and 73.81% MA, DA, and TA, respectively, were obtained under optimum conditions of temperature 110±2°C, G/AA mole ratio 1:10, and catalyst load 0.6 g in 3 h reaction time. On validation, all the model results exhibited good fit with good agreement between the predicted and the experimental data with the determination coefficient (R^2) > 0.9500 and adequate signal-to-noise ratio >4. The high performance of the synthesized carbon catalysts was attributed to the synergistic effect of good physicochemical characteristics, including good textural properties and high acidic site density and very importantly, the configuration of the surface acid moieties on the catalyst allowing unhindered access to the active sites during the reaction. On evaluating the reusability and stability of the selected catalysts in five reaction cycles each, they maintained excellent performance in glycerol conversion but inferior in TA selectivity after the first use. The DA selectivity became higher in the subsequent reaction cycles. The instability of TA was due to the leaching of active sites ($-SO_3H$).

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

PENGHASILAN PEMANGKIN BERASASKAN KARBON TERSULFON DARIPADA TEMPURUNG ISIRUNG SAWIT UNTUK PENGASETILAN GLISEROL

Oleh

NDA-UMAR USMAN IDRIS

Disember 2020

Pengerusi : Profesor Madya Irmawati bt Ramli, PhD
Fakulti : Sains

Peningkatan penghasilan dan penggunaan biodiesel telah menyebabkan berlakunya pertambahan produk sampingan iaitu gliserol yang menyumbang kepada lambakan dan kemerosotan nilai produk sampingan tersebut. Penukaran bermangkin gliserol kepada asetin merupakan salah satu kaedah untuk miningkatkan penggunaan biodisel kepada bahan kimia industri yang serba boleh. Pada masa kini, penggunaan mangkin homogen dikaitkan dengan banyak kesan negatif, manakala mangkin heterogen sedia ada mempunyai kepemilihan terhadap triasetin yang rendah iaitu produk yang paling bernilai. Bahan berasaskan karbon iaitu Tempurung isirung sawit (PKS) diproses dan dikarbonasi menggunakan kaedah langsung, kimia dan templat di dalam persekitaran CO_2 dan kemudiannya dirawat menggunakan agen pensulfonan tak organik, organik dan hibrid organik-tak organik. Mangkin yang terhasil diuji menggunakan pelbagai analisis termasuk analisis kehampiran, penitratan asid-bes, analisis CHNS, pembelauan sinar-X (XRD), spektroskopi infra-merah transformasi Fourier (FTIR), nyahjerapan terprogram suhu ammonia (TPD-NH_3), analisis fizijerapan N_2 (BET), mikroskopi elektron pengimbasan berpasangan spektroskopi sinar-X sebaran elektron (SEM-EDX), analisis gravimetri terma-pembezaan gravimetri terma (TGA-DTG), spektroskopi Raman, spektroskopi fotoelektron sinar-X (XPS) dan spektroskopi keadaan pepejal resonans magnet nukleus (NMR). Produk tindak balas telah dianalisis menggunakan kromatografi gas berpasangan dengan spektroskopi jisim (GC-MS), kromatografi gas dilengkapi dengan pengesan nyala pengionan (GC-FID), FTIR dan NMR. Pemangkin yang dihasikan pada suhu 800°C menggunakan menggunakan kaedah templat mampu menukarkan gliserol (GC) dengan sangat baik dengan kepemilihan triasetin yang tinggi.Pengoptimum mengunakan RSM dilakukan berdasarkan dua-aras, tiga-faktor, reka bentuk komposit pusat berpusatkan permukaan (2^3 CCD), 97% GC dan kepemilihan terhadap monoasetin (MA), diasetin (DA), dan triasetin (TA) masing-masing 4.9, 27.8, dan 66.5% yang dicapai dalam keadaan optimum iaitu pada suhu 126±2°C, nisbah mol gliserol-kepada-asid asetik (G/AA)

1:10.4, dan muatan mangkin (CL) 0.45 g untuk tindak balas selama 3 j. Asid etanasulfonik (ESA merupakan salah satu rawatan yang mengunakan reagen asid organosulfunik dan mempamerkan kepemilihan TA tertinggi dan pengoptimuman RSM, 99.03% GC dan kepemilihan 6.91, 54.86, dan 37.71% masing-masing MA, DA, and TA telah dicapai pada keadaan optimum suhu 120±2℃, nisbah mol G/AA 1:8, CL pada 0.69 g dan masa tindak balas selama 3 j. Seterusnya, mangkin yang dirawat menggunakan kaedah hibrid campuran asid pekat etanasulfonik dan asid sulfurik (1:9) menunjukkan keputusan yang baik iaitu 99.8% GC dan kepemilihan terhadap MA, DA dan TA adalah masing-masing 1.48, 24.64, and 73.81% setelah pemodelan dan pengoptimuman dalam keadaan suhu optimum 110±2℃, nisbah mol G/AA 1:10 dan CL 0.6 g dalam tindak balas selama 3 jam. Semasa pengesahan, kesemua model menunjukkan persamaan antara data ramalan dan data kajian dengan koefisien diperolehi (R^2) > 0.9500 dan memadai nisbah isyarat-kepada-hingar >4. Kecemerlangan prestasi mangkin karbon yang disintesis adalah disebabkan oleh kesan sinergistik ciri-ciri fizikal-kimia yang baik, termasuk tekstur yang baik, dan ketumpatan tapak asid yang tinggi dan faktor utama adalah disebabkan oleh konfigurasi lembapan asid permukaan mangkin yang membenarkan akses tanpa halangan kepada tapak aktif semasa tindak balas berlangsung. Kajian kebolehgunaan dan kestabilan untuk lima kitaran tindak balas dan di dapati mangkin tersebut mampu mengekalkan prestasi yang sangat baik dalam penukaran gliserol, walaubagaimanapun kepemilihan terhdap TA berkurang setelah penggunaan yang pertama dalam tindak balas. Kepemilihan terhadap DA bertambah pada kitaran yang selanjutnya. Keputusan yang diperolehi ini membuktikan ketakstabilan TA disebabkan pelarutlesapan tapak aktif (-SO_3H).

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In the name of Allah, the Most Beneficent, the Most Merciful.
"... if you are grateful, I will surely
increase you (in favour) … (Q14 V 7)."

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I pay tribute to my relations, friends and colleagues who passed on while I was away in Malaysia. Allah have mercy on their souls and reward them with Aljannatul firdausi. Ameen.

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:

Irmawati bt Ramli, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Taufiq-Yap Yun Hin, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Ernee Noryana bt Muhamad, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

ZALILAH MOHD SHARIFF, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 11 March 2021

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) were adhered to.

Signature: ______________________________
Name of Chairman
of Supervisory Associate Professor
Committee: Dr. Irmawati bt Ramli

Signature: ______________________________
Name of Member
of Supervisory Professor
Committee: Dr. Taufiq-Yap Yun Hin

Signature: ______________________________
Name of Member
of Supervisory
Committee: Dr. Ernee Noryana bt Muhamad

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LIST OF ABBREVIATIONS

AA	Acetic acid
ANOVA	Analysis of variance
BBD	Box-Behnken design
BDSA	Benzene-1,3-disulfonic acid (BDSA)
BET	Brunauer-Emmett-Teller (BET)
BJH	Barrett–Joyner–Halenda (BJH)
CCD	Central composite design
CHNS	Carbon, Hydrogen, Nitrogen, Sulfur
CL	Catalyst load
CP	Cross polarization
CV	Coefficient of variation
DA	Diacetin
DTG	Differential thermogravimetric
EDSA	1,2-ethane-1,2-disulfonic acid
ESA	Ethanesulfonic acid
FTIR	Fourier transform infra-red
G	Glycerol
G/AA	Glycerol-to-acetic acid mole ratio
GC	Glycerol conversion
GC-FID	Gas chromatography-Flame ionization detector
GC-MS	Gas chromatography-Mass spectroscopy
HBSA	4-hydroxybenzenesulfonic acid
HSO	Dilute sulfuric acid
MA	Monoacetin
MAS	Magic angle spinning
MR	Mole ratio

NMR	Nuclear magnetic resonance
OMSC	Optimized mesoporous sulfonic acid
P	PKS directly carbonized
P/P^o	Relative pressure
PC	PKS chemically carbonized
PKS	Palm kernel shell
PS	Pore size
PT	PKS template carbonized
PV	Pore volume
RSM	Response surface methodology
SA	Surface area
SAD	Sulfonic acid density
SEM-EDX	Scanning electron microscopy-energy dispersive X-ray
T	Temperature
TA	Triacetin
TAD	Total acid density
TAS	Total acid sites
TCD	Thermal conductivity detector
TGA	Thermogravimetric
TPD-NH_3	Temperature programmed desorption of ammonia
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Renewable energy sources are now considered viable and sustainable alternatives to the conventional oil. These renewables sources include solar, wind, geothermal and biomass. Biomass, which is a wide range of biological materials, contributes the highest share to the global energy supply of all the renewable resources and the energy has been deployed in heating, electricity and transportation (biofuels) purposes (REN21, 2020). Biofuel is a general name for fuels from biomass which include bioethanol, biodiesel, biomethanol, biogas, biohydrogen, bio-dimethyl ether, bio-ETBE (ethyl-tert-butyl-ether), bio-MTBE (methyl-tert-butyl-ether), synthetic biofuels (hydrocarbons) and bio-oil (vegetable) (Balat, 2011; EU-Commission, 2003; Thanh et al., 2012). Biodiesel, a monoalkyl ester of fatty acids obtained from vegetable oil or animal fat through esterification or transesterification reaction with alcohol in the presence of a catalyst, is the most researched and most viable for the transportation system at the moment owing to its advantages. It is biodegradable, non-toxic, renewable, of high cetane number, in-built oxygen content, higher combustion without or with low sulfur, aromatic components and other regulated emissions, complete carbon cycle, availability of raw materials and fit into the existing engines with little or no modification and with high flash point (Babajide, 2013; Gaurav et al., 2016; Knothe and Razon, 2017).

The directive by the European Union (EU) for member countries to add at least 5-20% of biofuels to conventional fuel by the year 2020 and the need to reduce CO_2 emission has increased the production of biodiesel (Dimitratos et al., 2009; EU-Commission, 2003). Biodiesel production in EU member countries increased from 1.93 million tons in 2004 to 10.37 million tons in 2013 (EBB, 2017). Similarly, the United State biodiesel production grew from 0.5 million gallons in 1999 to 250 million gallons in 2006 (Gliceryny and Ubocznego, 2011) and 2.89 billion gallons in 2016 (NBB, 2017). Generally, global biodiesel production is on the increase, as illustrated in Figure 1.1. Currently, over 40 billion litres is being produced with Indonesia, Brazil, United State, Germany and France among the top five producers, as indicated in Figure 1.2 (REN21, 2020).

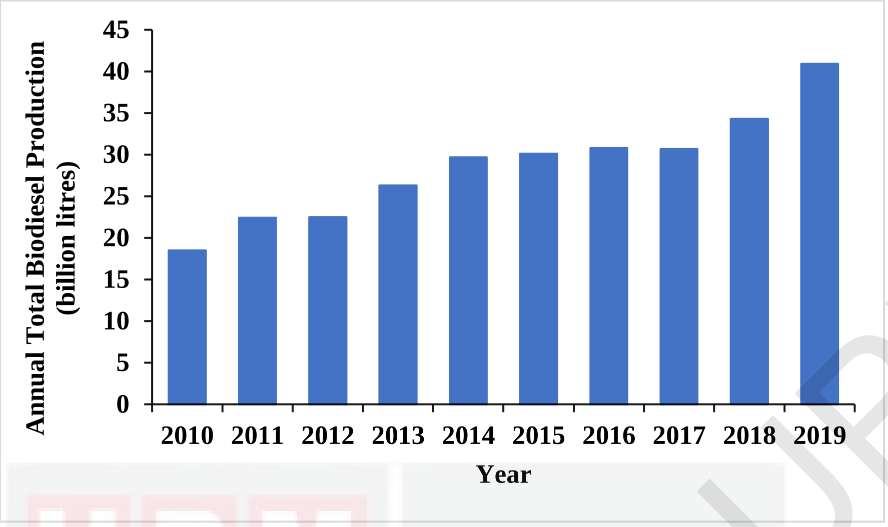

Figure 1.1 : Annual total biodiesel production for the last ten years (2010-2019) (REN21, 2013-2020)

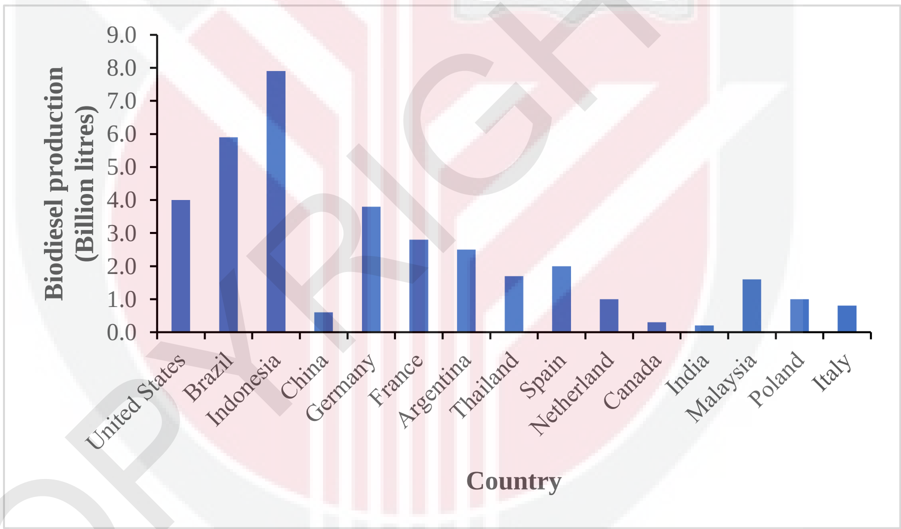

Figure 1.2 : The global biodiesel production of the top 15 countries in 2019 (REN21, 2020)

Given the above scenario of biodiesel production, huge volume of glycerol is expected to be generated. It has been reported that for every 100 kg of biodiesel produced, 10 kg (10%) of glycerol is obtained as the by-product leading to surplus in the market (Anuar and Zuhairi, 2016; Bauer and Hulteberg, 2013; Quispe et al., 2013). Recent literature indicates that by the year 2020, the global production of glycerol will move up to 41.9 billion litres (Nanda et al., 2014b). This number is expected to increase with the recent prediction that biodiesel will account for over 70% of the global transportation fuel by 2040 (Naylor and Higgins, 2017). This forecast is supported by many deliberate policies put in place by different countries and organizations to encourage biodiesel production and its utilization, such as the implementation of mandatory biodiesel blending targets, tax exemptions, government support, investment subsidies, and research and development programs (Naylor and Higgins, 2017).

Therefore, the current upsurge in biodiesel production will further depreciate the commercial value of glycerol (Trifoi et al., 2016) and underutilization may lead to some environmental challenges as such scientists around the world are developing new techniques in converting glycerol to high-value products or chemicals, which is expected to improve the economics of biodiesel. Of these techniques, catalysis and catalysts play a significant role in its transformation.

1.2 Catalysis and catalysts

Since the discovery of catalyst in the 17th century, catalysis has been playing significant roles in the chemical industry not only in promoting chemical reactions as it is traditionally known but also in enhancing selectivity of products, reducing reagent waste and unwanted products, removal or conversion of dangerous pollutants into products of lower toxicity amongst others (Singh and Tandon, 2015; Waclawek et al., 2018). Catalysts are now the heart of nearly all the chemical process because almost 85 - 95% of industrial products are produced through catalytic processes and the global catalyst market has been estimated to be about $15 billion per year (O’neill et al., 2015; Waclawek et al., 2018). Most chemical industries are traditionally accustomed to the use of acidic homogeneous catalysts like sulfuric acid, hydrochloric acid, nitric acid, etc, in their production processes due to their high catalytic activity and selectivity with little or no problem of diffusion. However, these catalysts are characterized with the formation of side products, low thermal stability, low water tolerance, corrosive tendency, energy consumption, difficulty of separation from the product, difficult to recycle, an additional step of washing, disposal challenge and general unfriendly environmental concern (Fauziyah et al., 2020; Ngaosuwan et al., 2016). To overcome the drawbacks of the homogeneous catalysts and to conform with the philosophy of green chemistry, extensive exploration of solid heterogeneous catalysts have been conducted and still ongoing to achieve similar efficiency and selectivity with less environmental impact. This is because solid acid heterogeneous catalysts are thermally more stable, easy to separate, reusable, corrosion-free, withstand harsh reaction conditions, low cost, and susceptible to wide applications (Nagasundaram et al., 2020; Waclawek et al., 2018). Given the gains made in the use of heterogeneous catalysis, approximately 85 % of it is used in various industries processes in the recent times with homogeneous and biocatalysts accounting for the remaining 15% (Waclawek et al., 2018). Though some of the heterogeneous catalysts have also exhibited low activity, selectivity, deactivation, and mass diffusion challenges, efforts are ongoing to improve these defects by way of functionalization and other measures leading to the introduction of heterogenized-homogeneous catalysts to improve the functionality of both classes of catalysts. The functionalization involves the immobilization or attachment of homogeneous active sites on solid, insoluble supports usually of large surface area and largely porous by covalent or non-covalent bonding (adsorption, electrostatic interaction, entrapment, etc.) to give room for high activity, high selectivity, easy separation and reusability (Barbaro and Liguori, 2009). This type of catalyst is seen as the catalyst of the present and the future. Glycerol valorisation to other high-value products will require the right catalysts with the appropriate technology. Figure 1.3 shows the classification of catalysts based on the state of aggregation in which they act.

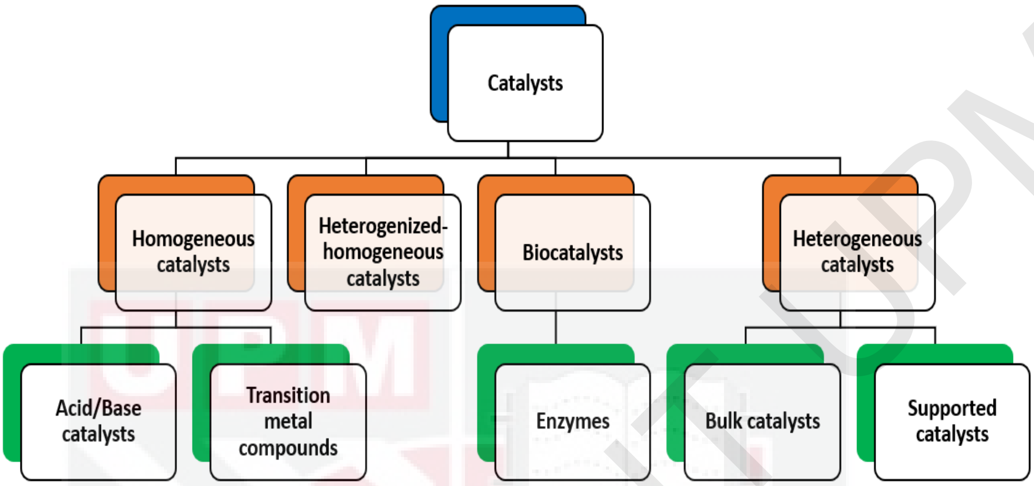

Figure 1.3 : Classification of catalysts

1.3 Problem statement

The global response to the production and utilization of biodiesel as an alternative renewable fuel to fossil fuels is throwing up the challenge of surplus glycerol in the environment. In view of the surplus, the value of glycerol has also fallen drastically in the international market. It is therefore imperative to convert glycerol to other high-value products to improve its commercial viability, improve biodiesel economics, and eliminate the perceived environmental concern of the surplus.

The conversion of glycerol to high-value products such as acetin (glycerol esters) is an acid-catalysed reaction and therefore requires appropriate catalysts. Currently, most of the catalysts deployed are associated with a number of defects. Use of homogeneous catalysts, though of high reaction rate, turnover frequency and selectivity but are associated with toxicity, corrosion problems, difficult in separation and production of unwanted or side products (Dalla Costa et al., 2017, Khayoon et al., 2014). The use of heterogeneous solid acid catalysts such as ion exchange resins, zeolites, heteropoly acids and metals have also been reported with the advantage of easy recovery, reusability, green process and amenable to modification for better performance. However, these catalysts have also been characterized with low thermal stability, low acid strength, narrow pore size, low mechanical stability, low surface area and ease of solubility in aqueous medium (Okoye et al., 2017, Dalla Costa et al., 2017, Balaraju et al., 2010).

Furthermore, the reports of glycerol conversion to acetin by various researchers using some of the above catalysts such as zeolites and heteropoly acids have indicated high glycerol conversion with high selectivity to monoacetin, average selectivity to diacetin and very little or no production of triacetin (Goncalves et al., 2012, Goncalves et al., 2008). While catalysts such as sulfonated clay (K-10) and sulfonated silica exhibits average selectivity to monoacetin, high selectivity to diacetin but low selectivity to triacetin (Kakasaheb et al., 2018, Dalla Costa et al., 2017). Despite the use of different catalysts, the selectivity to triacetin, the most sought-after product of acetylation, is still low. So, low selectivity towards triacetin is a major problem that requires appropriate attention.

It is in the light of above shortcomings that interest has now shifted to identifying new catalytic materials that are inexpensive, environmentally friendly, reusable, and easily amenable to functionalization to improve their surface characteristics (the surface area and the acid density) in order to improve the selectivity of triacetin. Carbon-based materials have been identified as a potential good material for such synthesis. Hence the study is focused on the development of sulfonated carbon-based catalysts derived from palm kernel shell for the purpose of catalysing glycerol acetylation to improve triacetin selectivity.

1.4 Objectives of the research

The objectives of this research include:

1. To investigate the effect of various carbonization methods on the development of sulfonated carbon-based catalysts derived from palm kernel shell (PKS) and their evaluation in glycerol acetylation with acetic acid.
2. To evaluate the effect of functionalization with sulfuric and organosulfonic acids reagents on the glycerol acetylation activity of the sulfonated carbon-based catalysts derived from palm kernel shell (PKS).
3. To optimize the glycerol acetylation reaction using the response surface methodology (RSM) with a view to improving the selectivity of triacetin.
4. To evaluate the reusability and stability of the selected sulfonated carbon-based catalysts.
5. To carry out spectroscopic analysis of the acetylation product.

1.5 Scope of the research

In this research, carbon-based solid catalysts were synthesized using palm kernel shell (PKS) as the precursor materials using direct, chemical and template carbonization methods under carbon dioxide (CO_2) environment and subsequently sulfonated using concentrated sulfuric acid. The template carbonized material was also sulfonated with different organosulfonic acid reagents as well as the hybrid of organic-inorganic sulfonic acid reagent (a mixture of sulfuric acid and ethanesulfonic acid). The precursor material and the resultants sulfonated carbon catalysts were characterized using proximate analysis, CHNS, EDX, XRD, FTIR, TPD, TGA, SEM, NMR, XPS, N_2 adsorption isotherm, and acid-base titration. The synthesized catalysts were evaluated for their activity in glycerol acetylation with acetic acid in a batch liquid phase reaction under atmospheric pressure. The catalyst identified with the best potential in each case was used for modelling and optimization, reusability and stability studies. The performance of the synthesized catalysts was also compared with the activities of commercial amberlyst-15 catalyst and homogeneous catalyst (concentrated sulfuric acid).

1.6 Thesis outline

The thesis has been divided into 9 chapters with the following content:

Chapter 1 gives a general overview of the status and trend of renewable energy production with emphasis on biofuel (biodiesel) and its by-product, glycerol. The chapter also gives a brief introduction on the field of catalysis and catalysts. Finally, the problem statement, objectives and scope of the research are also stated in the chapter.

Chapter 2 gives a detailed background on glycerol including its properties, synthesis route and applications. It also gives a detailed review of glycerol transformation into acetin via the acetylation reaction and the parameters that influences it. The chapter also provides a review of the synthesis of carbon-based catalysts derived from biomass materials. The basics of optimization are also discussed in the chapter.

Chapter 3 is the methodology section where all the materials, chemicals and equipment used in the research are outlined. It also described all the catalysts preparation methods, the theory and experimental procedures of the characterization techniques and the optimization method used. The procedure of the glycerol acetylation, product identification and quantification are also reported in this chapter.

Chapters 4 contains the characterization and activity test results of catalysts obtained via direct, chemical and template carbonization methods and their subsequent sulfonation with concentrated sulfuric acid. Chapter 5 presents the results and discussion on optimization of mesoporous carbon catalyst and their deployment in modelling and optimization of glycerol acetylation using RSM to improve triacetin selectivity. The results of reusability and stability of the catalyst are also discussed in this chapter. Chapter 6 deals with results and discussions arising from the synthesis and characterization of carbon catalysts obtained using organosulfonic acid functionalization. It also contains the results and discussion of the catalytic test, optimization of glycerol acetylation using RSM. The chapter also contains the results of reusability and stability of the catalyst. Chapter 7 contains the results and discussion of characterization and activity test of carbon catalysts obtained using organic-inorganic sulfonic acid hybrid functionalization. The results of the optimization of glycerol acetylation using RSM to improve triacetin selectivity, as well as, the reusability and stability of the catalyst are also reported in the chapter.

Chapter 8 is made up of the proposed structure of the synthesized catalyst, the plausible reaction mechanism of glycerol acetylation with acetic acid, and the spectroscopic analysis of the synthesized products. Chapter 9 summarizes the findings of this research, and the general conclusion of the research work. Recommendation for future studies is also contained in this chapter.

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BIODATA OF STUDENT

Usman Idris Nda-Umar had his Bachelor of Science Degree (B.Sc. Hons) in Chemistry and Master of Science Degree (M.Sc.) in Analytical Chemistry from the Usmanu Danfodiyo University, Sokoto, and the University of Ibadan, both in Nigeria. After his one-year youth service at Ogun State, he joined the services of the Federal Polytechnic, Bida, Nigeria, in 1995 as an Assistant Lecturer and gradually rose through the ranks to become a Chief Lecturer in the department of Science Laboratory Technology now the department of Chemical Sciences. He has several national and international conference papers, journal articles, and books to his credit. He has contributed immensely to the growth and development of the institution through various academic and administrative responsibilities. In view of his commitment and passion for fairness and justice to humanity, he served several labour organizations and associations selflessly, to the admiration of many, which earned him accolades and several awards from different organizations, including the Rotaract Club International District 9130 Nigeria, Azza Development Association, National Youth Council of Nigeria (NYCN), Bida district and Chemical Society of Nigeria (CSN). He is currently a Fellow of the Chemical Society of Nigeria and a member of the Institute of Chartered Chemist of Nigeria (ICCON). Usman joined the Catalysis and Advanced materials research group (UPM), headed by Prof. Madya Dr. Irmawati Binti Ramli for his PhD in 2017 and participated actively in her research endeavours leading to several publications in indexed journals and has successfully patented their research work on the synthesis of sulfonated carbon-based catalysts. Usman is married and blessed with four children. He enjoys reading, listening to news and discussions on national issues, travelling and sports as hobbies. His philosophy about life is ‘keep learning and treat people with dignity irrespective of their status.’

LIST OF PUBLICATIONS

Usman Idris Nda-Umar, Irmawati Ramli, Yun Hin Taufiq-Yap, Ernee Noryana Muhamad (2019). An overview of recent research in the conversion of glycerol into biofuels, fuel additives and other bio-based chemicals. *Catalysts*, 9 (1), 15. https://doi.org/10.3390/catal9010015 (**Q2 JCR, published**).

Usman Idris Nda-Umar, Irmawati Ramli, Ernee Noryana Muhamad, Yun Hin Taufiq-Yap & Norsahida Azri (2020). Synthesis and characterization of sulfonated carbon catalysts derived from biomass waste and its evaluation in glycerol acetylation. *Biomass Conversion and Biorefinery*. http://doi.org/10.1007/s13399-020-00784-0 (**Q2 JCR, published**).

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Usman Idris Nda-Umar, Shera Farisya Binti Mohamad Rasid, Nor Shafizah Ishak and Ernee Noryana Muhamad, Irmawati Ramli (2020). Carbon-based solid catalyst synthesized from palm kernel shell: Comparative study of organic and inorganic sulfonic acids functionalization at low concentration. *Materials* (**Q2 JCR, under review**).

Patent

Irmawati Binti Ramli, Ernee Noryana Muhamad, **Nda-Umar Usman Idris** (2020). A method to produce carbon catalyst from oil palm mill wastes with improved characteristics. (Patent appl. No.: PI22020002505).

Conference Paper

U. I. Nda-Umar, I. Ramli, E. N. Muhamad, Y. H. Taufiq-Yap. Glycerol acetylation over sulfonated carbon catalyst derived from biomass waste using different carbonization methods: synthesis, characterization and screening. 11th International Fundamental Science Congress. Palm Garden Hotel, IOI Resort city, Putrajaya, Malaysia. 30th – 31st October 2019.

Workshops

1. Workshop on Design of Experiment (DOE). Organized by College of Graduate Studies, The National Energy University (Universiti Tenaga National), Malaysia. 2nd, 9th & 16th August, 2017.

2. Fourier-Transform infrared spectroscopy (FTIR) workshop. Organize by Department of Chemistry, Universiti Putra Malaysia in partnership with Shimadzu. 28th September 2017.

3. Guide to getting published workshop. Organized by Emerald Group Publishing and Perpustakaan Sultan Abdul Samad, Universiti Putra Malaysia. 26th October 2017

4. Surface area and particle size distribution. Organized by Institut Tekhnogi Maju (ITMA), Universiti Putra Malaysia. 8th February 2018

5. Revealing the mysteries of solid-state materials. Organized by Department of Chemistry, Faculty of Science, Universiti Putra Malaysia. held 5-6th November 2019.

List of Other Publications

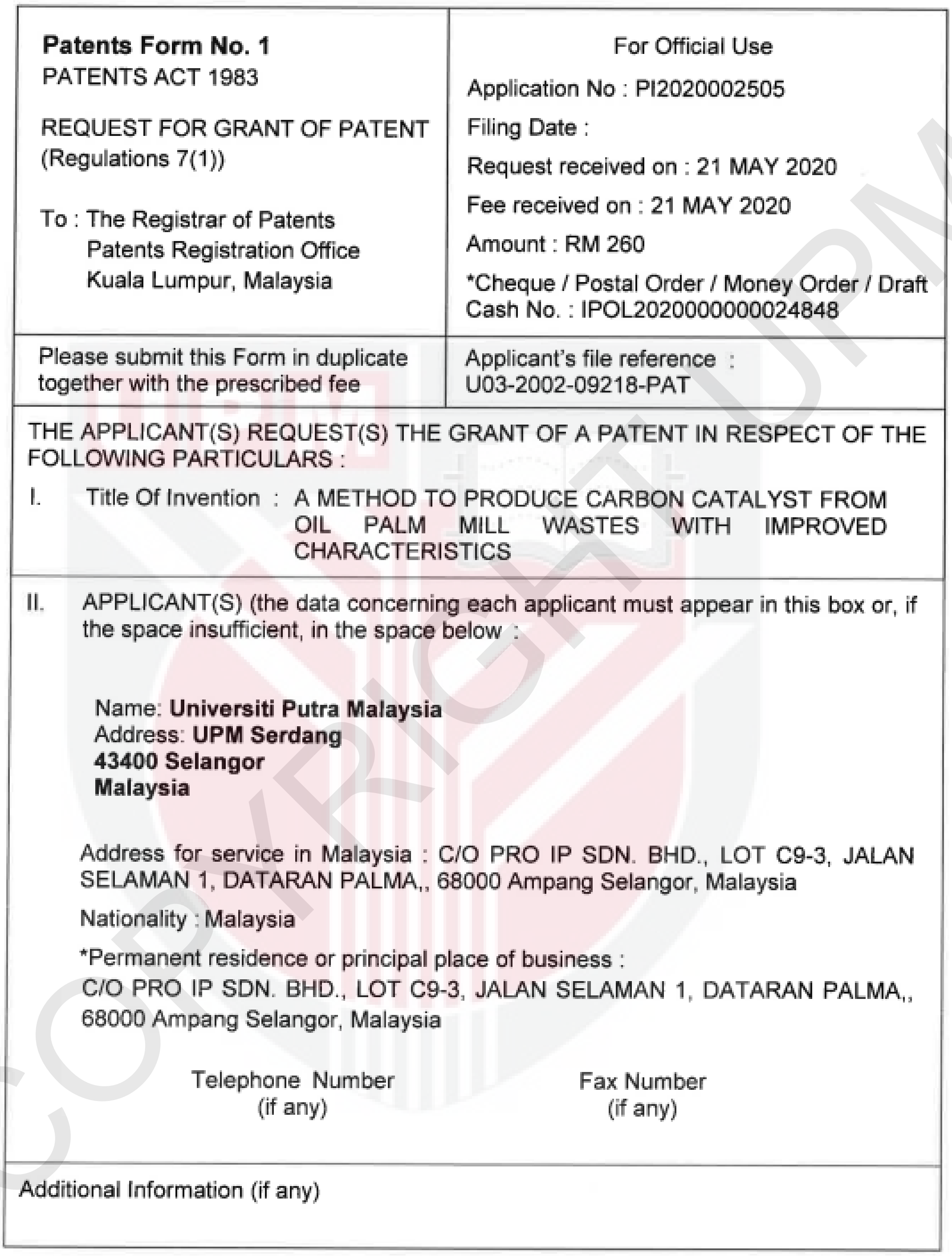
Muhammad Yahaya, Irmawati Ramli, Ernee Noryana Muhamad, Nor Shafizah Ishak, **Usman Idris Nda-Umar** and Yun Hin Taufiq-Yap. (2020). K_2O doped dolomite as heterogeneous catalyst for fatty acid methyl ester production from palm oil. *Catalysts*, 10 (7), 791. https://doi.org/10.3390/catal10070791 (**Q2 JCR, published**)

Norsahida Azri, Irmawati Ramli, **Usman Idris Nda-Umar**, Mohd Razali Shamsuddin Mohd Izham Saiman and Yun Hin Taufiq-Yap (2020). Copper-Dolomite as effective catalyst for glycerol hydrogenolysis to 1,2-propanediol. *Journal of the Taiwan Institute of Chemical Engineers,* 112, 34-51. https://doi.org/10.1016/j.jtice.2020.07.011 (**Q1 JCR, published**).

Norsahida Azri, Irmawati Ramli, **Usman Idris Nda-Umar**, Mohd Izham Saiman and Yun Hin Taufiq-Yap (2020). The Effect of Different Supports for Copper as Catalysts for Glycerol Hydrogenolysis to 1,2-Propanediol (2020). *Journal of King Saud University-Science* (**Q2 JCR, under review**).

Norsahida Azri, Irmawati Ramli, **Usman Idris Nda-Umar**, Mohd Izham Saiman and Yun Hin Taufiq-Yap (2021). Promotional Effect of Transition Metals (Cu, Ni, Co, Fe, Zn)–Doped Dolomite on Hydrogenolysis of Glycerol into 1,2-propanediol (2020). *Arabian Journal of Chemistry*, 14(4). https://doi.org/10.1016/j.arabic.2021.103047 (**Q2 JCR, published**).

PATENT FILING



Patents Form No. 1
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REQUEST FOR GRANT OF PATENT
(Regulations 7(1))

To : The Registrar of Patents
Patents Registration Office
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For Official Use
Application No : PI2020002505
Filing Date :
Request received on : 21 MAY 2020
Fee received on : 21 MAY 2020
Amount : RM 260
*Cheque / Postal Order / Money Order / Draft
Cash No. : IPOL2020000000024848

Please submit this Form in duplicate together with the prescribed fee

Applicant's file reference : U03-2002-09218-PAT

THE APPLICANT(S) REQUEST(S) THE GRANT OF A PATENT IN RESPECT OF THE FOLLOWING PARTICULARS :

I. Title Of Invention : A METHOD TO PRODUCE CARBON CATALYST FROM OIL PALM MILL WASTES WITH IMPROVED CHARACTERISTICS

II. APPLICANT(S) (the data concerning each applicant must appear in this box or, if the space insufficient, in the space below :

Name: **Universiti Putra Malaysia**
Address: **UPM Serdang**
43400 Selangor
Malaysia

Address for service in Malaysia : C/O PRO IP SDN. BHD., LOT C9-3, JALAN SELAMAN 1, DATARAN PALMA,, 68000 Ampang Selangor, Malaysia

Nationality : Malaysia

*Permanent residence or principal place of business :
C/O PRO IP SDN. BHD., LOT C9-3, JALAN SELAMAN 1, DATARAN PALMA,, 68000 Ampang Selangor, Malaysia

Telephone Number (if any)

Fax Number (if any)

Additional Information (if any)

III. INVENTOR :

Applicant is the inventor Yes ☐ No ☒

If the applicant is not the inventor:

Name: **IRMAWATI RAMLI**
Address: **FACULTY OF SCIENCE, UNIVERSITI PUTRA MALAYSIA, UPM SERDANG**
43400 SELANGOR
Malaysia

Name: **Ernee Noryana Muhammad**
Address: **Department of Chemistry, Faculty of Science, Universiti Putra Malaysia**
43400 Serdang Selangor
Malaysia

Name: **Nda-Umar Usman Idris**
Address: **Department of Chemistry, Faculty of Science, Universiti Putra Malaysia**
43400 Serdang Selangor
Malaysia

A statement justifying the applicant's right to the patent accompanies this Form :
Yes ☒ No ☐

Additional Information (if any)

IV. AGENT OR REPRESENTATIVE :

Applicant has appointed a patent agent in accompanying Form No. 17

Yes ☐ No ☒

Agent's registration No. : PA/2010/0224

Applicant has appointed MAD ISA BIN MOHAMED to be their representative

V. DIVISIONAL APPLICATION :

This application is a divisional application ☐ ☐

The benefit of the filing date priority date

of the initial application is claimed in as much as the subject-matter of the present application is contained in the initial application identified below :

Initial Application No. :
Date of Filing of initial application :

Additional Information (if any)