UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF SULFONATED CARBON-BASED CATALYSTS FROM GLYCEROL AND COW DUNG FOR BIODIESEL PRODUCTION FROM HIGH FREE FATTY ACID OILS

SHATESH KUMAR A/L SANGAR

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By

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

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October 2020

Chair: Prof Datuk Taufiq Yap Yun Hin, PhD

Faculty: Science

In this research, cost efficient and environmental friendly sulfonated carbon-based catalyst was prepared from glycerol (CG) and cow dung (CD) and subsequently functionalized with concentrated sulfuric acid (H_2SO_4) at different sulfonation time. The physico-chemical properties of the prepared catalysts were characterized by using X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption-ammonia (TPD-NH_3), Thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) surface area, variable pressure scanning electron microscope (VPSEM), high resolution transmission electron microscopy (HR-TEM), X-ray Fluorescene (XRF) analysis and CHNSO elemental analysis. The carbon that was sulfonated with H_2SO_4 for 10 h (SCG-$_{(10)}$ and SCD-$_{(10)}$ catalysts) were chosen to be used in optimization studies due to the synergistic effect of good physicochemical properties including high amount of acid sites and sulfur attached to carbon. The amount of sulfur and total acidity were increased significantly after being sulfonated at different time of reflux; whereas, the SCG-$_{(10)}$ and SCD-$_{(10)}$ catalysts showed the highest total amount of acidity 35117.14 µmol/g and 16653.49 µmol/g, respectively. The esterification of palm fatty acid distillate (PFAD) over SCG-$_{(10)}$ catalyst was optimized via the one-variable-at-a-time technique, and fatty acid methyl ester (FAME) of 97.8% was achieved at optimum conditions of 1 h reaction time, 90 °C reaction temperature, 5 wt% catalyst loading, and 18:1 methanol-to-oil molar ratio. The SCG-$_{(10)}$ catalyst was successfully reused for 7 cycles and it was found that the catalytic activity maintained with >96% of FAME yield for the first three run. The synthesized PFAD-derived biodiesel has complied with the international biodiesel standards of EN14214 and ASTM D6751. The amount of sulfur in biodiesel are lower than the maximum limit of ASTM D6751. Taguchi approach using four parameters at four-level, L-16 (4^4) of experiment design was employed to compare the experimental results. Reaction temperature was the most influenced control parameter on biodiesel production with high S/N ratio and F-value. The

optimum conditions for the highest biodiesel production was at reaction temperature at level 4 (90 ℃), methanol to PFAD molar ratio at level 3 (18:1), catalyst loading at level 4 (6 wt. %) and reaction time at level 3 (1.5 h). As SCG-$_{(10)}$ catalyst showed super catalytic performance in esterification of PFAD, it also been used for simultaneous esterification-transesterification of waste cooking oil (WCO) and chicken fat oil (CFO). The methyl ester production from WCO and CFO were also successfully performed by using SCG-$_{(10)}$ catalyst and obtained FAME yield 92.3% (optimum conditions of 5 wt% catalyst loading with 22:1 methanol to WCO molar ratio for 3 h reaction time and 100 ℃ reaction temperature) and 90.8% (optimised conditions of 5 wt% catalyst loading with 18:1 methanol to CFO molar ratio for 1 h reaction time and 70 ℃ reaction temperature), respectively. In addition, SCD-$_{(10)}$ catalyst was used in esterification of PFAD and achieved high FFA conversion of 96.5% at optimum parameter of 18:1 methanol to PFAD molar ratio, 4wt% of catalyst loading and 90 °C reaction temperature within 1 h reaction time. SCD-$_{(10)}$ catalyst is capable to convert PFAD to biodiesel with FFA conversion >90% for 3 consecutive cycles. As a conclusion, both SCG-$_{(10)}$ and SCD-$_{(10)}$ catalysts can be easily recovered, impressive catalytic activity and efficient for biodiesel production with high reusability.

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

PEMBANGUNAN MANGKIN BERASASKAN KARBON SULFONAT DARI GLISEROL DAN SISA HASIL PENCERNAAN LEMBU UNTUK PENGHASILAN BIODIESEL DARIPADA MINYAK ASID LEMAK BEBAS TINGGI

Oleh

SHATESH KUMAR A/L SANGAR

Oktober 2020

Pengerusi:Prof Datuk Taufiq Yap Yun Hin, PhD
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Dalam kajian ini, pemangkin berasaskan karbon sulfonat yang cekap dan mesra alam telah disediakan daripada gliserol (CG) dan sisa pencernaan lembu (CD) kemudian ianya difungsikan dengan asid sulfurik (H_2SO_4) pekat pada masa pensulfonan yang berbeza. Sifat fisiko-kimia pemangkin telah dikenalpasti dengan menggunakan pembelauan sinar-X (XRD), fourier mengubah inframerah spektroskopi (FTIR), spektroskopi fotoelektron sinar-X (XPS), analisis terma gravimetric (TGA), programsuhu-nyahjerapan ammonia (TPD-NH3), analisis luas permukaan Brunauer-Emmett-Teller (BET), tekanan ubah mikroskop imbasan elektron (VPSEM), mikroskop transmisi elektron resolusi tinggi (HR-TEM), pendarfluor sinar-X (XRF) dan analisis elemen CHNSO. Karbon yang telah disulfonasikan dengan H_2SO_4 selama 10 jam (pemangkin $SCG_{-(10)}$ dan $SCD-_{(10)}$) dipilih untuk digunakan dalam kajian pengoptimuman kerana kesan sinergistik sifat fiziko- kimia yang baik termasuk jumlah asid tinggi dan sulfur yang melekat pada karbon. Jumlah sulfur dan asid meningkat dengan ketara setelah disulfonasi pada masa yang berbeza; di mana, pemangkin $SCG_{-(10)}$ dan $SCD-_{(10)}$ menunjukkan jumlah keasidan tertinggi masing-masing iaitu 35117.14 µmol / g dan 16653.49 µmol / g. Pengesteran sulingan asid lemak sawit (PFAD) menggunakan pemangkin $SCG-_{(10)}$ telah dioptimumkan melalui teknik satu-pemboleh ubah pada satu masa, dan berjaya memperoleh FAME sebanyak 97.8% pada tahap optimum iaitu masa tindak balas 1 jam, suhu tindak balas 90 ° C, berat pemangkin 5 wt.%, dan nisbah molar metanol kepada minyak 18: 1. Pemangkin $SCG-_{(10)}$ berjaya digunakan semula sebanyak 7 kitaran dan didapati bahawa aktiviti pemangkin kekal dengan > 96% FAME bagi tiga kitaran pertama. Biodiesel yang telah dihasilkan memenuhi piawaian biodiesel antarabangsa iaitu EN14214 dan ASTM D6751. Jumlah sulfur dalam minyak biodiesel lebih rendah daripada had maksimum ASTM D6751. Pendekatan Taguchi dengan reka bentuk eksperimen empat parameter pada tahap empat, L-16 (4^4) digunakan untuk memandingkan dengan keputusan hasil eksperimen.

Suhu tindak balas adalah parameter kawalan yang paling banyak mempengaruhi bagi penghasilan biodiesel dengan nisbah S / N dan nilai F yang tinggi. Keadaan optimum untuk pengeluaran biodiesel tertinggi adalah pada suhu tindak balas pada tahap 4 (90 ℃), nisbah molar metanol kepada PFAD pada tahap 3 (18: 1), berat pemangkin pada tahap 4 (6 wt.%) dan masa tindak balas pada tahap 3 (1.5 jam). Oleh sebab pemangkin $SCG_{-(10)}$ menunjukkan prestasi pemangkin yang baik dalam pengesteran PFAD, maka ia turut digunakan bagi pengesteran-transesterifikasi serentak sisa minyak masak (WCO) dan minyak lemak ayam (CFO). Pengeluaran metil ester dari WCO dan CFO juga berjaya dilakukan dengan menggunakan pemangkin $SCG\text{-}_{(10)}$ dan memperoleh hasil FAME 92.3% (keadaan optimum berat pemangkin 5 wt% dengan nisbah molar metanol kepada WCO, 22:1 selama 3 jam masa tindak balas dan 100 ℃ suhu tindak balas) dan 90.8% (keadaan dioptimumkan berat pemangkin 5 wt% dengan nisbah molar metanol kepada CFO 18: 1 untuk masa tindak balas 1 jam dan suhu tindak balas 70 ℃), masing-masing. Tambahan pula, pemangkin $SCD\text{-}_{(10)}$ digunakan dalam pengesteran PFAD dan mencapai penukaran FFA tinggi 96.5% pada parameter optimum nisbah molar metanol kepada PFAD 18:1, 4 wt% berat pemangkin dan suhu tindak balas 90 ° C bagi 1 jam masa tindak balas. Pemangkin $SCD_{-(10)}$ mampu menukarkan PFAD menjadi biodiesel dengan FAME> 90% untuk 3 kitaran berturut-turut. Kesimpulannya, kedua-dua pemangkin $SCG\text{-}_{(10)}$ dan $SCD_{-(10)}$ dapat dipulihkan dengan mudah, aktiviti pemangkin yang mengagumkan dan cekap untuk pengeluaran biodiesel dengan kebolehan guna pakai semula yang tinggi.

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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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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) are adhered to.

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LIST OF ABBREVIATIONS

FAME	Fatty acid methyl ester
FFA	Free fatty acid
TGs	Triglycerides
GHG	Greenhouse gases
NO_x	Nitrogen dioxide
AOAC	American Society for Testing and Materials
EN	European Standard
AV	Acid Value
SV	Saponification Value
XRD	X-Ray diffraction spectroscopy
TGA	Thermogravimetric Analysis
BET	Brunauer-Emmett-Teller
CHNS	Carbon, Hydrogen, Nitrogen, Sulfur element analysis
FTIR	Fourier Transform Infrared Spectroscopy
NH3-TPD	Ammonia-Temperature Programmed Desorption
VPSEM	Variable Pressure Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray
GCMS	Gas Chromatography-Mass Spectrometer
GCFID	Gas Chromatography-Flame Ionization
Wt. %	Weight percentage
CG	Carbon derived glycerol
$SCG\text{-}_{(2)}$	Sulfonated carbon derived glycerol catalyst reflux at 2 hours
$SCG\text{-}_{(5)}$	Sulfonated carbon derived glycerol catalyst reflux at 5 hours
$SCG\text{-}_{(10)}$	Sulfonated carbon derived glycerol catalyst reflux at 10 hours
CD	Carbon derived Cow dung
$SCD\text{-}_{(2)}$	Sulfonated carbon derived cow dung catalyst reflux at 2 hours
$SCD\text{-}_{(5)}$	Sulfonated carbon derived cow dung catalyst reflux at 5 hours
$SCD\text{-}_{(10)}$	Sulfonated carbon derived cow dung catalyst reflux at 10 hours
CFO	Chicken fat Oil
PFAD	Palm Fatty Acid Distillate
WCO	Waste Cooking Oil
H_2SO_4	Sulfuric Acid
OECD	Organization for Economic Cooperation and Development
IEA	International Energy Association
MPOB	Malaysia Palm Oil Board
DOE	Design of experiment
ANOVA	Analysis of variance
S/N ratio	Signal to noise ratio

CHAPTER 1

INTRODUCTION

1.1 World Energy Demand

The earth is facing with double crisis of increment in environmental pollution and declination of fossil fuels which due to high consumption of petroleum as main source of energy (Nur Syazwani *et al*., 2019). Petroleum consists of hydrocarbon with various molecular weight and it used in many industries in the world. There are many products that can be produced from the raw petroleum (crude oil) such as gasoline, jet fuel, bitumen and wax. Several process are required in order to produce particular products from the petroleum. Generally the process is known as petroleum refining where the first step is separation by using crude oil distillation unit which often referred to the atmospheric distillation because it operates slightly above atmospheric pressure. The high consumption of petroleum caused many environmental problems such as global warming, increased in greenhouse gasses (GHG) emissions and brought the earth to unsustainable environment (Kumar *et al*., 2019).

The world oil consumption for OECD and Non-OECD countries from 1990 to 2035 (International Energy Outlook EIA, 2019) as shown in Figure 1.1. World marketed energy consumption grows by 52% from 2008 to 2035. Total world energy use rises from 505 quadrillion British thermal units (Btu) in 2008 to 619 quadrillion Btu in 2020 and 770 quadrillion Btu in 2035. The most rapid growth in energy demand from 2008 to 2035 occurs in nations outside the Non-OECD countries. The most increases in energy consumption came from non-OECD countries due to strong economic growth, increased access to marketed energy, and rapid population growth that led to rising of energy consumption.

In 2035, fossil fuels mainly petroleum will continue become the dominant fuel choice with only 14% of renewable energy consumption. This is also correlated to the current situation which rising in energy use in developing countries such as China and India. Energy International Association (EIA) estimated that the world energy consume will increase by around 53% by 2035 (BP Statistical Review, 2019). According to EIA, China is targeted to use around 68% more energy than the United States by 2035 as recently China became the world's top energy consumer.

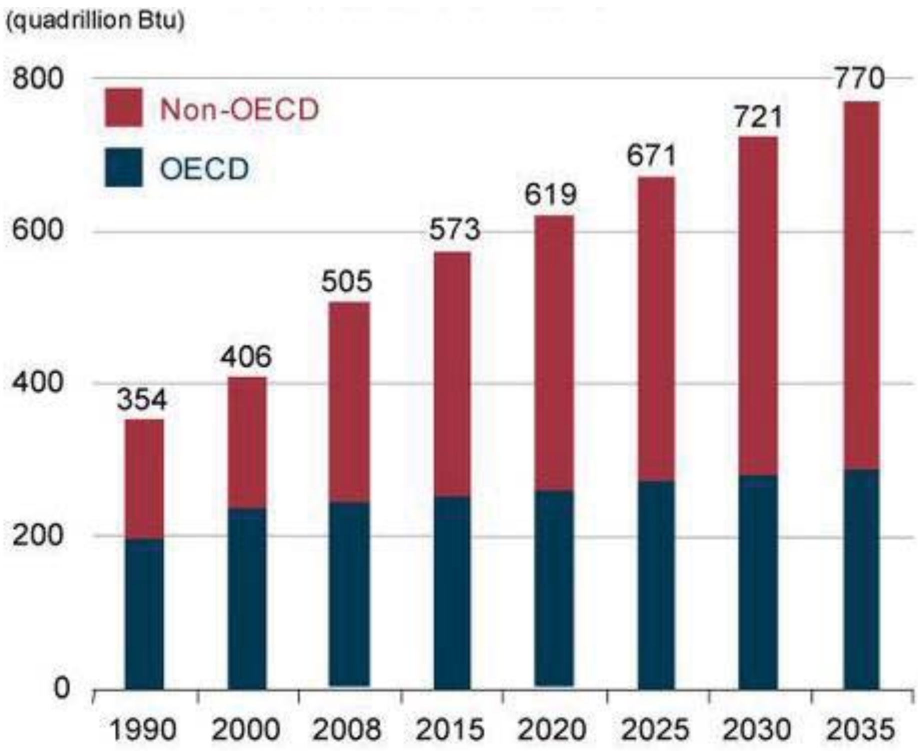

Figure 1.1: World oil consumption for OECD and non-OECD countries 1990 – 2035 [Source: International Energy Outlook EIA, 2019]

The highest world energy consumption is the crude oil because many industries depends on the crude oil as the main source of the energy and the demand of crude oil always increases. The demand increase as industry that use oil as source of energy increase and this condition is not parallel to the supply of crude oil in the world. According to International Energy Agency, the crude oil are used in different sectors and transportation sector showed the highest percentage for the usage of crude oil as shown in Figure 1.2 (IEA Key World Energy Statistic, 2019). Global transportation energy consumption is dominated by two fuels: motor gasoline (including ethanol blends) and diesel (including biodiesel blends). The transportation sector has been the largest consumer of petroleum products since at least 1949, the earliest year for which EIA has data. After transportation, the industrial sector accounts for the second-largest share of petroleum consumption, accounting for about 23%. Examples of industrial use of petroleum products include hydrocarbon gas liquids used as feedstock for chemicals and plastics, as well as asphalt and road oil used for construction and road maintenance.

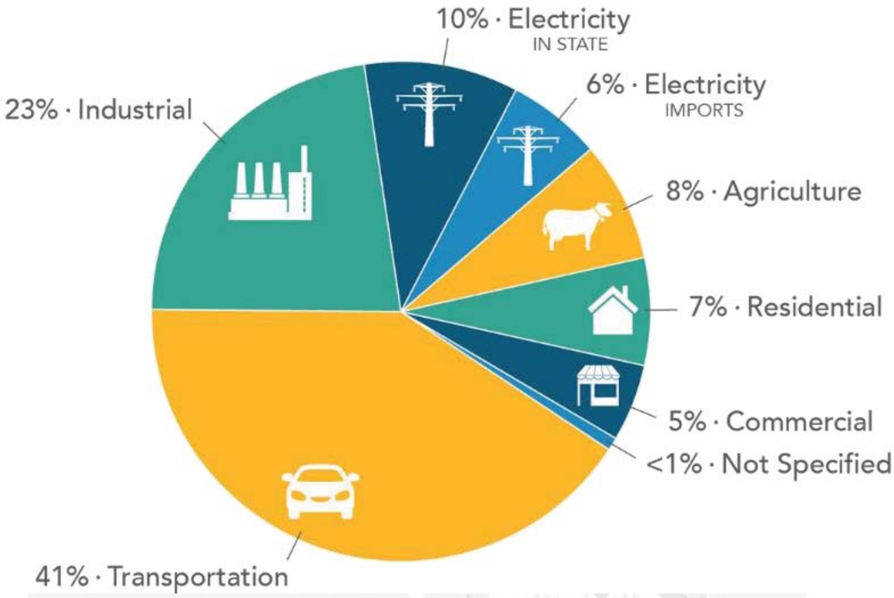

Figure 1.2: Global crude oil consumption by sectors [Source: IEA Key World Energy Statistic 2019]

United Nations recently reported that the atmosphere predicted to warm up by 1.5 °C in 20 years' time that may causes massive food shortages and other destruction. The consumption of fossil fuels lead to rapid increase in carbon dioxide emission (Huang et al., 2017) . The increased in global average temperature will also increases the amount of greenhouse gas emissions (Hewage *et al*., 2019). The Industrial Revolution and high consumption of fossil fuels led to increment in concentration of CO_2 to 400 ppm for the first time in 800,000 years. Meanwhile, the global average temperature also rise about more than 1 °C since the pre-industrial times. There are two source of carbon emission which is embodied carbon (transportation, manufacturing and construction) and operational carbon (building). According to Global Carbon Project 2019, last year China emitted CO_2 about 28%, United States at 15%, followed by European Union around 9%, India at 7% and Russia 6%. From Figure 1.3, in 2019 reported that around 36.8 Gt CO_2 emissions was produced and it was 62% higher than the year 1990 (United Nations Climate Change Annual Report, 2019). The global carbon emission also was increased from 2 Gt CO2 to above 36.8 Gt CO_2 after 119 years. Due to high emission of carbon dioxide (CO_2) worldwide which contribute towards negative impact such as global warming and greenhouses effect, there are essential to identify the best alternative renewable energy to replace the diesel fuel that may overcome the high demand of energy consumption (Farabi *et al*., 2019).

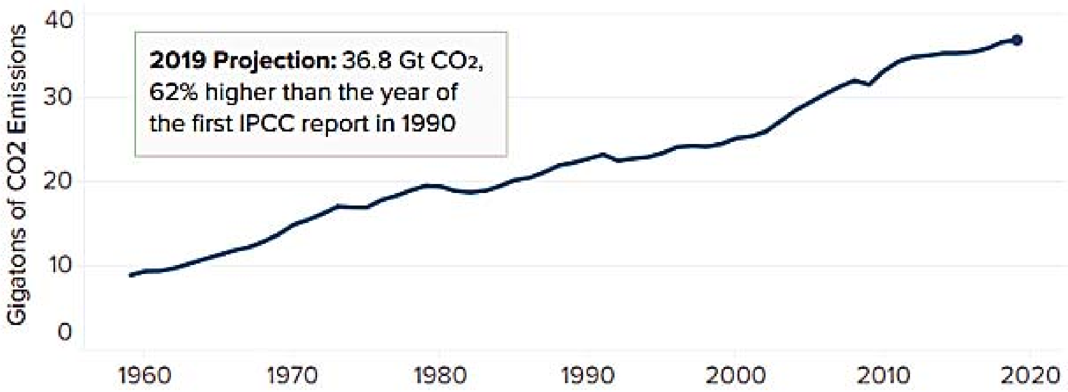

Figure 1.3: Global carbon dioxide emissions [Source: United Nations Climate Change Annual Report 2019 & Global Carbon Project 2019]

1.2 Renewable Energy

Renewable energy sources (RESs) is also well-known as alternative energy. Commonly RESs are primary energy resources that readily available in nature. It is derived from those natural through mechanical, thermal and growth processes that continuously reproduce certain quantities of energy when required. RESs use local resources have potential to provide energy with zero or low emission of air pollutant and greenhouse gases (Pandey *et al*., 2010). Renewable energy technologies produced profitable and commercial energy by converting natural materials into useful form of energy (A. Kumar *et al*., 2010).

Producing energy from the renewable sources promises as clean energy and provides few benefits such as reduce the dependency towards fossil fuels (Kumar et al., 2019). Generally, renewable energy sources are easily generated or produced but it is restricted in the amount of energy that is accessible per unit of time (A. Kumar et al., 2010). The significant benefits of using renewable energy resources are providing energy efficiency over wide geographical areas. Rapid consumption of renewable energy would resulted in high energy security and sustainable economic development. Therefore, renewable energy also minimise the environmental effects such as air pollution by burning of fossil fuels and also decrease the premature mortalities due to pollution (Lokman *et al*., 2015).

Figure 1.4 shows that renewable energy contributed around 11% towards total world energy consumption in 2018. One of the highest contributor to percentage of renewable energy is biofuels. Biomass fuels hold great promises as a component of Clean

Development Mechanism (CDM) strategies in the Kyoto Protocol to reduce greenhouse gas emissions to acceptable levels (Luiz *et al.*, 2008). Renewable energy such as biofuel promising alternative solution.

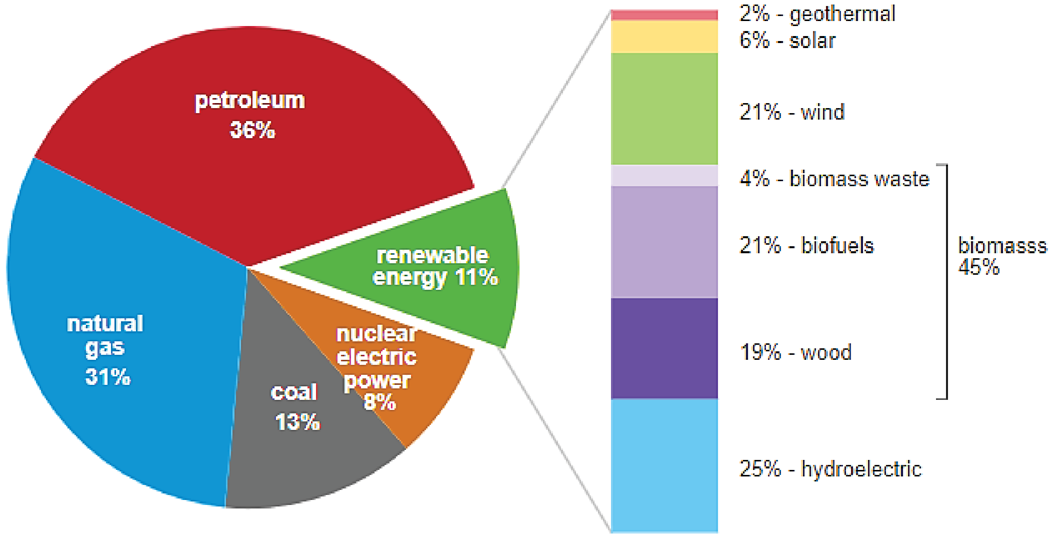

Figure 1.4: Total world energy consumption in 2018 [Source: Statistic, K. W. E. (2019)]

1.3 Biodiesel as alternative sources of petroleum

Biodiesel is an efficient, clean and 100% natural energy alternative to petroleum based fuels. Biodiesel is non-toxic, biodegradable, produces lower greenhouse gaseous (GHG) emission (HC, CO_2, SOx and NOx) and high lubricity which has potential to replace the non-renewable energy (Kirubakaran *et al.*, 2018; and Koberg *et al.*, 2011). It can be produced from raw materials containing fatty acid that are linked to other molecules or present as free fatty acid. Feedstock such as edible oil, animal fats, waste greases, and edible oil processing waste can be used for biodiesel production (Patil & Deng, 2009). In addition, biodiesel can be defined as a vegetable oil or animal fat-based diesel fuel consisting of long chain alkyl such as methyl, propyl or ethyl esters (Feyzi *et al.*, 2013). Biodiesel is not only used for transportation but have many other uses. Since biodiesel are composed by alkyl ester of fatty acids, it becomes an effective solvent for oil. It can clean oil spills caused by petroleum since it is biodegradable.

Even though petro-diesel and biodiesel are different in sources, both can be used as burning materials of various industries. Petro-diesel are one of petroleum product that contain about 95% saturated hydrocarbon and 5% aromatic compounds (Ciolkosz *et al.*, 2015). Biodiesel which has higher lubricity and oxygen content consist almost entirely of chemicals called fatty acid methyl esters (FAME) and unsaturated "olefin"

(Ciolkosz *et al*., 2015). High oxygen content in biodiesel reduces emission of unwanted gaseous hence can reduce pollution (J. Gupta *et al*., 2016). With appearance of golden to dark brown liquid, biodiesel has higher flash point compared to petroleum. This proved that biodiesel are stable thus easier to handle and store. Green diesel is known as renewable diesel or second generation of biodiesel (Kalnes *et al*., 2007). It derived from biological sources and biomass that are chemically not ester which are lighter than the average density required diesel. Table 1.1 shows the different between biodiesel, green-diesel and petroleum diesel properties respectively.

Table 1.1: Physico-chemical properties of biodiesel, green diesel and petroleum (Kalnes *et al*., 2007; Alsultan *et al*., 2017; Smith *et al*., 1939; and Mansir *et al*., 2017)

	Petroleum	**FAME Biodiesel**	**Green Diesel**
Oxygen %	0	11	0
Cetane	40-55	50-65	75-90
Energy Density, MJ/kg	43	38	44
Sulfur,ppm	<10	<2	<2
Cold Flow	Baseline	Poor	Excellent
Oxidative Stability	Baseline	Poor	Excellent

There is also advantages when the use of biodiesel as an alternative to or when blended with petroleum diesel where it gives out benefits such as reduce carbon dioxide emission, reduce emission of particulate matter, reduce emission of unburned hydrocarbon and sulfur and benzene free product (Zillillah *et al*., 2012).

1.4 Problem Statement

Homogeneous catalyst is difficult to remove as its required a lot of water to purify the produced biodiesel and subsequently the cost of biodiesel production will increase (Nur Syazwani *et al*., 2015). Furthermore, low cost material contain high FFAs that are not compatible with base catalyst used in esterification causing problem like incomplete recovery catalyst and it make the high purification cost and reduce yield (Lokman, IM *et al*., 2015). It also can lead to saponification process that must be avoided in biodiesel production. (Kawashima *et a*l., 2008) claimed that heterogeneous catalyst is low cost and showed minimal environment impact which also effective for biodiesel production due to the purification processes under mild conditions and possibility of simplifying the production. Thus, heterogeneous acid catalyst is more preferable. As reported previously, the esterification reaction using high FFA feedstock was conducted using heterogeneous catalyst such as sulphated metal oxide *(Taufiq-Yap et al*., 2014; Nur Syazwani *et al*., 2015; Wan *et al*., 2015; Taufiq-Yap *et al*., 2011) and functionalised carbon nanotubes (Shuit *et al*., 2013; Shuit *et al*., 2015; Shu *et al*., 2009). The production cost of these catalysts are expensive meanwhile it need complex synthesis process or route to prepare the catalyst. Thus, utilization of carbon based catalyst be the best choice for the biodiesel production.

Due to highly abundant and available of waste materials which are sources for preparation of carbon catalyst that commonly used in FAME production as heterogeneous catalyst. The use of carbon-based catalysts offers certain advantages over metal catalysts showing to their durability, temperature resistant, and low cost. Carbon-based solid acid catalyst considered as an ideal and promisingly catalyst for many reactions due to their thermal stability and mechanical properties. However, utilization of carbon catalyst without any acid activation process is not suitable for high FFA feedstock such as PFAD and WCO since it will cause an unfavour saponification reaction. Thus, synthesis of sulfonated carbon derived glycerol and cow dung catalyst are expected to produce low cost heterogeneous catalyst which applicable and reasonable for biodiesel production. Due to large amount of glycerol availability and production, it is feasible and viable to be utilise in few applications such as biodiesel production. Meanwhile, previously the cow dung was used as bio-fertiliser, bio-pesticides and as a feedstock for the production of bio-char and bio-oil via pyrolysis method. This proves that cow dung is viable to be use in various application and showed remarkable result. Both glycerol and cow dung are waste material which will reduce the cost of biodiesel production.

Furthermore, process duration is a main problem in biodiesel production industry where it took relatively long time to obtain a satisfy FAME yield. Rao *et al*., (2011) took high relative reaction time about 24 h to convert Canola Oil to FAME using de-oiled canola meal derived carbon catalyst. Meanwhile, Hosseini *et al*., (2015) obtained 89% FFA conversion for esterification of PFAD using carbon coated monolith catalyst at reaction time 4 h. The reaction took longer time to convert FFA to FAME is due to low amount of acidity in the catalyst and low surface area. Generally, the acidity in catalyst will helps to enhance the conversion of FFA to FAME with shorter time of reaction. Besides, Zhao *et al.,* (2018) claimed that higher time of reaction will cause the reaction to reverse and degrade the solid catalyst. The shorter reaction time has potential to reduce the cost of biodiesel production. To overcome this problem, the use of catalyst with highly sulfonated via acid activation process using concentrated acid may help to improve the production of the biodiesel yield.

It has been reported that the cost of feedstock contribute around 75 % of the overall cost of FAME production (Atabani *et al*., 2013). The usage of edible oil has raises up the food price and increases the area of arable land, thus edible oil cannot be considered as a sustainable feedstock. Therefore, one of the best solution of overcoming this limitation is by using non-edible oils as low cost biodiesel feedstock for biodiesel production (Bhuiya *et al*., 2014). The utilization of low cost feedstock such as chicken fat oil (CFO), palm fatty acid distillate (PFAD), and waste cooking oil (WCO) with low cost catalyst precursor which also produce from waste product for the biodiesel production are more economical as they can reduce the production cost can reduce the overall cost of biodiesel production.

1.5 Objectives

This research aims to synthesize sulfonated solid acid carbon based catalyst derived from two sources which are glycerol and cow dung. This research also focused on the physicochemical properties of the synthesized catalysts and the feasibility of the FAME production from the low cost feedstock such as PFAD, WCO and CFO. There are five main objectives in this research.

1) To synthesize and investigate the physico-chemical properties of sulfonated solid acid carbon based catalysts derived glycerol and cow dung
2) To optimize condition for the esterification reaction of PFAD by using prepared sulfonated carbon based catalysts via traditional method and Taguchi approach.
3) To optimise condition for the simultaneous esterification and transesterification reaction of WCO and CFO using sulfonated carbon catalyst derived glycerol.
4) To investigate the reusability of synthesized catalysts.
5) To evaluate and determine the fuel properties of PFAD methyl ester.

1.6 Scope of Research

In this study, the catalyst is prepared from glycerol (by product of biodiesel industry) via partial carbonization and sulfonated processes. The sulfonation process was conducted in different time (2, 5 and 10 h). The catalyst produced undergoes characterization by FTIR, XRD, VPSEM, NH_3-TPD, TGA, BET and CHNS. The catalytic performance for all catalysts were screen and determined at certain condition parameter in order to choose the best catalyst with high catalytic performance for the optimization study. The effect of the molar ratio of methanol to oil, catalyst loading, reaction temperature and reaction time were investigated by conducting esterification reaction of PFAD. The methanol ratio that been used 12:1 to 24:1. Meanwhile, the temperature that use is 60 – 110 ^{o}C and time from 1-5h was varied with catalyst loading form 1-6wt%. Reusability test is a test applied on catalyst where several cycle of reaction conducted by using same catalyst without modifying the catalyst and the amount of sulfur leached was determined by using CHNS. The catalyst also used in simultaneous esterification and transesterification of WCO and CFO. Taguchi approach was used in optimization of esterification from PFAD to determine the optimal condition and the most influenced control parameter in biodiesel production. The biodiesel produced is analysed using GC. The quality assessment and PFAD methyl ester properties was determined by using ASTM D6751 and EN 14212 standard.

Next, the carbon derived cow dung was synthesized and sulfonated at different time of sulfonation (2, 5 and 10 h). The synthesized catalysts were characterized by using XRD, FTIR, NH3-TPD, BET, CHNS, XRF and FESEM to determine the physic-chemical properties of the prepared catalysts. The catalyst with high catalytic performances was chosen by conducting esterification reaction at certain operating condition. The esterification reaction of PFAD was conducted by investigating the effect of reaction parameter such as reaction temperature, reaction time, methanol to PFAD molar ration and catalyst loading. The reusability was performed under optimized reaction parameter. The amount of sulfur leached in biodiesel was determined using CHNS analyser.

1.7 Organization of the Thesis

The thesis consisted of **six chapters**. The **Chapter One** introduces regarding the world energy demand mainly the consumption and production of oil, renewable energy and the advantage of using biodiesel as alternative transportation fuel in daily life. It also consists of the problem statements, the main objectives of research, and scope of research. The **Chapter Two** consists of comprehensive literature review that based on previous reported research of biodiesel. Besides, it also explains the types of feedstock for biodiesel production, methyl ester production methods and technologies in biodiesel production. The types of catalysts such as homogeneous, heterogeneous and enzyme were explained in detail in this chapter. Meanwhile, **Chapter 3** covers the method and process for the catalyst preparation, oil and catalyst characterization. It also consists of experimental set up for biodiesel production using conventional reflux system for esterification reaction. **Chapter 4** discusses and explains regarding the characterization of sulfonated carbon catalyst derived glycerol, characterization of PFAD, WCO and CFO as low cost feedstock, optimization reaction for esterification of PFAD, WCO and CFO, the optimization of biodiesel production PFAD by using Taguchi method using four parameters at four-level L-16 (4^4) of experiment design and the reusability test. The amount of sulfur leached into FAME, qualitative analysis of biodiesel and fuel properties of PFAD methyl ester according to ASTM D6751 and EN14121 standards also discussed in this chapter. Therefore, **Chapter 5** explains regarding characterization of sulfonated carbon derived cow dung catalyst, optimization reaction for esterification of PFAD and the reusability test. Lastly, **Chapter 6** concludes the significant results and outcomes of this research with few recommendation for future work.

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