BIODIESEL PRODUCTION USING AMINATED FIBROUS POLYMER CATALYST IN PACKED CONTINUOUS REACTOR

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To my beloved parents and my sisters who are always supporting and encouraging me

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ABSTRACT

A solid polymer catalyst in a form of aminated ion exchange fibers having basic functionality was prepared by amination (treatment with triethylamine) of a fibrous grafted copolymer precursor obtained by radiation induced grating of glycidyl methacrylate (GMA) onto polyethylene (PE) fibers. The obtained aminated fibrous catalyst was characterized with Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and thermal gravimetric analysis (TGA) to confirm the presence of the functional (amine) groups. Degree of amination of 30.65% was obtained together with an amine group density of 1.89 mmol/g. The performance of the obtained fibrous polymer catalyst was tested for biodiesel production by the transesterification of triacetin with methanol using packed bed column under dynamic conditions (temperature, methanol/oil ratio and residence time). The ranges of independent variables were reaction temperature (50°C-90°C), residence time (1-5 h) and methanol:triacetin ratio (12:1-24:1). The obtained product was characterized by GC-MS to provide evidence for the conversion of triacetin to methyl acetate. The highest conversion of 90.06% was obtained at 90°C with 18:1 molar ratio and 2 h for residence time. Meanwhile, kinetic model and studies was applied. Reaction rate was calculated k=0.383 liter2 mol-2 hour-1 for the order of the reaction 2. Activation energy was calculated 46.89 kJ/mol with pre-exponential factor 6.016×10^6 based on Arrhenius equation. The fixed bed reactor with the fibrous solid polymer catalyst set a modular process for production of biodiesel based on transesterification of triacetin. The obtained solid polymer catalyst under the optimum conditions provides sufficient conversion without purification and separation for biodiesel which might affect the properties of the product.

ABSTRAK

Sejenis pemangkin polimer dalam bentuk serabut pernukaran ion yang diaminasi dengan kefungsian bes telah disediakan melalui pengaminasian (rawatan dengan triethylamine) serabut kopolimer pelopor yang diperolehi menggunakan cantuman secara sinaran radiasi oleh glycidyl methacrylate (GMA) ke atas serat polyethylene (PE). Penyifatan pemangkin berserabut yang diaminasi tersebut dilakukan dengan spektroskopi inframerah jelmaan Fourier, mikroskop elektron penskanan dan analisis gravimetri terma mengesahkan kehadiran kumpulan berfungsi. Darjah aminasi 30.65% bersama dengan ketumpatan kumpulan amina 1.89 mmol/g diperolehi. Prestasi pemangkin polimer berserabut tersebut diuji untuk pengeluaran biodiesel melalui transesterifikasi trisetin dengan metanol menggunakan ruang katil dibungkus pada kondisi-kondisi dinamik (suhu, metanol / nisbah minyak dan masa mastautin). Julat pembolehubah tak bersandar ialah suhu tindak balas (50°C-90°C), masa mastautin (1-5 h) dan nisbah metanol:trisetin (12:1-24:1). Produk yang diperolehi disifatkan menggunakan GC-MS untuk memberi bukti penukaran trisetin kepada methyl acetate. Penukaran tertinggi 90.06%. diperolehi pada 90°C dengan 18:1 nisbah molar dan 2 jam untuk masa mastautin. Sementara itu, model kinetik dan kajian telah diaplikasikan. Kadar tindakbalas dikira, k=0.383 mol2liter-2jam-1 untuk order tindak balas 2. Tenaga pengaktifan dikira 46.89 kJ / mol dengan faktor pra eksponen 6.016×10^6 berdasarkan persamaan Arrhenius. Reaktor katil tetap berisi pemangkin polimer berserabut menetapkan satu proses bermodul untuk pengeluaran biodiesel berdasarkan transesterifikasi trisetin. Pemangkin polimer yang diperolehi dibawah keadaan optimum memberikan penukaran mencukupi tanpa penulenan dan pemisahan untuk biodiesel yang mungkin mempengaruhi sifat produk akhir.

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LIST OF ABBREVIATION

ASTM	-	American society for testing and materials
B100	-	Pure biodiesel
B20	-	20% biodiesel blend with fuel
B6	-	6% biodiesel blend with fuel
CEN	-	European committee for standardization
CFFP	-	Cold filter plug point
CN	-	Cetane number
СР	-	Cloud point
DAG	-	Diacylglycerol
DETA	-	Diethylenetriamine
DMF	-	Dimethylformamide
DSC	-	Differential scanning calorimetry
EGR	-	Exhaust gas recirculation
FA	-	Fatty acid
FAME	-	Fatty acid methyl esters
FFA	-	Free fatty acid
GHG	-	Greenhouse gas
GMA	-	Glycidyl methacrylate
HHV	-	Higher heating value
LHV	-	Lower heating value
MAG	-	Monoacylglycerol
NVO	-	Neat sunflower oil
NWPE	-	Nonwoven polyethylene
PE	-	Polyethylene
РР	-	Poor point

PS	-	Polystyrene
PVF	-	Polyvinyl Fluoride
RSM	-	Response surface methodology
SCR	-	Selective catalytic reduction
SEM	-	Scanning electron microscope
TAc	-	Triacein
TAG	-	Triacylglycerol
TEA	-	Triethylamine
TETA	-	Triethylenetetramine
THF	-	Tetrahydrofuran
Tw	-	Polyoxyethylene sorbitan monolaurate
WVOD	-	Domestic waste oil
WVOR	-	Fast food restaurant waste oil

LIST OF SYMBOLS

А	-	Alcohol
D	-	Di-glyceride
d	-	Inner column diameter
D_{g}	-	Degree of grafting
E	-	Free acid ester
h	-	Bed height
Ma	-	Molecular weight of TEA
M_{G}	-	molecular weight of GMA
S (H ⁺)	-	Cation exchange resin
S(OH ⁻)	-	Anion exchange resin
Т	-	Triglyceride
Wa	-	Mass of the aminated PE-g-GMA
\mathbf{W}_{i}	-	Polymer weight after grafting
Wo	-	Polymer weight before grafting
τ	_	Residence time

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CHAPTER 1

INTRODUCTION

1.1 Background

The quick development of population, transport and urbanization is today's energy crisis. Fossil fuel as a non-renewable source, chips in 80% of the world's energy demand (Demain, 2009; Huang et al., 2012; Ng et al., 2010). Due to this unsustainable energy system, demand for other renewable power/fuel is increasing. Major alternatives to fossil fuels are nuclear power and hydroelectricity (Cseke et al., 2009). Biofuels are coming out as one of the green option for alternative and renewable energy. In developed countries there is an increasing trend towards the use of modern technologies and efficient bioenergy systems using a range of biofuels, which are more economical than fossil fuels. Biofuels are produced from biomass. Biomass is biological material come from living, or recently living, organisms. Biofuel refers to solid, liquid or gas material for the transport sector that are predominantly produced from biomass or organic matter. Biofuels offer many benefits, including sustainability, reduction of greenhouse gas emissions (Bessou et al., 2011; Demain, 2009). According to the state of the biofuels at room temperature, they can be classified easily. There are gaseous bio-fuels, like biogas from different sources and syngas (coal gas); liquid biofuels including biodiesel, bioethanol, vegetable oil and bio-oil; and solid biofuels such as wood and charcoal. Bioethanol and biodiesel are two general biomass products in liquid form that can replace gasoline and diesel fuel (Figure 1.1). Bioethanol is obtained from the aerobic fermentation of carbohydrate-rich biomass, often used in blends. In plant materials,

carbohydrates (e.g. cellulose and hemicelluloses) can be hydrolyzed and formed into sugars. The fermentation is an anaerobic biological process in which the sugars are converted into alcohol by the action of microorganisms, generally yeast. The obtained alcohol is ethanol. The reaction between animal fat or vegetable oil with alcohol produces biodiesel. This reaction is called transesterification (Bessou, et al., 2011; Cseke, et al., 2009; Demain, 2009; Huang, et al., 2012; Murphy, 2011; Ng, et al., 2010; Romano and Sorichetti, 2011; Roy, 2007).



Figure 1.1 Major Sources of Biofuels

1.2 Biodiesel

Many years before Rudolf Diesel's presented his diesel engine, oil crops and animal fats have been used as sources of fuels, for a long time. Vegetable oil's Transesterification was done by J. Patrick and E. Duffy, in early 1853. 40 years later (on August 10, 1893), Mr. Diesel invited a cylinder with a flywheel at its base, made from iron in 3meter which use up its own power for the first time (Cseke, et al., 2009). Diesel ran his car on pure peanut oil at the 1901 in Paris (Murphy, 2011). Biodiesel as a clean burning fuel for diesel engines is made from internally produced, renewable fats and oils like sunflower oil, without aromatic or sulfur compounds. Most of the Plant oils are contained long-chain triacylglycerol which can be used directly as fuels or lubricants, while it is usable to a few of engine types. On the other hand, the triacylglycerol can be formed to methyl esters somehow similar to petroleum hydrocarbons, and glycerol. Recently environmental assesses have made effect and decreased price differences for vegetable oils as an alternative source. Although the World use fossil petroleum, propensity to vegetable oils as fuels in inner combustion engines were afforded in several countries between 1920s and 1930 (Cseke, et al., 2009). Biodiesel can be used in engines without adjustment or with blending. It is a great alternative choice for our environment due to reducing dependence on our fossil fuel and bringing more value and credit for agricultural product markets. As shown in Figure 1.2, the usage of feedstock related with local region and climate conditions. Therefore different soils are using different types of oil. At present, the dominant feed stocks are rapeseed oil in Europe, soybean oil in the U.S., and palm oil in South East Asia. Animal fats (especially beef tallow) and used cooking oil (also known as yellow grease) are small but important market for biodiesel in many places. Other vegetable oils with a real or potential commercial interest that supply biodiesel stocks are canola, coconut, corn, sunflower and jatropha (Huang, et al., 2012).



Figure 1.2 Main sources of biodiesel in worldwide

1.3 Problem Statement

The most important obstacle for biodiesel production is feedstock and catalyst for the process which more expensive than the petroleum diesel. Technologies for Biodiesel processes will cost-effective, in case of reduction material costs. In addition, according to the demands for renewable fuel instead of petroleum, there is no processes which can provide the high production of biodiesel in sufficient quality, quantity and production speed to be acceptable for total demands and Industrial scale. Pyrolysis has some drawbacks include corrosivity, low calorific value, high viscosity characteristic of aging, making improper crude biodiesel to its direct use as an alternative fuel. Most of the produced biodiesel are blended with petro-diesel. Every day, scientists introduce new methods and technologies, but biodiesels still is not completely substitutable choice for fuels and need more qualifications in processes and materials that use.

Upgrade catalyst methods give a low yield improved oil and could produce undesirable products (e.g., deposition of coke on the catalyst surface), giving high cost of product recovery. According to this, for known feed-stocks, oils and fats and specific technologies for reaction, catalyst and reaction variables still have a wide variety to improve biodiesel production.

Solid polymer catalyst as a heterogeneous catalyst can provide many advantages to overcome these problems. Solid catalysts are recyclable and have longer lifetime for processes. Usually they are used for membrane processes to remove impurities like heavy metals as ion exchange resins. With strong functional group on solid catalysts, it can be used in transesterification reactions as membrane too. They provide easy separation process, simple ester and glycerol purification and make the process potentially cheaper. In addition homogenous catalyst must be separated from products which can effect products, while heterogeneous catalyst is not needed. Anion ion exchange fibrous for lower crosslinking density and smaller particle size comparing to cation form, is superior option due to high basic activity, selectivity and non-corrosiveness provide high conversion and reaction rate. Polyethylene grafted by Glycidyl methacrylate as a common base polymer, modified by Triethylamine as a strong ammonium function group was used as an efficient solid polymer catalyst for biodiesel production.

1.4 Research Objectives

The main objective of this research is to explore the performance of the obtained catalyst for biodiesel production under dynamic conditions. The objectives of this study are listed as below:

- i. To prepare solid polymer catalyst by activating the precursor by animation reaction.
- ii. To characterize the obtained solid polymer catalyst.
- iii. To investigate the effects of reaction parameters on the conversion of triacetin to biodiesel in a packed bed column system under dynamic conditions.

1.5 Scope of Research

To achieve the objectives of this study, the following scope of work was pursued.

- i. Firstly, NWPE which was grafted with glycidyl methacrylate (GMA) was modified by triethylamine solution at 90°C for 24 h to introduce amine groups. The aminated catalyst was then alkalinized by a treatment with NaOH.
- The prepared solid polymer catalyst was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and thermal gravimetric analysis (TGA) to confirm the incorporation of the amine group on catalyst.

- iii. Catalyst was tested under various conditions to evaluate the catalyst performance in continuous mode. Catalyst was cut into discs and inserted into the column to have a packed bed. Temperature, residence time and ratio in specific ranges were examined to analyze the conversion of the reaction. Temperature from 50°C to 90°C, molar ratio from 12:1 to 24:1 methanol:triacetin and residence time from 1 hour to 5 hours for 7 cm catalyst in the column were analyzed for single factor analysis.
- iv. Determination of the best reaction combination for obtaining the highest conversion. Dependence variables like sampling time in range of 2-10h, reusability of the catalyst after 40times cycles and bed height of the catalyst in the column in range of 2-11cm were analyzed. Kinetic model was obtained to calculate the reaction rate order, reaction rate constant and activation energy of triacetin transesterification with a functionalized aminated PE-g-GMA solid polymer catalyst.

1.6 Dissertation Outline

This study investigates the preparation of the solid polymer catalyst by amination and its activity by transesterification of the triacetin. Chapter 1 introduced the biodiesel and transesterification reactions. Meanwhile it covered the problem statement, the objectives and scope of study. Chapter 2 fully covered the biodiesel properties and specifications. Furthermore, different methods for transesterification was fully observed and ion exchange materials were introduced. Finally ion exchange transesterification was introduced. Chapter 3 introduced the methodologies of the research step-by-step to achieve the objectives. Chapter 4 included the results and the discussion including interpretation of the findings and comparing with prior studies. Finally chapter 5 contained the conclusions and recommendation for further studies.

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