DEVELOPMENT OF MILLIMETRIC HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION

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UNIVERSITI MALAYSIA SABAH
2011

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THESIS SUBMITTED IN FULFILLMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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UNIVERSITI MALAYSIA SABAH
2011

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TITLE : **DEVELOPMENT OF MILLIMETRIC HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION**

DEGREE : **DOCTOR OF PHILOSOPHY (CHEMICAL ENGINEERING)**

VIVA DATE : **12 DECEMBER 2011**

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ACKNOWLEDGEMENT

First and foremost, I would like to express my profound sense of gratitude and indebtedness to my supervisor, Professor Dr. Pogaku Ravindra, Department of chemical engineering, School of Engineering and Information Technology, University Malaysia Sabah, Malaysia. His generosity, encouragement and the overwhelming enthusiasm were invaluable for the completion of this research.

I would like to convey my sincere gratitude to Dr. Eng Seng Chan, Department of chemical engineering, School of Engineering and Information Technology, University Malaysia Sabah (UMS), Malaysia, for his inspiring, helpful suggestions and persistent encouragements as well as close and consistent supervision throughout the period of my PhD program.

I am most grateful to Dr. Chu Chi Ming, Program Head, Chemical Engineering Programme, School of Engineering and IT, UMS, for his encouragement and support throughout this research. I would like to convey my regards to Dr. Rachel Fran Mansa for her support during my research. I would like to extend my deep gratitude to Prof. Dr. Taufik Yap Yun Hin, Faculty of Science, Universiti Putra Malaysia, Malaysia, for giving me opportunity to perform some of my experimental works at Center of Excellence for Catalysis Science and Technology. My special thanks also go to all the catalysis science group members for their help and support to carry out my works.

I would also like to thank the fellow students. I had the pleasure to work with during this project: Catherine Voo, Joreen Lim, Lim Tek Kaun, Bala Krishna. I would specially thank Yim Zhi Hui for his friendship and support in the workplace. I would like to extend my appreciation to the laboratory assistant, Noor Aemi Dawalih, Noridah Abas and the other laboratory assistants for the help offered to me. The financial support provided by ministry of science and technology innovation (MOSTI) and fundamental research grant scheme (FRGS) are gratefully acknowledged.

My special gratitude to my parents, brothers, and sister whose love and affection is the source of inspiration and encouragement for my studies. Last, but not least, I extend thanks and appreciation to everyone who helped directly or indirectly to get this work done.

ABSTRACT

DEVELOPMENT OF HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION

Biodiesel is a renewable, biodegradable and nontoxic fuel. Biodiesel production using various types of heterogeneous metal oxide catalysts has been studied in the past. However, most of these catalysts have been prepared in the form of powders with size ranging from nano- to micrometer. The small particle size may offer high catalytic activity but it gives rise to several problems such as high pressure drops, poor mass/heat transfer, poor contact efficiency and difficulties in handling and separation. Until now, there has been limited work to prepare alkali metal based catalyst in macroscopic form to catalyze the transesterification reaction for biodiesel production. The aim of this work was to develop a heterogeneous catalyst in the form of milimetric spherical beads and to evaluate its performance in biodiesel production in terms of biodiesel yield and catalyst reusability. Preliminary studies involved synthesis of the beads from commercial boehmite powders by the sol-gel method using two different approaches: integrated gelling process and oil-drop granulation process. The gelled beads were then calcined to produce the γ-Al_2O_3 support beads. It was found that the beads produced by the oil-drop granulation process had higher mechanical strength, thus the process was used for bead production in subsequent works. The γ-Al_2O_3 support beads were activated by impregnating with aqueous solution of KF $NaNO_3$ and KI, as catalyst. The surface properties of the supported catalysts were analyzed using BET and the basicity properties, evaluated in terms of number and strength of basic sites, were analyzed using CO_2-TPD. Bead morphology was studied using SEM. The supported catalysts were used in transesterification reaction with methanol at 60 ^oC in batch process. The composition of biodiesel was evaluated by the gas chromatography method and the effects of catalyst properties, reaction time, molar ratio of methanol to oil, catalyst loading on biodiesel yield were studied. The reusability of the catalyst was also determined and the leachate of catalyst into the reaction product was verified by XRF. Results show that boehmite was transformed to γ-Al_2O_3 at 800 ^oC where crystalline structure was formed, as verified by XRD. The highest FAME yield obtained from KI/γ-Al_2O_3 catalyst was 98% after 4 h of reaction time at 60 ^oC and the yield was found to directly correspond to the catalyst basicity. It can be correlated with their generation of K_2O, $KAlO_2$ for KI/γ-Al_2O_3 catalyst as evident from XRD which were possibly the main active sites for the transesterification reaction. Similarly, the activity of KF/Al_2O_3 catalysts was remarkably improved when the catalysts loading were 0.30g ($g_{Cat}/g_{\gamma\text{-}Al2O3}$) for $NaNO_3$/γ-Al_2O_3 and 0.24g ($g_{Cat}/g_{\gamma\text{-}Al2O3}$) for KF/γ-$Al_2O_3$. The high activity towards the transesterification reaction corresponds to the generation of Na_2O, $NaAlO_2$ on $NaNO_3$/γ-Al_2O_3 catalyst, K_2O, $KAlF_4$ on KF/γ-Al_2O_3 catalyst. The high FAME yield could also be attributed to the mesoporous characteristic of the catalyst with pore diameter of 7-9 nm since the smaller triglycerides molecules could diffuse into the catalyst. Moreover, the catalyst exhibited good operational stability with biodiesel yield of 79% after 11 cycles of successive reuse. In conclusion, a heterogeneous catalyst in the form of milimetric spherical beads with potential application in biodiesel production has been developed.

ABSTRAK

Biodiesel adalah satu sumber yang boleh diperbaharui, mesra alam dan tidak bertoksik. Penghasilan biodiesel menggunakan pelbagai jenis mangkin heterogen oksida logam telah dikaji sebelum ini. Walau bagaimanapun, kebanyakan pemangkin yang dibuat adalah dalam bentuk serbuk dengan saiz antara nano hingga mikrometer. Saiz zarah kecil mungkin menawarkan aktiviti pemangkin yang tinggi tetapi saiz zarah kecil ini mungkin juga menimbulkan beberapa masalah seperti penurunan tekanan yang tinggi, pemindahan jisim/haba yang lemah, kecekapan hubungan yang lemah dan masalah dalam pengendalian dan pengasingan. Sehingga kini, penyelidikan adalah terhad dalam penyediaan pemangkin logam alkali dalam bentuk makroskopik untuk memangkinkan tindak balas transesterifikasi untuk penghasilan biodiesel. Tujuan kerja ini adalah untuk membangunkan satu pemangkin heterogen dalam bentuk manik bulat milimetrik dan menilai prestasi dalam penghasilan biodiesel dari segi hasil biodiesel dan sifat penggunaan semula pemangkin. Kajian awal yang melibatkan sintesis manik dari serbuk boehmite komersil dengan kaedah sol-gel menggunakan dua pendekatan yang berbeza: proses pengelan integrasi dan proses granulasi titisan-minyak. Manik gel kemudian dikalsinasi untuk menghasilkan manik sokongan γ-Al_2O_3. Didapati bahawa manik yang dihasilkan oleh proses granulasi titisan-minyak mempunyai kekuatan mekanikal yang lebih tinggi, oleh itu proses ini digunakan untuk penghasilan manik dalam kerja-kerja seterusnya. Manik sokongan γ-Al_2O_3 diaktifkan dengan mengimpregnat dengan larutan KF $NaNO_3$ dan KI, sebagai pemangkin dan kalsinasi bagi kali kedua pada pelbagai suhu. Ciri-ciri permukaan pemangkin sokongan dianalisis dengan menggunakan BET dan sifat kebesan, dinilai dari segi bilangan dan kekuatan tapak bes, dan dianalisis dengan menggunakan CO_2-TPD. Morfologi manik dikaji dengan menggunakan SEM. Pemangkin sokongan digunakan dalam tindak balas pengtransesteran dengan metanol pada suhu 60 ^oC dalam proses kelompok. Komposisi biodiesel dinilai dengan menggunakan kaedah kromatografi gas dan kesan ciri-ciri pemangkin, tempoh reaksi, nisbah molar metanol dengan minyak, penyaratan mangkin terhadap keputusan biodiesel juga dikaji. Sifat penggunaan semula pemangkin ditentukan dan sifat leachate pemangkin terhadap reaksi produk juga disahkan oleh XRF. Keputusan menunjukkan bahawa boehmite berubah kepada γ-Al_2O_3pada 800 ^oC di mana struktur kristal telah dibentuk, seperti yang disahkan oleh XRD. Hasil FAME yang tertinggi diperolehi daripada pemangkin KI/γ-Al_2O_3 adalah 98% selepas 4 jam tindak balas pada 60 ^oC dan hasil didapati berkadar secara langsung kebesan pemangkin. Ia boleh dikaitkan dengan penghasilan K_2O, $KAlO_2$ untuk pemangkin KI/γ-Al_2O_3 seperti yang terbukti daripada XRD yang mungkin tapak aktif utama untuk reaksi pengtransesteran. Begitu juga dengan aktiviti pemangkin KF/Al_2O_3 adalah bertambah bagus apabila beban pemangkin ialah 0.30g ($g_{Cat}/g_{\gamma\text{-}Al2O3}$) untuk $NaNO_3$/γ-Al_2O_3dan 0.24g ($g_{Cat}/g_{\gamma\text{-}Al2O3}$) untuk KF/γ-$Al_2O_3$. Aktiviti tinggi terhadap reaksi pen gtransesteran adalah disebabkan oleh penghasilan Na_2O, $NaAlO_2$ pada pemangkin $NaNO_3$/γ-Al_2O_3, K_2O, $KAlF_4$ pada pemangkin KF/γ-Al_2O_3.

Keputusan FAME yang tinggi mungkin juga disebabkan oleh ciri-ciri mesoliang mangkin dengan diameter liang sekitar 7-9 nm di mana trigliserida molekul kecil dapat meresap ke dalam mangkin. Selain itu, mangkin ini menunjukkan kestabilan operasi yang baik dengan penghasilan biodiesel sebanyak 79% selepas 11 kitaran gunasemula berturut-turut. Sebagai kesimpulan, mangkin heterogen dalam bentuk manik-manik sfera dalam ukuran milimetric telah dihasilkan dengan potensi untuk diaplikasikan dalam penghasilan biodiesel.

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A	Temperature dependent pre-exponential term
A_{is}	Area of internal standard
A_{iss}	Area of internal standard in the sample
A_{RS}	Area of reference standard
A_{FCS}	Area of individual FAMEs compound in the sample.
C_{is}	Concentration of internal standard in reference standard solution.
C_{iss}	Concentration of internal standard in the sample
C_{RS}	Concentration of reference standards in solution
C	Equilibrium constant of adsorption in the first adsorption layer at the measuring temperature.
d_a	Diameter of the particle after air-drying (mm)
d_f	Diameter of the particle while falling (mm)
d_g	Diameter of the particle after gelling (mm)
d_{max}	Maximum diameter passing through a beads centroid (mm)
d_p	Overall particle diameter (mm)
d_c	Diameter of the particle after calcining (mm)
d_{per}	Diameter perpendicular to d_{max} passing through the bead centroid (mm)
d_T	Tip diameter (mm)
g	Gravitational force (m/s^{-2})
k_a	Shrinkage factor of particle after air-drying
k_c	Shrinkage factor of particle after calcining
k_g	Shrinkage factor of particle after gelling

k_{LF}	Liquid lost factor
k	Consistency index (pa.s)
k	Overall size correction factor (mm)
N_A	Avogadro's number
n	Flow behavior index
P_o	Saturated vapor pressure of nitrogen
P	Equilibrium pressure
R	Gas constant (8.314 J/mol.K)
RF_{RS}	Response factor of the respective reference standard
T	Reaction temperature
V_{ads}	Amount of adsorbed gas
V_m	Amount of adsorbed gas at one monolayer
γ	Shear rate per second (s^{-1})
γ	Surface tension (mN/m)
η	Viscosity of the suspension (mPa.s)
θ	Angle between the incoming X-rays and the normal to the reflecting lattice plane.
λ	Wave length of X-rays.
ρ	Density (kg/m^3) of the suspensions
σ	Molecular cross sectional area for nitrogen
τ	Shear stress in dyne per cm^2

CHAPTER 1

INTRODUCTION

1.1 Research Background

The enormous worldwide use of diesel fuel and the rapid depletion of crude oil reserves have prompted keen interest and exhaustive research into suitable alternative fuel. Currently, attention is focused on human and environmental safety, in relation to the release of hydrocarbons into the environment. Petroleum derivatives contain benzene, toluene, ethylbenzene and xylene isomers the major components of fossil fuel, which are hazardous substances subject to regulations in many parts of the world (Serrano *et al.,* 2006)**.** As a consequence, the demand of green energy is increasingly gaining international attention. When green energy is used, the primary objective is to reduce air pollution, and minimize or eradicate completely any impacts to the environment (Burgess**,** 1990). Among many possible sources, apparently, biodiesel is a viable alternative energy to conventional diesel fuel, which is of environmental concern and is under legislative pressure to be replaced by biodegradable substitutes.

The most common way to produce biodiesel is by transesterification which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol (Freedman *et al.,* 1984; Lottero *et al.,* 2006), as shown in Figure 1.1. Triglycerides, as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol structure. When triglycerides react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the methanol to yield fatty acid methyl esters (FAME). Glycerol is produced as a by-product. The transesterification reaction can be carried out using homogeneous, heterogeneous or enzymatic catalysts (Lopez *et al.,* 2005; Dossin *et al.,* 2006; Jenannathan *et al.,* 2008).