

**SULFATED ZIRCONIA SUPPORTED ON SBA-15
FOR SELECTIVE GLYCEROL
ESTERIFICATION WITH PALMITIC ACID TO
MONOPALMITIN**

MOHD HIZAMI BIN MOHD YUSOFF

UNIVERSITI SAINS MALAYSIA

2016

**SULFATED ZIRCONIA SUPPORTED ON SBA-15 FOR SELECTIVE
GLYCEROL ESTERIFICATION WITH PALMITIC ACID TO
MONOPALMITIN**

by

MOHD HIZAMI BIN MOHD YUSOFF

**Thesis submitted in fulfillment of the
requirements for the degree of
Doctor of Philosophy**

September 2016

ACKNOWLEDGEMENT

In the name of Allah, The Most Beneficent and The Most Merciful, who is listening to all prayers from His humble servants, I would like to first and foremost express my boundless gratitude to Him for giving me courage, strength, patience and guidance to successfully finish this PhD thesis. The completion of this research would be impossible without the assistance and supports from many individuals who have lent me their hands. First of all, I would like to thank my dedicated supervisor, Prof. Dr Ahmad Zuhairi Abdullah for his endless support, invaluable advices and guidance throughout my PhD study. Both, his patience and never ending help are very much appreciated. I would also love to express my deepest gratitude to both of my beloved parents, Mohd Yusoff Abdullah and Zainab Che Mat for their endless love, prayers and tolerance. They are always encouraging me when I am in difficulties and never failed to remind me about being a successful person. My appreciation also goes to the Dean, Deputy Deans and administrative staffs of School of Chemical Engineering for their supports and assistance during my study. Not to forget, all technical staffs for their technical guidance and assistances in my experimental works. I would also like to thank all of my colleagues for helping me and sharing useful ideas to improve my research. Last but not least, I would like to thank to people who has directly and indirectly helped me throughout my study. Finally, I would like to acknowledge the funding from Universiti Sains Malaysia (Grant No. 814144 and 814181) and financial support from Ministry of Higher Education Malaysia in the form of MyPhD. Thank you very much.

Mohd Hizami bin Mohd Yusoff

September 2016

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	viii
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xv
LIST OF SYMBOLS	xvii
ABSTRAK	xix
ABSTRACT	xxi
CHAPTER ONE : INTRODUCTION	
1.1 Introduction	1
1.1.1 Surplus of glycerol from biodiesel overproduction	1
1.1.2 Conversion of glycerol to value added products	5
1.2 Monoglycerides	7
1.3 Palmitic acid for monoglyceride production	8
1.4 Problem statement	10
1.5 Objectives	12
1.6 Scopes of study	12
1.7 Thesis organization	15
CHAPTER TWO : LITERATURE REVIEW	
2.1 Introduction	17
2.2 SBA-15	17
2.2.1 Mechanism formation of SBA-15	18
2.2.2 Textural and morphological properties	20
2.3 Sulfated zirconia as an efficient catalyst	22
2.3.1 Nature of active sites	24
2.3.2 Application of sulfated zirconia in esterification	25
2.4 Sulfated zirconia in SBA-15	30
2.4.1 Method of preparation	33
2.4.1.1 Incipient wetness impregnation	34

2.4.1.2	Direct synthesis method	35
2.4.1.3	Vapor-induced internal hydrolysis	35
2.4.1.4	Urea hydrolysis method	37
2.4.2	Application of SZSBA-15 in various areas	38
2.5	Effect of catalyst preparation on physicochemical properties of catalyst	42
2.5.1	Effect of zirconia loading	42
2.5.2	Effect of calcination temperature	46
2.6	Esterification of fatty acids with glycerol	49
2.6.1	Autocatalytic reaction	51
2.6.2	Heterogeneous catalysts for fatty acid esterification	53
2.6.2.1	Ion exchange resin	55
2.6.2.2	Zeolite	56
2.6.2.3	Montmorillonite	57
2.6.2.4	Metal oxides or salts catalysts	58
2.6.2.5	Functionalized mesoporous silica-based catalysts	59
2.7	Factors influencing esterification reaction	63
2.7.1	Effect of reaction temperature	63
2.7.2	Effect of catalyst loading	65
2.7.3	Effect of glycerol to fatty acid molar ratio	67
2.7.4	Effect of reaction time	68
2.8	Kinetic of glycerol esterification with fatty acids	70
2.8.1	Reaction pathways	70
2.8.2	Proposed kinetic model for monoglyceride production	73
2.9	Concluding remarks	76

CHAPTER THREE : MATERIALS AND METHODS

3.1	Introduction	78
3.2	List of chemicals	78
3.3	Experimental flow chart	79
3.4	Equipment	81
3.5	Catalyst preparation	82
3.5.1	Preparation of SBA-15	82

3.5.2	Incorporation of sulfated zirconia into SBA-15	84
3.5.2.1	Effect of zirconia loading	84
3.5.2.2	Effect of final calcination temperature	86
3.5.3	Synthesis of sulfated zirconia	86
3.6	Characterization of SBA-15 and SZSBA-15 catalysts	86
3.6.1	Surface analysis	86
3.6.2	Scanning electron microscopy (SEM)	87
3.6.3	Transmission electron microscopy (TEM)	87
3.6.4	X-ray diffraction (XRD)	88
3.6.5	Fourier transformed-infrared (FT-IR) spectroscopy	88
3.6.6	Energy dispersive X-ray (EDX)	88
3.6.7	Thermogravimetric analysis (TGA)	89
3.6.8	Temperature-programmed desorption of ammonia (NH ₃ -TPD)	89
3.6.9	Surface acidity determination by titration	89
3.7	Catalytic activity	90
3.7.1	Esterification of glycerol with palmitic acid	90
3.7.2	Product analysis	90
3.8	Reusability of SZSBA-15 catalyst	93
3.9	Kinetic study of esterification of glycerol with palmitic acid	94

CHAPTER FOUR : RESULTS AND DISCUSSION

4.1	Introduction	96
4.2	Performance of SZSBA-15 catalyst in glycerol esterification with palmitic acid	97
4.2.1	Characterization of SBA-15 before and after the incorporation of sulfated zirconia	97
4.2.1.1	Textural analysis	97
4.2.1.2	Energy dispersive X-ray (EDX)	100
4.2.1.3	X-ray diffraction (XRD)	101
4.2.1.4	Scanning electron microscopy (SEM)	102
4.2.1.5	Transmission electron microscopy (TEM)	104
4.2.1.6	Fourier transform infrared spectroscopy (FTIR)	106

4.2.1.7	Thermogravimetric analysis (TGA)	107
4.2.2	Activity study	108
4.3	Influence of zirconia loading on glycerol esterification with palmitic acid	110
4.3.1	Characterization of the catalysts	110
4.3.1.1	Physicochemical properties	110
4.3.1.2	Morphological structure	116
4.3.1.3	Fourier transform infrared spectroscopy (FTIR)	119
4.3.1.4	Thermogravimetric analysis (TGA)	120
4.3.1.5	Temperature-programmed desorption of ammonia (NH ₃ -TPD)	121
4.3.2	Activity study	125
4.4	Influence of catalyst calcination temperature on glycerol esterification with palmitic acid	130
4.4.1	Characterization of the catalyst	130
4.4.1.1	Physicochemical properties	130
4.4.1.2	Morphological structure	136
4.4.1.3	Thermogravimetric analysis (TGA)	140
4.4.1.4	Temperature-programmed desorption of ammonia (NH ₃ -TPD)	141
4.4.2	Activity study	144
4.5	Influence of reaction conditions on palmitic acid conversion and monopalmitin yield	147
4.5.1	Effect of catalyst loading	147
4.5.2	Effect of reaction time	149
4.5.3	Effect of nitrogen flow rate	152
4.5.4	Effect of reaction temperature	154
4.5.5	Effect of glycerol to palmitic acid molar ratio	156
4.6	Catalyst stability and reusability	159
4.6.1	Reusability experiment	160
4.6.2	Characterization of the fresh and spent catalysts	162
4.7	Reaction kinetic study for glycerol esterification with palmitic acid	164

CHAPTER FIVE : CONCLUSIONS AND RECOMMENDATIONS	
5.1	Conclusion 174
5.2	Conclusions 174
5.3	Recommendations 176
REFERENCES 177	
APPENDICES	
LIST OF PUBLICATIONS	

LIST OF TABLES

		Page
Table 1.1	Products from glycerol	6
Table 1.2	Typical fatty acids composition of crude palm oil (Hossain <i>et al.</i> , 2016)	9
Table 2.1	Solid superacids and their acid strength (Arata <i>et al.</i> , 2003)	24
Table 2.2	The application of sulfated zirconia and its modified forms in esterification of fatty acids with various alcohols	26
Table 2.3	Textural properties of sulfated zirconia on SBA-15	33
Table 2.4	Application of sulfated zirconia on SBA-15 in various fields	38
Table 2.5	Textural properties of ZrO ₂ -SBA-15 with different zirconia loadings (Gutiérrez <i>et al.</i> , 2009)	43
Table 2.6	Autocatalytic reaction involving fatty acids with glycerol	52
Table 2.7	Heterogeneous catalysts for glycerol esterification with fatty acids	54
Table 2.8	Functionalized mesoporous catalyst for glycerol esterification with fatty acids	60
Table 2.9	Kinetic studies of glycerol esterification with fatty acids using various catalysts	74
Table 3.1	List of chemicals used in the preparation of catalysts, reaction study and product analysis	78
Table 3.2	List of equipment used	81
Table 4.1	Textural characteristics of SBA-15, ZrSBA-15 and SZSBA-15	98
Table 4.2	EDX results of the catalyst and support	101
Table 4.3	Physical characteristics of the SBA-15 and SZSBA-15 catalysts	111
Table 4.4	Chemical properties of the catalysts	115
Table 4.5	Physical characteristics of the support and SZSBA-15 catalysts	131
Table 4.6	Chemical properties of the catalysts	135

Table 4.7	Textural properties of the fresh and spent catalysts	163
Table 4.8	EDX results of the fresh and spent catalysts	163
Table 4.9	Physicochemical properties of catalysts used for kinetic study	165
Table 4.10	Specific rate constants for various reaction temperatures using second-order kinetic model	168
Table 4.11	Kinetic parameters of glycerol esterification with palmitic acid	170
Table 4.12	Comparison of monopalmitin yield calculated from the developed model with the experimental results for different reaction temperatures	172
Table B-1	Concentration of each compound in the reaction mixture measured by gas chromatography	
Table C-1	Parameters used in the kinetic model	

LIST OF FIGURES

		Page
Figure 1.1	Production of biodiesel in Malaysia from 2010 to 2014 (Johari <i>et al.</i> , 2015)	2
Figure 1.2	Transesterification of triglyceride to produce FAME and glycerol (Tan <i>et al.</i> , 2013)	3
Figure 1.3	World biodiesel (bars) and crude glycerol (lines) productions between 2000 and 2011 (Gholami <i>et al.</i> , 2014)	3
Figure 1.4	Chemical structure of glycerol	5
Figure 1.5	Chemical structure of monoglyceride	7
Figure 2.1	Schematic representation of the synthesis of SBA-15 (Johansson, 2008)	19
Figure 2.2	SEM images of SBA-15 (a) with ropelike domains (Gagea <i>et al.</i> , 2009) and (b) aggregated into wheat-like morphology (Liu and Baker, 2008)	21
Figure 2.3	TEM images of SBA-15 (a) in the direction perpendicular to the pore axis and (b) SBA-15 in the direction of the pore axis (Li <i>et al.</i> , 2009)	22
Figure 2.4	The Brønsted and Lewis sites on the surface of sulfated zirconia (Hino <i>et al.</i> , 2006)	25
Figure 2.5	TEM images of (a) SBA-15 and (b) 35%SZSBA-15 (Garg <i>et al.</i> , 2009)	30
Figure 2.6	NH ₃ temperature-programmed-desorption profiles of (1) SiO ₂ -SZ and (2) SZ (Chen <i>et al.</i> , 2007)	32
Figure 2.7	Schematic illustration of mechanism for SZ/MS catalyst by the VIH method (Chang <i>et al.</i> , 2012)	36
Figure 2.8	TEM images of unsulfated SBA-15 with (a) 0 (b) 15 (c) 25 mol% ZrO ₂ loading and sulfated SBA-15 with (d) 0 (e) 15 (f) 25 mol% ZrO ₂ (Degirmenci <i>et al.</i> , 2007)	44
Figure 2.9	Esterification of glycerol with fatty acids (Kotwal <i>et al.</i> , 2011)	50

Figure 2.10	Consecutive reactions of the glycerol esterification as proposed by (a) Szeląg and Zwierzykowski, (1998) and (b) Macierzanka and Szeląg, (2004)	71
Figure 2.11	Irreversible parallel reactions for glycerol esterification with fatty acid (Sánchez <i>et al.</i> , 1997)	72
Figure 2.12	Combination of consecutive and parallel irreversible reactions of glycerol esterification with oleic acid (Singh <i>et al.</i> , 2013)	73
Figure 3.1	Flowchart of overall experimental works	80
Figure 3.2	Schematic diagram for the reactor used in the esterification study	82
Figure 3.3	Flow chart on the procedure used for the synthesis of SBA-15	83
Figure 3.4	Flow chart on the procedure used for the synthesis of SZSBA-15	85
Figure 4.1	N ₂ adsorption-desorption isotherms of SBA-15, ZrSBA-15 and SZSBA-15	99
Figure 4.2	Pore size distribution of SBA-15, ZrSBA-15 and SZSBA-15 catalysts	100
Figure 4.3	Small angle XRD patterns of (a) SBA-15 (b) ZrSBA-15 and (c) SZSBA-15 catalysts.	102
Figure 4.4	SEM images of SBA-15 at a (a) magnification of 20000 X and (b) magnification of 3000 X	103
Figure 4.5	SEM images of SBA-15 at a magnification of 5000 X (a) after being incorporated with zirconia and (b) after subsequent sulfation with sulfuric acid	104
Figure 4.6	TEM images of SBA-15 (a) in the direction perpendicular to the pore axis (b) SBA-15 in the direction of the pore axis	105
Figure 4.7	TEM images of SBA-15 after (a) incorporation of zirconia and (b) after sulfation	105
Figure 4.8	FTIR spectra of SBA-15, ZrSBA-15 and SZSBA-15	106
Figure 4.9	TGA profiles of SBA-15 and SZSBA-15 catalyst	108

Figure 4.10	Comparison of palmitic acid conversions and monopalmitin yield using SBA-15, ZrSBA-15, SZSBA-15 and without catalyst	109
Figure 4.11	N ₂ adsorption-desorption isotherms of (a) 5SZSBA-15, (b) 10SZSBA-15, (c) 15SZSBA-15 and (d) 20SZSBA-15 catalysts	113
Figure 4.12	Pore size distribution of the SZSBA-15 catalysts prepared at different zirconia loadings	114
Figure 4.13	SEM images of (a) 5SZSBA-15, (b) 10SZSBA-15, (c) 15SZSBA-15 and (d) 20SZSBA-15 catalysts with magnification of 10000X	116
Figure 4.14	TEM images of (a) 5SZSBA-15, (b) 10SZSBA-15, (c) 15SZSBA-15 and (d) 20SZSBA-15 catalysts	118
Figure 4.15	FTIR spectra of SZSBA-15 catalysts prepared at different zirconia loadings between 1700 – 400 cm ⁻¹	120
Figure 4.16	TGA profiles of 5SZSBA-15, 10SZSBA-15, 15SZSBA-15 and 20SZSBA-15 catalysts	121
Figure 4.17	NH ₃ -TPD profiles of 5SZSBA-15, 10SZSBA-15, 15SZSBA-15 and 20SZSBA-15 catalysts	122
Figure 4.18	Palmitic acid conversion and monopalmitin yield over SZSBA-15 catalysts (Reaction temperature = 170 °C, reaction time = 3 h, glycerol/palmitic acid = 4:1, catalyst loading = 2 wt. %)	125
Figure 4.19	Selectivity of monopalmitin, dipalmitin and tripalmitin SZSBA-15 catalysts (Reaction temperature = 170 °C, reaction time = 3 h, glycerol/palmitic acid = 4:1, catalyst loading = 2 wt. %)	128
Figure 4.20	N ₂ adsorption-desorption isotherms of (a) SZSBA-15(450), (b) SZSBA-15(500), (c) SZSBA-15(550) and (d) SZSBA-15(650) catalysts	133
Figure 4.21	Pore size distribution of (a) SZSBA-15(450), (b) SZSBA-15(500), (c) SZSBA-15(550) and (d) SZSBA-15(650) catalysts	134
Figure 4.22	SEM images of (a) SZSBA-15(450), (b) SZSBA-15(500), (c) SZSBA-15(550) and (d) SZSBA-15(650) catalysts at a magnification of 1000 X	137

Figure 4.23	SEM images of (a) SZSBA-15(450), (b) SZSBA-15(500), (c) SZSBA-15(550) and (d) SZSBA-15(650) catalysts at a magnification of 10000 X	138
Figure 4.24	TEM images of (a) SZSBA-15(450), (b) SZSBA-15(500), (c) SZSBA-15(550) and (d) SZSBA-15(650) catalysts	139
Figure 4.25	TGA profiles of SZSBA-15(450), SZSBA-15(500), SZSBA-15(550) and SZSBA-15(650) catalysts	140
Figure 4.26	NH ₃ -TPD profile of SZSBA-15(450), SZSBA-15(500), SZSBA-15(550) and SZSBA-15(650) catalysts	143
Figure 4.27	Effects of SZSBA-15 catalysts prepared at different calcination temperatures on the palmitic acid conversion and monopalmitin yield (Reaction temperature = 170 °C, reaction time = 3 h, glycerol/palmitic acid = 4:1, catalyst loading = 2 wt. %)	144
Figure 4.28	Effects of SZSBA-15 catalysts prepared at different calcination temperatures on the selectivity of mono-, di- and tripalmitin (Reaction temperature = 170 °C, reaction time = 3 h, glycerol/palmitic acid = 4:1, catalyst loading = 2 wt. %)	145
Figure 4.29	Effect of catalyst loadings on palmitic acid conversion (Reaction time = 3 h, reaction temperature = 170 °C, glycerol/palmitic acid = 4:1)	148
Figure 4.30	Effects of catalyst loading on the yield of monopalmitin (Reaction time = 3 h, reaction temperature = 170 °C, glycerol/palmitic acid = 4:1)	149
Figure 4.31	Effect of reaction time on the palmitic acid conversion (Catalyst loading = 2 wt. %, reaction temperature = 170 °C, glycerol/palmitic acid = 4:1)	150
Figure 4.32	Effect of reaction time on the yield of monopalmitin, dipalmitin and tripalmitin (Catalyst loading = 2 wt. %, reaction temperature = 170 °C, glycerol/palmitic acid = 4:1)	151
Figure 4.33	Effects of nitrogen flow rate on the conversion of palmitic acid and monopalmitin yield (Catalyst loading = 2 wt. %, reaction time = 3 h, reaction temperature = 170 °C, glycerol/palmitic acid = 4:1)	153

Figure 4.34	Effect of reaction temperature on palmitic acid conversion (Catalyst loading = 2 wt. %, reaction time = 3 h, glycerol/palmitic acid = 4:1)	154
Figure 4.35	Effect of reaction temperature on monopalmitin yield (Catalyst loading = 2 wt. %, reaction time = 3 h, glycerol/palmitic acid = 4:1)	156
Figure 4.36	Effect of molar ratio on palmitic acid conversion (Catalyst loading = 2 wt. %, reaction time = 3 h, reaction temperature = 170 °C)	157
Figure 4.37	Effect of molar ratios on monopalmitin yield (Catalyst loading = 2 wt. %, reaction time = 3 h, reaction temperature = 170 °C)	158
Figure 4.38	Palmitic acid conversion and monopalmitin yield over 10SZSBA-15(500) catalyst for four consecutive runs (Catalyst loading = 2 wt. %, reaction time = 3 h, reaction temperature = 170 °C, glycerol/palmitic acid = 4:1)	160
Figure 4.39	Selectivities of monopalmitin, dipalmitin and tripalmitin for each catalytic run (Catalyst loading = 2 wt. %, reaction time = 3 h, reaction temperature = 170 °C, glycerol/palmitic acid = 4:1)	161
Figure 4.40	Comparison of the surface morphologies between the (a) fresh and (b) reused catalyst after four cycles (Spent 3)	164
Figure 4.41	Arrhenius plot of reaction rate constant versus inverse of reaction temperatures for (a) 5SZSBA-15, (b) 10SZSBA-15(500) and (c) 20SZSBA-15 catalysts	169
Figure 4.42	Parity plot for the experimental monopalmitin yield and calculated values from second order kinetic model	173
Figure A-1	GC typical chromatogram of palmitic acid	
Figure A-2	GC typical chromatogram of monopalmitin	
Figure A-3	GC typical chromatogram of dipalmitin	
Figure A-4	GC typical chromatogram of tripalmitin	
Figure A-5	GC typical chromatogram of product obtained from the reaction at 170 °C, reaction time of 3 h and catalyst loading of 2 wt. %	

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CPO	Crude palm oil
CTAB	Cetyltrimethyl ammonium bromide
DAG	Diglyceride
EDX	Energy dispersive X-ray
FAME	Fatty acid methyl ester
FTIR	Fourier transformed infrared
G	Glycerol
GHG	Greenhouse gases
GMO	Glycerol monooleate
GMP	Glycerol monopalmitate
HCl	Hydrochloric acid
HMF	5-hydroxymethyl-2-furfural
HPW	12-tungstophosphoric acid
HRTEM	High resolution transmission electron microscopy
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
MAG	Monoglyceride
MCM-41	Mobile Composition of Matter No. 41
MPIC	Malaysia's Ministry of Plantation Industries and Commodities
NaOH	Sodium hydroxide
NH ₃ -TPD	Temperature-programmed desorption of ammonia
PA	Palmitic acid
PFAD	Palm fatty acid distillate
SBA-15	Santa Barbara Amorphous No. 15

SEM	Scanning electron microscopy
STP	Standard temperature and pressure
SZ	Sulfated zirconia
SZSBA-15	Sulfated zirconia supported SBA-15
TAG	Triglyceride
TBAB	Tetrabutyl ammonium bromide
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
TPD	Temperature – programmed desorption
VIH	Vapor – induced hydrolysis
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbols	Description	Unit
A	Pre-exponential factor	$L \cdot mol^{-1} g_{cat}^{-1} h^{-1}$
A_i	Peak area of mono, di- or tripalmitin in the sample	Dimensionless
A_{IS}	Peak area of internal standard	Dimensionless
$A_{SD,i}$	Peak area of mono, di- or tripalmitin in the standard reference	Dimensionless
C_G	Concentration of glycerol	mol/L
C_i	Concentration of mono-, di- or tripalmitin	mol/L
C_{PA}	Concentration of palmitic acid	mol/L
C_{PAO}	Initial concentration of palmitic acid	mol/L
$C_{SD,i}$	Concentration of mono-, di- or tripalmitin for standard reference	mol/L
D_f	Dilution factor	Dimensionless
E_a	Activation energy	kJ/mol
H_o	Hammett acidity function	Dimensionless
k_s	Specific rate constant	$L \cdot mol^{-1} h^{-1}$
M	Molar ratio	Dimensionless
R	Universal gas constant	$cal \cdot K^{-1} \cdot mol^{-1}$
r_{PA}	Rate of reaction	$mol \cdot g_{cat}^{-1} \cdot h^{-1} \cdot L^{-1}$
R_{SD}	Ratio of peak area of mono-, di- or tripalmitin in the standard reference to peak area of the internal standard	Dimensionless
S_{Mono}	Selectivity of monopalmitin	Dimensionless
S_{Di}	Selectivity of dipalmitin	Dimensionless
S_{Tri}	Selectivity of tripalmitin	Dimensionless
t	Time	h

T	Temperature	K
W	Weight of catalyst	g
X_{G0}	Initial glycerol conversion	Dimensionless
X_{PA}	Conversion of palmitic acid	Dimensionless
X_{PA0}	Initial palmitic acid conversion	Dimensionless
Y_M	Monopalmitin yield	Dimensionless

**ZIRKONIA TERSULFAT BERPENYOKONG SBA-15 UNTUK
PENGESTERAN TERPILIH GLISEROL DENGAN ASID PALMITIK
KEPADA MONOPALMITIN**

ABSTRAK

Peningkatan pesat dalam pengeluaran biodiesel di Malaysia menjana lebih gliserol mentah sebagai produk utama yang mempunyai aplikasi yang terhad dalam industri tempatan. Berdasarkan keadaan semasa, penukaran gliserol kepada produk bernilai tinggi seperti monogliserida adalah satu alternatif yang menarik. Dalam kajian ini, mangkin meso liang SZSBA-15 telah disintesis dengan muatan zirkonia (5 – 20 % berat) dan suhu pengkalsinan akhir (450 – 650 °C) yang berbeza. Mangkin-mangkin yang disintesis telah dicirikan melalui analisis permukaan, SEM, TEM, XRD, FTIR, EDX, TGA, NH₃-TPD dan penentuan keasidan melalui titratan. Ciri-ciri mangkin tersebut kemudiannya dikaitkan dengan aktiviti mangkin dalam pengesteran gliserol dengan asid palmitik dan prestasinya ditunjuk berdasarkan penukaran asid palmitik dan hasil monopalmitin. Kesan keadaan tindak balas seperti masa (1 – 6 jam), kadar aliran N₂ (5 – 40 cm³/min), suhu tindak balas (160 – 180 °C), muatan mangkin (1 – 3 % berat), nisbah bilangan mol gliserol/asid palmitik (2:1 – 6:1) juga dijelaskan dan dikaitkan dengan ciri-ciri mangkin. Didapati bahawa mangkin SZSBA-15 yang disediakan menggunakan 10 % berat muatan zirkonia dan dikalsin pada 500 °C (10SZSBA-15(500)) menunjukkan aktiviti yang tinggi dalam penghasilan monopalmitin. Peningkatan masa tindakbalas, kadar aliran N₂, suhu tindakbalas dan muatan mangkin telah meningkatkan penukaran asid palmitik. Sebaliknya, perubahan dalam penukaran asid palmitik tidak ketara apabila nisbah bilangan mol melebihi 4:1.

Tambahan pula, keadaan tindak balas terbaik telah diperolehi pada masa tindak balas 3 jam, suhu tindak balas 170 °C, muatan mangkin 2 % berat dan nisbah gliserol/asid palmitik 4:1. Di bawah keadaan ini menggunakan mangkin 10SZSBA-15(500), sebanyak 86 % penukaran asid palmitik dan 43 % hasil monopalmitin telah diperolehi. Dari segi kebolegunaan semula, mangkin ini boleh digunakan semula sehingga empat kali dalam tindak balas ini dengan sedikit penurunan dalam aktiviti pemangkin. Ini disebabkan oleh kehilangan kumpulan sulfur daripada mangkin. Walau bagaimanapun, struktur liang tidak terjejas setelah empat kitaran pemangkin. Pengesteran gliserol dengan asid palmitik didapati menepati model kinetik tertib kedua terhadap gliserol dan asid palmitik dengan tenaga pengaktifan yang rendah sebanyak 38.2 kJ/mol. Sebagai kesimpulan, mangkin 10SZSBA-15(500) yang menunjukkan aktiviti yang baik merupakan mangkin aktif dan sesuai digunakan dalam tindak balas melibatkan molekul-molekul besar.

**SULFATED ZIRCONIA SUPPORTED ON SBA-15 FOR SELECTIVE
GLYCEROL ESTERIFICATION WITH PALMITIC ACID TO
MONOPALMITIN**

ABSTRACT

The rapid increase of biodiesel production in Malaysia generates an excess of crude glycerol as the primary co-product which has limited application in local industries. Based on the current situation, the conversion of glycerol to higher value products like monoglyceride is an attractive alternative. In the present work, mesoporous SZSBA-15 catalyst has been synthesized with different zirconia loadings (5 - 20 wt. %) and final calcination temperatures (450 – 650 °C). The synthesized catalysts were characterized by means of surface analysis, SEM, TEM, XRD, FTIR, EDX, TGA, NH₃-TPD and determination of acidity by titration. The characteristics of the catalyst were then correlated with the catalytic activity in glycerol esterification with palmitic acid and the performance was demonstrated based on the palmitic acid conversion and monopalmitin yield. Effects of reaction conditions such as time (1 – 6 h), N₂ flow rate (5 – 40 cm³/min), reaction temperature (160 – 180 °C), catalyst loading (1 – 3 wt. %) and glycerol/palmitic acid molar ratio (2:1 – 6:1) were also elucidated and correlated with the characteristics of the catalysts. It was found that SZSBA-15 catalyst prepared using 10 wt. % of zirconia loading and calcined at 500 °C (10SZSBA-15(500)) demonstrated high activity in the production of monopalmitin. An increase in the reaction time, nitrogen flow rate, reaction temperature and catalyst loading increased the conversion of palmitic acid. On the contrary, changes in the palmitic acid conversion were insignificant when the molar ratio exceeded 4:1. On top

of that, the best reaction conditions were obtained at a reaction time of 3 h, a reaction temperature of 170 °C, 2 wt. % of catalyst loading and 4:1 of glycerol/palmitic acid molar ratio. Under these conditions using 10SZSBA-15(500) catalyst, 86 % of palmitic acid conversion and 43 % monopalmitin yield were obtained. In terms of reusability, this catalyst was reusable for up to four times in this reaction with slight decrease in the catalytic activity. This was attributed to the loss of sulfur groups from the catalyst. Nevertheless, the pore structure remained unaffected after four catalytic cycles. The glycerol esterification with palmitic acid was found to follow a second order kinetic model with respect to glycerol and palmitic acid with a low activation energy of 38.2 kJ/mol. As a conclusion, 10SZSBA-15(500) catalyst which exhibited good activity was as an active catalyst and suitable to be used in the reaction involving bulky molecules.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Energy is one of the essential inputs for economic, social and industrial development of any nation. A sustainable and continuous supply of energy resources is essential to maintain and improve the socio-economic conditions. However, in the current era of energy shortage, conventional energy sources which are mainly derived from fossil fuels are depleting at very fast rate. They are also facing major challenges with respect to high price and environmental problems such as emission of greenhouse gasses (GHG). In the light of current and future status of energy demand coupled with the availability of fossil fuel resources and their environmental impacts, Malaysia along with international communities are in urgent search for alternative energy resources.

1.1.1 Surplus of glycerol from biodiesel overproduction

Biodiesel which comes from renewable resource has been gaining more attention as an alternative fuel option for future due to its enormous resources, environmental benefits and potential as a substitute for petroleum-based diesel fuels (Yusoff *et al.*, 2013). In Malaysia, as of October 2011, a total of 60 palm oil-based biodiesel manufacturing licenses had been approved by the Malaysia's Ministry of Plantation Industries and Commodities (MPIC) with a total annual capacity of 6.79 million tonnes. Until recently, there were 11 active biodiesel plants in the country with a total capacity of 1.65 million tonnes per year (Kheang and May, 2012).