

**PRODUCTION OF BIODIESEL BY
ESTERIFICATION OF FREE FATTY ACID
USING MICROWAVE SYNTHESIZED RICE
HUSK SULPHONATED CATALYST**



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UNIVERSITI MALAYSIA SABAH

**FACULTY OF ENGINEERING
UNIVERSITI MALAYSIA SABAH
2019**

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HUSK SULPHONATED CATALYST**

**THESIS SUBMITTED IN FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF MASTER
OF ENGINEERING**



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**FACULTY OF ENGINEERING
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DEGREE : **MASTERS OF ENGINEERING
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ACKNOWLEDGEMENT

Praise and thanks to God the Father, God the Son, and God the Holy Spirit, who created me in His image and likeness; great, capable, and unique. God has always been my anchor of hope, my source joy, my pillar of strength to face every obstacles and difficulties throughout the process of completing my master degree. He is my source of inspiration and wisdom. I praise Him for He is true to His promises, for whenever I ask, it will be given to me, whenever I seek, I will find, and whenever I knock, the door will be opened.

Firstly, I would like to express my gratitude to my supervisor, Assoc. Prof. Dr. Jidon Janaun for being a great coach to me. Thank you for the guidance and efforts to ensure my research can be done smoothly, and also for looking at me as a person full of potential. I am grateful that I am guided by you. Thanks for unleashing me to my fullest potential by allowing me to grow through every opportunity that came by. I would like also to thank my co-supervisor, Dr. Sariah Abang for supervising and guiding me throughout the entire period of my studies.

Secondly, my sincere appreciation goes to mummy and daddy, for giving me the freedom to choose the path that I think best for me. I am very grateful to have very supportive parents. They always give their best especially in providing me with good financial, supporting me in prayers and trusting me with my decision.

I would like also to express my sincere appreciation to all friends and families for the continuous encouragement and supports. You have been giving wonderful support, physically and mentally, in order to help me to complete my studies. Million thanks to all my lab mates for the motivations and suggestions you have given to me.

Winnie Sinan Balan

4th February 2019

ABSTRACT

Discovery of carbon based catalyst or also known as sugar catalyst has gained attention due to its high catalytic activity on biodiesel production despite possessing a low surface area. Many have tried to hybrid carbon with other inorganic materials to provide higher surface area and further improve the performance of carbon catalyst. However, most of the materials used were expensive. Furthermore, tedious procedures need to be done in order to synthesize a hybrid catalyst. Thus, rice husk (RH) came into the picture. RH has high carbon and silica content, and it is naturally porous material. To obtain rice husk char (RHC), pyrolysis of RH can be done using conventional furnace. However, long pyrolysis time (12-15 h) is needed. Recently, microwave technology has gained much attention due to its ability to pyrolyze biomass at a shorter time. For this study, pyrolysis and sulphonation of RH using microwave (MW) technology was proposed. The performance of MW synthesized catalysts was tested through esterification reaction of oleic acid, as well as, esterification of oil extracted from palm oil mill effluent (POME). Carbon-silica hybrid based acid catalysts derived from RH were successfully synthesized using MW. RHC can be obtained by MW pyrolysis at power level as low as 200 W. The elemental compositions results showed increase in S content after MW sulphonation. S content of sulphonated rice husk chars (SRHCs) were 17.2 – 18.5 times higher than S content in raw RH. FTIR results for all SRHCs further proved the presence of $-SO_3H$ on the catalysts by the appearance of peak at 1035 cm^{-1} which corresponded to $O=S=O$ stretching of sulphonic group. Besides, FTIR detected that peak related to silica (788 cm^{-1}) remained even after MW pyrolysis and sulphonation which suggest that silica did not decompose. XRD results showed that all SRHCs have an amorphous structure. Through SEM magnification, it was observed that MW pyrolysis and sulphonation caused broadening of the RH voids and also formation of pores. EDX analysis showed that silica content was higher on the outer surface of RH and carbon is higher on the inner surface. Meanwhile, S was only detected on the inner surface only. SRHCs were all mesoporous with pore diameter ranging from 3.89 nm to 5.41 nm. All SRHCs showed high catalytic activity for esterification of oleic acid (model compound for free fatty acids, FFA) with methanol with RH600 had the highest initial formation rate ($6.33\text{ mmol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$) and yield 97.19%. Reusability of catalyst showed gradually drop in yield for every reuse. The declination of catalytic performance might due to leaching of $-SO_3H$, due to washing of catalyst with methanol. Kinetic study of SRHCs showed that esterification of oleic acid with methanol under the reaction condition used fitted pseudo-first order. RH600 had low activation energy of 15.19 kJ/mol. Finally, esterification of oil recovered from under reaction condition of temperature 70°C , 40:1 molar ratio of methanol to recovered oil, stirring rate of 1200 rpm and 5 wt.% of catalyst loading able to convert 87.3% of FFA into fatty acid methyl ester (FAME). RH catalysts were successfully synthesized using MW technology and able to esterify FFA with high yield and initial formation rate. Further improvement of this work is to study the washing method for reusability purpose of the catalyst.

ABSTRAK

Penemuan pemangkin berasaskan karbon atau juga dikenali sebagai pemangkin gula telah mendapat perhatian kerana aktiviti pemangkinnya yang tinggi bagi pengeluaran biodiesel meskipun ianya mempunyai luas permukaan yang rendah. Ramai yang mencuba untuk menghasilkan karbon hibrid dengan bahan bukan organik bagi menyediakan luas permukaan yang lebih tinggi dan meningkatkan lagi prestasi pemangkin karbon. Walau bagaimanapun, kebanyakan bahan yang digunakan adalah mahal. Selain itu, langkah yang panjang perlu dilaksanakan bagi menghasilkan pemangkin hibrid. Oleh itu, sekam padi mendapat perhatian kerana kandungan karbon dan silikanya yang tinggi, dan sifatnya yang semula jadi berliang. Untuk mendapatkan karbon dari sekam padi, pirolisis sekam padi boleh dilaksanakan dengan menggunakan relau konvensional. Walau bagaimanapun, masa pirolisis memakan masa yang panjang (12-15 jam). Baru-baru ini, teknologi gelombang mikro (MW) telah banyak mendapat perhatian kerana keupayaannya untuk melancarkan pirolisis bahan bio-jisim dalam masa yang lebih singkat. Untuk kajian ini, pirolisis dan sulfonasi sekam padi menggunakan teknologi MW telah dicadangkan. Prestasi pemangkin yang disintesis oleh MW diuji melalui tindak balas pengesteran asid oleik, serta pengesteran minyak yang diekstrak daripada efluen kilang minyak sawi. Pemangkin asid berasaskan karbon-silika berasal dari sekam padi tersebut telah pun berjaya disintesis menggunakan MW. RHC boleh diperolehi oleh pirolisis MW pada paras kuasa serendah 200 W. Komposisi elemen menunjukkan peningkatan dalam kandungan S selepas sulfonasi. Kandungan S bagi sekam padi yang telah disulfonasi (SRHCs) adalah 17.2 - 18.5 kali lebih tinggi daripada kandungan S pada sekam padi mentah. Hasil FTIR bagi semua SRHC membuktikan kehadiran $-SO_3H$ pada pemangkin dengan kemunculan puncak pada 1035 cm^{-1} . Selain itu, FTIR turut mengesan silika (788 cm^{-1}). Keputusan XRD menunjukkan bahawa semua SRHC mempunyai struktur amorfus. Melalui SEM, SRHC kelihatan lompong dan berliang. Analisis EDX menunjukkan bahawa kandungan silika lebih tinggi pada permukaan luar SRHC dan karbon lebih tinggi pada permukaan dalaman. Sementara itu, S hanya dikesan di permukaan dalam sahaja. Kesemua SRHC mempunyai diameter pori antara 3.89 nm hingga 5.41 nm. SRHC menunjukkan aktiviti pemangkin yang tinggi dalam proses pengesteran asid oleik (sebatian model untuk asid lemak bebas, FFA) dengan metanol. RH600 mempunyai kadar pembentukan awal tertinggi ($6.33\text{ mmol.L}^{-1}.\text{min}^{-1}$) dan menghasilkan 97.19% metil ester. Apabila pemangkin diguna semula, hasil (%) semakin merosot secara beransuran. Penurunan prestasi pemangkin mungkin disebabkan oleh pelupusan $-SO_3H$, akibat dibasuh dengan metanol. Kajian kinetik SRHC menunjukkan bahawa esterifikasi asid oleik dengan metanol mengikut reaksi pseudo-pertama. RH600 mempunyai tenaga pengaktifan yang rendah (15.19 kJ/mol). Akhirnya, esterifikasi minyak dengan metanol berjaya menghasilkan 87.3% asid lemak metil ester. Pemangkin RH telah berjaya dihasilkan dengan menggunakan teknologi MW dan mampu mengolah FFA dengan hasil dan kadar pembentukan awal yang tinggi. Penambahbaikan bagi kerja ini adalah untuk mengkaji kaedah pencucian untuk kegunaan penggunaan semula pemangkin.

LIST OF CONTENTS

	Page
TITLE	i
DECLARATION	ii
CERTIFICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
<i>ABSTRAK</i>	vi
LIST OF CONTENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xvii
LIST OF APPENDICES	xix
CHAPTER 1: INTRODUCTION	
1.1 Research background	1
1.2 Problem statement	2
1.3 Research topics	3
1.4 Research novelty	4
1.5 Research objectives	4
1.6 Hypothesis	4
1.7 Scope of work	5
CHAPTER 2: LITERATURE REVIEW	
2.1 Biodiesel: An overview	6
2.1.1 Catalytic reactions based on feedstocks	6

2.1.2	Classification of feedstock for biodiesel production: Advantages and disadvantages	10
2.2	Oil recovered from Palm Oil Mill Effluent (POME) as potential feedstock in Malaysia	12
2.3	Solid acid catalyst for biodiesel production	16
2.3.1	Development of sulphonated carbon-based acid catalysts	17
2.4	Rice husk as carbon based catalyst: Synthesis, characterization and activity	20
2.4.1	Routes for preparation of char from rice husk	25
2.5	Reaction conditions for transesterification/esterification catalyzed by sulphonated solid catalyst	26
2.6	Microwave heating mechanism	30
2.6.1	Conventional heating versus microwave heating	33
2.6.2	Microwave assisted pyrolysis	34
CHAPTER 3: METHODOLOGY		
3.1	Material	37
3.2	Preparation of rice husk for synthesis of catalyst	38
3.3	Catalyst preparation	38
3.3.1	Pyrolysis of RH by using microwave	39
3.3.2	Sulphonation of rice husk char	41
3.4	Characterization of SRHCs	42
3.4.1	Elemental compositions	42
3.4.2	Total acidity	42
3.4.3	Functional group	42
3.4.4	Carbon structure	43
3.4.5	Surface morphology and element detection	44
3.4.6	Specific surface area and pore volume	45
3.4.7	Thermal stability	45

3.5	Catalytic activity of SRHCs	45
3.5.1	Esterification of oleic acid	46
3.5.2	Product analysis	46
3.5.3	Recovery and reusability of SRHC	48
3.5.4	Activation energy of SRHC	48
3.6	Esterification of oil recovered from Palm Oil Mill Effluent (POME) catalyzed by SRHC	49
3.6.1	Recovery of oil from POME	49
3.6.2	Properties of oil recovered from POME	50
3.6.3	Reaction condition	52
3.6.4	Titration analysis	52
CHAPTER 4: RESULTS AND DISCUSSION		
4.1	Preparation of sulphonated rice husk catalyst	54
4.2	Characterization of SRHCs	58
4.2.1	Elemental analysis and total acidity of RH and SRHCs	58
4.2.3	Functional group	60
4.2.4	Carbon structure	63
4.2.5	Surface morphology	67
4.2.6	Surface area	71
4.2.7	Thermal stability of SRHC	73
4.3	Catalytic activity of SRHC	74
4.3.1	Calibration curve of methyl oleate	74
4.3.2	Esterification of oleic acid and comparative study	75
4.3.3	Effect of temperature on SRHC	79
4.4	Kinetic analysis of SRHC	80
4.5	Activation energy of SRHC	86
4.6	Reusability of SRHC	88

4.7	Esterification of oil from palm oil mill effluent	89
CHAPTER 5: CONCLUSION		
5.1	Conclusions	91
5.2	Recommendation	93
REFERENCES		94
APPENDICES		106



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LIST OF TABLES

Table 1:	Generation of biodiesel feedstocks	10
Table 2:	Chemical properties and fatty acid composition of palm oil residual of from POME	14
Table 3:	Ultimate analyses and proximate analyses of RH	20
Table 4:	Summary of surface area analysis of porous carbons	24
Table 5:	Optimum condition for reaction catalyzed by sulphonated solid acid catalyst	29
Table 6:	Char yield from microwave pyrolysis of biomasses	36
Table 7:	Operating conditions of GC to analyze quantity of methyl oleate produced	47
Table 8:	Weight of RH before and after washing	54
Table 9:	C, H, N, S content in RH and SRHCs	59
Table 10:	Total acidity and sulphonic acid density of SRHCs	60
Table 11:	Elemental compositions of RH and SRHCs using EDX	69
Table 12:	Surface characterization of RH and SHRCs	72
Table 13:	Data based on area from GC-FID	75
Table 14:	Comparison of characteristics and activity of SRHCs with other acid catalysts	77
Table 15:	The effect of temperature on initial formation rate of reactions	80
Table 16:	Kinetics parameters for reaction catalyzed by SRHCs at temperature 333.15 K	84
Table 17:	Summary of kinetics for RH600 at three different temperatures	86
Table 18:	Physicochemical properties of oil recovered from POME	89
Table 19:	Esterification of oil recovered from POME	90
Table 20:	Supplementary data on pyrolysis using power level of 450 W at different times	107
Table 21:	Weight loss and char yield after MW pyrolysis at different power levels	108
Table 22:	Raw data from back-titration method to determine total acidity of RH450	110

Table 23:	Volume of stock solution needed to obtain desired concentration for calibration curve	126
Table 24:	Table of concentration of methyl oleate over time for reaction catalyzed by H ₂ SO ₄ at temperature 60°C	129
Table 25:	Table of concentration of methyl oleate over time for reaction catalyzed by SRHC at temperature 60°C	130
Table 26:	Table of concentration of methyl oleate over time for reaction catalyzed by RH600 at temperature 70°C and 80°C	130
Table 27:	Concentration of methyl oleate over time catalyzed by RH700 and its standard deviation	131
Table 28:	Molar balance of reaction catalyzed by H ₂ SO ₄ at temperature 60°C calculated using excel	132
Table 29:	Molar balance of reaction catalyzed by RH200 at temperature 60°C calculated using excel	132
Table 30:	Molar balance of reaction catalyzed by RH300 at temperature 60°C calculated using excel	132
Table 31:	Molar balance of reaction catalyzed by RH450 at temperature 60°C calculated using excel	133
Table 32:	Molar balance of reaction catalyzed by RH600 at temperature 60°C calculated using excel	133
Table 33:	Molar balance of reaction catalyzed by RH600 at temperature 70°C calculated using excel	133
Table 34:	Molar balance of reaction catalyzed by RH600 at temperature 80°C calculated using excel	134
Table 35:	Molar balance of reaction catalyzed by RH700 at temperature 60°C calculated using excel	134
Table 36:	Yield of methyl oleate over time for esterification reaction catalyzed by H ₂ SO ₄ at temperature 60°C	136
Table 37:	Yield of methyl oleate over time for esterification reaction catalyzed by SRHCs at temperature 60°C	136
Table 38:	Yield of methyl oleate over time for esterification reaction catalyzed by RH600 at temperature 70°C and 80°C	137
Table 39:	Density of POME	144
Table 40:	Data for determination of saponification value	145
Table 41:	Data for experiment on determination of acid value	145

LIST OF FIGURES

Figure 1:	Transesterification reaction of triglycerides with methanol	7
Figure 2:	Effect of the presence of water alkali -catalyzed reaction	8
Figure 3:	Esterification reaction of fatty acids with methanol	8
Figure 4:	Summary on classification of typical biodiesel production pathways	9
Figure 5:	Flow chart of typical milling process in Malaysia	13
Figure 6:	Polycyclic aromatic carbon sheet	17
Figure 7:	Preparation of carbon based catalyst	18
Figure 8:	XRD patterns for pyrolysed D-glucose (A) before and (B) after sulfonation	18
Figure 9:	Preparation steps for composites solid acid catalyst	19
Figure 10:	Electromagnetic spectrum	30
Figure 11:	Movement of electromagnetic field	32
Figure 12:	The propagation process of MW penetration into sample followed by thermal energy being transferred outwards	33
Figure 13:	Heating mechanism of conventional heating and microwave heating	34
Figure 14:	The size of the RH particle was measured using ruler. The range was 8 – 10 mm long and 1.5 – 2.5 mm wide	37
Figure 15:	Colour of the washed water after several washing. (a) 1st wash (b) 2nd wash (c) 3rd wash (d) 4th wash (e) 5th wash.	38
Figure 16:	Flow diagram of catalyst preparation.	39
Figure 17:	Modified microwave equipped with N ₂ gas inlet and outlet.	40
Figure 18:	Glass round bottom flask in microwave chamber.	40
Figure 19:	Cary 630 FTIR, Agilent	43
Figure 20:	Photo on left is an automatic sputter coater, model Q 150R S, Quorum. This machine was used to coat sample with Au.	

	Meanwhile, photo on the right is the image of SEM-EDX, model S-3400N, Hitachi.	44
Figure 21:	RH after MW pyrolysis at power (a) 100 W, (b) 200 W, (c) 300 W, (d) 450 W, (e) 600 W and (f) 700 W. Some unburned RHs were observed when pyrolysed at power 100 W to 450 W.	55
Figure 22:	Graph of weight loss and yield at different power.	57
Figure 23:	FTIR spectrum of RH feedstock	61
Figure 24:	FTIR spectrum of RH600	62
Figure 25:	IR spectrum for RH and all MW synthesized catalysts	63
Figure 26:	XRD spectra of RH feedstock	64
Figure 27:	XRD spectra of RH600	65
Figure 28:	XRD spectrum of RH and SRHCs	66
Figure 29:	SEM images of RH particle.	67
Figure 30:	SEM images of SRHC pyrolyzed at 600 W.	68
Figure 31:	Point on an outer surface of RH600 for EDX analysis	70
Figure 32:	Point on the inner surface near voids on RH600 for EDX analysis	70
Figure 33:	Proposed illustration of SRHC with hybrid carbon-silica support	71
Figure 34:	Nitrogen adsorption-desorption of RH and RH600	73
Figure 35:	Curve fits for experimental data from esterification of oleic acid at 60° C for 12 h reaction time	76
Figure 36:	Activity of RH600 at three different temperatures	79
Figure 37:	First order reaction based on pseudo-homogeneous model for RH600	83
Figure 38:	Second order reaction based on pseudo-homogeneous model for RH600	84
Figure 39:	Pseudo-first order graphs of RH600 at three different temperatures	85
Figure 40:	Relationship between $\ln k$ and $1/T$ for reaction catalyzed by RH600	87

Figure 41:	Reusability performance of RH600	89
Figure 42:	Rice husk collected from Kilang Seri Padi Dusun on 18th April 2017 and was kept in a sealed bag	106
Figure 43:	Approximately 100 g of RH was weighed before washing	106
Figure 44:	Removal of unburned RH from product of MW pyrolysis at power 200 W	108
Figure 45:	FTIR spectra of RH200	112
Figure 46:	FTIR spectra of RH300	113
Figure 47:	FTIR spectra of RH450	113
Figure 48:	FTIR spectra of RH700	114
Figure 49:	XRD spectra of RH200	115
Figure 50:	XRD spectra of RH300	115
Figure 51:	XRD spectra of RH450	116
Figure 52:	XRD spectra of RH700	116
Figure 53:	SEM images of RH200	117
Figure 54:	SEM images of RH300	118
Figure 55:	SEM images of RH450	118
Figure 56:	SEM images of RH700	119
Figure 57:	N ₂ adsorption-desorption for RH200	120
Figure 58:	N ₂ adsorption-desorption for RH300	120
Figure 59:	N ₂ adsorption-desorption for RH450	121
Figure 60:	N ₂ adsorption-desorption for RH700	121
Figure 61:	TGA-DTA analysis of RH200	122
Figure 62:	TGA-DTA analysis of RH300	122
Figure 63:	TGA-DTA analysis of RH450	123
Figure 64:	TGA-DTA analysis of RH600	123
Figure 65:	TGA-DTA analysis of RH700	124

Figure 66:	GC raw data for concentration of 100 ppm. Peak of methyl oleate was observed at t=4.99.	126
Figure 67:	R value generated from GC was 0.999377	127
Figure 68:	Slope at t=0 to determine initial formation rate of methyl oleate catalzed by RH200	135
Figure 69:	First order reaction based on pseudo-homogeneous model for esterification at temperature 60°C catalyzed by RH200	138
Figure 70:	Second order reaction based on pseudo-homogeneous model for esterification at temperature 60°C catalyzed by RH200	139
Figure 71:	First order reaction based on pseudo-homogeneous model for esterification at temperature 60°C catalyzed by RH300	139
Figure 72:	Second order reaction based on pseudo-homogeneous model for esterification at temperature 60°C catalyzed by RH300	140
Figure 73:	First order reaction based on pseudo-homogeneous model for esterification at temperature 60°C catalyzed by RH450	140
Figure 74:	Second order reaction based on pseudo-homogeneous model for esterification at temperature 60°C catalyzed by RH450	141
Figure 75:	First order reaction based on pseudo-homogeneous model for esterification at temperature 60°C catalyzed by RH700	141
Figure 76:	Second order reaction based on pseudo-homogeneous model for esterification at temperature 60°C catalyzed by RH700	142

LIST OF ABBREVIATIONS

AV	-	Acid Value
BOD	-	Biochemical Oxygen Demand
CaO	-	Calcium Oxide
COD	-	Chemical Oxygen Demand
-COOH	-	Carboxyl Group
CPO	-	Crude Palm Oil
DTA	-	Derivative Thermal Analysis
Ea	-	Activation Energy
EDX	-	Energy Dispersive X-ray
FAME	-	Fatty Acid Methyl Ester
FFA	-	Free Fatty Acid
FFB	-	Fresh Fruit Bunches
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared Spectrometry
GC	-	Gas Chromatography
HCl	-	Hydrochloric Acid
H ₂ SO ₄	-	Sulphuric Acid
KOH	-	Potassium Hydroxide
MeOH	-	Methanol
MgO	-	Magnesium Oxide
MNF	-	Micro/Nano Fiber
MW	-	Microwave
N ₂	-	Nitrogen gas
NaOH	-	Sodium Hydroxide
OA	-	Oleic Acid
-OH	-	Hydroxyl Group

POME	-	Palm Oil Mill Effluent
PTSA	-	p-Toluenesulfonic Acid
RH	-	Rice Husk
RHC	-	Rice Husk Char
SBA-15	-	Santa Barbara Amorphous-15
SC	-	Sugar Catalyst
SD	-	Standard Deviation
SEM	-	Scanning Electron Microscopy
-SO ₃ H	-	Sulphonic Group
SO ₄ ²⁻	-	Sulfates
SO ₄ ²⁻ /SnO ₂	-	Sulfated Stannous Oxide
SO ₄ ²⁻ /ZrO	-	Sulfated Zirconium Oxide
SPO	-	Sludge Palm Oil
SRHC	-	Sulphonated Rice Husk Char
SrO	-	Strontium Oxide
TFMSA	-	Trifluoromethanesulfonic Acid
TG	-	Triglyceride
TGA	-	Thermal Gravimetric Analysis
W	-	Watt
WO	-	Tungsten
wt.%	-	Weight Percentage
XPS	-	X-Ray Photoelectron Spectroscopy
XRD	-	X-Ray Diffraction

LIST OF APPENDICES

Appendix A	:	Catalyst preparation	106
Appendix A.1	:	Images of RH feedstock	106
Appendix A.2	:	Pyrolysis of rice husk using microwave	107
Appendix B	:	Characterization of catalyst	109
Appendix B.1	:	Sample calculation on mole ratio of O/C, H/C and S/C based on elemental analyzer	109
Appendix B.2	:	Sample calculation for total acidity of RH450	110
Appendix B.3	:	Sample calculation for SO ₃ H density based on elemental analyzer	111
Appendix B.4	:	FTIR spectrum of SRHCs	111
Appendix B.5	:	XRD spectrum of SRHCs	114
Appendix B.6	:	SEM images of SRHCs	116
Appendix B.7	:	N ₂ adsorption-desorption of SRHCs	118
Appendix B.8	:	TGA analysis on SRHCs	120
Appendix C	:	Catalytic activity of SRHCs	123
Appendix C.1	:	Calculation for preparation of methyl oleate standard for calibration curve	123
Appendix C.2	:	Dilution factor and determination of real concentration of sample	125
Appendix C.3	:	Esterification reaction of oleic acid	126
Appendix C.3.1	:	Calculation of weight and volume of reactants based on molar ratio of 1:12.	126
Appendix C.3.2	:	Results on concentration of methyl oleate (mol/L) obtained from esterification reaction of oleic acid using H ₂ SO ₄ and SRHCs	127
Appendix C.3.3	:	Calculation of standard deviation of esterification reactions	128

Appendix C.3.4:	Molar balance of esterification reactions the yield	129
Appendix C.3.5:	Sample calculation for initial formation rate	132
Appendix C.3.6:	Calculation of yield of methyl oleate	133
Appendix D :	Kinetic analysis	136
Appendix D.1 :	Determination of order of reaction using integral method	136
Appendix D.2 :	Sample calculation for determination of rate constant, k	141
Appendix E :	Characterization of Palm Oil Mill Effluent (POME)	142
Appendix E.1 :	Sample calculation for determination of oil density	142
Appendix E.2 :	Sample calculation of saponification value	142
Appendix E.3 :	Determination of acid value	143
Appendix F :	List of publications and achievements	144
Appendix G :	Examiners comments and corrective action	145



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CHAPTER 1

INTRODUCTION

1.1 Research background

On late 18th and early 19th century, the inauguration of industrial revolution had put energy to become one of the most important factors for economic growth as well as to maintain an urban living standard (Atabani, Silitonga, Badruddin, Mahlia and Mekhilef, 2012). Since then, fossil fuels play an important role as primary source for electricity, heating, transportation and etc. However, the demand on fossil fuels is still on a rise which will cause depletion of the fossil fuels near future. Though, it is still the primary source for transportation fuel, globally. To reduce the dependency on fossil fuels, biodiesel came into the picture as an alternative fuel. Biodiesel was first discovered by Rudolf Diesel on 1890s. The development and advancement study on biodiesel continue to bloom after the first discovery.

Biodiesel is an alternative fuel that can be derived from any feedstock containing triglycerides (TG) and/or free fatty acids (FFA). Vegetables oil, waste oil and grease are the examples of biodiesel feedstock. Biodiesel can be produced through transesterification of any feedstock with methanol producing fatty acid methyl esters (FAME) and glycerol with or without catalyst. In Malaysia context, palm oil is the most suitable feedstock for biodiesel production due to the abundant source available. However, palm oil is expensive and it causes competition with food source. Another alternative biodiesel feedstock that is oil recovered from palm oil mill effluent (POME). Based on information extracted from Sumathi, Chai, and Mohamed (2008), it was calculated that Malaysia produces approximately 16 – 26 million m³ of POME every year. Around 90 000 – 156 000 m³ of residual oil can be recovered for biodiesel production, annually. The properties of oil recovered from

POME reported to be comparable with palm oil but it has high FFA and moisture content (Primandari, Yaakob, Mohammad, and Mohamad, 2013).

A "green" catalyst that can convert feedstock with high FFA content into FAME had been discovered by Hara and co-workers. It was reported that pyrolysis of D-glucose at optimum temperature of 400°C produced an amorphous carbon which can easily be functionalized and has high reactivity (Okamura, Takagaki, Toda, Kondo, Domen, Tatsumi, Hara, and Hayashi, 2006). Carbon-based catalyst can also be derived from lignocellulosic material such as biomass (Nakajima and Hara, 2012). Rice husk (RH) is a potential biomass due to its availability, compositions and naturally containing high surface area (Touhami, Zhu, Balan, Janaun, Haywood, and Zein, 2017). However, pyrolysis using conventional heating is time and energy consuming. Pyrolysis through irradiation heating using microwave was reported to be fast and efficient, as well as producing better properties of char (Touhami *et al.*, 2017). Therefore, in this study, catalysts derived from RH will be synthesized using microwave (MW) technology. The activity of synthesized catalysts will be evaluated through esterification of oleic acid and methanol. The kinetics and activation energy of catalyst and the reactions will also be evaluated. Finally, performance of the catalysts converting FFA in oil recovered from POME into FAME will also be tested through esterification with methanol.

1.2 Problem statement

Discovery of sugar catalyst by Hara *et al.* has gained attention due to its high catalytic activity on biodiesel production and comparable performance with sulphuric acid, H₂SO₄ despite possessing a low surface area. Many had tried to hybrid carbon with other inorganic material such as Santa Barbara Amorphous-15 (SBA-15), Platinum, Ferum and etc., to provide higher surface area and further improve the performance of carbon catalyst. However, the material used for a hybrid catalyst is expensive. Furthermore, tedious procedures need to be done in order to synthesize a hybrid catalyst.