

**BIODIESEL PRODUCTION FROM WASTE PALM OIL
USING WASTE BIOMASS DERIVED SOLID ACID
CATALYSTS**

BY

PAHALAGEDARA INDIKA THUSHARI

**A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY (ENGINEERING AND TECHNOLOGY)
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A Dissertation Presented

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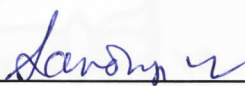
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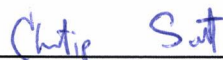
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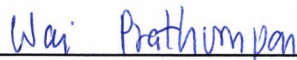
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Abstract

BIODIESEL PRODUCTION FROM WASTE PALM OIL USING WASTE BIOMASS DERIVED SOLID ACID CATALYSTS

by

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Production of biodiesel from waste palm oil (WPO) can provide alternative energy and at the same time reduce the problems created by disposal of WPO. In addition, use of solid acid catalysts (SACs) derived from waste biomass for biodiesel production, makes the overall process more economical and sustainable.

In this study, desired carbon based SACs were synthesized from palm empty fruit bunch (PEFB), coconut meal residue (CMR), and coconut coir husk (CCH) as waste biomass, adapting two simple protocols; direct in-situ one step concentrated H₂SO₄ carbonization (DS) and sulfonation of incompletely carbonized biomass (BCS). Prepared catalysts were duly characterized for physical and chemical properties. The activity of the catalysts was studied for biodiesel production from WPO (5.2%) in an open (using a reflux reactor) and closed (using a laboratory scale autoclave and microwave assisted reactor) systems. The fatty acid methyl ester (FAME) yield was determined by gas chromatography.

The presence of active functional groups, such as SO₃H, COOH, and OH on the surface of the catalysts was confirmed by Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Results showed that the

catalysts prepared from DS protocol have high sulfonic acid groups compared to BCS protocol. Despite the high acid density, they have low surface area compared to the catalysts prepared from BCS protocol. Among the catalysts prepared from DS protocol, PEFB-DS-SO₃H and CMR-DS-SO₃H showed the highest FAME yields of 91% and 92.7%, respectively, under optimum conditions in an open reflux reactor. For CMR-DS-SO₃H, the highest FAME yield of 95.5% was obtained at 150 °C and 3 h reaction time in an autoclave assisted reactor, and 94.7% FAME yield at 70 °C and 40 min in a microwave assisted reactor. However, CCH-DS-SO₃H catalyst which showed a poor activity in an open reflux reactor was able to give a maximum FAME yield of 89.8% using 10 wt. % catalyst at 130 °C and 3 h using an autoclave reactor. It was also found that PEFB-DS-SO₃H, CMR-DS-SO₃H, and CCH-DS-SO₃H can be re-used for at least four cycles without significant loss of the catalytic activity. Even though, PEFB-BCS-SO₃H, CMR-BCS-SO₃H, and CCH-BCS-SO₃H showed poor activity during biodiesel production in an open reflux reactor, they showed higher catalytic activity in a microwave assisted reactor.

This study indicated that PEFB, CMR, and CCH as waste biomass can be used for SACs preparation and sustainable biodiesel production. DS is a simple and economical protocol for SAC preparation and prepared catalysts can be successfully employed for biodiesel production from WPO (5.2% FFA). The presence of high amounts of both strong (SO₃H-contributing to a high acid density) and weak (COOH and OH-acting as the anchoring sites) acid groups bonded to the hydrophobic carbon structure is a possible reason for the high activity of the catalysts. Biodiesel production using an autoclave and a microwave assisted reactor provided a good yield at relatively low reaction time compared to an open-reflux reactor. However, it is required to understand the cost-effectiveness and sustainability of the overall process through a life cycle assessment. It was found that the fuel properties of the produced biodiesel meet the international standards.

Keywords: Biodiesel; Direct sulfonation; Waste biomass; Waste palm oil; Solid acid catalysts; Fuel properties

Table of Contents

Chapter	Title	Page
	Signature Page	i
	Acknowledgments	ii
	Abstract	iii
	Table of Contents	v
	List of Figures	ix
	List of Tables	xiv
	List of Abbreviations	xv
1	Introduction	1
	1.1 Background	1
	1.2 Objectives of the study	4
	1.3 Scope of the study	5
2	Literature review	7
	2.1 WCO as a potential biodiesel feedstock	7
	2.2 Conventional catalysts used in biodiesel production	11
	2.3 Carbon based SACs used in biodiesel production	13
	2.3.1 Biochar based SACs for biodiesel production	14
	2.3.1.1 Physically activated carbon based SACs for biodiesel production	15
	2.3.1.2 Chemically activated carbon based SACs for biodiesel production	17
	2.3.1.3 Nano-scale carbon based SACs for biodiesel production	18
	2.3.2 In-situ H ₂ SO ₄ carbonized carbon based SACs for biodiesel production	19
	2.4 Features of carbon based SACs	23
	2.4.1 Acid strength	24
	2.4.2 Surface hydrophobicity	24
	2.4.3 Porosity, surface area, and surface structure	25
	2.5 Current biodiesel production processes	29

2.5.1	Conventional open reflux reactor assisted biodiesel production	29
2.5.2	Autoclave assisted biodiesel production	30
2.5.3	Microwave assisted biodiesel production	32
2.6	Fuel properties of biodiesel	35
2.6.1	Acid value	35
2.6.2	Viscosity	36
2.6.3	Density	36
2.6.4	Heating value	36
2.6.5	Cetane number	41
2.6.6	Oxidation stability	41
2.6.7	Flash point	41
2.6.8	Cloud point and pour point	42
2.6.9	Water and sediments content	42
2.6.10	Ash content	42
3	Materials and methodology	43
3.1	Materials	43
3.2	Catalyst preparation	44
3.2.1	Direct in-situ concentrated H ₂ SO ₄ carbonization of waste biomass	45
3.2.2	Sulfonation of incompletely carbonized waste biomass	46
3.3	Characterization of carbon based SACs	46
3.3.1	Total acid density and sulfonic acid density	46
3.3.2	Elemental composition	47
3.3.3	Surface area and pore size distribution	47
3.3.4	Surface morphology	47
3.3.5	Presence of surface functional groups	47
3.3.6	Chemical states of functional groups	47
3.3.7	Thermal stability	48
3.4	Evaluation of the catalytic activity	48
3.4.1	Esterification of palmitic acid	48
3.4.2	Biodiesel production from WPO	51
3.4.2.1	Biodiesel production from WPO using a conventional	

open reflux reactor	51
3.4.2.2 Biodiesel production from WPO using an autoclave reactor	52
3.4.2.3 Biodiesel production from WPO using a microwave reactor	54
3.4.3 Reusability of the catalysts	55
3.4.4 Ester separation and purification	55
3.5 Characterization of biodiesel produced from WPO	55
3.5.1 FAME yield	55
3.5.2 Fuel properties of produced biodiesel	56
3.5.2.1 Acid value and FFA content	56
3.5.2.2 Viscosity	57
3.5.2.3 Density	57
3.5.2.4 Flash point	58
3.5.2.5 Pour point	58
3.5.2.6 Heating value	58
3.5.2.7 Oxidation stability	59
3.5.2.8 Ash content	59
3.5.2.9 Sulfur content	60
3.6 Comparison of energy consumption of three reactors	60
4 Results and Discussion	62
4.1 Characterization of biodiesel feedstock	62
4.2 Characterization of the catalysts	64
4.2.1 Total acid density and sulfonic acid density	64
4.2.2 Surface area, pore size distribution, and surface morphology	68
4.2.3 Presence of surface functional groups	73
4.2.4 Chemical states of surface functional groups	79
4.2.5 Thermal stability	82
4.3 Catalyst activity for esterification of palmitic acid	87
4.4 Catalyst activity for biodiesel production from WPO	89
4.4.1 Biodiesel production using an open reflux reactor	89
4.4.2 Biodiesel production using an autoclave assisted reactor	95
4.4.3 Biodiesel production using a microwave assisted reactor	102
4.4.4 Comparison of biodiesel production from WPO and CMR-DS-SO ₃ H	

using three different reactors	108
4.5 Fuel characteristics of produced biodiesel	111
4.5.1 Acid value	112
4.5.2 Viscosity	112
4.5.3 Density	113
4.5.4 Heating value	115
4.5.5 Oxidation stability	115
4.5.6 Flash point	116
4.5.7 Pour point	116
4.5.8 Ash content	116
4.5.9 Sulfur content	117
5 Conclusions and Recommendations	118
5.1 Conclusions	118
5.2 Recommendations for future work	120
References	122
Appendices	138
Appendix A	139
Appendix B	144
Appendix C	147

List of Figures

Figures	Page
1.1 SAC catalyzed simultaneous esterification and trans-esterification	3
2.1 Cost distribution in biodiesel production process	8
2.2 Wholesale prices for biodiesel and vegetable oil (as mean values of rapeseed, soybean, palm, and sunflower oil prices) in Germany	8
2.3 Price of biodiesel and raw materials in Thailand	9
2.4 Feedstocks used in biodiesel production, worldwide in 2015	9
2.5 (a) Acid or base catalyzed trans-esterification, (b) esterification, and (c) saponification	12
2.6 SAC catalyzed simultaneous esterification and trans-esterification	13
2.7 Catalyst preparations by sulfonation of carbonized biomass	14
2.8 Different proposed graphical structures for carbon based SACs	23
2.9 Bronsted and Lewis acid sites in $\text{SO}_4^{2-}/\text{ZrO}_2$	24
2.10 A conventional open reflux reactor	29
2.11 A closed autoclave reactor	31
2.12 Mechanism of conventional and microwave assisted heating	33
2.13 Microwave assisted (a) a batch reactor, (b) a flow reactor	34
3.1 Waste biomass used as carbon precursors; (a) PEFB, (b) CMR, and (c) CCH	44
3.2 Schematic diagram for catalyst preparation	45
3.3 Schematic diagram of biodiesel production (a) using palmitic acid, (b) using WPO	49
4.1 EDS of (a) PEFB-DS- SO_3H , (b) PEFB-BCS- SO_3H , (c) CMR-DS- SO_3H , (d) CMR-BCS- SO_3H , (e) CCH-DS- SO_3H , and (f) CCH-BCS- SO_3H	67

4.2	Adsorption-desorption isotherms of (a) PEFB-DS-SO ₃ H, (b) PEFB-BCS-SO ₃ H, (c) CMR-DS-SO ₃ H, (d) CMR-BCS-SO ₃ H, (e) CCH-DS-SO ₃ H, and (f) CCH-BCS-SO ₃ H	70
4.3	Pore-size distribution of (a) PEFB-DS-SO ₃ H, (b) PEFB-BCS-SO ₃ H, (c) CMR-DS-SO ₃ H, (d) CMR-BCS-SO ₃ H, (e) CCH-DS-SO ₃ H, and (f) CCH-BCS-SO ₃ H	71
4.4	SEM of (a) PEFB-DS-SO ₃ H, (b) PEFB-BCS-SO ₃ H, (c) CMR-DS-SO ₃ H, (d) CMR-BCS-SO ₃ H, (e) CCH-DS-SO ₃ H, and (f) CCH-BCS-SO ₃ H	72
4.5	FT-IR spectra of (a) Raw PEFB, (b) PEFB-DS-SO ₃ H, and (c) PEFB-BCS-SO ₃ H	74
4.6	FT-IR spectra of (a) Raw CMR, (b) CMR-DS-SO ₃ H, and (c) CMR-BCS-SO ₃ H	75
4.7	FT-IR spectra of (a) Raw CCH, (b) CCH-DS-SO ₃ H, and (c) CCH-BCS-SO ₃ H	75
4.8	FT-IR spectra of (a) PEFB-DS-SO ₃ H, (b) used catalyst after first run, and (c) used catalyst after second run in an open reflux reactor	76
4.9	FT-IR spectra of (a) CMR-DS-SO ₃ H, (b) used catalyst after first run, and (c) used catalyst after third run in an open reflux reactor	77
4.10	FT-IR spectra of (a) CMR-DS-SO ₃ H, (b) used catalyst after first run, and (c) used catalyst after third run in an autoclave reactor	77
4.11	FT-IR spectra of (a) CMR-DS-SO ₃ H, (b) used catalyst after first run, and (c) used catalyst after third run in a microwave reactor	78
4.12	FT-IR spectra of (a) CCH-DS-SO ₃ H, (b) used catalyst after first run, and (c) used catalyst after third run in an autoclave reactor	78
4.13	XPS of (a) PEFB-DS-SO ₃ H, (b) PEFB-BCS-SO ₃ H, (c) CMR-DS-SO ₃ H, (d) CMR-BCS-SO ₃ H, (e) CCH-DS-SO ₃ H, and (f)	

	CCH-BCS-SO ₃ H	80
4.14	De-convoluted spectra of (a) S2p, (b) C1s, and (c) O1s peaks of PEFB-DS-SO ₃ H	81
4.15	De-convoluted spectra of (a) S2p, (b) C1s, and (c) O1s peaks of CMR-DS-SO ₃ H	81
4.16	De-convoluted spectra of (a) S2p, (b) C1s, and (c) O1s peaks of CCH-DS-SO ₃ H	81
4.17	S2p of used catalysts (a) PEFB-DS-SO ₃ H (b) CMR-DS-SO ₃ H	82
4.18a	TGA of PEFB-DS-SO ₃ H	84
4.18b	TGA of CMR-DS-SO ₃ H	84
4.18c	TGA of CCH-DS-SO ₃ H	85
4.18d	TGA of PEFB-BCS-SO ₃ H	85
4.18e	TGA of CMR-BCS-SO ₃ H	86
4.18f	TGA of CCH-BCS-SO ₃ H	86
4.19	Effect of reaction time and temperature on esterification efficiency of palmitic acid in an open reflux reactor with 5 wt. % PEFB-DS-SO ₃ H and 4:1 methanol to palmitic acid molar ratio	87
4.20	Effect of methanol loading on esterification efficiency of palmitic acid in an open reflux reactor with 5 wt. % PEFB-DS-SO ₃ H at 80 °C for 5 h	88
4.21	Reusability of PEFB-DS-SO ₃ H for esterification of palmitic acid in an open reflux reactor with 5 wt. % catalyst and 6:1 methanol to oil molar ratio at 80 °C for 5 h	88
4.22	Effect of methanol:oil (molar ratio) on FAME yield (%) in an open reflux reactor with 5 wt.% catalyst at 65-70 °C for 8 or 10 h	90
4.23	Effect of reaction time on FAME yield (%) in an open reflux reactor (5 wt. % catalyst, 14:1 and 12:1 methanol to oil molar ratio) for PEFB-DS-SO ₃ H and CMR-DS-SO ₃ H, at 65-70 °C	91
4.24	Effect of CMR-DS-SO ₃ H loading on FAME yield (%) in an open reflux reactor with 12:1 methanol to oil molar ratio at 65-	

	70 °C for 12 h	92
4.25	Effect of PEFB-DS-SO ₃ H loading on FAME yield (%) in an open reflux reactor with 14:1 methanol to oil molar ratio at 65-70 °C for 10 h	92
4.26	Reusability of CMR-DS-SO ₃ H for FAME production from WPO in an open reflux reactor with 5 wt. % catalyst and 12:1 methanol to oil molar ratio at 65-70 °C for 12 h	93
4.27	Reusability of PEFB-DS-SO ₃ H for FAME production from WPO in an open reflux reactor with 5 wt. % catalyst and 14:1 methanol to oil molar ratio at 65-70 °C for 14 h	93
4.28	Effect of reaction temperature on FAME yield (%) in an autoclave reactor with 5 wt. % CCH-DS-SO ₃ H and 12:1 methanol to oil molar ratio for 3 h	98
4.29	Effect of reaction time on FAME yield (%) in an autoclave reactor with 5 wt. % CCH-DS-SO ₃ H and 12:1 methanol to oil molar ratio at 130 °C	98
4.30	Effect of CCH-DS-SO ₃ H loading on FAME yield (%) in an autoclave reactor with 12:1 methanol to oil molar ratio at 130 °C for 3 h	98
4.31	Reusability of CCH-DS-SO ₃ H for FAME production from WPO in an autoclave reactor with 10 wt. % catalyst and 12:1 methanol to oil molar ratio at 130 °C for 3 h	98
4.32	Effect of reaction temperature on FAME yield (%) in an autoclave reactor with 5 wt. % CMR-DS-SO ₃ H and 12:1 methanol to oil molar ratio after 3 h	99
4.33	Effect of reaction time on FAME yield (%) in an autoclave reactor with 5 wt. % CMR-DS-SO ₃ H and 12:1 methanol to oil molar ratio at 150 °C	99
4.34	Reusability of CMR-DS-SO ₃ H for FAME production from WPO in an autoclave reactor with 5 wt. % CMR-DS-SO ₃ H and 12:1 methanol to oil molar ratio at 150 °C for 3 h	100
4.35	Effect of reaction temperature on FAME yield (%) in an	

	autoclave reactor with 5 wt. % PEFB-DS-SO ₃ H and 6:1 methanol to oil molar ratio for 3 h	101
4.36	Effect of reaction time on FAME yield (%) in a microwave assisted reactor with 5 wt. % catalyst and 12:1 methanol to oil molar ratio at 70 °C	103
4.37	Effect of methanol:oil molar ratio on FAME yield (%) in a microwave assisted reactor with 5 wt.% catalyst at 70 °C for 60 min	104
4.38	Effect of reaction temperature on FAME yield (%) in a microwave assisted reactor with 5 wt. % catalyst and 16:1 methanol to oil molar ratio for 60 min	104
4.39	Reusability of PEFB-BCS-SO ₃ H, CMR-BCS-SO ₃ H, and CCH-BCS-SO ₃ H for FAME production from WPO in a microwave assisted reactor with 5 wt. % catalyst and 16:1 methanol to oil molar ratio at 70 °C for 60 min	105
4.40	Effect of reaction time on FAME yield (%) in a microwave assisted reactor with 5 wt. % CMR-DS-SO ₃ H and 12:1 methanol to oil molar ratio at 70 °C	106
4.41	Effect of reaction temperature on FAME yield (%) in a microwave assisted reactor with 5 wt. % CMR-DS-SO ₃ H and 12:1 methanol to oil molar ratio and 40 min	106
4.42	Effect of CMR-DS-SO ₃ H loading on FAME yield (%) in a microwave assisted reactor with 12:1 methanol to oil molar ratio at 70 °C for 40 min	107
4.43	Reusability of CMR-DS-SO ₃ H for FAME production in a microwave assisted reactor with 5 wt. % catalyst and 12:1 methanol to oil molar ratio at 70 °C for 40 min	107
4.44	Comparison of the activity of CMR-DS-SO ₃ H using different reactors	110

List of Tables

Tables	Page	
2.1	Recent studies on use of waste biomass for SACs development	21
2.2	Recent studies on use of carbon based SAC for biodiesel production	27
2.3	Biodiesel Standards ASTM D 6751 and EN 14214	38
2.4	Fuel properties of biodiesel produced using different feedstocks	40
3.1	Composition of carbon precursors	44
3.2	Esterification of palmitic acid using PEFB-DS-SO ₃ H catalyst	50
3.3	Biodiesel production using conventional reflux reactor	52
3.4	Biodiesel production using CMR-DS-SO ₃ H catalyst in an autoclave reactor	53
3.5	Biodiesel production using CCH-DS-SO ₃ H catalyst in an autoclave reactor	53
3.6	Biodiesel production using CMR-DS-SO ₃ H catalyst in a microwave assisted reactor	54
3.7	Biodiesel production using X-BCS-SO ₃ H catalysts in a microwave assisted reactor	54
4.1	Composition and physicochemical properties of WPO	63
4.2	Total acid density of carbon precursors and catalysts	66
4.3	Elemental composition of carbon precursors and catalysts	66
4.4	Surface area and pore size distribution of the catalysts	68
4.5	Surface functional groups and band locations in FT-IR spectra of catalysts	74
4.6	Thermal degradation of the catalysts	83
4.7	Comparison of the activity of CMR-DS-SO ₃ H catalyst using different reactors	109
4.8	Comparison of energy consumption by three different methods	109
4.9	Fuel properties of produced biodiesel	114

List of Abbreviations

ATR	Attenuated Total Reflectance
ASTM	American Society for Testing Materials
AV	Acid Value
BCS	BioChar Sulfonation (Sulfonation of incompletely carbonized biomass)
BET	Brunauer-Emmet-Teller
BJH	Barrett, Joyner, and Halenda
CCH	Coconut Coir Husk
CMR	Coconut Meal Residue
CPO	Crude Palm Oil
DS	Direct in-situ Sulfuric carbonization
EDS	Energy Dispersive X-ray Spectroscopy
EN	European Standards
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acids
FID	Flame Ionization Detector
FT-IR	Fourier Transform Infrared spectrometer
FW	Feedstock Weight
SACs	Solid Acid Catalysts
SWNH	Single Walled Carbon Nano-Horn
MWCNTs	Multi Walled Carbon Nano Tubes
PA	Palmitic Acid
PEFB	Palm Empty Fruit Bunch
TGA	Thermo Gravimetric Analysis
TGs	Triglycerides
THB	Thai Baht
UCO	Used Cooking Oil
USDA	United States Department of Agriculture
WCO	Waste Cooking Oil
WPO	Waste Palm Oil
XPS	X-ray Photoelectron Spectroscopy



Chapter 1

Introduction

1.1 Background

Industrialization, economic, and population growth has continuously increased the global energy demand. A higher amount of energy requirement of the world is still satisfied by fossil fuels. However, depletion of fossil fuel sources together with its soaring price, and potential health and environmental concerns triggered by fossil fuel burning, have prompted researchers to find new alternative fuel derivatives. Biodiesel has gained more attention as an alternative for conventional diesel fuel due to various benefits, such as ability to derive from renewable biomass through cleaner production process, low emission profiles, and biodegradability. Biodiesel is a liquid biofuel which consists of mono alkyl esters of long chain fatty acids. Various types of renewable biomass, such as edible oils (Issariyakul & Dalai, 2014), non-edible oils and fats; rubber seed oil (Pillai et al., 2017), *Jatropha curcas* oil (Mardhiah et al., 2017), *Silybum marianum* L. seed oil (Fadhil et al., 2016), algal oil (Chisti, 2007), and waste oils and fats; waste cooking oil (Tran et al., 2016), animal fats (Cunha et al., 2013) have been studied for biodiesel production.

Among the feed stocks which have been used for biodiesel production, waste cooking oil (WCO) is considered as one of the most economical assortment (Phan & Phan, 2008). Since used cooking oils are unhealthy to reuse in food processing, WCOs are generated in large quantities worldwide. Only a small portion of WCO is being utilized as raw materials for fodder and soap production while the rest is discarded (Gómez & Machado, 2015; Issariyakul & Dalai, 2014; Michael et al., 2017). Therefore, reuse of WCOs as a biodiesel feedstock provides various benefits. WCO as an alternative biodiesel feedstock can address some issues, such as food crisis and environmental degradation when using edible and non-edible virgin oils (Banani et al., 2015). In addition, use of WCO as a biodiesel feedstock reduces waste treatment cost and secondary environmental problems, which may arise due to improper disposal behaviors (Lam et al., 2010). An increase of edible oil demand for increasing

global population increases the available WCO as a potential biodiesel feedstock (César et al., 2017). A large portion of the global edible oil demand is for palm oil (Shankar et al., 2016). As stated by United States Department of Agriculture (USDA), 64.5 million metric tons of palm oil will be produced globally in 2016-2017 (Foreign Agricultural Service 2017), making it the most consumed oil. Thailand uses 2160 thousand metric tons of palm oil for domestic consumption, out of 2200 thousand metric tons of total production (Foreign Agricultural Service 2017) . This increases the available amount of used palm oil as a waste. Therefore, waste palm oil (WPO) which is generated after a cooking process is identified as a promising biodiesel feedstock for present study.

However, use of WCOs/WPOs as low-cost biodiesel feedstocks is a challenge, as the quality of these feedstocks is very low compared to the virgin oils. These feedstocks contain a high amount of free fatty acids (FFA) and water, in addition to the triglycerides (TGs) (Yaakob et al., 2013). The presence of a high amount of FFA in the feedstock makes the biodiesel production and downstream processes more complex and expensive during conventional alkaline catalyzed trans-esterification by soap formation during saponification (Zong et al., 2007). Therefore, conventional biodiesel production using low quality feedstocks is consisting of two main steps; where, at the first step, convert FFA in the system into ester by using acid catalysts, and at the second step, convert remain TGs into esters using alkaline catalysts (Zong et al., 2007). High catalysts and alcohol consumption, complex and expensive downstream processes in this conventional method increases the ultimate biodiesel cost, overcoming the advantage of WCO as a low cost feedstock.

There are several attempts have been developed to overcome these barriers associated with biodiesel production from low quality feedstocks, such as WCO. Reduction of processing steps and use of low cost alternatives in various steps of the entire biodiesel production processes have proposed, considering technical feasibility, and economic and environmental benefits. Among these, development of bi-functional and cheap, solid acid catalysts (SACs) have gained much interest. SACs can convert both FFA and TGs into their esters, simultaneously, by catalyzing both esterification

and trans-esterification reactions, respectively (Fig. 1.1). Also, use of SAC eliminates further washing and neutralization steps allowing easy separation of the final product, compared to the homogeneous catalysts (Dehkhoda, 2010; Nakajima et al., 2007). In addition, SACs can be easily decanted or filtered from the reaction mixture for re-use.

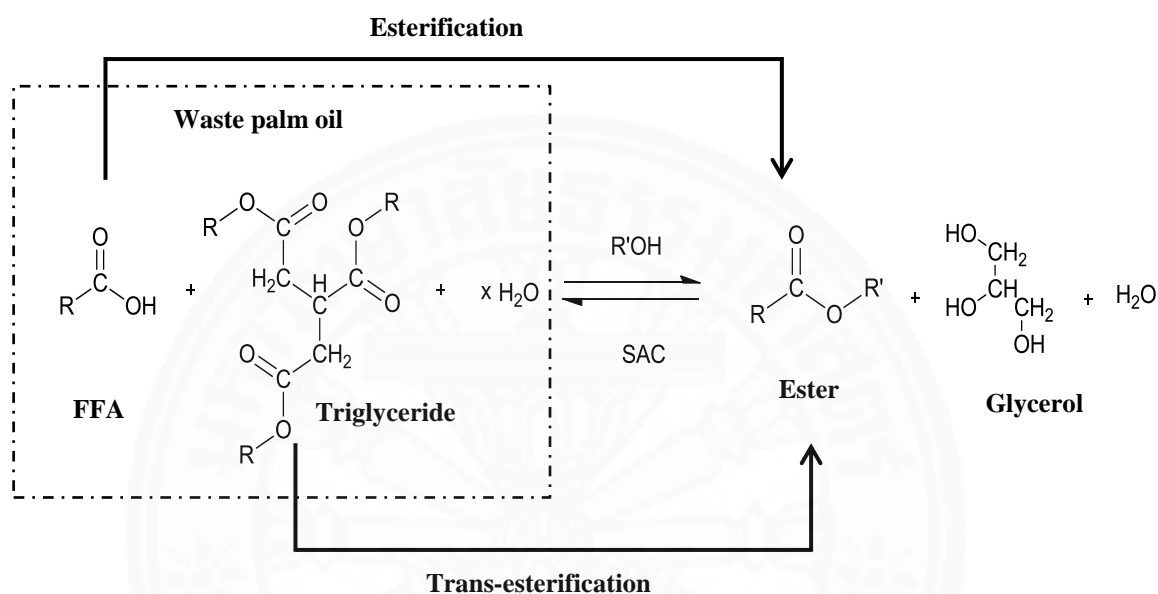


Fig. 1.1 SAC catalyzed simultaneous esterification and trans-esterification

Commercially available SACs, such as sulfated metal oxides ($\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{ZrO}_2$, etc.), ion exchange resin (nafion, amberlyst), modified template silica materials, and heteropolyacid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) are favorable for biodiesel production (Su & Guo, 2014). However, the activity and the stability of these SACs are very low compared to the homogeneous acid catalysts. In addition, the high cost of the catalyst and possible environmental damages caused by these catalysts have limited their use in biodiesel production (Dehkhoda, 2010). Therefore, there is an increasing demand for development of novel and economical SACs with a high catalytic activity and stability.

Among different types of SACs used for biodiesel production, use of carbon based SACs for biodiesel production is being popular recently due to various reasons. Carbon materials are abundant and relatively inexpensive. Carbon based SAC can be

prepared by using simple protocol. They show relatively high stability in the reaction medium (Nakajima et al., 2007). Successful use of carbon based SAC prepared from D-glucose (Nakajima et al., 2007), sucrose (Zong et al., 2007), starch (Lou et al., 2008), and glucose-starch mixture (Chen & Fang, 2011) for biodiesel production from low quality feedstocks are reported. Since, glucose, sugar, and starch are relatively expensive carbohydrates, use of waste biomass for catalyst preparation is recommended. Waste biomass, such as oil mill effluent; vegetable oil asphalt (Shu et al., 2010b), agricultural waste; corn straw (Liu et al., 2013), rice husk (Li et al., 2014), *Albizia lebbek* Pods (Pillai et al., 2017), and *Ceiba pentandra* stalks (Parthiban & Perumalsamy, 2015), microalgae residue (Fu et al., 2013), and coffee residue (Ngaosuwan et al., 2016), have been used for SAC preparation and effectively employed for biodiesel production.

Even though, use of waste biomass decreases the cost of catalyst, multiple processing steps, including pretreatment of biomass, use of extreme conditions during carbonization and activation (excessive use of chemicals, high reaction temperatures, and longer reaction times), as reported by many studies (Parthiban & Perumalsamy, 2015; Zong et al., 2007), make the overall catalyst preparation more complex and expensive. This increases the ultimate cost of biodiesel production and environmental degradation. Therefore, possibility of use of whole lignocellulose biomass for SAC preparation using simple protocol is explored in this study. Palm empty fruit bunch (PEFB), Coconut meal residue (CMR), and Coconut coir husk (CCH), are abundant agricultural waste biomass. It is expected that presence of high carbon content in this biomass supports for a rigid structure in the catalyst while oxygenated functional groups present in lignocellulose biomass support for a greater activation during catalyst preparation. Therefore, use of these waste biomasses for SAC preparation is an economical and sustainable approach.

1.2 Objectives of the study

Waste utilization is necessary and challenging. It reduces the problems associated with environmental pollution and waste treatment. This study explores the possibility

of employing abundant agricultural waste biomass for synthesis of SACs and their potential application in biodiesel production from WPO. The main purpose of this study is to develop promising carbon based SACs from PEFB, CMR, and CCH, using a simple protocol, since a carbon based SAC can catalyze both esterification and trans-esterification reactions. Use of these catalysts for biodiesel production from WPO makes the overall process more sustainable and economical. In order to gain ultimate benefit of WPO as low cost feedstock, different approaches are applied for biodiesel production process. To achieve the goal of the sustainable and economical biodiesel production from WPO, following objectives are derived:

1. Synthesis of carbon based SACs from PEFB, CMR, and CCH, and characterization of synthesized catalysts investigating the effect of two different preparation methods on the activity of the catalyst for biodiesel production
2. Determination of optimum conditions for biodiesel production from WPO using prepared catalyst in a conventional open reflux reactor, a closed autoclave assisted reactor, and a microwave assisted reactor and also investigate the reusability
3. Analysis of fuel properties of prepared biodiesel and compare with the international standards

1.3 Scope of the study

There are various factors affecting the quality and the economy of the biodiesel production. This study mainly focuses on biodiesel production from low quality WPO with high FFA content, in an economically feasible way.

WPO produced during food (snack) processing is used as the biodiesel feedstock without any pretreatment. Characterization of WPO is done in order to identify the effect of the quality of feedstock for biodiesel quality and the catalytic activity. The possibility of use of low cost raw materials, such as agricultural waste biomass for the preparation of carbon based SAC, is examined. Therefore, PEFB, CMR, and CCH are

used as the carbon precursors for catalysts development. Carbon based SACs are derived basically from two simple methods, such as direct in-situ incomplete sulfuric carbonization and sulfonation of pre-incompletely carbonized biomass. Activity of the catalysts prepared in this study is compared with the activity of common carbon based SACs reported in the literature. Characterization based on several analytical and instrumental techniques is adapted in order to understand the behavior of the catalyst in the reaction medium. Optimum conditions for biodiesel production using the prepared catalysts are evaluated by using atmospheric condition (using an open reflux reactor), closed auto clave reactor assisted condition, and microwave assisted condition.

Fuel properties, such as acid value, kinematic viscosity, density, flash point, pour point, heating value, oxidation stability, ash content, and sulfur content of produced biodiesel under optimum conditions are investigated using the standard methods. They were compared with American Society for Testing Materials (ASTMD 6751), European Standards (EN 14214), and Thailand biodiesel standards. However, engine performance, and the emission profiles of the biodiesel are not evaluated at this stage. Also, life cycle evaluation of biodiesel production using WPO using carbon based SACs in different production process is not an objective of this study.

Chapter 2

Literature review

The aim of this chapter is to describe the current literature relevant to the sustainable and economical biodiesel production by using waste biomass derived SACs. Various types of feedstocks have been explored and their potential towards biodiesel production is being investigated. Use of WCO as a biodiesel feedstock is identified as a better option to minimize the high cost associated with biodiesel production. In addition, there are various protocols have developed for sustainable biodiesel production from WCO. International standards were developed in order to identify the required specification of biodiesel for general use. Therefore, this chapter describes the potential of WCO as a biodiesel feedstock, progress of waste biomass derived SACs development, and the standard specifications of biodiesel properties.

2.1 WCO as a potential biodiesel feedstock

WCO is the residual oil product obtained after food frying processes in households, restaurants, and other food industries. WCO must be disposed safely in order to overcome the potential health concerns which may arise due to the accumulation of toxic substances produced during the frying process. Therefore, proper utilization of this waste in a way that is not harmful to human being and environment is essential. This further reduces the waste treatment cost and the secondary environmental problems due to improper disposal behaviors (Gnanaprakasam et al., 2013; Phan & Phan, 2008; Talebian-Kiakalaieh et al., 2013a).

The major barrier of commercialization of biodiesel is its higher cost, compared to diesel fuel. About 70-80% of the cost of biodiesel production is related with the feedstock cost (Fig 2.1), and the price of biodiesel increases with the price of the feedstock (Fig. 2.2 and 2.3). As shown in Fig. 2.4, virgin vegetable oils still play the key role as conventional biodiesel feedstocks.

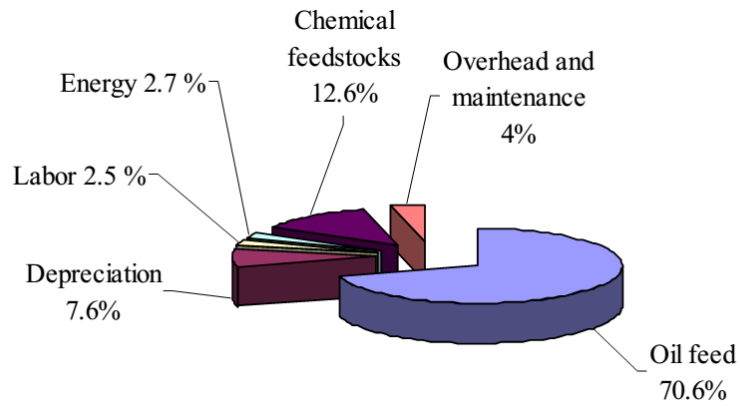


Fig. 2.1 Cost distribution in biodiesel production process (taken from (Kemp & 2006))



Fig. 2.2 Wholesale prices for biodiesel and vegetable oil (as mean values of rapeseed, soybean, palm, and sunflower oil prices) in Germany (taken from (Oel, 2017))

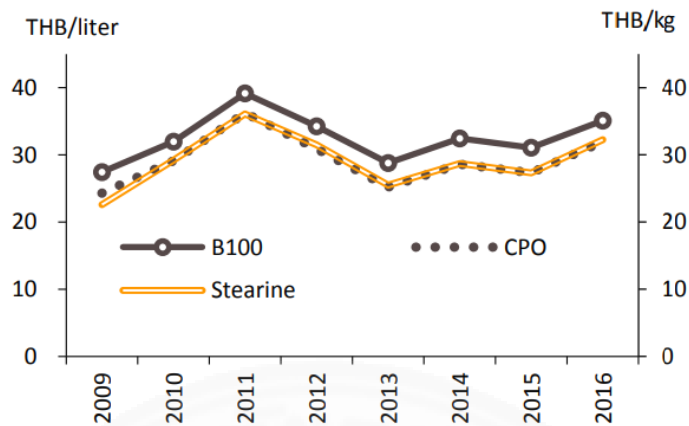


Fig. 2.3 Price of biodiesel and raw materials in Thailand (taken from (Krungsri, 2017)).

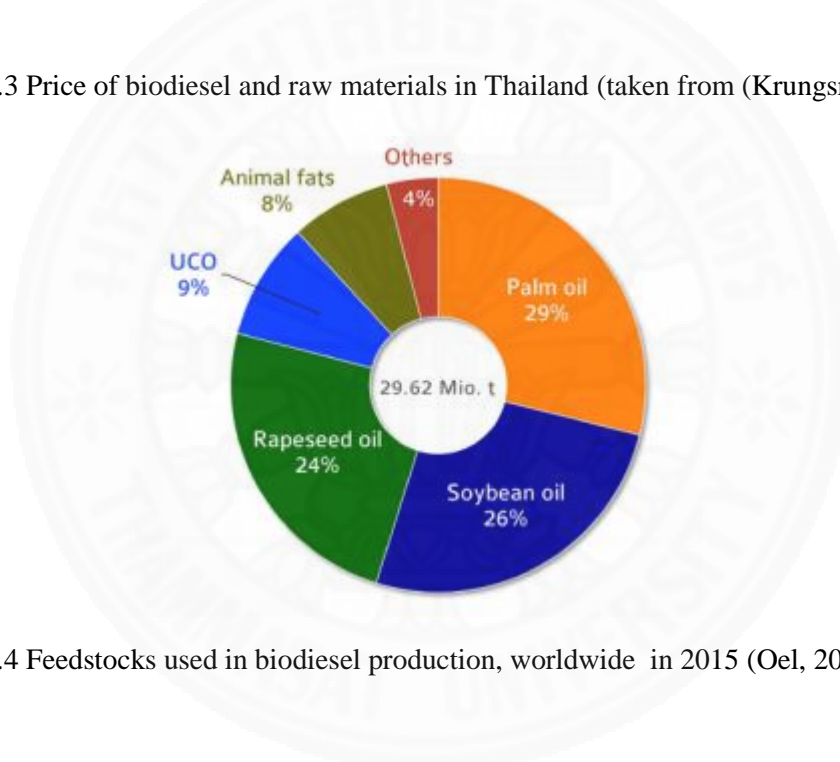


Fig. 2.4 Feedstocks used in biodiesel production, worldwide in 2015 (Oel, 2017)

Thailand is ranked 8th among global biodiesel producers (OECD & Food, 2017). The main feedstock used for biodiesel production in Thailand is crude palm oil (CPO) while refined palm oil, palm stearin, free fatty acids of palm oil, and recycled vegetable oil are partly being used (Krungsri, 2017). Therefore, the cost of biodiesel is fluctuated according to the price of the crude palm oil (Fig. 2.3). As reported by Kungsri research Thailand Industry Outlook (Krungsri, 2017), 40% (0.89 million tons) of the palm oil produced in Thailand is used in biodiesel industry. Use of edible oils for biodiesel production triggers the threat of food crisis and possible environmental damages while increasing the cost of biodiesel (Oel, 2017). Therefore,

use of waste oil as biodiesel feedstock can reduce the manufacturing cost of the biodiesel (Glisic et al., 2016). According to Araújo et al. (2013), use of WCO reduces about 45% of biodiesel production cost even considering complex pretreatment steps and downstream processes.

The use of WCO as an alternative biodiesel feedstock decreases the cost of vegetable oil while increasing the availability of vegetable oil as a food source (César et al., 2017). However, the available the amount of WCO generated in each country is different, depending on the used vegetable oil for food processing. According to Patil et al. (2012), per capita WCO generation per year is 4.1 kg. As reported by Maddikeri et al., more than 29 million tons of WCO is generated per year (Maddikeri et al., 2012). However, as summarized by Yaakob et al. (2013) and Maddikeri et al. (2012), United states, China, Europe, Japan, Malaysia, Canada, and Taiwan produced, 10.0, 4.5, 0.7-10, 0.5, 0.45-0.57, 0.12 and 0.07 million tons of WCO, respectively. An increase of edible oil consumption for increasing global population increases the amount of WCO generated. However, regardless of the amount of WCO generated, only a small amount is reused. César et al. (2017), reported that only 2.5% of oil is reused (which is account for 0.5% of biodiesel production in 2015) in Brazil while the rest is disposed improperly to the environment. This study suggested a requirement of integrated social network (with public and private initiatives) to collect WCO in order to get better advance of WCO as a low cost biodiesel feedstock. Otherwise, even though, WCO is widely available, the cost of collection, transportation, and the required infrastructures increases the cost of WCO (César et al., 2017).

In general, WCO is 2 to 3 times cheaper than the virgin vegetable oils (Chhetri et al., 2008; Felizardo et al., 2006; Phan & Phan, 2008). According to Sharma et al. (2008), the price of WCO is between \$ 0.04 to \$ 0.09 for yellow grease and \$ 0.004 to \$ 0.014 for brown grease, respectively. However, an increase of a demand for WCO as feasible biodiesel feedstock increases the price of WCO. According to USDA national round up report, 2015, the price of the waste vegetable oil has increased to \$3.30 per gallon.

2.2 Conventional catalysts used in biodiesel production

Trans-esterification is one of the most common method used for biodiesel production. In which triglycerides are converted into esters and glycerol, in the presence of suitable catalysts (Fig. 2.5a). In addition, esterification of FFAs also produces respective esters (Fig. 2.5b) (Ma & Hanna, 1999). Three main types of catalysts (either chemical or biological), such as alkaline, acid, and enzyme are used in trans-esterification. The homogeneous alkaline catalysts, such as NaOH and KOH, are well known in conventional industrial biodiesel production using the high quality feedstocks, such as virgin edible oils with low FFA content. However, these catalysts are corrosive to the equipment used and caused for environmental degradation. In addition, these catalysts make the entire biodiesel production process complex and expensive due to undesired saponification (Fig. 2.5c) during biodiesel production from low quality feedstocks with high FFAs content. Homogeneous acid catalysts, such as HCl and H₂SO₄ are effective for biodiesel production from low quality feedstocks. Serious issues, such as corrosion of appliances, requirement of high reaction conditions, difficulty in catalyst separation have limited their use in biodiesel production (Nakajima et al., 2007). High cost of the enzyme lipase, slower reaction rate, and inactivation of the lipase enzyme at the presence of short chain alcohol and glycerol has limited the use of biological catalysts in biodiesel production (Gog et al., 2012).

Therefore, use of heterogeneous catalysts has recently gained much attention as these catalysts can be easily removed and recycled during biodiesel production (Parthiban & Perumalsamy, 2015). Heterogeneous solid catalysts are of two types, i.e. heterogeneous solid base catalysts and heterogeneous solid acid catalysts (SACs). SACs are preferable over solid base catalysts for biodiesel production from low quality feed stocks, such as WCO, since they are not sensitive to FFA presence in the feedstock. As depicted in Fig. 2.6, SACs catalyze both esterification and trans-esterification reactions, simultaneously eliminating further neutralization and washing steps (Zong et al., 2007). There are several different heterogeneous SACs have been investigated for biodiesel production, recently. As reported by several studies; sulfated metal oxides, such as sulfated ZrO₂, TiO₂, and Ta₂O₅, etc., (Melero et al.,

2009) (Wen et al., 2010), ion exchange resins, such as Amberlyst (Gan et al., 2012), heteropoly acids (Anitha & Dawn, 2010; Noshadi et al., 2012; Talebian-Kiakalaieh et al., 2013b), mesoporous silica and sulfated zirconia (Saravanan et al., 2016) have used in biodiesel production. However, reasons, such as high cost and relatively low activity and the stability limit the usage of these catalysts in biodiesel production.

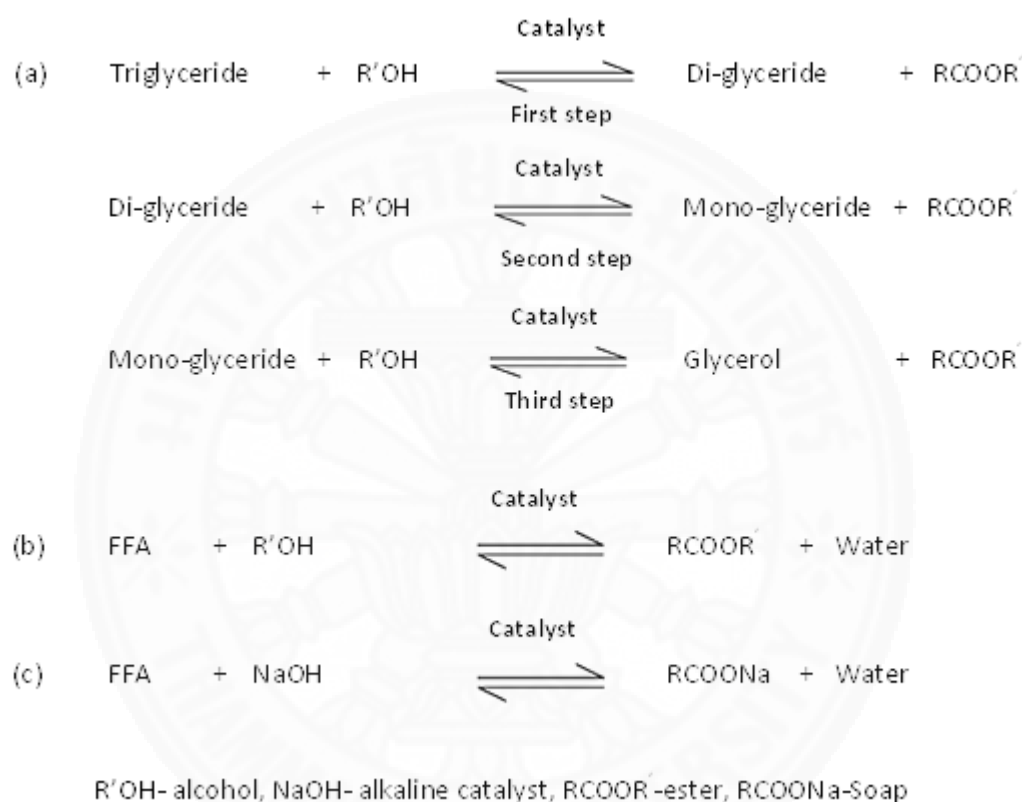


Fig. 2.5 (a) Acid or base catalyzed trans-esterification, (b) esterification, and (c) saponification

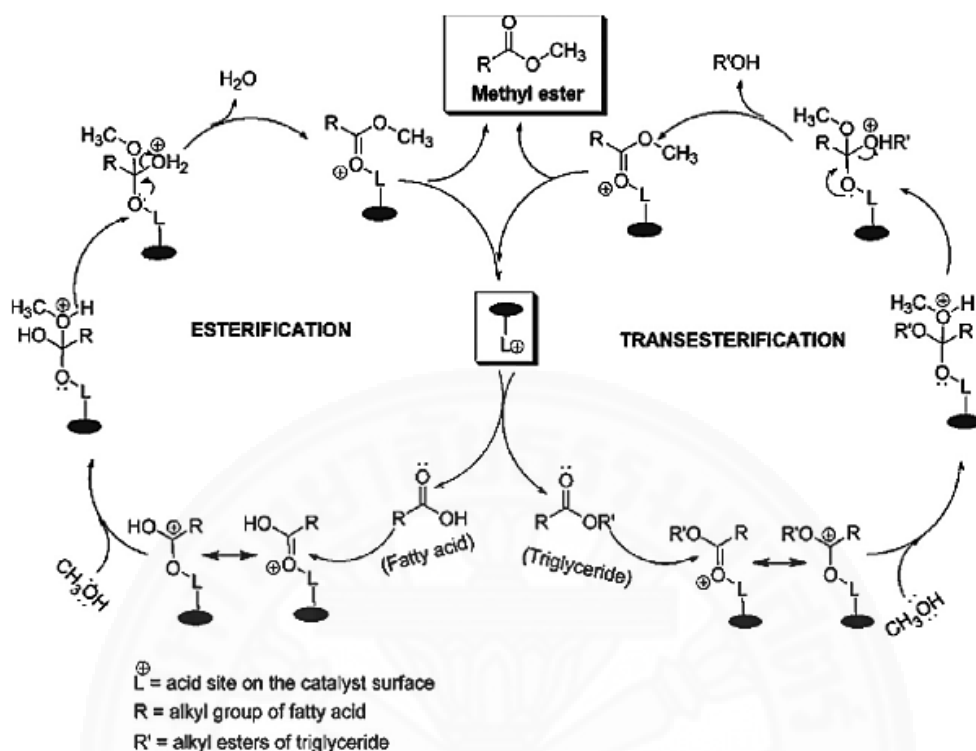


Fig. 2.6 SAC catalyzed simultaneous esterification and trans-esterification (taken from (Kulkarni et al., 2006))

2.3 Carbon based SACs used in biodiesel production

Carbon based SACs have gained recent attention in biodiesel production, due to higher catalytic activity, stability in the reaction medium, low cost, and easy preparation steps (Nakajima et al., 2007). The SACs prepared from D-glucose (Nakajima et al., 2007), sucrose (Zong et al., 2007), starch (Lou et al., 2008), and glucose-starch mixture (Chen & Fang, 2011) for successful use in biodiesel production from low quality biodiesel feedstocks are reported. Glucose, sugar, and starch are relatively expensive carbohydrates. Use of waste biomass for SAC preparation is recommended, since they are largely available at low or no cost. There are several studies have investigated preparation of SAC from various biomass, including agricultural waste (Kastner et al., 2012) (Liu et al., 2013) (Zhou et al., 2016), food waste (Ngaosuwan et al., 2016), algal residues (Fu et al., 2013), and even

from the bi-product or waste generated during biodiesel production (Devi et al., 2009).

Preparation of the carbon based SAC have been identified as a green approach, in which various carbon based materials are subjected to carbonization (hydrothermal conversion, pyrolysis, etc.) and sulfonation (under fuming/concentrated H_2SO_4 , hydroxyethylsulfonic acid, etc.) operations under relatively low temperature (Kang et al., 2013). However, a proper design of efficient and stable SACs for biodiesel production is challenging. The ideal SAC for biodiesel production should be capable of catalyzing both esterification and trans-esterification reactions. The activity of carbon based SACs mainly depends on various factors, such as acid strength, surface area, pore size, etc. Therefore, there are various methods have been adapted to develop the activity of carbon based SACs (Kang et al., 2013). These methods are discussed in this section.

2.3.1 Biochar based SACs for biodiesel production

Carbonization of the biomass at 250-650 °C by processes, such as pyrolysis, gasification, and hydrothermal conversion followed by sulfonation is widely used in this method (Fig. 2.7) (Kang et al., 2013).

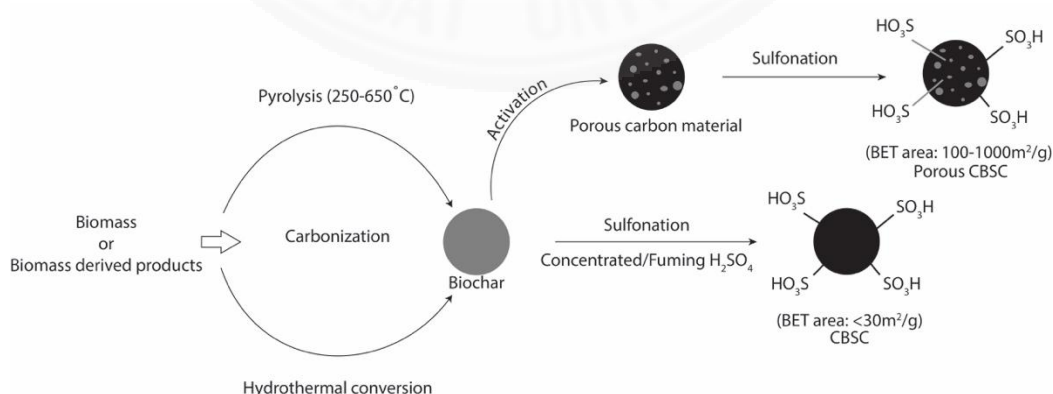


Fig. 2.7 Catalyst preparations by sulfonation of carbonized biomass (taken from (Kang et al., 2013))

A major drawback of the reported sulfonated carbon catalysts is relatively low surface area (Zhou et al., 2016), which in turn limits the catalytic activity by limiting the mass diffusion. In general, char obtained from carbonization of cellulose is microporous. Therefore, many methods, including chemical and physical activation have been developed to synthesize porous carbon materials with high surface area. In general, physical activation of carbon material is achieved by partial gasification by CO₂, steam, and air (Poonjarernsilp et al., 2014; Shu et al., 2010a). Chemicals, such as phosphoric acid, ZnCl₂, and KOH are used to activate the carbon materials chemically (Konwar et al., 2014b; Ngaosuwan et al., 2016). In addition, template based SACs preparation using mesoporous silica, carbon nano-tubes are also reported (Guan et al., 2017; Poonjarernsilp et al., 2014). However, most of the reported studies used combination of chemical and physical activation methods in order to develop catalysts with higher activity. Following section discussed various approaches reported in literature to develop surface area of carbon based SACs and their use in biodiesel production.

2.3.1.1 Physically activated carbon based SACs for biodiesel production

Shu et al. (2010a), have prepared a carbon based SAC with 2.04 mmol g⁻¹ and 7.48 m² g⁻¹ total acid density and surface area, respectively, from vegetable oil asphalt (VOA). During catalyst preparation, pretreated VOA (10 g) was carbonized at 500-700 °C under Ar environment after oxidizing the sample for 1 h at 280 °C in steam of air (300 ml min⁻¹). Sulfonation was achieved by mixing carbonized VOA (5 g) and 100 ml concentrated H₂SO₄ (96%) at 210 °C in an oil bath for 10 h. Resultant catalyst was used for esterification and trans-esterification of synthetic waste vegetable oil (>50% FFA) and received a maximum yield of 94.8% and 80.5%, respectively, under the reaction conditions of 16.8:1 ethanol to oil molar ratio, 0.2 wt. % catalyst at 220 °C after 4.5 h in an autoclave assisted reactor. However, they reported a decrease of catalytic activity during recycling due to the deactivation of the catalyst. They identified that high acid density due to Bronsted acid sites (OH) and SO₃H, hydrophobicity that prevent the hydration (due to carbon frame work), and porous structure of the catalyst are the reasons for observed higher catalytic activity.

Use of agricultural waste, such as peanut hulls, pine logging residues, and wood chips for SAC preparation was reported (Kastner et al., 2012). Waste biomass derived biochar/activated carbon was derived by pyrolyzing biomass at 400-500 °C. Sulfonation was achieved by two methods, during catalyst preparation. At the first method, 12.5 g of biochar mixed with 20% concentrated H₂SO₄ (20 ml) and heated the mixture at 100 °C for 12-18 h in a muffle furnace. Then, in the second method, 5 g of biochar and activated carbon mixture has exposed to solid SO₃ (20 g) in a sealed glass jar. Prepared catalyst (sulfonated using SO₃) was used for 97% conversion of FFA in vegetable oil and animal fats. They have stated that reported high activity is due to high surface area (1137 m²g⁻¹), and sulfonic acid group density of the catalyst (0.81 mmolg⁻¹). In addition, Liu et al. (2013), have reported the use of SAC catalyst prepared using corn straw (2.64 mmolg⁻¹ acid density) for esterification of oleic acid. They received 90% of ester yield, using 3:1 methanol: oil (molar ratio), 3 wt. % of catalyst, at 60 °C and 4 h. The catalyst was synthesized by using two steps; in which, carbonization was achieved by heating corn straw under N₂ flow at 250 °C in a tube reactor for 1 h, the resultant was soaked in fuming H₂SO₄ in an oil bath at 80 °C for 4 h for the sulfonation. Zhou et al. (2016), have reported the use of bamboo derived carbon acid catalyst for biodiesel production from oleic acid. They derived the catalyst with a total acid density 1.74 mmolg⁻¹ and a surface area of 0.25 m²g⁻¹ after carbonization of bamboo at 350 °C for 2 h and successive sulfonation by concentrated H₂SO₄ at 105 °C for 2 h. A highest esterification efficiency of 98.4% was shown by the catalyst under optimum reaction conditions of 6 wt. % of the catalyst, 7:1 ethanol to oleic acid molar ratio at 90 °C after 2 h. However, it is reported a decrease of the catalytic activity from 98.4 to 27.8% after five runs, though the catalyst was able to reactivate to have 93.6% esterification efficiency.

In addition, xylose based SAC preparation from hydrothermal carbonization (190 °C, 24 h in an autoclave reactor) and sulfonation (1 g in 20 ml of concentrated H₂SO₄, 150 °C, 15 h in an autoclave reactor) was reported (Tran et al., 2016). Xylose based SAC (86 m²g⁻¹ surface area and 1.38 mmolg⁻¹ total acid strength) was used for biodiesel production from WCO (1.54% FFA). They reached a maximum 89.6%

biodiesel yield with 10 wt. % catalyst, 9.35:1 methanol to oil molar ratio, at 110 °C and 4 h. However, they have reported 9% decrease of biodiesel yield at each run when investigating reusability of the catalyst. Yet, they claimed that xylose derived SAC as a green catalyst, since it is non-toxic, and synthesized from waste biomass.

2.3.1.2 Chemically activated carbon based SACs for biodiesel production

Chemical activation increases the surface area and the porosity of the char by limiting the tar formation during carbonization (Dehkhoda, 2010). There are some investigations reported, carbon based SAC preparation by chemical activation (or integrated chemical and physical activation) and their use in biodiesel production.

Konwar et al. (2014b), have reported catalyst preparation by phosphoric acid activation and two-step carbonization and sulfonation of oil-cake waste. Oil cake waste derived SACs were synthesized by phosphoric acid activation (soak 20 g oil cake powder in 50% ortho-phosphoric acid, 2:1 wt/wt.), consequent carbonization (500 °C, 1 h), and sulfonation (covalent attachment of 4-Benzenediazoniumsulfonate, 30-32 % H_3PO_2 , at 3-5 °C for 1.3 h or 4-Benzenediazoniumsulfonate, HCl 5 °C, 12 h). They have invented two SACs with high surface area (698, 555 m^2g^{-1}), total acid strength (2.2, 2.4 mmolg^{-1}), and employed for pre-treatment of acidic oil (43.7% FFA). Even though, reported catalyst is not successful in trans-esterification, they reported an excellent activity (97-99% FFA conversion) and high stability of the catalyst. In addition, the use of coffee residue derived SAC for esterification of caprylic acid was reported (Ngaosuwan et al., 2016). During the catalyst preparation, dried coffee residues were mixed with ZnCl_2 (1:3 wt/wt) at 110 °C for 12 h. Then, activated coffee residue was carbonized at 600 °C for 4 h under CO_2 atmosphere. It was expected that ZnCl_2 as activation agent promote carbonization in order to facilitate higher porosity while acting as a template for mesoporous carbon. After removing residual ZnCl_2 , resultant product was sulfonated (1 g: 20 ml concentrated H_2SO_4 , 200 °C for 18 h) in an autoclave reactor. Even though preparation method supported to have very high surface area (1091 m^2g^{-1}), catalyst showed a low total acid density (0.99 mmolg^{-1}) and sulfonic acid density (0.45 mmolg^{-1}). In addition,

catalyst showed a lower stability and gave only a 71.4 % conversion using 5 wt. % catalyst, 3:1 methanol: caprylic acid molar ratio, at 60 °C and 4 h during first cycle.

2.3.1.3 Nano-scale carbon based SACs for biodiesel production

Nano scale carbon, such as carbon nano-tubes are popular due to their high surface area and thermal stability (Poonjarernsilp et al., 2014). Even though, cost of the nano-scale carbon preparation is high, the use of nano-scale sulfonated carbon for biodiesel production is reported (Guan et al., 2017; Parthiban & Perumalsamy, 2015; Poonjarernsilp et al., 2014).

Poonjarernsilp et al. (2014), have reported biodiesel production from palmitic acid, using a sulfonated single walled carbon nano-horn (SWNH), synthesized via arc discharge in water with nitrogen gas injection. Prepared catalyst with 418 m²g⁻¹ surface area and 0.5 mmolg⁻¹ acid density showed a better activity giving 93% methyl palmitate yield using 33:1 methanol:palmitic acid, 0.15 g catalyst, at 64 °C after 4 h. However, as they reported, even though, oxidization (500 °C for 30 min) increases the surface area of the catalyst (ox-SWNH), oxidized catalyst were able to give only a 50% methyl palmitate yield. Parthiban and Perumalsamy (2015), have reported preparation of nano-scale carbon acid catalyst with a high surface area of 714 m²g⁻¹ and an average pore size of 4.8 nm using *C. pentandra* stalks in their study. Carbonized biomass in a muffle furnace at 250 °C for 4 h were grounded in a planetary mill for 5 h to obtained nano-scale carbon and resultant was allowed to react with 20% concentrated H₂SO₄ for 24 h for sulfonation. They have reported a highest FAME conversion of 99% at 220 °C, 18:1 methanol to oil molar ratio, and 1.5 wt. % catalysts after 150 min using *C. pentandra* oil (13.4% FFA). Even though, they have reported a decrease of catalytic activity during recycling, they claimed that the higher surface area and the larger pore size are contributed for higher activity. In addition, use of sulfonated multi walled carbon nano tubes (MWCNTs) for trans-esterification of trilaurin was reported (Guan et al., 2017). The catalyst was synthesized using commercially available MWCNTs. MWCNTs were treated with concentrated H₂SO₄ and HNO₃ (1:1, 40 ml), and functionalized by keeping the mixture under ultrasonication for 5 h to have the catalyst with 198.9 m²g⁻¹ surface area. They received a

90% of trilaurin conversion using 20:1 ethanol to trilaurin molar ratio, 3.7 wt. % catalyst, at 170 °C after 20 min. They have claimed that, reasons such as the presence of high density of acid sites, high surface area, and the porous nature of the catalyst are caused for the superior activity of the catalyst.

Even though, reported carbon based SAC catalysts successfully used for biodiesel production, their preparation is very complex. Multiple processing steps, including pre-treatment, carbonization and activation are involved with high reaction temperatures, reaction time and chemicals, making the whole process very expensive and intricate. Therefore, a design of a carbon based SAC under mild reaction condition has recommended.

2.3.2 In-situ H₂SO₄ carbonized carbon based SACs for biodiesel production

Direct incomplete concentrated H₂SO₄ carbonization and sulfonation have been reported as a simple and low cost method for SAC preparation. Since there is no pre-carbonization process prior to sulfonation, this simplify the process while saving a large amount of cost of energy (Kang et al., 2013). In this approach, natural and abundant carbon sources, such as cellulose, lignin, starch, and sugar or derivatives are used as carbon precursors. They are incompletely carbonized under low temperature, in order to produce amorphous carbon with small carbon sheets and sulfonated, simultaneously (Kang et al., 2013). However, there are very few studies have focused on SAC preparation from the direct in-situ concentrated H₂SO₄ carbonization.

Devi et al. (2009), have reported catalyst preparation by in situ one-pot partial carbonization and sulfonation using glycerol (a by-product of biodiesel production) as carbon support. They have mixed glycerol and concentrated H₂SO₄ (1:4 wt. %) at 180 °C for 20 min. Resultant catalyst obtained after filtering and drying in an oven, for 2 h, at 120 °C showed 1.6 mmolg⁻¹ of acid density and 1.0 m²g⁻¹ of surface area. Prepared catalyst was used for esterification of palmitic acid to obtained 99% of ester yield using 10 wt. % of the catalyst. They claimed that Glycerol based SAC showed a better activity compared to amberlyst-15 and ZSM-5 zeolite with excellent stability

after 8 cycles. This group reported the activity of another catalyst, prepared by in-situ partial carbonization of glycerol at 220 °C and 20 min using 1:3 wt. % of concentrated H₂SO₄. Despite the low acid density (1.6 mmolg⁻¹) and low surface area (1.0 m²g⁻¹) catalyst exhibited an excellent activity for biodiesel production from Karanja oil (7.5% FFA) in a pressure tube (Table 2.1).

Fu et al. (2013) have reported use of a SAC prepared from microalgae residue, for esterification of oleic acid and trans-esterification of triolein. The SAC was prepared by in-situ concentrated H₂SO₄ carbonization (1:12 wt. %) for 2 h in an autoclave reactor. Similar to Devi et al. (2009), catalyst showed a higher activity compared to Amberlyst-15 catalyst giving 98% FAME conversion by esterification of oleic acid and 24% ester yield for trans-esterification of triolein with methanol, and 5 wt. % of catalyst at 80 °C after 12 h. Even though prepared catalyst had a very small surface area with non-porous aromatic carbon sheets, catalyst afforded for a higher catalytic activity (> 88% FFA conversion). This is perhaps due to the higher acid density of the catalyst (4.25 mmolg⁻¹). However, the catalyst was not successful for trans-esterification of triolein which was able to give only 22% yield. In addition, it was observed that the stability of the catalyst decreases with usage after 5 cycles, which is due to the deactivation of the catalyst by methanol absorption or possible leaching of active sites.

Further, a similar approach was reported for preparation of bagasse based SAC through one step concentrated H₂SO₄ carbonization (Savaliya & Dholakiya, 2015). A sulfonated carbon catalyst with 1.9 mmolg⁻¹ of total acid density, 1.27 m²g⁻¹ of surface area and 0.003 cm³g⁻¹ of pore volume was obtained by heating bagasse powder (5 g) with 30 ml of concentrated H₂SO₄ at 180 °C under N₂ flow. Catalyst showed a good activity for esterification of FFA (97.2% conversion) in soap stock oil using 15:1 methanol to oil molar ratio, 5 wt.% catalyst, at 65 °C after 11 h reaction time in a reflux system. Reusability tests confirmed that the stability of the catalyst was remained unchanged for three repetitive cycles.

Table 2.1 Recent studies on use of waste biomass for SACs development

C precursor	Preparation method	Total acid density (mmolg ⁻¹)	Sulfonic acid density (mmolg ⁻¹ /wt.%)	Surface area (m ² g ⁻¹)	Pore size (nm)	Pore volume (cm ³)	Reference
Glycerol	Simultaneous carbonization and sulfonation: Con. H ₂ SO ₄ , (1:4 wt.%) 180 °C , 20 min	1.6	-	1.0	-	-	(Devi et al., 2009)
Glycerol	Simultaneous carbonization and sulfonation: Con. H ₂ SO ₄ , (1:4 wt.%) 220 °C , 20 min	1.6	-	0.21	-	-	(Devi et al., 2014)
Bagasse	Simultaneous carbonization and sulfonation: Con. H ₂ SO ₄ , (5 g:30 ml) 180 °C , 10 h	1.9	-	1.27	-	0.003	(Savaliya & Dholakiya, 2015)
vegetable oil asphalt (VOA)	Carbonization: carbonized at 500-700 °C under Argon environment after oxidizing the sample for 1 h at 280 °C in steam of air (300 ml/min) Sulfonation: mixing carbonized VOA (5 g) and 100 ml concentrated H ₂ SO ₄ (96%), 210 °C in an oil bath for 10 h	2.04	-	7.48	43.9	-	(Shu et al., 2010a)
Oil cake waste	Activation : soak 20 g oil cake powder in 50% ortho-phosphoric acid (2:1 wt/wt,) carbonization : 500 °C, 1 h Sulfonation: 1) covalent attachment of 4-Benzenediazoniumsulfonate, 30-32 % H ₃ PO ₂ , at 3-5 °C for 1.3 h or 2) 4-Benzenediazoniumsulfonate, HCl 5 °C, 12 h	1) 2.2 2) 2.4	-	1) 698 2) 555	-	-	(Konwar et al., 2014b)
Single wall carbon nano-horn	Carbonization: Carbon nano tube- arc discharge in water with nitrogen gas injection, oxidation by heating in air with an electric furnace at 500 °C for 30 min	1) 0.5 2) 0.2	-	418 855	-	-	(Poonjarernsil p et al., 2014)

	Sulfonation: Immersed (1 g) in 20 ml concentrated H ₂ SO ₄ (95%), 200 °C in an oil bath for 18 h (1-SWCNH, 2-ox-SWCNH)						
<i>C. pentandra</i> stalks powder	Carbonization: 250 °C for 4 h (muffle furnace) Grounded in a planetary mill for 5 h to obtain nano-scale carbon Sulfonation : 20% concentrated H ₂ SO ₄ , 24 h	-	18.0%	714	4.8	-	(Parthiban & Perumalsamy, 2015)
Banana peel	Activation : Fragments of banana peel (1.2 kg) submerged in an aqueous FeCl ₃ (1.8 L, 80 °C , 1 week) Carbonization : 650 °C, 3 h under N ₂ environment	1.43-2.68	0.9-4.8%	156-1097	6.1-11.4	0.17-0.74	(Liu et al., 2015)
Rice husk	Activation : calcined for 450 °C, 15 h under N ₂ environment (leaching with NaOH, 100 °C, 5 h) Sulfonation: Concentrated H ₂ SO ₄ (98%), 150 °C, 12 h under N ₂ environment	5.25	-	1233	38.9	0.74	(Zeng et al., 2016)
Xylose	Carbonization: 190 °C , 24 h Sulfonation: Concentrated H ₂ SO ₄ , 150 °C, 15 h	1.38	0.31	86.3	6.6	0.09	(Tran et al., 2016)
Coffee residue	Activation: mixed with ZnCl ₂ (1:3 wt/wt) at 110 °C for 12 h Carbonization: 600 °C for 4 h under CO ₂ atmosphere Sulfonation: 1 g: 20 ml concentrated H ₂ SO ₄ , 200 °C for 18 h	0.99	0.45	1091	3.5	3.5	(Ngaosuwan et al., 2016)
<i>Jatropha curcas</i> seed cake	Carbonization: 350 °C , 4 h Sulfonation: 10 g: Concentrated H ₂ SO ₄ , 90 °C, 5 h	2.24	-	1.92	6.67	3.20	(Mardhiah et al., 2017)

Use of agricultural waste biomass for SAC preparation is a promising approach because they are abundant and available at low or no cost. There are very few studies have focused on SAC preparation from direct in-situ concentrated H_2SO_4 carbonization and using abundant waste biomass (Guo et al., 2012). Reported studies reveal that one-step direct in-situ H_2SO_4 carbonized sulfonated carbon shows superior activity for biodiesel production (Table 2.1). Therefore, it is crucial to identify possible waste biomass which can be employed for SAC preparation. This reduces the entire cost of the catalyst preparation and the biodiesel production, eventually.

2.4 Features of carbon based SACs

Carbon based SACs are identified as a substitute for homogeneous acid catalyst, in which they can be used in biodiesel production from low quality feedstocks. According to the reported studies, a wide range of carbon rich materials can be used as precursors for catalyst development. Pre-treatment, subsequent carbonization, and activation, change the properties of carbon precursors into active SACs with unique surface and structural properties (Konwar et al., 2014a).

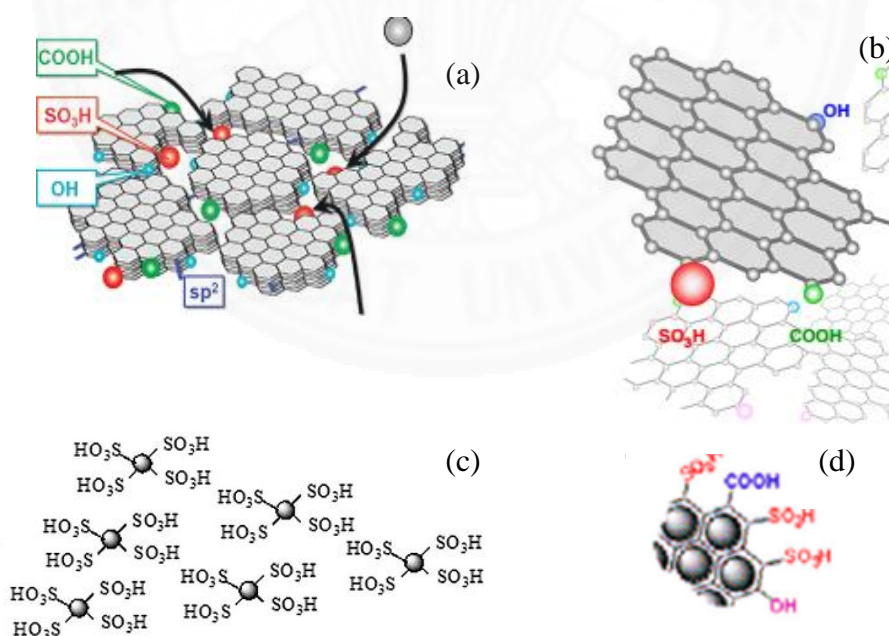


Fig. 2.8 Different proposed graphical structures for carbon based SACs (a) cellulose derived SAC (Nakajima & Hara, 2012), (b) D-glucose derived SAC (Nakajima et al., 2007), (c) *Ceiba pentandra* stalks nano catalyst (Parthiban & Perumalsamy, 2015), (d) micro algae derived SAC (Fu et al., 2013; Lee et al., 2014)

Different structures proposed for carbon based SACs are shown in Fig. 2.8.

2.4.1 Acid strength

An ideal SAC should contain many protonic acid sites, including both Bronsted and Lewis acid sites (Fig 2.9). In which, highly polarized hydroxyl groups on the surface of the catalyst are acting as H^+ donors (Bronsted acid sites) while coordinative unsaturated cationic sites (Lewis acid sites), which leave the exposed M^+ ion to interact with guest molecules (Rinaldi & Schuth, 2009; Su & Guo, 2014). However, carbon based SACs are incorporated with high densities of acidic functional groups, such as OH, COOH, and SO_3H on the surface of the catalyst. Among them, catalytic activity is mostly influenced by SO_3H groups. SO_3H acid sites are stronger ($pK_a \approx 7$) and more active than COOH and OH acid sites. However, they are susceptible for deactivation due to water and bonded reactant, such as methanol. Hence, high activity of the carbon based SAC is perhaps due to possibility of COOH and OH groups to behave as anchoring sites for attaching the reactants, together with high acid strength of Bronsted acid sites (Hara, 2010; Ngaosuwan et al., 2016). On the other hand, this exposure leads for leaching of SO_3H groups and loss of catalyst activity during reuse (Konwar et al., 2014a).

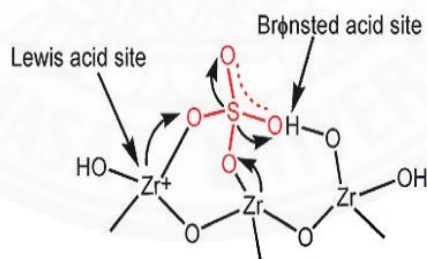


Fig. 2.9 Bronsted and Lewis acid sites in SO_4^{2-}/ZrO_2 (taken from (Su & Guo, 2014))

2.4.2 Surface hydrophobicity

Since, carbon based SACs incorporate with large number of hydrophilic functional groups, such as COOH, OH, and SO_3H , these catalysts can incorporate a large amount of hydrophilic groups into the flexible carbon bulk (Nakajima & Hara, 2012). This brings reactants to the strongly acidic SO_3H functional groups, regardless of small

surface area of the catalyst. In addition, surface hydrophobicity of the catalyst due to carbon bulk, attracts organic reactants reducing the possible unfavorable reactions (Konwar et al., 2014a). These reasons cause for relatively higher activity of carbon based SACs.

2.4.3 Porosity, surface area, and surface structure

It is found that, usually surface area of carbon based SACs are relatively low. The low surface area of the catalyst limits mass diffusion during the reaction, which ultimately causes a decrease of catalytic activity (Su & Guo, 2014). However, despite the low surface area, these catalysts have shown excellent catalytic activity for esterification and trans-esterification (Devi et al., 2014; Savaliya & Dholakiya, 2015). In addition, some studies reported poor catalytic activity, even though prepared catalysts has significantly higher surface area (Ngaosuwan et al., 2016). On the other hand, as stated by North (2016), possible swelling of carbonaceous catalysts in the solvent, provides a great access to reactants pointing out that the low surface area may not be significant during the reaction. Also, as stated by Konwar et al. (2014a), high pore volume of the catalyst, in addition to presence of high density of SO₃H groups favored high catalyst activity. However, it is found that catalysts prepared from hydrothermal carbonization and sulfonation showed high mechanical and thermal stabilities (<260 °C) (Devi et al., 2009), with high surface area compared to catalyst prepared from direct sulfuric carbonization. This may help catalyst to maintain their unique structure during reaction.

In general, therefore, it can be concluded that remarkably improved activity of the carbon based SAC is due to various integrated factors of the catalysts, such as high sulfonic acid group density, the presence of both hydrophilic (SO₃H, COOH, and OH groups) and hydrophobic structures (carbon framework) in the catalyst, large pore volume, and specific large surface area (Su & Guo, 2014).

Carbon based SACs are identified as a promising, economical and sustainable alternative for commercially available SACs and homogeneous acid catalysts.

However, use of SAC is reported mainly for direct esterification of fatty acids, or pre-treatment (esterification) of FFA in acidic feedstocks (Devi et al., 2009; Konwar et al., 2014b; Liu et al., 2015; Poonjarernsilp et al., 2014; Zeng et al., 2016). A very few studies have reported use of carbon based SAC for simultaneous esterification and trans-esterification of low quality acidic feedstock for biodiesel production (Devi et al., 2014; Shu et al., 2010a) (Table 2.2). Therefore, the investigation of possible waste biomass materials for SACs preparation and the possible use of biodiesel production using low quality feedstocks are crucial.



Table 2.2 Recent studies on use of carbon based SAC for biodiesel production

Catalyst	Catalyst preparation	Reaction conditions Feedstock/reaction/Methanol loading(molar ratio)/ Catalyst loading (wt. %) /Reaction temperature (°C)/reaction time (h)	Activity FAME yield (%)/ Reusability	Reference
Esterification				
Glycerol based SAC	Direct in situ sulfuric carbonization	Palmitic acid, esterification/25 ml for 2.56 g/ 10/ 65 / 4 in a reflux reactor	99%/ 8 cycles	(Devi et al., 2009)
Single wall carbon nano-horn	Two step carbonization and hydrothermal sulfonation of single walled carbon nano horn	Palmitic acid, esterification/ 33:1/0.5 g/ 64 /4, in a reflux reactor	93%/ 3 cycles	(Poonjarernsilp et al., 2014)
Banana peel derived SAC	Direct impregnation with FeCl ₃ and subsequent carbonization	Oleic acid, esterification / 150 mg:5 g/150 mg/80/2 in a reflux reactor	63-94%/ 4 cycles	(Liu et al., 2015)
Bagasse based SAC	Direct in situ sulfuric carbonization	Esterification of soap stock oil/ 15:1/ 5 / 65/ 11 in a reflux reactor	97.2%/ 3 cycles	(Savaliya & Dholakiya, 2015)
Rice husk derived SAC	Incompletely carbonization, sodium hydroxide leaching and subsequent sulfonation.	Oleic acid, esterification /5:1/0.015 g catalyst (20 mmol oleic acid)/80/9 in a reflux reactor	91%/ 10 cycles	(Zeng et al., 2016)
Coffee residue derived SAC	Chemically activated, two step carbonization and sulfonation	Caprylic acid, esterification/3:1/ 5/60/4 in an autoclave reactor	71.4%/4 cycles (very low reusability)	(Ngaosuwan et al., 2016)
Pre-treatment of acidic feedstock				
Oil cake derived SAC	Phosphoric acid activation and two- step carbonization and sulfonation	Pre-treatment of acidific oil (43.7% FFA)/43:1/5/80/8 in an autoclave reactor	97-99%/ 5 cycles	(Konwar et al., 2014b)

Palm Empty fruit bunch derived SAC	Direct impregnation with $\text{Fe}_2(\text{SO}_4)_3$	Pre-treatment of WCO /-/1/65/1	90.9%,	(Koguleshun et al., 2015)
<i>Jatropha curcas</i> seed cake derived SAC	Two step carbonization and sulfonation	Pre-treatment of <i>J.curcus</i> oil (12.7)/12:1/7.5/60/1 in a reflux reactor	99.13%/3 cycles	(Mardhiah et al., 2017)
Simultaneous esterification and trans-esterification				
vegetable oil asphalt (VOA) derived SAC	Two step carbonization and sulfonation	Waste vegetable oil (>50% FFA)/ 16.8:1/0.2/220/4.5 in an autoclave reactor	94.8% FFA conversion 80.5% ester yield for trans-esterification, 5 cycles	(Shu et al., 2010a)
Glycerol based SAC	Direct in situ sulfuric carbonization	Karanja oil (7.5% FFA), /45:1/20/ 160/ 4 in a ACE pressure tube	> 99%/5 cycles	(Devi et al., 2014)
<i>C.Pentandra</i> seed cake derived SAC	Two step carbonization (nano sized) and sulfonation	<i>C.Pentandra</i> seed oil (13.4% FFA)/1.5/18:1/ 220/150 min in an autoclave reactor	99%/ 4 cycles	(Parthiban & Perumalsamy, 2015)
Xylose derived SAC	Hydrothermal carbonization and sulfonation	Waste cooking oil (1.54% FFA) /10:1/10/110/2 in an autoclave reactor	89.6%/ 3 cycles	(Tran et al., 2016)
Biochar based SAC	Two step pyrolysis and sulfonation	Waste cooking oil(6.4% FFA)/ 10:1/10/140/15 min in microwave reactor	90%/6 cycles	(González et al., 2017)

2.5 Current biodiesel production processes

There are several technologies associated with biodiesel production from various feedstocks. Direct use, blending with petro-fuels, micro-emulsions, thermal cracking (pyrolysis), and trans-esterification (alcoholysis), are the main methods to obtain biodiesel from various feedstocks (Ma & Hanna, 1999b; Schwab et al., 1987). Among them, the most commonly used method for biodiesel production is trans-esterification, in which oils are converted into esters by reaction with alcohol in the presence of a catalyst. There are several different processes, such as batch and continuous reactive distillation methods, mechanical stirring, ultrasound assisted processes, microwave assisted processes, and membrane reactor assisted processes have been employed in order to improve the biodiesel production. However, three main biodiesel production technologies which are used in this study are discussed in this session.

2.5.1 Conventional open reflux reactor assisted biodiesel production

Most of the laboratory scale biodiesel production processes are associated with open batch system due to its simple operational conditions (Banani et al., 2015). A typical reactor consists with a simple round bottom glass vessel which is considered as the main reactor vessel, and a reflux condenser (Fig. 2.10). Oil or water bath equipped with a magnetic stirrer is used to maintain reaction temperature and agitation speed, respectively.

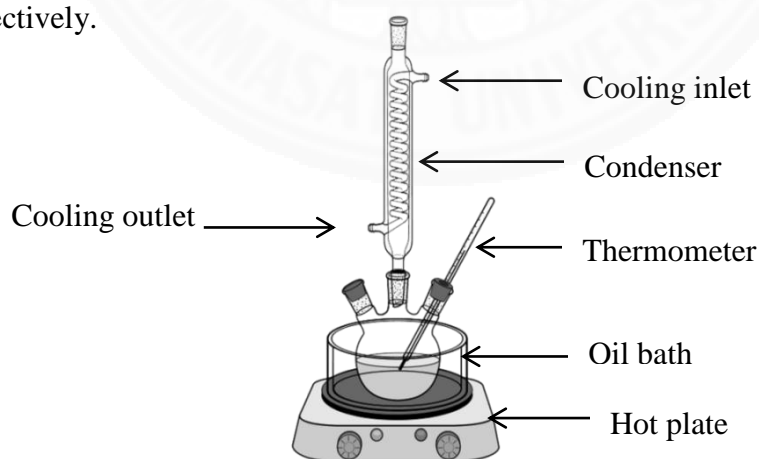


Fig. 2.10 A conventional open reflux reactor

Successful use of a conventional reflux reactor for both acid and alkaline catalyzed biodiesel production, to have a higher biodiesel yield at relatively low reaction temperature is reported in many studies. Banani et al. (2015), used conventional open reflux reactor for biodiesel production from WCO (with 0.21% of FFA) at 60 °C and received 98% of ester yield. Kai et al. (2012), reported two step biodiesel production from WCO at 37 °C using KOH. The use of Ca based solid base catalyst produced from industrial waste for biodiesel production (>90 %) from WCO at 60 °C is reported (Viriya-Empikul et al., 2012). Dawodu et al. (2014), reported biodiesel production from soya bean oil and dimethyl carbonate at 90 °C and potassium methoxide as catalysts. They have received 92% of ester yield after 5 h. However, acid catalyzed biodiesel production requires a high reaction temperature to initiate the reaction. Since, maintenance of high reaction temperature is not easy in the conventional reflux reactor and due to possible evaporation of methanol, a longer reaction time at low reaction temperature is used in acid catalyzed biodiesel production. As reported by Savaliya and Dholakiya (2015), a reflux reactor assisted esterification of soap stock oil yield 97.2% conversion at 65 °C and 11 h using bagasse based SACs. It is reported a 99% conversion during esterification of palmitic acid using glycerol based SACs at 65 °C and 4 h (Devi et al., 2009). In addition, use of an open reflux reactor for esterification, pre-treatment of acidic feedstocks, and simultaneous esterification and trans-esterification, using SACs is reported in several studies (Table 2. 2).

However, difficulty in maintaining high reaction temperature and pressure conditions specially when using SACs (Gnanaprakasam et al., 2013), and limitations in large scale biodiesel production have limited the use of open system only for lab scale.

2.5.2 Autoclave assisted biodiesel production

Biodiesel production from low quality feedstocks with high acid value prefers acid catalysts in order to prevent unnecessary downstream processes. In general, acid catalyzed reactions require high reaction temperature for activation during the

reaction. A closed system which can control high reaction temperature and pressure, minimizes the possible methanol loss during biodiesel production (Gude et al., 2013). The pressure inside the autoclave is the methanol vapour pressure at the reaction condition. A typical reactor consists with a stainless steel vessel and a stirrer motor which is considered as the main reactor vessel, connected to a temperature and a motor controller (Fig. 2.11).

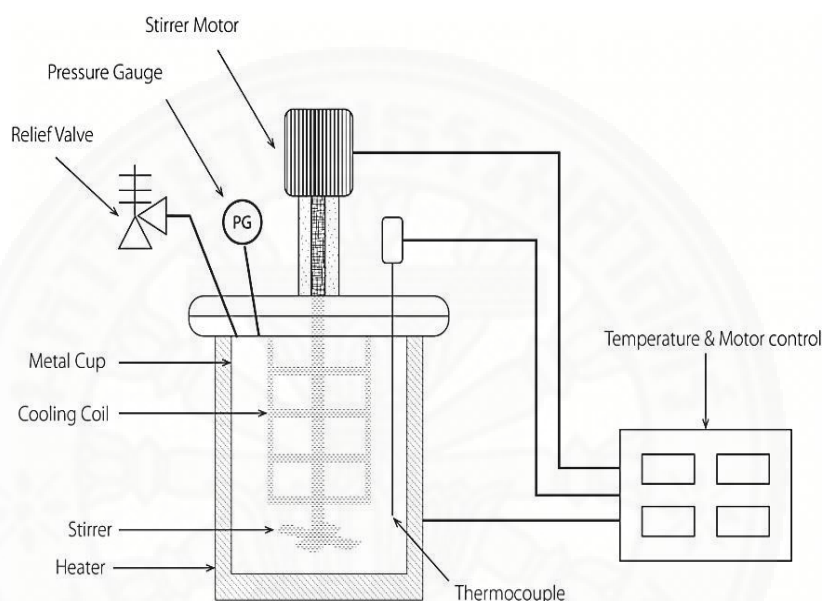


Fig. 2.11 A closed autoclave reactor

The use of an autoclave reactor for acid catalyzed biodiesel production is reported in several studies. Shu et al. (2010a), reported use of vegetable oil asphalt derived SAC for biodiesel production from WCO in an autoclave reactor. They obtained a maximum biodiesel yield of 94.8% at optimum conditions of 16.8:1 methanol to oil molar ratio, 0.2 wt.% of the catalysts, at 220 °C and 4.5 h. Parthiban and Perumalsamy (2015) have used autoclave reactor (100 ml) for biodiesel production from *C. pentandra* oil to receive a 99% ester conversion at optimum conditions of 18:1 methanol: oil, 1.5 wt.% *C. pentandra* seed cake derived SAC, at 220 °C after 2.5 h. Tran et al. (2016), reported 89.6% maximum ester yield when producing biodiesel from WCO using an autoclave reactor at optimum reaction conditions of 10:1 methanol:oil molar ratio, 10 wt.% Xylose derived SAC, at 110 °C and 2 h. Results

show that an autoclave reactor is efficient than a conventional reflux reactor and achieve higher biodiesel yield at high temperature and shorter reaction time (Table 2.2).

However, an autoclave assisted biodiesel production also requires comparatively longer overall processing time, mainly due to the long heating-up and cooling times (Gude, 2017). This increases the requirement of energy for biodiesel production. In addition, reasons, such as the presence of chemically active metal surface, poor temperature control and difficulty in sampling during the reaction, are identified as failures of this reactor (Shumate & Riley, 1984).

2.5.3 Microwave assisted biodiesel production

Microwave assisted biodiesel production has gain increased attention over conventional biodiesel production process in terms of the higher energy efficiency. Reduction of overall reaction time due to rapid, selective, and uniform heating (Fig. 2.12), reduction of overall process steps and the cleaner production during microwave assisted process have facilitated, recent attention for their use in the biodiesel production (Gude et al., 2013). According to Özçimen and Yücel (2011), microwaves are electromagnetic radiations that influence on the molecular motions. Microwaves change the electric field of the system, facilitating a rapid rotation of the oil, alcohol, and catalyst in the system by dipolar polarization and ionic conduction (Fig. 2.12). This improves the mixing of reactants and increases the rate of reactants.

The application of the microwave assisted biodiesel production using both batch and continuous reactors have been investigated. The batch process is relatively simple, although it requires a large reactor size and a longer reaction time. There are different types of batch reactors, including borosilicate glass or Teflon vessels, and round bottom flask equipped with reflux condenser are reported in the lab scale experiments (Barnard et al., 2007; Fernandes et al., 2014; Hernando et al., 2007; Khemthong et al., 2012; Zhang et al., 2012). A continuous-flow reactor avoids the limitation of

penetration depth of microwaves compared to a batch reactor, when up-scaling the biodiesel production (Tangy et al., 2017). Microwave assisted a batch reactor and a flow type reactor is shown in Fig.2.13.

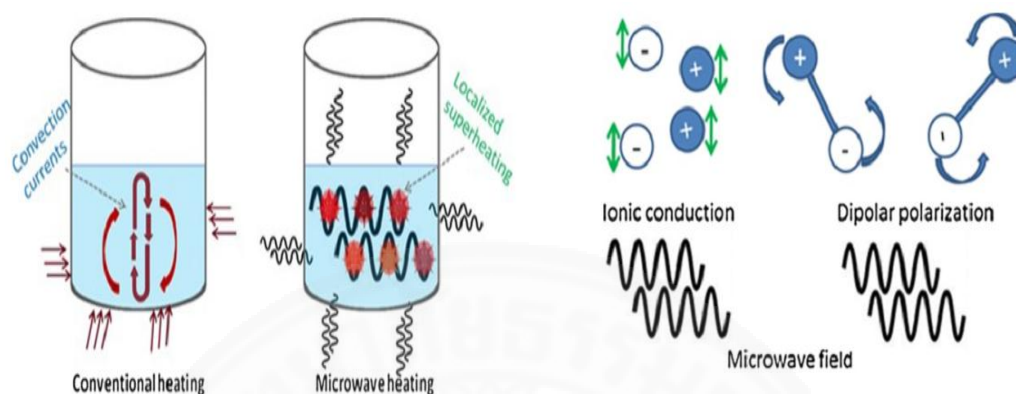


Fig. 2.12 Mechanism of conventional and microwave assisted heating (Gude et al., 2013)

Biodiesel production using microwave assisted batch and flow reactors, and alkaline catalyst in a very short reaction time is reported. Chen et al. (2012), obtained a maximum 97.6 % FAME yield from WCO within 3 min, using CH_3ONa as a catalyst and 6:1 methanol to oil molar ratio. A study by Choedkiatsakul et al. reported a 99.4% yield only in 1.75 min residence time at 70 °C using 1% NaOH and 12:1 methanol to oil molar ratio, from palm oil in a flow type microwave assisted reactor (Choedkiatsakul et al., 2015). Indarti (2016), reported a maximum FAME yield of 96% from palm oil within 10 min using 5:1 methanol to oil molar ratio and 0.5 wt.% of seashell derived solid base catalyst in a batch reactor. Tangy et al. (2017), reported the use of continuous flow microwave assisted reactor for large scale biodiesel production from WCO using SrO based catalyst. They received >99% FAME yield in 8.3 min using 41 wt. % of catalyst and 12:1 methanol:oil (molar ratio). However, only few studies are reported that uses acid catalyst for microwave assisted biodiesel production. Yual et al., reported a maximum FAME yield of 94% from castor oil using 12:1 methanol to oil ratio and 5% carbon based sulfonated catalyst after 60 min at 65 °C (Yuan et al., 2008) in a batch reactor. Gonzalez et al. have reported a 90% FAME yield from WCO after 15 min at 140 °C using 10% oat hull based carbon acid catalyst and 10:1 methanol to oil molar ratio (González et al., 2017). It is observed

that acid catalyzed, microwave assisted biodiesel production also requires a longer reaction time compared to the alkaline catalyzed biodiesel production.

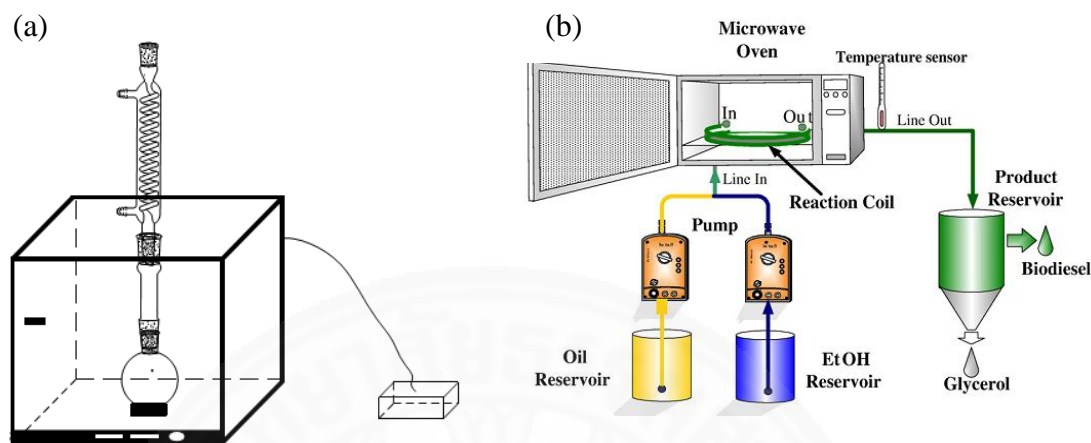


Fig. 2.13 Microwave assisted (a) a batch reactor, (b) a flow reactor (Motasemi & Ani, 2012)

However, as summarized by Talebian-Kiakalaieh et al. (2013a) ability of damaging triglycerides due to high microwave power, safety aspects and limitations of the process when scaling up to large scale are considered as limitations of microwave assisted biodiesel production. In addition, the strong microwave interactions increase the rate of possible methanol evaporation (Gude et al., 2013; Yuan et al., 2008).

An ultrasound assisted biodiesel production reduces the requirement of alcohol, catalyst, and the reaction time compared to other process due to high chemical activity (Singh et al., 2007; Yaakob et al., 2013). Biodiesel production using ultrasound reactors (Gupta et al., 2015), and combined ultrasound and microwave irradiation assisted processes (Ma et al., 2015), are reported. In addition, non-catalytic supercritical alcohol method is used to produce biodiesel at very high temperature and pressure conditions (García-Martínez et al., 2017; Leung et al., 2010). High energy requirement and the safety issues are the disadvantages of this method. Membrane reactor assisted biodiesel production is popular in order to obtain pure biodiesel without impurities and due to low wastewater production. However, the cost,

durability of the membrane, and slow reaction limits the wide use of them in industries (Yaakob et al., 2013).

2.6 Fuel properties of biodiesel

The fuel properties of biodiesel depend on several factors, such as the quality and the composition of the feedstock, production technologies, downstream processes, and the handling and storage. Therefore, it is vital to evaluate the fuel properties in order to understand the suitability of biodiesel for usage. As reported by Barabás and Todoruț (2011), the current standards for quality of biodiesel are defined based on several factors. The biodiesel standards are varying mainly according to the region. Also, the type of diesel engine use, emission regulations, and climatic properties of the region are mainly influenced for the biodiesel standards. ASTM D6751 and EN 14214 are established specifications for key fuel properties of biodiesel and tabulated below (Table 2.3). The properties of biodiesel can be classified according to different factors, such as the influence on the engine performance and engine parts (ignition qualities, heating value, viscosity, etc.), storage and transport (oxidation stability, flash point, microbial contamination, etc.), and cold properties (cloud point and pour point) (Barabás & Todoruț, 2011).

2.6.1 Acid value

The acid value is a direct measure of the corrosiveness of the biodiesel. It is measured in terms of required amount of KOH in milligram per gram of the sample to neutralize the acids present. The presence of residual mineral acid from the production process, residual free fatty acids, and by-products of biodiesel oxidation contribute for the acid value. Therefore, the acid value is also a measure of the freshness, and cleanness of biodiesel. The acid value of biodiesel should be less than $0.50 \text{ mgKOH g}^{-1}$ in order to fit for the ASTM 6751 and EN 14214 international standards.

2.6.2 Viscosity

The viscosity of biodiesel is one of the most important property which influences on the easiness of starting the engine, the quality and size of the particles, and quality of fuel-air mixture combustion (Barabás & Todoruț, 2011). Viscosity has both upper and lower limits, as both too low and very high viscosities create problems due to incomplete combustion. Due to formation of a very fine spray with a very low mass and a speed which limits sufficient penetration, a too low viscous biodiesel makes black smoke during combustion. Also, due to formation of too big drops, a too high viscous biodiesel makes blue smoke by disturbing combustion (Barabás & Todoruț, 2011; Bățaș et al., 2003). The viscosity of biodiesel should be in the range of 1.9-6.0, and 3.5-5.0 mm²s⁻¹ according to ASTM 6751 and EN 14214 standards. Biodiesel derived from frying oil has higher viscosity compared to those produced from vegetable oil due to the presence of less unsaturated fatty acids (Knothe, 2006). The viscosities of different biodiesel feedstocks are shown in Table 2.4.

2.6.3 Density

Density of biodiesel is an important physical property and the information of which is required in storage facilities, reactors, and fluid flow designs (Phankosol et al., 2014). Also, fuel properties, such as cetane number, and heating value are related with the density of biodiesel (Gülüm & Bilgin, 2015). Since the density of biodiesel depends on the molar mass, the free fatty acid and water content, that is varies mainly depending on the type of feedstock (Table 2.4). Even though, ASTM 6751 has no specific requirement documented, the density of biodiesel should be in the range of 860-900 kgm⁻³ at 15 °C according to EN 14214.

2.6.4 Heating value

The heating value or heat of combustion is the amount of heat released when a unit quantity of biodiesel is combusted in oxygen. There are two types of heating values are concerned; the gross heating value (high) and the net heating value (lower)

(Barabás & Todoruț, 2011). As stated by Barabás and Todoruț (2011), the heating value of biodiesel increases with the length and the degree of saturation of carbon chains. In general, the heating value of biodiesel is measured using bomb calorimeter following ASTM D240.



Table 2.3 Biodiesel Standards ASTM D 6751 and EN 14214

Property	ASTM D6751-12			EN 14214:2012	
	2-B	1-B	Test		Test
Flash point, min	93 °C		D93	101 °C	EN ISO 2719
Water & sediment, max	0.050% <u>vol</u>		D2709		
Water, max				500 mgkg ⁻¹	EN ISO 12937
Total contamination, max				24 mgkg ⁻¹	EN 12662
Kinematic viscosity	1.9-6.0 mm ² s ⁻¹		D445	3.5-5.0 mm ² s ⁻¹	EN ISO 3104
Density				860-900 kgm ⁻³	EN ISO 3675 EN ISO 12185
Sulfated Ash, max	0.020% mass		D874	0.02% mass	ISO 3987
Sulfur, max (by mass)	Two grades: S15 15 ppm S500 0.05%		D5453	10.0 mgkg ⁻¹	EN ISO 20846 EN ISO 20884 EN ISO 13032
Copper strip corrosion, max	No 3		D130	class 1	EN ISO 2160
Cetane number, min	47		D613	51.0	EN ISO 5165
Cloud point	Report		D2500	Location & season dependent	EN 23015
Pour point	-15 to 10		D 5358	-15 to 10	ISO 3016
Carbon residue on 10% distillation residue, max	0.050% wt ⁵		D4530		
Acid number, max	0.50 mg KOHg ⁻¹		D664	0.50 mg KOHg ⁻¹	EN 14104
Oxidation stability	3 h min		EN 14112	6 h min	EN 14112
Iodine value, max				120 ¹ g Iod/100g	EN 14111 EN 16300
Linolenic acid methyl ester, max				12.0% <u>wt</u>	EN 14103
Polyunsaturated methyl esters, max				1.00% <u>wt</u>	EN 15779
Alcohol control	0.2% <u>wt</u> methanol max, or		EN14110	0.20% <u>wt</u> methanol max	EN 14110
	130°C flash point min		D93		

Monoglycerides, diglycerides & triglycerides, max		MG 0.40% wt	D6584	MG 0.70% wt DG 0.20% wt TG 0.20% wt	EN 14105
Group I metals (Na + K), max	5 mgkg ⁻¹		EN 14538	5.0 mgkg ⁻¹	EN 14108 EN 14109 EN 14538
Group II metals (Ca + Mg), max	5 mgkg ⁻¹		EN 14538	5.0 mgkg ⁻¹	EN 14538
Free glycerin, max	0.020% wt		D6584	0.02% wt	EN 14105 EN 14106
Total glycerin, max	0.240% wt		D6584	0.25% wt	EN 14105
Phosphorous, max	0.001% wt		D4951	4.0 mgkg ⁻¹	EN 14107 EN 16294
Cold soak filtration time (CSFT), max	360 s ⁴	200 s	D7501		

Table 2.4 Fuel properties of biodiesel produced using different feedstocks

Feedstock and used catalyst	Acid value (mg KOH g ⁻¹)	Kinematic viscosity (at 40 °C mm ² s ⁻¹)	Density (kgm ⁻³)	Heating value (MJkg ⁻¹)	Oxidation stability (h)	Cetane number (min)	Pour point (°C)	Cloud point (°C)	Flash point (°C)	Ash content (wt. %)	S content (wt. %)	Reference
Spirulina algae Water pond algae and con. H ₂ SO ₄ as catalysts	0.45 0.40	5.66 5.82	860 872	41.36 40.8	-	-	-18 -15	-	130	-	-	(Nautiyal et al., 2014)
Soap stock oil and carbon based SAC	-	3.9	886.2	-	-	51.2	-	-4.8	180	-	-	(Savaliya & Dholakiya, 2015)
WCO and carbon based SAC	0.45	4.15 (at 15 °C)	876.6 (at 15 °C)	9.912	2.6	50	2	-	194	-	0.003	(Maneechakr et al., 2015)
<i>C. pentandra</i> oil and carbon based SAC	0.12	4.30	867	38.12	4.12	47	-2	3	164	-	-	(Parthiban & Perumalsamy, 2015)
WCO and carbon based SAC	0.72	6.4	-	-	-	-	-22	-	167	0.057	-	(Tran et al., 2016)
Rubber seed oil Fe/C based SAC	0.1	4.85	870	45.1	-	51	-10	-7	155	-	-	(Dhawane et al., 2017)
Spent coffee ground and Two step con. H ₂ SO ₄ , and KOH as catalysts	0.80, 0.79	5.36, 5.27	-	-	6.62, 33.42	-	-	-	-	-	-	(Liu et al., 2017)

2.6.5 Cetane number

The cetane number is a measure of the combustion quality of biodiesel. In general, cetane number is defined in the range of 15-100, while the minimum recommended value is 47 in the United States and 51 in the Europe. A too low cetane number biodiesel leads incomplete combustion with an improper engine function. A too high cetane number biodiesel ignites quickly close to the injector. This overheats the injector and insufficient of air results in incomplete combustion (Barabás & Todoruț, 2011). Therefore, the cetane number of biodiesel should be within the standard limit in order to have a better combustion.

2.6.6 Oxidation stability

Biodiesel can be degraded during storage due to oxidation by contact with air or water. The susceptibility of oxidation of biodiesel increases with increasing amount of unsaturated fatty acid composition. Therefore, stability of biodiesel during long time storage is important as the oxidation changes the composition and other properties, such as acid value, viscosity, and heating value (Agarwal et al., 2015; Barabás & Todoruț, 2011). Oxidation stability of biodiesel is measured mainly by two methods: the rancimat analysis (EN 14214) and the oxidative stability index (ASTM D6751). According to the standards the oxidation stability of biodiesel should be minimum values of 3 h (ASTM 6751) and 6 h (EN 14214). As stated by Agarwal et al. (2015) poor oxidation stability is a major barrier for commercialization of biodiesel. Therefore, several types of antioxidants are used to enhance the oxidation stability of biodiesel.

2.6.7 Flash point

The flash point of biodiesel is an important parameter and is used to classify fuels according to hazard level. Even though the flash point is not directly affects to the combustion efficiency, it is a measure of residual methanol or ethanol present in biodiesel. The flash point is measured by using open cup or closed cup methods. The

minimum recommended flash point for biodiesel in the United States is 93 °C while 101 °C in Europe. However, if the flash point is considered as a measure of residual methanol, and it should be minimum 130 °C according to ASTM 6751 (Barabás & Todoruț, 2011).

2.6.8 Cloud point and pour point

The cloud point (ASTM D 2500) determines the temperature, at which biodiesel form crystalline or cloudy appearance. Generally, the cloud point of biodiesel is higher than the conventional diesel. It should be less than -1 °C for effective use of biodiesel in cold climates. The pour point determines the temperature, at which biodiesel losses its flow characteristics. It is measured by standard test method of ASTM D 5358 and ISO 3016. Both the cloud point and the pour point depend on the type of biodiesel feedstock and minimum values are defined based on the location of which biodiesel is intending to use (Barabás & Todoruț, 2011).

2.6.9 Water and sediments content

The water content and the sediments are measurements of purity of biodiesel. Water can accumulate in biodiesel during transportation and storage even though they are dried after preparation. This enhances the microbial growth forming sediments. The water content of biodiesel can be measured in terms of volume after centrifugation of known sample (Barabás & Todoruț, 2011).

2.6.10 Ash content

As reported by Barabás and Todoruț (2011), sulfated ash is a measure of ash from inorganic metallic compounds and carbon residue is a measure of residual catalysts, glycerol, and FFA. Therefore, ash content is a measure of purity of biodiesel.

Chapter 3

Materials and methodology

This study investigates sustainable biodiesel production from WPO using waste biomass derived SACs. The main focus of this study was to synthesize carbon based SACs from waste biomass using a simple and economical protocol for biodiesel production. In addition, optimum reaction conditions for biodiesel production from WPO and energy consumption in open and closed reactors are studied. Fuel properties of produced biodiesel are also investigated.

3.1 Materials

All chemicals were of analytical grade. Acetone (C_3H_6O , RCI Lab scan), anhydrous sodium sulfate (Na_2SO_4 , Loba Chemi), ethanol (C_2H_6O , Fisher Scientific), heptane (C_7H_{16} , Fisher Scientific), hexane (C_6H_{14} , Fisher Scientific), methanol (CH_4OH , Wako), methyl heptadecanoate ($C_{17}:0$, Fluka), Palmitic acid ($CH_3(CH_2)_{14}COOH$, Wako), sulfuric acid (H_2SO_4 , Wako), and potassium hydroxide (KOH, Wako), were used as received.

WPO was used as the biodiesel feedstock and collected from Useful Food Co. Ltd, Thailand. Composition of WPO was analyzed using an in-house method based on a compilation of methods for food analysis, Thailand (Standards, 2003). Other properties, such as acid value, viscosity, density, flash point, pour point, sulfur and ash content were also analyzed. WPO was used as received without pre-treatment during carbon based SACs catalyzed biodiesel production.

Three types of abundant waste biomass; Palm empty fruit bunch (PEFB), Coconut meal residue (CMR), and Coconut coir husk (CCH) were selected as the carbon supports for catalysts preparation. The PEFB was harvested from a palm tree at Thammasat University, Pathum Thani, Thailand, while CMR and CCH were collected

from a local market, Pathum Thani, Thailand. The composition of carbon precursors used in this study is shown in Table 3.1 and 4.1.

Table 3.1 Composition of carbon precursors

	Cellulose (wt. %)	Hemicellulose (wt. %)	Lignin (wt. %)	Ash content (wt. %)	Reference
PEFB	42.85	24.01	11.7	0.52	(Rahman et al., 2007)
CMR	72.6	2.00	1.8	0.23	(Ng et al., 2010)
CCH	43.44	0.25	45.84	2.22	(Verma et al., 2013)

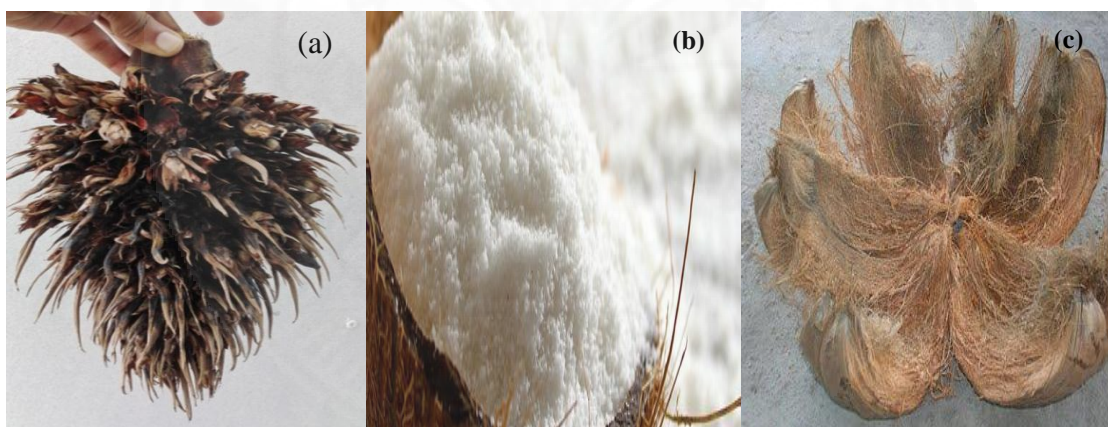


Fig. 3.1 Waste biomass used as carbon precursors; (a) PEFB, (b) CMR, and (c) CCH

3.2 Catalyst preparation

Three types of carbon precursors, i.e., PEFB, CMR, and CCH were selected for catalyst preparation due to high carbon content of these popular waste biomasses (Table 3.1). They were thoroughly washed for several times and allowed for drying under the sun. After that, waste biomass was ground and dried in an oven (FED 115, BINDER) at 110 °C for 5 h in order to remove moisture. Then, the oven

dried, biomass powder was used to produce desired carbon based SACs by two methods under defined reaction conditions. The schematic diagram of the catalysts preparation is shown in Fig. 3.2.

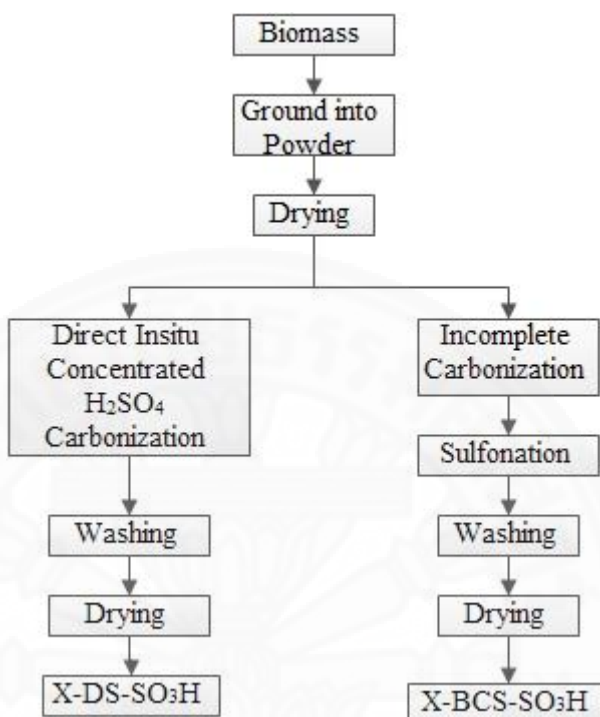


Fig. 3.2 Schematic diagram for catalyst preparation

3.2.1 Direct in-situ concentrated H₂SO₄ carbonization of waste biomass

For this method, oven dried waste biomass powder (10 g) and concentrated H₂SO₄ were mixed (1:5 wt/wt) at 100 °C in a flat glass beaker for 1 h, using a hot plate (C-MAG HS7, IKA) to facilitate in-situ incomplete sulfuric carbonization. After 24 h, the reaction mixture was diluted and filtered using a suction filtration kit equipped with a Buchner funnel and an Erlenmeyer flask. The resultant was repeatedly washed with hot distilled water thoroughly until the excess H₂SO₄ acid was removed. Then, the resultant was kept in an oven at 120 °C for 2 h to remove all moisture. The prepared carbon based SAC was denoted as X-DS-SO₃H and used for biodiesel production (where, 'X' is the type of biomass used for catalyst preparation).

3.2.2 Sulfonation of incompletely carbonized waste biomass

For this method, oven dried waste biomass powder was heated in low oxygen environment using a lid closed porcelain crucible in a muffle furnace (CWF 1200, Carbolite) at 400 °C for 5 h to facilitate incomplete carbonization. Then, the resultant product (biochar) was mixed with 25% concentrated H₂SO₄ (5 g in 100 ml H₂SO₄) in an Erlenmeyer flask using an orbital mechanical shaker (NB-205V, N-BioTeck) at 200 rpm for 24 h to facilitate sulfonation. After that, sulfonated black solid residue was separated by vacuum filtration using a suction filtration kit equipped with a Buchner funnel and an Erlenmeyer flask. The residue was washed with hot distilled water until the pH was neutral in the effluent. Prepared sulfonated carbon based SACs kept in an oven at 120 °C for 2 h to remove moisture, were denoted as X-BCS-SO₃H and used for biodiesel production (where 'X' is the type of biomass used for catalyst preparation).

3.3 Characterization of carbon based SACs

3.3.1 Total acid density and sulfonic acid density

Three acid groups, such as sulfonic, carboxyl, and phenolic groups, are associated with biomass derived SACs contributing to the catalytic activity. Total acid density of the catalyst was measured by standard acid base back titration, similar to method reported by (Dehkhoda, 2010). The catalysts were dried in an oven at 110 °C for 2 h prior to use for titration. Dried catalyst (0.1 g) was thoroughly mixed with 60 ml of 0.008 mol dm⁻³ of KOH and back titrated with 0.02 mol dm⁻³ of H₂SO₄. The total acid density was measured with respect to consumed volume of H₂SO₄. It is assumed that the sulfur content of each catalyst sample is mainly in the form of sulfonic acid groups. A small amount of sulfur present in the raw material is also assumed to be converted to sulfonic groups during preparation of the catalyst. This was also reported by other researches (Dehkhoda, 2010; Nakajima et al., 2007). Thus, sulfonic acid density was measured on the basis of weight percentage of sulfur in the catalysts.

3.3.2 Elemental composition

The composition of raw biomass changes during the catalyst preparation due to various reactions. Therefore, the carbon, hydrogen, nitrogen, oxygen, and sulfur contents of carbon precursors and prepared catalysts were analyzed via elemental analysis using CHNSO analyzer (628 series, Leco Corporation) and energy dispersive X-ray spectroscopy (EDS) (S-3400N, HITACHI), using Edax Genesis software.

3.3.3 Surface area and pore size distribution

The specific surface area and pore size distribution of the catalysts were studied by N₂ adsorption and desorption isotherm data, using liquid nitrogen at 77 K (BELSORP miniII, Japan). The Brunauer-Emmet-Teller (BET) specific surface area was calculated by using nitrogen adsorption isotherm (Brunauer et al., 1938). The total pore volume was calculated based on methods develop by Barrett, Joyner, and Halenda (BJH) method (Barrett et al., 1951).

3.3.4 Surface morphology

Surface morphology of the catalyst was examined by a scanning electron microscope (SEM-VE-8800, Keyence, Japan).

3.3.5 Presence of surface functional groups

Surface functional groups of the catalyst were analyzed by using a Fourier transform infrared (FT-IR) spectrometer (NICOLET iS50, FT-IR, Thermo scientific) with attenuated total reflectance (ATR) mode.

3.3.6 Chemical states of functional groups

The chemical states of the functional groups on the surface of the catalyst were analyzed by X-ray photoelectron spectroscopy (XPS) (PH15000 Versa Probe II @ Ulvac- PHI Inc, Japan) with Al K α radiation.

3.3.7 Thermal stability

The thermal stability of the catalysts was analyzed by thermo gravimetric (TG) analysis (TGA/DSC3+HT/1600/219) under a N₂ flow (25 ml min⁻¹) at heating rate of 10 °C min⁻¹ at 25-900 °C temperature range.

3.4 Evaluation of the catalytic activity

The activity of the catalysts was evaluated for esterification of palmitic acid and biodiesel production from WPO (5.2% FFA). The schematic diagram of biodiesel production from palmitic acid and WPO using prepared catalysts was shown in Fig. 3.3. All the experiments were conducted in duplicate, and average values were reported and discussed.

3.4.1 Esterification of palmitic acid

Esterification is faster than trans-esterification. Palmitic acid is the second largest abundant fatty acid present in WPO (Table 4.1). Therefore, activity of the catalyst (PEFB-DS-SO₃H) for esterification of palmitic acid was evaluated as a preliminary experiment.

Experiments were carried out in a 250 ml round bottom flask equipped with a reflux condenser and a thermometer on a hot plate with a magnetic stirrer, under following reaction conditions (Table 3.2). The control experiments were carried out without using the catalyst at optimum reaction conditions.

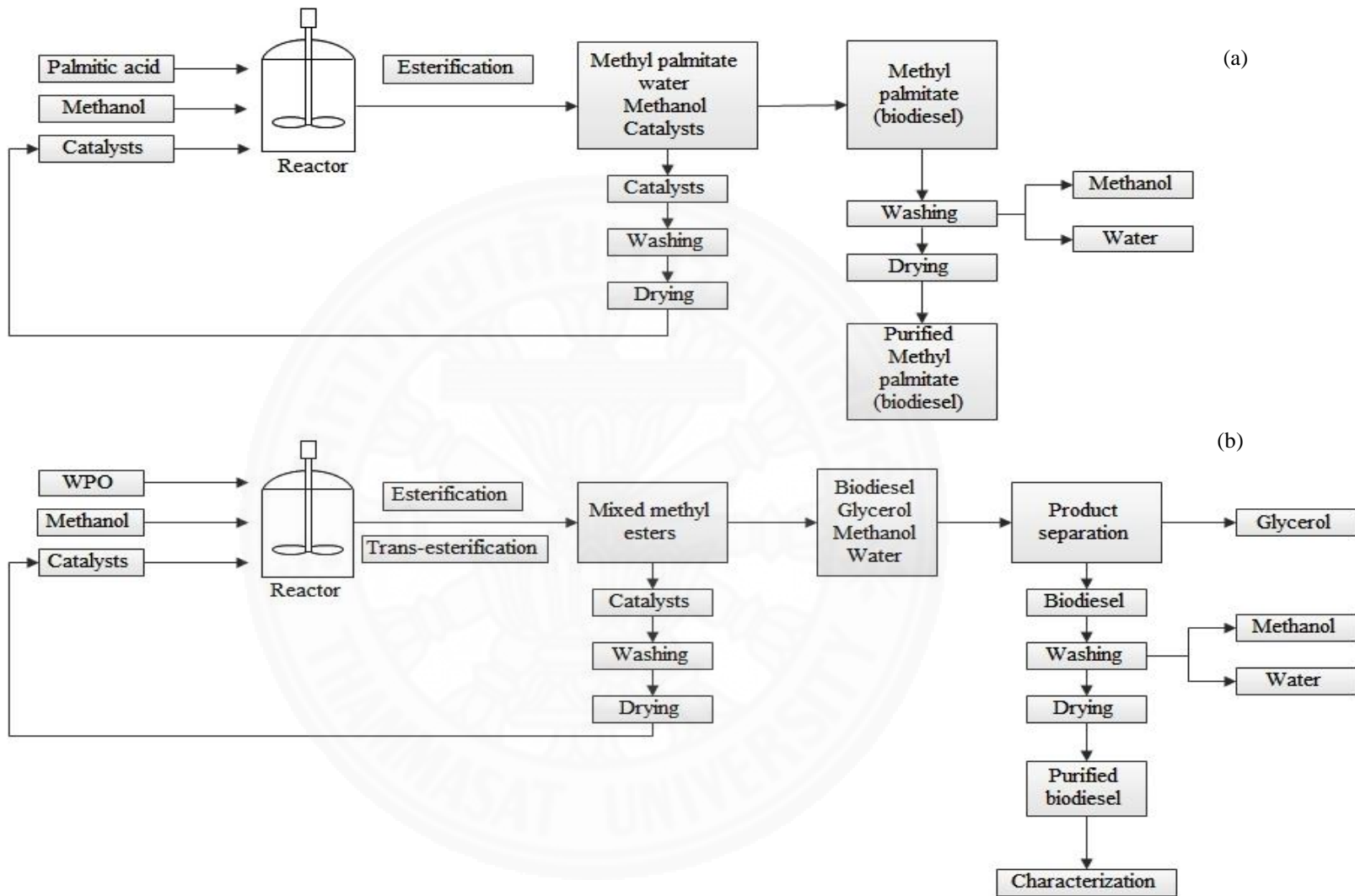


Fig. 3.3 Schematic diagram of biodiesel production (a) using palmitic acid, (b) using WPO

Table 3.2 Esterification of palmitic acid using PEFB-DS-SO₃H catalyst

Varied parameters		Fixed parameters
Parameters	Values	
Temperature (°C)	40, 60, 80	PA=10, C=0.5, t=3, A:PA=4:1
Reaction time (h)	1, 2, 3, 4, 5	PA=10, C=0.5, T=80, A:PA=4:1
Methanol:palmitic acid (molar ratio)	2:1, 4:1, 6:1, 8:1	PA=10, C=0.5, T= 80, t=5

Remarks: PA=Palmitic acid weight (g), C=Catalyst weight (g),

A:PA=Methanol:Palmitic acid (molar ratio), T=Temperature °C, t=Reaction time (h)

After the reaction, the catalyst was separated for reuse by vacuum filtration and oven dried for 2 h at 105 °C after washing with ethanol. Excess methanol from the final product was removed by evaporation at 80 °C in a water bath. Finally, the acid value of the medium was determined by titration according to the method described in GB/T 5530-2005 (National standards of people republic China) ("GB/T 5530 (2005) The National Standard of P.R. China," 2005). In the typical procedure, a known amount of the final product (0.5 g) was vigorously dissolved in ethanol (50 ml) by heating the mixture for 10 min. Then, the mixture was titrated against 0.1M KOH solution using phenolphthalein as the indicator. The esterification efficiency of the catalyst was determined by following equation.

$$\text{Esterification efficiency (\%)} = \frac{(AV_0 - AV_1)}{AV_1} \times 100 \quad (1)$$

Where, AV₀ and AV₁ are acid values (mg KOH g⁻¹) of the original feedstock and final product, respectively.

Reusability of the catalysts was studied using the optimum reaction conditions.

3.4.2 Biodiesel production from WPO

The biodiesel production from WPO was carried out using an open (using a conventional reflux reactor) and a closed (using a high pressure laboratory scale autoclave assisted reactor and a microwave assisted reactor) systems.

3.4.2.1 Biodiesel production from WPO using a conventional open reflux reactor

The screening experiments were carried out by using conventional reflux reactor. The effect of methanol:oil (molar ratio), reaction time (h), and catalyst loading (wt. %), on fatty acid methyl ester (FAME) yield and the reusability of the catalysts were investigated for which showed an acceptable activity.

Experiments were carried out in a 500 ml three-neck round bottom flask, equipped with a reflux condenser and a thermometer. The reactor was placed in a hot plate with an oil bath to maintain the reaction temperature. A magnetic stirrer was placed in the reactor in order to facilitate high mixing rate in the reaction medium. Optimum conditions for biodiesel production were evaluated using the reaction parameters shown in Table 3.3. The controlled experiments were carried out without using the catalyst, with non-functionalized carbon precursor, and H₂SO₄ acid at the optimum reaction conditions.

Table 3.3 Biodiesel production using conventional reflux reactor

Varied parameters		Fixed parameters
Parameters	Values	
A:O (molar ratio)	6:1, 8:1, 10:1, 12:1, 14:1, 16:1	FW=20, C=5, T=65-70, t=8 or 10
Time (h)	6, 8, 10, 12, 14, 16	FW=20, C = 5, T = 65-70, A:O= 12:1 or 14:1
Catalyst loading (wt. %)	5, 10, 15, 20	FW=20, A:O =12:1 or 14:1, T= 65-70, t=10 or 12

Remarks: FW=Feedstock weight (g), C=catalyst weight (wt.%), A:O=methanol:oil (molar ratio), T=Temperature (°C), t=Reaction time(h)

3.4.2.2 Biodiesel production from WPO using an autoclave reactor

Both esterification and trans-esterification reactions are endothermic. SAC catalyzed reactions are favorable under high reaction temperatures. Therefore, the activity of the catalysts under high reaction temperature was studied using selected catalysts; CMR-DS-SO₃H and CCH-DS-SO₃H which showed a higher FAME yield and a lower FAME yield under a conventional open reflux system, respectively. The effects of reaction temperature, reaction time, and catalyst loading on FAME yield were studied using selected catalysts and the optimum conditions were found from open reflux reactor assisted biodiesel production.

Experiments were carried out in a high pressure laboratory autoclave reactor (400 ml, Amar Equipment, India) which can maintain the temperature and agitation speed. Experimental conditions investigated using autoclave is presented in Table 3.4.

Table 3.4 Biodiesel production using CMR-DS-SO₃H catalyst in an autoclave reactor

Varied parameters		Fixed parameters
Parameters	Values	
Temperature (°C)	90,120, 150, 180	FW=20, C=5, A:O=12:1, t =3, a=500
Reaction time (h)	1, 2, 3, 4	FW=20, C=5, A:O=12:1, T=150, a=500

Remarks: FW= Feedstock weight (g), C =Catalyst weight (wt. %), A:O=methanol:oil (molar ratio), T=Temperature (°C), t=Reaction time (h), a=agitation speed (rpm)

Table 3.5 Biodiesel production using CCH-DS-SO₃H catalyst in an autoclave reactor

Varied parameters		Fixed parameters
Parameters	Values	
Temperature (°C)	90, 110, 130, 150	FW=20, C=5, A:O=12:1, t=3, a=500
Reaction time (h)	1, 2, 3, 4	FW=20, C=5, A:O=12:1, T=130, a=500
Catalyst loading (wt. %)	5, 10, 15, 20	FW=20, A:O=12:1, t=3, T=130, a=500

Remarks: FW= Feedstock weight (g), C =Catalyst weight (wt. %), A:O=methanol:oil (molar ratio), T=Temperature (°C), t=Reaction time (h), a=agitation speed (rpm)

Since, CCH-DS-SO₃H showed a poor activity during biodiesel production in the open-reflux reactor, activity of CCH-DS-SO₃H catalyst for biodiesel production using an autoclave reactor was studied (Table 3.5). The controlled experiment was carried out without using the catalyst at optimum reaction conditions.

3.4.2.3 Biodiesel production from WPO using a microwave reactor

Microwave assisted biodiesel production was carried out in a microwave reactor (240/50 MARS 6a) using easy prep reaction vessels (100 ml). Experiments were conducted for CMR-DS-SO₃H catalyst (which showed the best activity for open reflux and autoclave reactors), and PEFB-BCS-SO₃H, CMR-BCS-SO₃H, and CCH-BCS-SO₃H catalysts, using conditions presented in Table 3.6 and 3.7. The controlled experiments were carried out without the catalyst using optimum reaction conditions.

Table 3.6 Biodiesel production using CMR-DS-SO₃H catalyst in a microwave assisted reactor

Varied parameters		Fixed parameters
Parameters	Values	
Time (min)	20, 40, 60	FW=10, C=5, P=400, T=70, A:O=12:1
Temperature (°C)	70, 90, 110	FW=10, C=5, P=400, A:O=12:1, t=40
Remarks: FW= Feedstock weight (g), C =Catalyst weight (wt. %), P=microwave power (W) A:O=methanol: oil (molar ratio), T=Temperature °C, t=Reaction time (min)		

Table 3.7 Biodiesel production using X-BCS-SO₃H catalysts in a microwave assisted reactor

Varied parameters		Fixed parameters
Parameters	Values	
Time (min)	20, 40, 60	FW=10, C=5, P=350, T=70, A:O=12:1
A: O (molar ratio)	8:1,12:1,16:1, 20:1	FW=10, C=5, P=350, T=70, t=60
Temperature (°C)	70, 90, 110	FW=10, C=5,P=350, A:O=16:1, t=60
Remarks: FW= Feedstock weight (g), C =Catalyst weight (wt. %), P=microwave power (W) A:O=methanol: oil (molar ratio), T=Temperature °C, t=Reaction time (min)		

3.4.3 Reusability of the catalysts

After the reaction, the catalyst was separated for reuse by vacuum filtration and oven dried for 2 h at 105 °C after washing with hexane or acetone. Reusability was studied for catalysts which showed good activity, using optimum reaction conditions as found in each method. In addition, the presence of functional groups in the used catalysts was confirmed by FT-IR spectroscopy.

3.4.4 Ester separation and purification

Resultant mixture after the reaction is composed of a mixture of esters, glycerol, di and mono glycerides, and unreacted alcohol. Therefore, the remaining reaction medium was left to settle for about 8 h in a separating funnel for complete phase separation. After that, the crude methyl ester upper layer was washed with hot distilled water (>80 °C) in the separating funnel, in order to remove residuals of methanol and acidity. Then, remaining moisture of the ester portion is dried by using anhydrous Na₂SO₄ bed. All the samples were stored in amber color glass bottles and kept in the refrigerator (<10 °C) to avoid possible degradation.

3.5 Characterization of biodiesel produced from WPO

3.5.1 FAME yield

The FAME yield was determined by gas chromatography system (Clarus 580, PerkinElmer) equipped with a flame ionization detector (FID), a flow split injector, and a capillary column (HP-INNOWax – 30 m, 0.25 mm, 0.25 µm length, internal diameter, and film thickness, respectively). The column temperature program was set as: initial temperature 80 °C, first rate of 15 °C min⁻¹ increase from 80 to 200 °C, and second rate of 10 °C min⁻¹ increase from 200 to 250 °C (held for 5 min). Helium and Nitrogen (1 ml min⁻¹) were used as the carrier gas and the makeup gas, respectively. Methyl heptadecanoate was used as the internal standard. Finally, FAME yield was calculated by using following equation and according to the analytical conditions of the standard method of EN 14103.

$$\text{FAME yield (\%)} = \frac{(\Sigma A) - (A_{EI})}{A_{EI}} \times \frac{(C_{EI}) - (V_{EI})}{m} \times 100 \quad (2)$$

Where, ΣA is the total peak area from the methyl ester in C_{14} to $C_{24:1}$; A_{EI} is the peak area corresponding to $C_{17:0}$; C_{EI} is the concentration of the $C_{17:0}$ (mg ml^{-1}); V_{EI} is the volume of the methyl heptadecanoate solution (ml); m is the mass of the product (mg).

3.5.2 Fuel properties of produced biodiesel

Fuel properties of produced biodiesel and WPO, such as acid value (AV), kinematic viscosity, density, flash point, pour point, heating value, oxidation stability, ash content, and sulfur content were tested using standard methods. Resultant values were compared with biodiesel standards, such as ASTM D 6751 (US), EN 14214 (Europe), and Thailand standards.

3.5.2.1 Acid value and FFA content

Acid value represents the amount of acids present in the sample. Acid value and FFA content of biodiesel was determined by titration with KOH and using following equations (Banani et al., 2015). About 5 g of the biodiesel sample (or WCO), and 50 ml of neutralized ethanol were transferred in to a 250 ml conical flask. The mixture was heated gently using a hot plate for 10 min until all contents are dissolved. Then, the sample was titrated with 0.1 mol dm^{-3} KOH solution. Acid value is expressed as milligrams of KOH required to neutralize free acids in the system. AV and FFA content were calculated using the following equation 3 and 4.

$$\text{AV} = \frac{\text{KOH (mg)} \times N \times 56}{\text{Weight of the sample (mg)}} \quad (3)$$

$$\% \text{ FFA content} = \text{AV} \times 0.503 \quad (4)$$

3.5.2.2 Viscosity

The viscosity of a fluid is a measure of resistance to pouring. This is an important parameter which is related with the combustion efficiency and the carbon deposition on the injector. The viscosity of the produced biodiesel was tested at 40 °C, using an ubbelohde viscometer (525 23, capillary viscometer) according to ASTM D 446 (ASTM D446, 2017). In a typical procedure, biodiesel sample was charged to the viscometer and mounted in a constant temperature (40 °C) bath (CT 72/2, SI Analytics). The sample was then allowed to flow through the gravity and the time required to pass the marked edges of the viscometer was recorded to the nearest 0.1 s. Then, the viscosity of the samples was calculated using the following equation (equation 5).

$$\text{Kinematic viscosity} = K \cdot t \quad (5)$$

Where, K is the viscometer constant ($0.2831 \text{ mm}^2 \text{ s}^{-2}$) and t is flow time (s)

3.5.2.3 Density

The density affects fuel performance and combustion, since it is connected with various fuel properties. In addition, the density of biodiesel varies depending on several factors, such as molar mass, water and FFA content, and temperature. The density of the biodiesel was measured by using following equation (equation 6) at 30 °C.

$$\text{Density} = \frac{m}{V} \quad (6)$$

Where, m is the unit mass (mg) and the unit volume (ml) of biodiesel measured at 30 °C

3.5.2.4 Flash point

The flash point is the minimum temperature at which a fuel starts to ignite when given an ignite source. It is an indicator of the residual methanol in the biodiesel and decreases with an increase of the residual methanol (Barabás & Todoruț, 2011). The flash point of produced biodiesel was determined by open cup method using an open cup apparatus (D-12279, Petrotest) equipped with a test cup, a heating plate with a heater, a thermometer, and a test flame applicator according to ASTM D 92 (ASTM D92-16b, 2016). Approximately, 70 ml of the sample was filled into an open cup and heated at a slow constant rate while a flame test was passed across the cup. The temperature at which the test flame causes the sample to ignite was recorded. Vapor pressure of the biodiesel increases as the temperature increases. This increases available combustible vapor in the air and induce the ignition when an ignition source is provided. Therefore, this temperature was reported as the flash point of the biodiesel.

3.5.2.5 Pour point

The pour point determines the temperature at which biodiesel loses its flow characteristics. Pour point of the biodiesel was measured by cooling the fuel under controlled conditions according to ASTM D 97 (ASTM D97-15, 2015) . In which, biodiesel sample was kept at 40 °C in an oven to form a homogenous medium. Then, the sample was poured into a test glass jar until the marked level. The closed test jar was then kept in an acetone cooling bath in a pour point measurement apparatus (NR0127, Petrotest). The flow characteristic of the sample was observed at intervals of about 3 °C and the temperature, at which the cloudy or crystalline appearance occurs, was recorded as the pour point.

3.5.2.6 Heating value

During a complete combustion, all carbon, hydrogen, and any sulfur or nitrogen presence in biodiesel are converted into CO₂, H₂O, SO₂ and nitrogen oxides,

respectively. Therefore, the heating value of biodiesel represents the energy content/heat released by combusting a unit volume of the fuel at constant pressure, volume or temperature. The heating value of produced biodiesel was measured according to ASTM D 240 (ASTM D240-02, 2002) using an isoperibol bomb calorimeter (AC500, LECO). In a typical procedure, a weighted sample was placed in a bomb calorimeter vessel with about 1 ml of water. A firing wire which is suspended in the sample is act as an ignition source, and oxygen (about 30 bar) was used for the combustion. The heating value of biodiesel was calculated when the combustion is complete and using the temperature rise in the bomb and cooling water.

3.5.2.7 Oxidation stability

Biodiesel can be degraded due to the presence of unsaturated compounds, during storage and handling. Features, such as acid value, viscosity, and heating value of biodiesel are changed with the degradation of biodiesel (Barabás & Todoruț, 2011). The oxidation stability of the prepared biodiesel was measured using rancimat method according to EN 15751:2009 (EN 15751, 2014) at PTT public company Ltd. Bangkok, Thailand. In a typical procedure, a stream of air is passed through the sample at constant elevated temperature in order to facilitated oxidization. The vapors of oxidized products together with the air flow, are transported to a flask containing deionized water. The accelerated conductivity of the water which is due to the absorption of these products is continuously measured. The time at which a rapid increase in the conductivity starts is considered as the induction time and taken as a measurement of the oxidation stability (EN 15751, 2014).

3.5.2.8 Ash content

Ash content of a fuel means the amount of inorganic substances in the fuel which can come from various ways. Ash content of the biodiesel was measured according to ASTM-D 482-13 (ASTM D482-13, 2013). A preheated (700 °C, 15 min) porcelain crucible was weighted after cooling down to the room

temperature. Then, about 1 g of the prepared biodiesel sample was taken into the crucible and allowed to burn in a muffle furnace (CWF 1200, Carbolite) at 775 °C for 1 h. The weight of the sample with porcelain crucible was measured at room temperature and ash content was calculated as a percentage of the original sample weight.

3.5.2.9 Sulfur content

Since, this study used sulfonated carbon based SACs for biodiesel production, it is possible to remain leached sulfur from the catalysts in biodiesel. Therefore, it is vital to analyze remaining sulfur content in biodiesel. Sulfur content of produced biodiesel was measured using CHNSO elemental analyzer (628 series, Leco Corporation).

3.6 Comparison of energy consumption of three reactors

The energy consumption for biodiesel production by using each method was calculated according to Patil et al. (2009), Motasemi and Ani (2012), and (Gude & Martinez-Guerra, 2017). The maximum energy requirement for each reactor was considered for the calculations. The heating capacity of the hot plate (C-MAG HS7, IKA) (heating source for an open reflux reactor) was 500 W. The heating capacity of the lab scale autoclave reactor was 1073 W including the energy requirement for the motor and the heater (Amar Equipment, 2017). For the microwave assisted biodiesel production, 400 W was used. Optimum considered reaction time for each reactor is tabulated in Table 3.8. Since a maximum of 50 g of biodiesel can be produced from reactors per time the energy requirement for each technology to produce 1 kg of biodiesel was calculated.

$$\text{Total equipment energy load (W)} = \text{Heating capacity for heater (W)} + \text{Energy for stirrer motor (W)} \quad (7)$$

$$\begin{aligned} \text{Total energy consumption (kW h kg}^{-1}\text{)} \\ = \frac{\text{Total energy capacity (kW)} \times \text{Reaction time (h)}}{50 \text{ (g)}} \times 1000 \text{ (g)} \end{aligned} \quad (8)$$

Table 3.8 Optimum required reaction time for biodiesel production

Type of the reactor	Optimum reaction time (h)
Reflux reactor	12
Autoclave reactor	3
Microwave reactor	0.67

In addition, the cost for 1 kg of biodiesel production from WPO using CMR-DS-SO₃H catalyst in each reactor was calculated.

These calculations are based on the current study which was carried out in a lab scale. However, the energy consumption may change when used in large scale and certain processes may become more economical.

Chapter 4

Results and Discussion

This chapter describes the characteristic of WPO as the biodiesel feedstock used in this study. The result of the catalyst characterization for the catalysts prepared from two approaches and using three different carbon precursors are detailed. The effects of different reaction conditions on FAME yield by using different catalysts and different biodiesel production process are discussed. The fuel properties of produced biodiesel are presented and compared with international standards.

4.1 Characterization of biodiesel feedstock

The physicochemical properties of the oil can be changed due to various reactions, such as hydrolysis, oxidation, and polymerization during frying (Sanli et al., 2011). Therefore, it is vital to identify physicochemical properties of waste oil after frying process in order to know the quality of the feedstock. The composition and physicochemical properties of WPO are shown in Table 4.1.

The acid value and FFA contents are key parameters which influence on the potential of biodiesel production via direct trans-esterification reactions. According to Meher et al. (2006), higher acid value in the feedstock is responsible for the lower rate of conversion with conventional alkaline catalysts trans-esterification reactions. The acidity of the feedstock is mainly due to the FFA content. In general, it is necessary to have a FFA content less than 0.5% (Ma & Hanna, 1999), or 3% (Gnanaprakasam et al., 2013) in order to proceed alkaline catalyzed trans-esterification reaction effectively. An increase of the FFA content of WCO beyond the recommended value, leads for an increase rate of saponification when using alkaline catalyst. This decreases the available alkaline catalysts for biodiesel production. In addition, water formed as a result of saponification increases the hydrolysis of triglycerides, forming more FFA in the medium. This decreases the biodiesel yield. It is found that the acid

value of used WPO is 10.3 mgKOH g⁻¹ (5.2% FFA), which is higher than the recommended value for alkaline catalyzed biodiesel production (Table 4.1). Therefore, use of a carbon based SAC is desired to avoid unnecessary side reactions (Su & Guo, 2014), since a carbon based SAC can catalyze both esterification and trans-esterification reactions, simultaneously (Fig 2.5).

It is found that WPO used in this study contains comparatively higher amount of unsaturated fatty acid composition (52.9%) than saturated fatty acid composition (42.7%). The major fatty acids found in the WPO are oleic acid (42.39%), followed by palmitic acid (36.63%), and linoleic acid (9.85%). The composition of biodiesel is a major factor which determines the quality of the biodiesel (Chhetri et al., 2008).

Table 4.1 Composition and physicochemical properties of WPO

Property	
Acid value (mgKOH g ⁻¹) ASTM D664	10.3
% FFA	5.2
Kinematic viscosity at 40 °C (mm ² sec ⁻¹) ASTM D446	24.1
Density at 30 °C (kgm ⁻³)	970
Flash point (°C) ASTM D92	300
Pour point (°C) ASTM D97	-23
Ash content (wt. %) ASTM D482-13	0.43
Sulfur content (wt. %)	0.002
Fatty acid composition (%)	
Unsaturated fatty acid	52.9
Saturated fatty acid	42.7
Lauric acid (C12:0)	0.39
Myristic acid (C14:0)	0.88
Palmitic acid (C16:0)	36.63
Palmitoleic acid (C16:1)	0.16
Stearic acid (C18:0)	4.18
Cis-9-Oleic acid (C18:1)	42.39
Linoleic acid (C18:2n6c)	9.85
Alpha-Linolenic acid (C18:3n3)	0.23
Arachidic acid (C20:0)	0.34
Cis-11-Eicosenoic acid (C20:1n11)	0.16

4.2 Characterization of the catalysts

Altogether, six different types of carbon based SACs are derived using three carbon precursors and two preparation methods. Catalysts derived from the direct in-situ sulfuric carbonization (DS) and catalysts derived from sulfonation of incompletely carbonized biomass (BCS) are named as X-DS-SO₃H and X-BCS-SO₃H, respectively (where 'X' is replaced by the relevant carbon precursor used in the catalyst preparation).

4.2.1 Total acid density and sulfonic acid density

The total acid density of biomass derived SACs is associated with three types of functional groups, such as sulfonic, carboxyl, and phenolic groups (Su & Guo, 2014). Among them, sulfonic acid groups significantly contribute for catalyzing esterification and trans-esterification reactions. Therefore, the total acid density and the sulfonic acid groups' density of the catalysts are investigated. The total acid density and the elemental composition of the raw biomass, fresh catalysts, and used catalysts are given in Table 4.2, and Table 4.3. The highest total acid density is found to be in PEFB-DS-SO₃H (5.40 mmolg⁻¹) followed by PEFB-BCS-SO₃H, CMR-DS-SO₃H, CMR-BCS-SO₃H, CCH-DS-SO₃H, and CCH-BCS-SO₃H catalysts. The weight percentage of sulfur as found by elemental analysis are CMR-DS-SO₃H (3.89%) > CCH-DS-SO₃H (1.99%) > PEFB-DS-SO₃H (1.10%) > PEFB-BCS-SO₃H (0.38%) > CCH-BCS-SO₃H (0.16%) > CMR-BCS-SO₃H (0.11%). Since the highest contribution for both esterification and trans-esterification reaction is shown by sulfonic acid groups, it is important to have more sulfonic acid groups in the catalyst. Results showed that direct sulfonation is more efficient in catalyst preparation in order to have high sulfonic acid groups. Low temperature carbonization during one-step direct sulfonation, decreases the degree of de-oxygenation of functional groups, facilitating a higher degree of sulfonation during catalysts preparation (North, 2016).

According to the EDS results (Fig.4.1), weight percentage of sulfur on the surface of the catalysts are found as 1.54, 0.96, 2.26, 1.83, 0.75, and 0.28 in PEFB-DS-SO₃H, PEFB-BCS-SO₃H, CMR-DS-SO₃H, CMR-BCS-SO₃H, CCH-DS-SO₃H, and CCH-BCS-SO₃H catalysts, respectively. However, these data may not be the real representative of sulfur content of the catalyst because EDS spectroscopy is able only to give information related to surface of the catalyst. Thus, the sulfur content measured by using CHNSO analyzer is an appropriate measure for the sulfonic acid density of the catalysts.

It is also found that the content of carbon and sulfur increases while the content of hydrogen and oxygen decreases in the catalysts compared to raw biomass (Table 4.3). Carbonization of raw biomass during the catalyst preparation increases the carbon content of the catalysts. Decrease of oxygen and hydrogen content is due to de-oxygenation and de-hydration of carbon precursors during conversion of raw biomasses into partially carbonaceous products and also in the presence of concentrated H₂SO₄. However, sulfonation increases both oxygen and sulfur contents of the catalysts. Similar phenomena were reported by Zhou et al. (2016) and Malins et al. (2016) during SACs preparation using bamboo and cellulose, respectively. In addition, results show that carbon content of the catalyst prepared from two step activation is higher while oxygen content is lower compared to the catalysts prepared from in-situ concentrated sulfuric acid carbonization. This confirms the degree of carbonization and de-oxygenation is high in two step catalyst preparation.

Higher O to C ratio indicates increase of weak acid groups in the carbon based SACs (Fraile et al., 2014; Ngaosuwan et al., 2016). It is found that the O:C ratio is higher in CCH-DS-SO₃H (0.63) followed by CMR-DS-SO₃H (0.58) and PEFB-DS-SO₃H (0.53) indicating that CCH-DS-SO₃H possess higher density of weak acid groups, such as COOH and OH. However, it is found that X-BCS-SO₃H catalysts showed a very low O:C ratio (<0.35), which is attributed to the de-oxygenation of the biomass during carbonization. Therefore, it can be concluded that X-DS-SO₃H catalysts may be incorporated with a high density of both strong

(SO₃H) and weak (COOH, OH) acid sites compared to X-BCS-SO₃H catalysts. As reported by Hara (2010), it is an advantage to have more COOH and OH groups on the catalysts. These groups act as the anchoring sites for attaching the reactants and increase the rate of reaction.

However, it is found that the total acid density and the sulfur content of the catalyst decreases after the first run (Table 4.2 and 4.3). This may be due to the possible deactivation of the catalyst during the reaction.

Table 4.2 Total acid density of carbon precursors and catalysts

	Total acid density (mmol g ⁻¹)		
	Fresh catalysts	after 1 st run	
		Reflux reactor	Autoclave reactor
Raw PEFB	0.49		
Raw CMR	0.52		
Raw CCH	0.25		
PEFB-DS-SO ₃ H	5.40	5.26	
CMR-DS-SO ₃ H	3.80	3.25	3.15
CCH-DS-SO ₃ H	2.50		1.90
PEFB-BCS-SO ₃ H	4.79		3.00
CMR-BCS-SO ₃ H	3.75		2.45
CCH-BCS-SO ₃ H	2.80		1.80

Table 4.3 Elemental composition of carbon precursors and catalysts

	C (wt. %)	H (wt. %)	N (wt. %)	O (wt. %)	S (wt. %)	O:C
Raw PEFB	44.18	5.08	0.58	39.75	0.21	0.89
Raw CMR	50.33	7.70	0.79	36.53	0.09	0.72
Raw CCH	45.91	5.08	0.58	35.06	0.05	0.76
PEFB-DS-SO ₃ H	58.20	2.23	0.37	31.02	1.10	0.53
CMR-DS-SO ₃ H	56.95	3.34	0.40	32.84	3.89	0.58
CCH-DS-SO ₃ H	55.20	2.38	0.23	34.80	1.99	0.63
PEFB-BCS-SO ₃ H	72.54	1.93	1.26	17.54	0.38	0.24
CMR-BCS-SO ₃ H	65.09	2.54	2.85	24.07	0.11	0.37
CCH-BCS-SO ₃ H	67.46	2.62	1.46	23.45	0.16	0.35

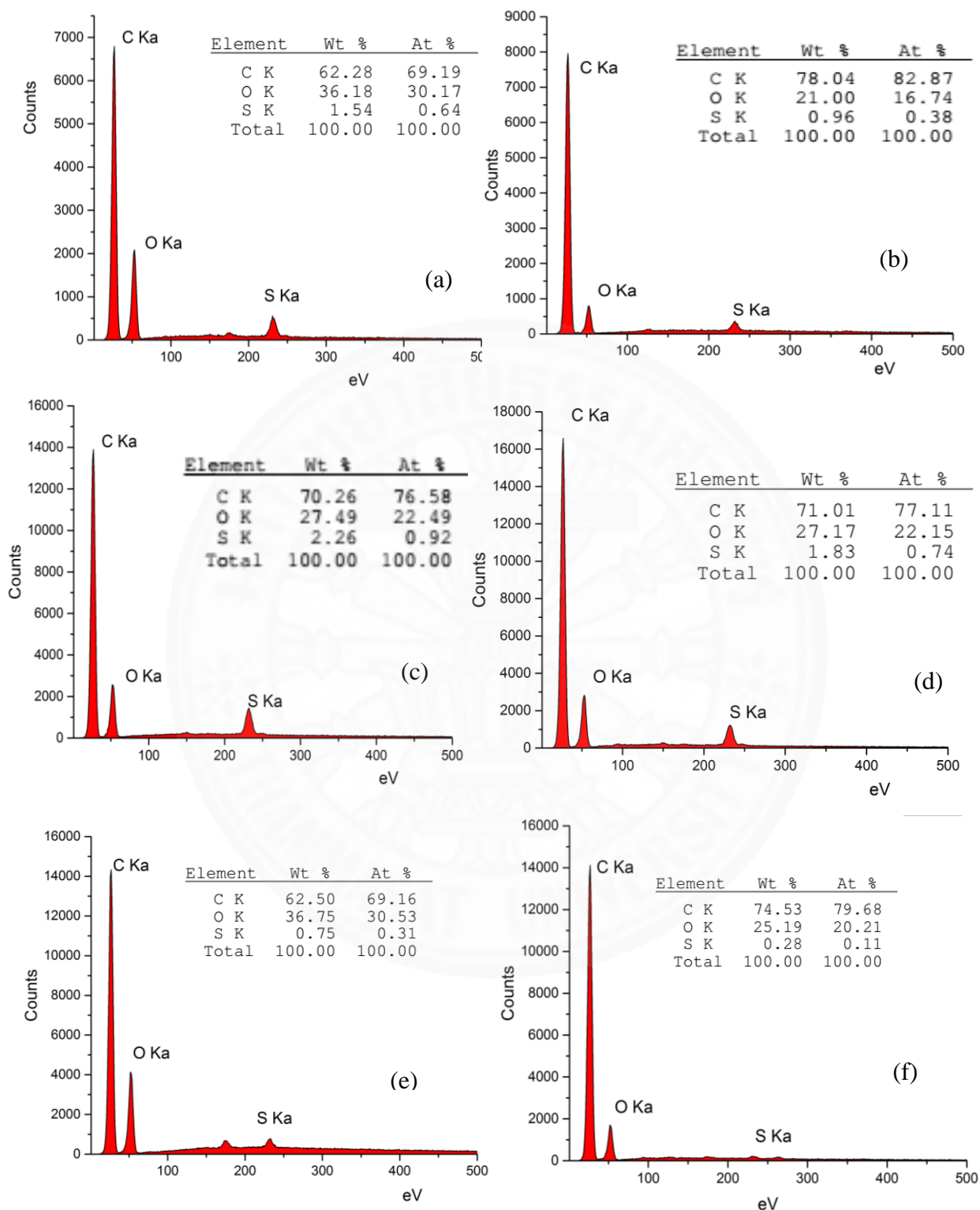


Fig. 4.1 EDS of (a) PEFB-DS-SO₃H, (b) PEFB-BCS-SO₃H, (c) CMR-DS-SO₃H, (d) CMR-BCS-SO₃H, (e) CCH-DS-SO₃H, and (f) CCH-BCS-SO₃H

4.2.2 Surface area, pore size distribution, and surface morphology

Nitrogen adsorption and desorption isotherm for catalysts PEFB-DS-SO₃H, PEFB-BS-SO₃H, CMR-DS-SO₃H, and CCH-DS-SO₃H are found similar to type-III and/or type-IV at lower p/p_0 values ((Fig. 4.2 (a), (b), (c), and (e)) indicating the presence of nonporous and mesoporous phases of the catalysts (Brunauer et al., 1938). In addition, it is found that nitrogen adsorption and desorption isotherms for CMR-BCS-SO₃H and CCH-BCS-SO₃H are type I at lower p/p_0 values ((Fig. 4.2 (d) and (f)) indicating the presence of microporous structure of the catalysts (Brunauer et al., 1938). The surface area, mean pore volume, and pore diameter of the catalysts are shown in Table 4.4.

Table 4.4 Surface area and pore size distribution of the catalysts

Carbon based SACs	Surface area (m ² g ⁻¹)	Mean pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
PEFB-DS-SO ₃ H	5.50	0.13	17.07
CMR-DS-SO ₃ H	1.33	0.31	13.92
CCH-DS-SO ₃ H	1.37	0.32	10.63
PEFB-BCS-SO ₃ H	739.0	154.65	3.20
CMR-BCS-SO ₃ H	89.77	20.63	2.34
CCH-BCS-SO ₃ H	61.50	14.19	2.58

In addition to the acid strength, the activity of the catalyst relies on easiness of diffusion of reactants and products in the reaction medium. It was found that the catalysts prepared from two-step protocol (carbonization followed by sulfonation) have higher surface area and pore volume compared to the catalysts prepared from direct sulfonation protocol. It is obvious that the physical activation of the biomass at 400 °C in a muffle furnace gives higher surface area to the catalysts. The presence of a porous structure with lower surface area (X-DS-SO₃H) may block the reactants and products, lowering the catalytic activity. However, it is

found that X-DS-SO₃H catalysts have higher pore diameters compared to the X-BCS-SO₃H catalysts. This provides good access for reactants to acid sites during the reaction. The pore size distribution of the catalysts is depicted in Fig. 4.3.

However, results show that the acid density is not greatly depended on the surface area of the catalysts. On the other hand, large pore diameter of X-DS-SO₃H would increase the accessibility of the H₂SO₄ and then decrease the pore volume by covalently bonding carbon with SO₃H (Savaliya & Dholakiya, 2015). In addition, as stated by North (2016), carbonaceous catalysts swell in solvent, pointing out that a low surface area may not cause a significant effect during the reaction. Carbon based SACs can incorporate large amounts of hydrophilic molecules into the carbon framework due to the presence of hydrophilic functional groups (SO₃H, COOH, and OH). Such incorporation leads to adsorb large amounts of hydrophilic solvents, including water into the carbon framework (Suganuma et al., 2010). This causes swelling in the carbon catalysts which provides a good access for reactants to the functional groups. Therefore, catalysts show high activity despite the low surface area. This phenomenon is reported in various studies (Fraile et al., 2014; Suganuma et al., 2008; Suganuma et al., 2010).

The SEM image of each catalyst, as shown in Fig. 4.4, further confirms their amorphous nonporous, microporous, and/or mesoporous carbon structure in line with adsorption isotherm data. However, it is shown that the porous carbon structure is modified with some irregular cracks and deposits, which may be due to the partial oxidation, condensation, and destruction of the catalyst during carbonization (Ngaosuwan et al., 2016).

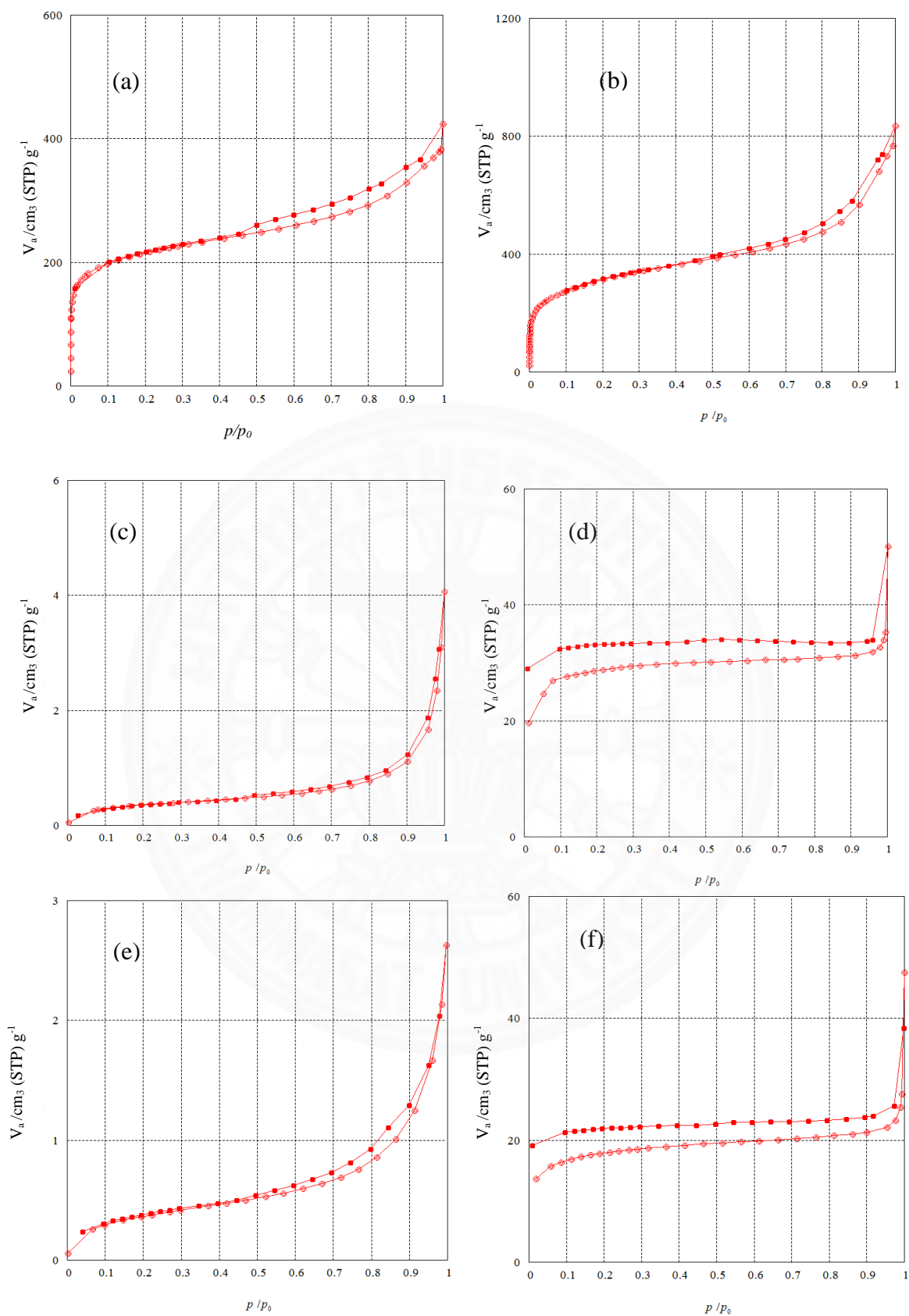


Fig. 4.2 Adsorption-desorption isotherms of (a) PEFB-DS-SO₃H, (b) PEFB-BCS-SO₃H, (c) CMR-DS-SO₃H, (d) CMR-BCS-SO₃H, (e) CCH-DS-SO₃H, and (f) CCH-BCS-SO₃H

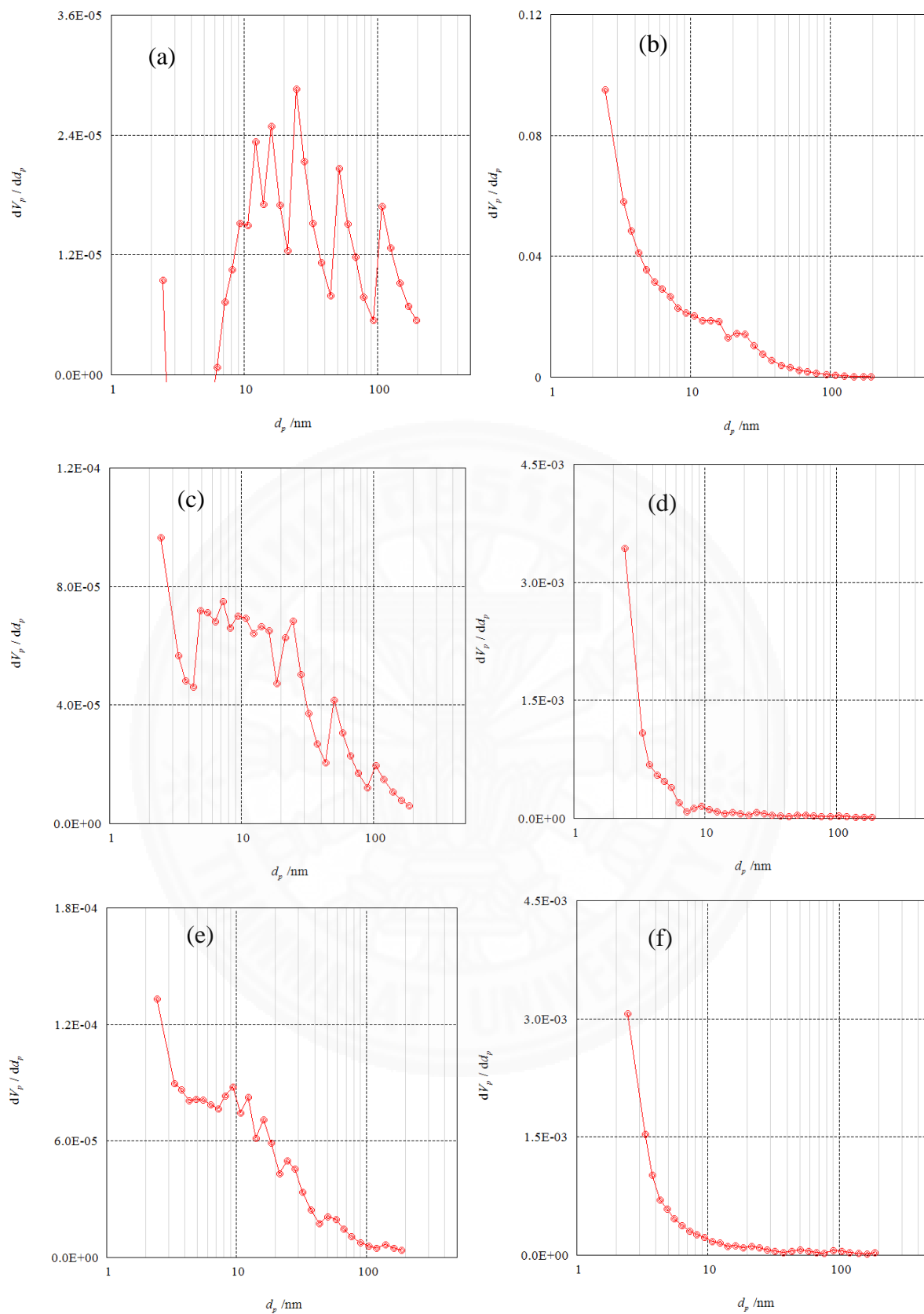


Fig. 4.3 Pore-size distribution of (a) PEFB-DS-SO₃H, (b) PEFB-BCS-SO₃H, (c) CMR-DS-SO₃H, (d) CMR-BCS-SO₃H, (e) CCH-DS-SO₃H, and (f) CCH-BCS-SO₃H

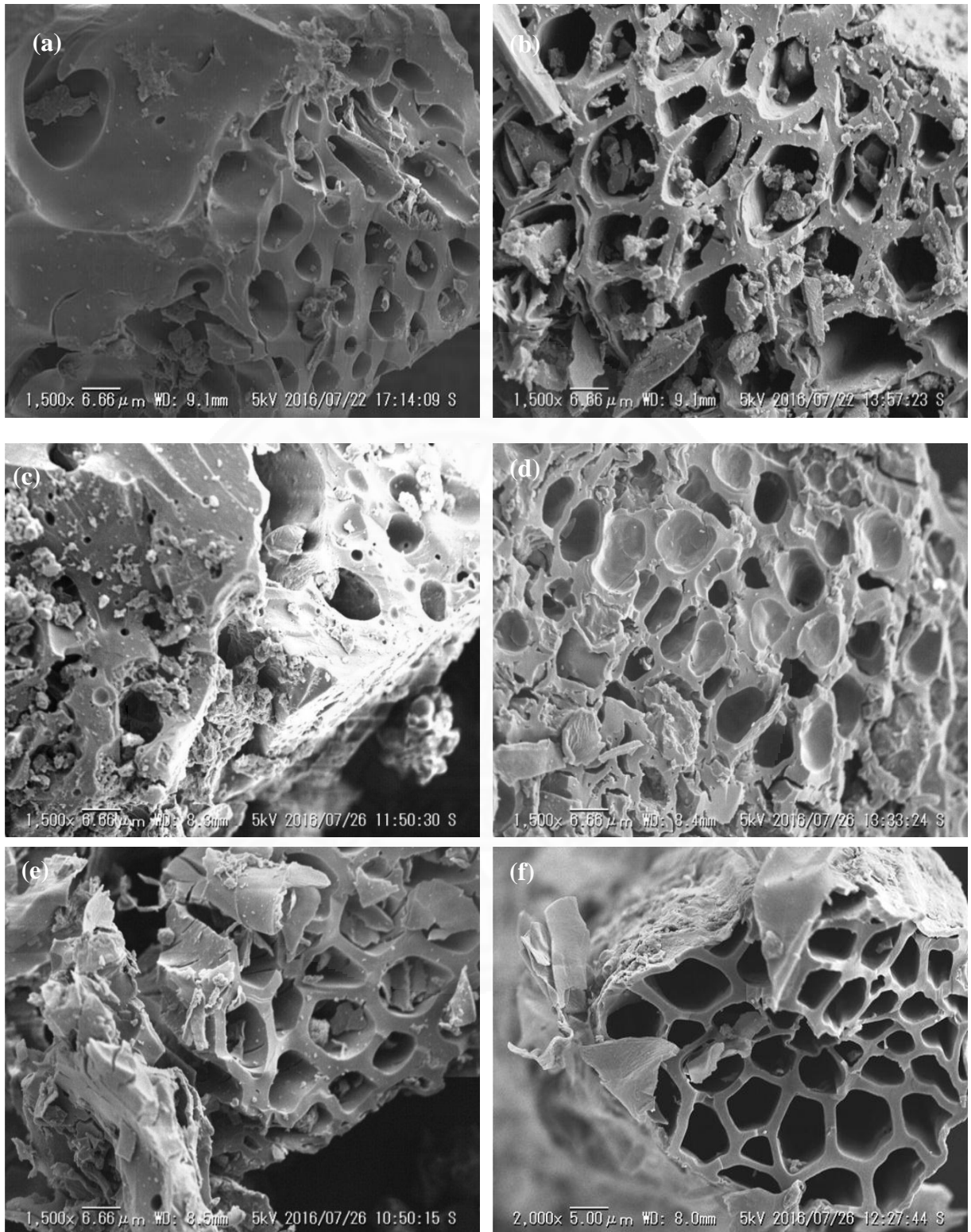


Fig. 4.4 SEM of (a) PEFB-DS-SO₃H, (b) PEFB-BCS-SO₃H, (c) CMR-DS-SO₃H, (d) CMR-BCS-SO₃H, (e) CCH-DS-SO₃H, and (f) CCH-BCS-SO₃H

4.2.3 Presence of surface functional groups

The FT-IR spectra of raw carbon precursors, and catalysts prepared under different activation conditions are shown in Fig. 4.5, 4.6, and 4.7. Table 4.5 summarizes the band locations and the possible surface functional groups in FT-IR spectra of the catalysts. The FT-IR spectra confirm the presence of important functional groups which are associated with catalyzing esterification and transesterification, on the surface of the catalysts. As shown in all the spectra, the characteristic strong and broad peaks at around $3600\text{-}2800\text{ cm}^{-1}$ are attributed to the OH functional groups in the raw precursors, fresh catalysts, and the used catalysts. Peaks at around $3000\text{-}2800\text{ cm}^{-1}$ are attributed for C-H groups while the sharp peaks at 2916 cm^{-1} and 2848 cm^{-1} are contributed for the anti-symmetric and symmetric vibrations of CH_2 groups of raw samples (Coates, 2000). It is found that the peak intensities of these functional groups decreases in catalysts compared to the raw biomass. This is attributed to the de-hydration of biomass during catalyst preparation. As reported by Allen et al., the peaks present at around $1800\text{-}1500\text{ cm}^{-1}$ is responsible for carbonyl/carboxyl region (Allen et al., 2007). According to Coates et al., the peak at around 1700 cm^{-1} may be assigned to SO_3H (1712 cm^{-1}) (Coates, 2000). It is found that all catalysts prepared from direct in-situ sulfonation had a prominent peak at around 1700 cm^{-1} indicating the presence of sulfonic acid groups. It can be concluded that PEFB-DS- SO_3H , CMR-DS- SO_3H , and CMR-DS- SO_3H catalysts are successfully sulfonated compared to X-BCS- SO_3H (Fig. 4.5, 4.6, and 4.7). In addition, the sharp strong stretching at around $1230\text{-}1120\text{ cm}^{-1}$ is attributed for S=O group which is coming from sulfonic acid group or sulfonate ion group, or O=S=O symmetric and asymmetric stretching vibrations of SO_3H (Fu et al., 2012). The vibrational bands at around 1401 cm^{-1} and $1200\text{-}1100\text{ cm}^{-1}$ are attributed to asymmetric or symmetric stretching of SO_2 , indicating that the catalyst bears SO_3H (Coates, 2000). These groups are conspicuous in catalysts produced after sulfonation of incompletely carbonized biomass (Nakajima et al., 2007). These data confirms the presence of SO_3H , COOH , and OH functional groups on the surface of the catalysts.

Table 4.5 Surface functional groups and band locations in FT-IR spectra of catalysts

Band positions (cm ⁻¹)	Possible assignments
3600-2800	OH Stretching vibration
2900-2800	C-H ₂ symmetric or asymmetric stretching vibration
1800-1500	C=O/ COOH
1712	SO ₃ H
1725-1700	COOH
1631-1629	C=C aromatic stretch
1410-1310	Phenolic OH/C-O-C
1230-1120	S=O stretching
1200-1100	SO ₂ stretching
1130-1080/680-610	Sulfate ion
1055-925	Cyclohexane ring vibration/ C-O

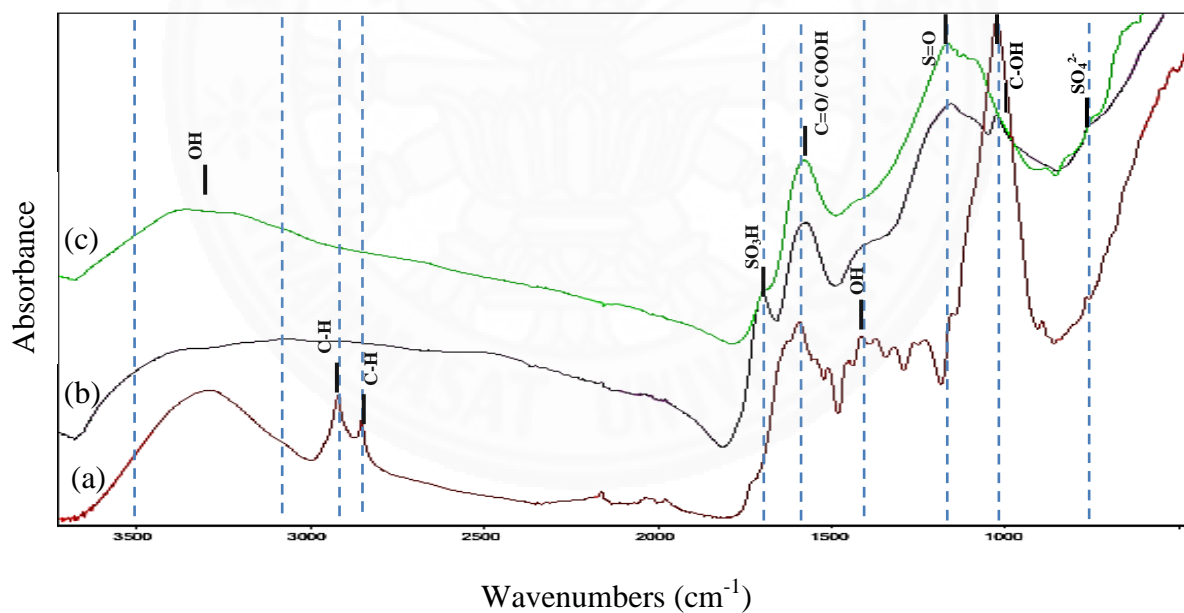


Fig. 4.5 FT-IR spectra of (a) Raw PEFB, (b) PEFB-DS-SO₃H, and (c) PEFB-BCS-SO₃H

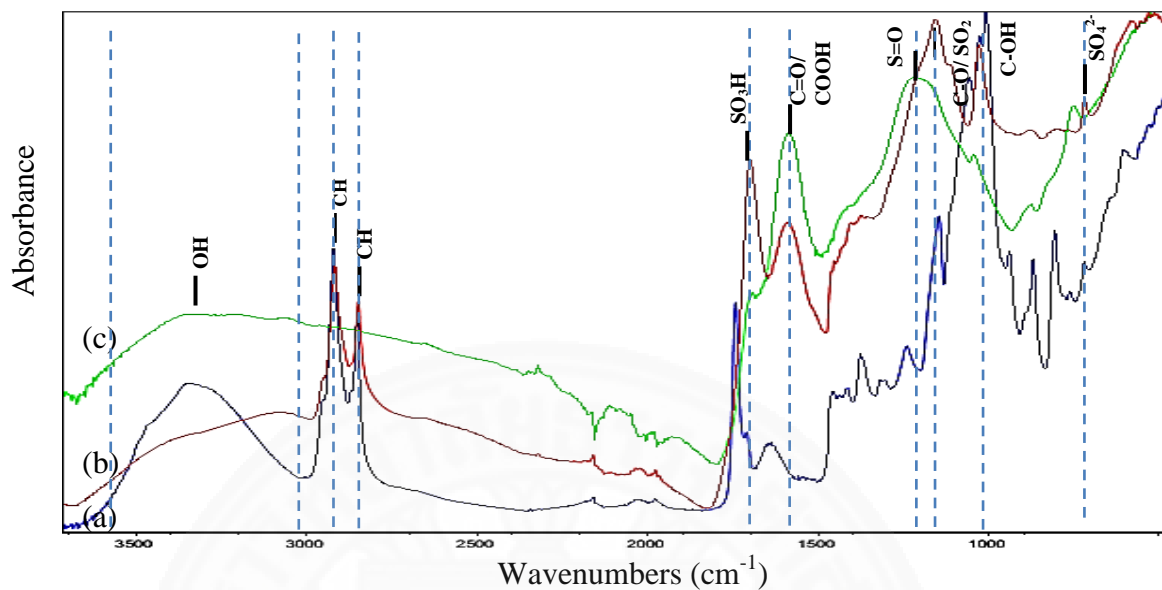


Fig. 4.6 FT-IR spectra of (a) Raw CMR, (b) CMR-DS-SO₃H, and (c) CMR-BCS-SO₃H

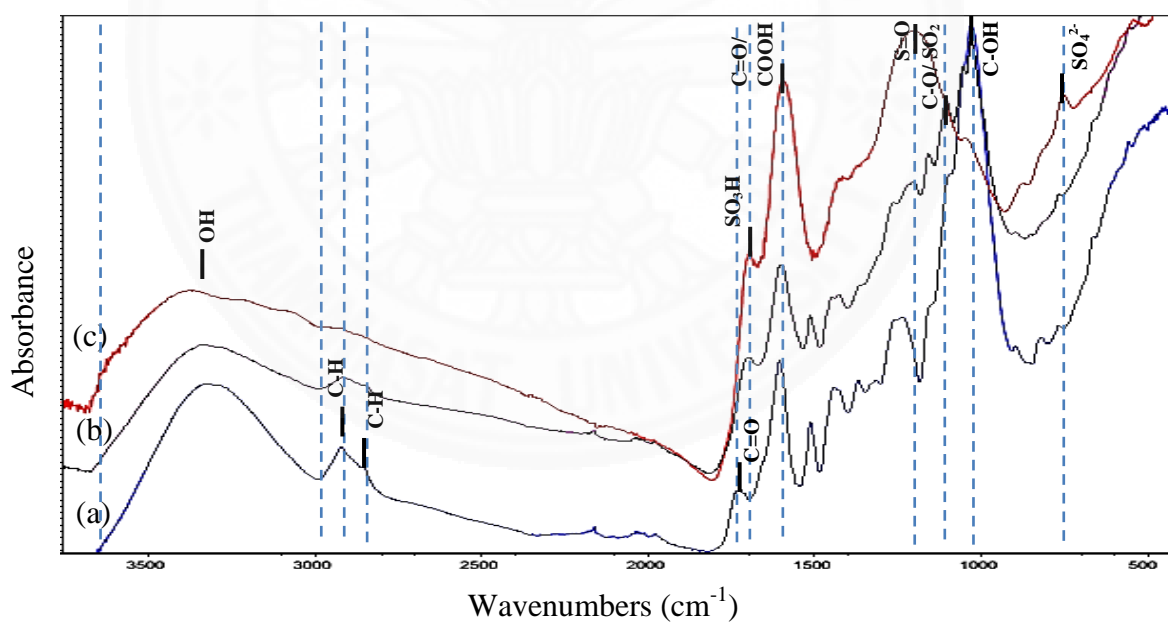


Fig. 4.7 FT-IR spectra of (a) Raw CCH, (b) CCH-DS-SO₃H, and (c) CCH-BCS-SO₃H

The stability of the catalysts (X-DS-SO₃H) was investigated by FT-IR analysis after first and second runs for the catalyst which gave an acceptable activity. The FT-IR

spectra of PEFB-DS-SO₃H used in open reflux reactor; CMR-DS-SO₃H used in open reflux reactor, autoclave reactor, and microwave reactor; and CCH-DS-SO₃H used in autoclave reactor are shown in Fig. 4.8, 4.9, 4.10, 4.11, and 4.12, respectively. It is found that peaks of the functional groups of recovered catalysts are consistent with the functional groups of the fresh catalysts. This indicates that there is no significant change to the catalyst surface structure after the use. This may be attributed to the covalent attachment of catalytic active sites to the carbon structure.

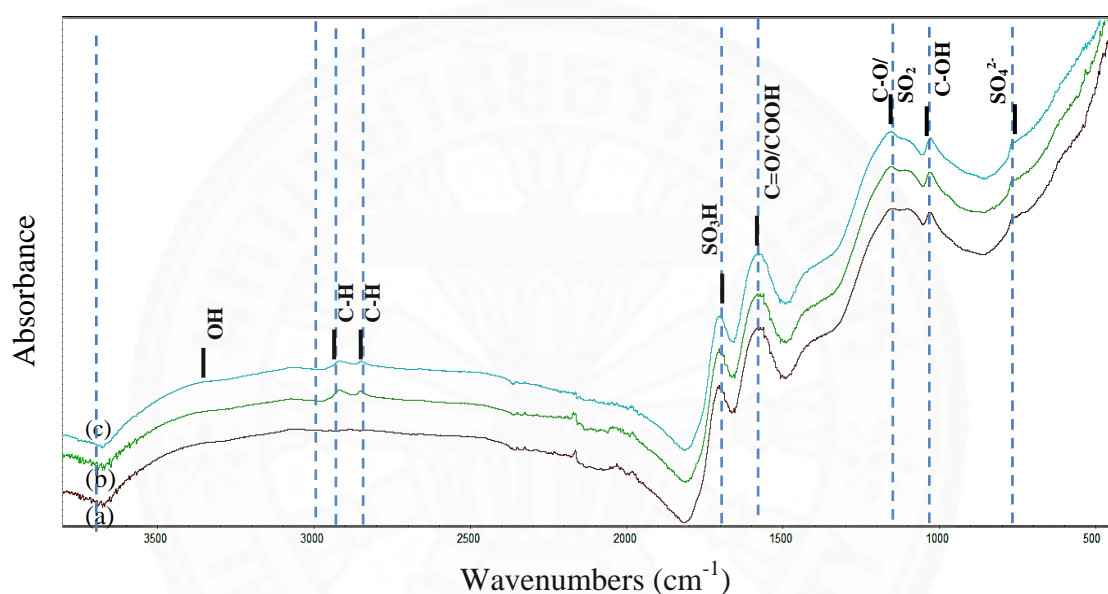


Fig. 4.8 FT-IR spectra of (a) PEFB-DS-SO₃H, (b) used catalyst after first run, and (c) used catalyst after second run in an open reflux reactor

However, it is found that the sharp peaks around 2800-3000 cm⁻¹ which are attributed for CH, slightly increased for recycled catalysts when used in biodiesel production with conventional reflux reactor. This may be due to hydration of the catalyst during the reaction. However, FT-IR is not likely to be used as a quantitative analysis technique for the presence of functional groups. It is required to have a detailed quantitative analysis for a stronger conclusion of the status of functional groups present in used catalysts.

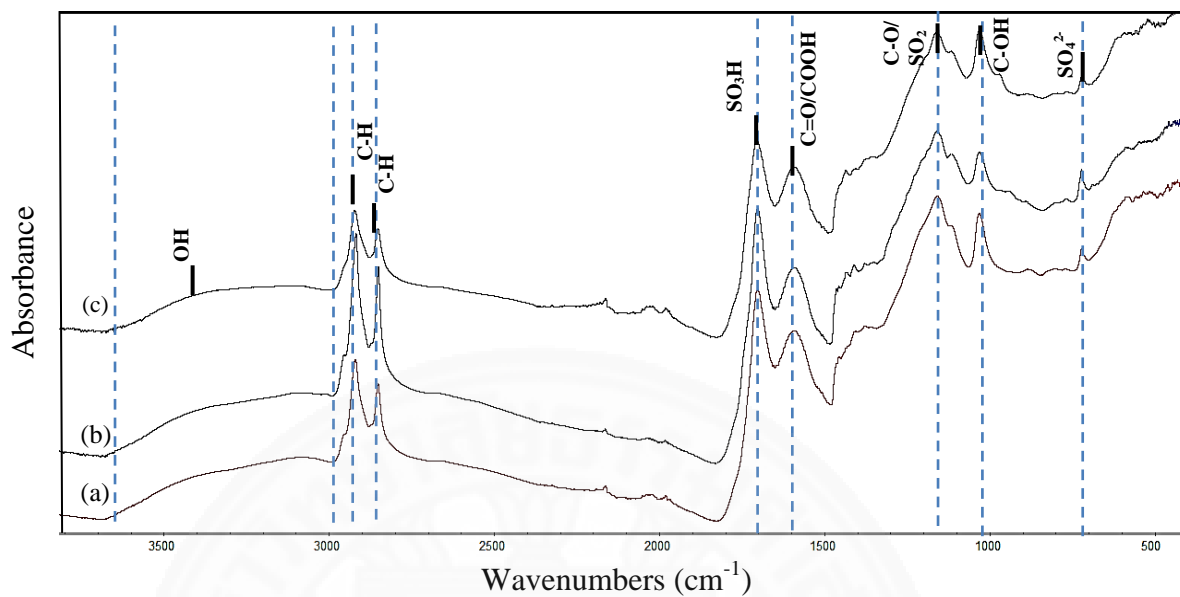


Fig. 4.9 FT-IR spectra of (a) CMR-DS-SO₃H, (b) used catalyst after first run, and (c) used catalyst after third run in an open reflux reactor

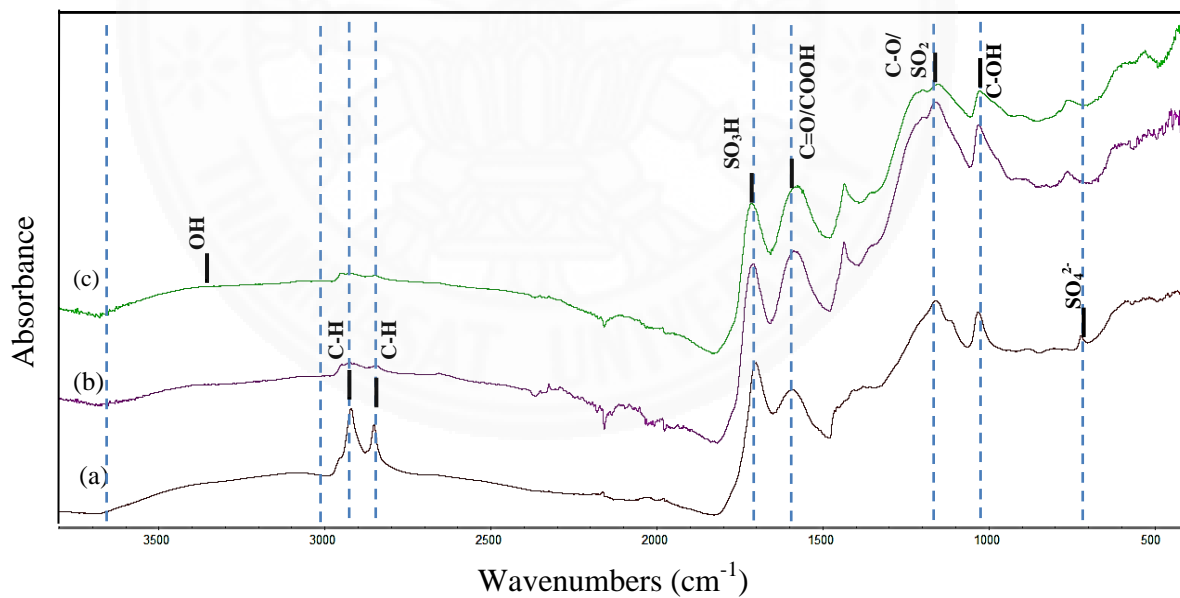


Fig. 4.10 FT-IR spectra of (a) CMR-DS-SO₃H, (b) used catalyst after first run, and (c) used catalyst after third run in an autoclave reactor

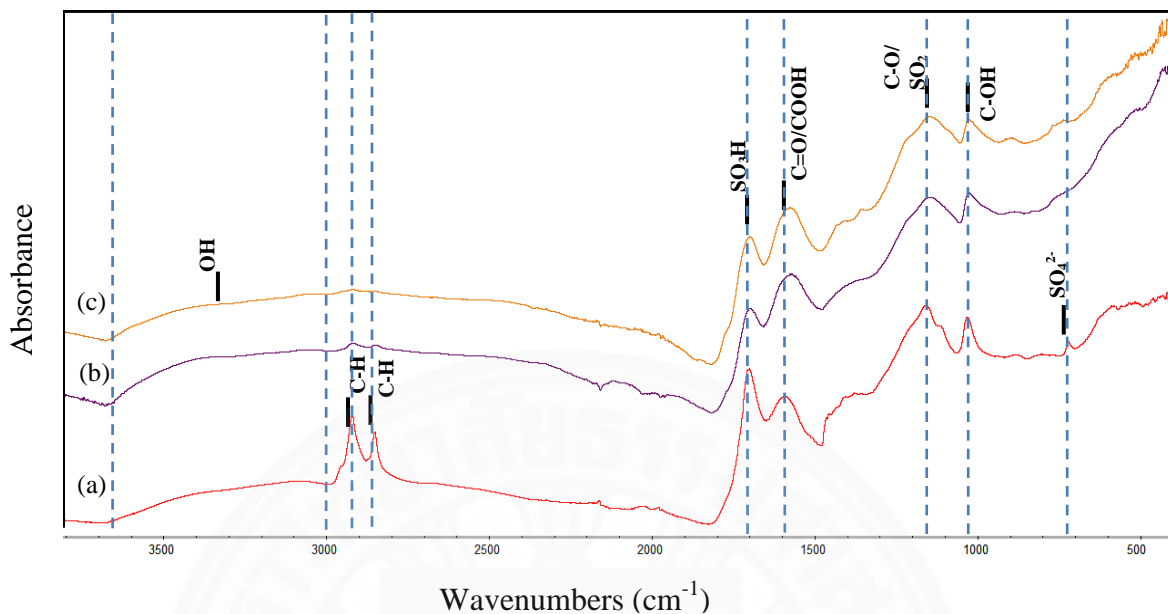


Fig. 4.11 FT-IR spectra of (a) CMR-DS-SO₃H, (b) used catalyst after first run, and (c) used catalyst after third run in a microwave reactor

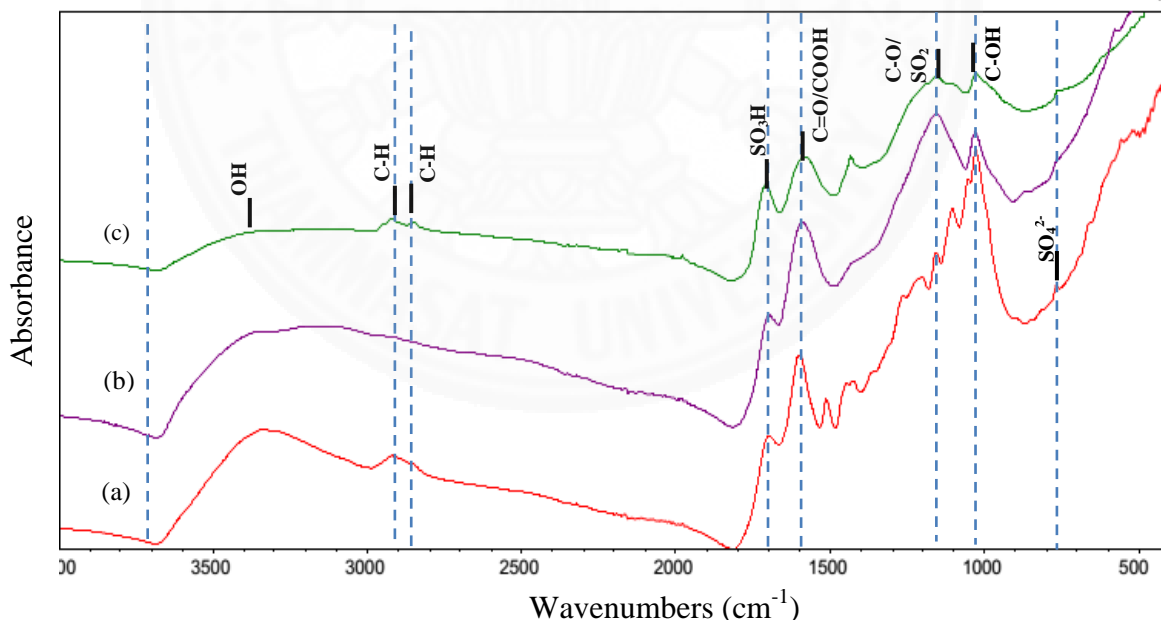


Fig. 4.12 FT-IR spectra of (a) CCH-DS-SO₃H, (b) used catalyst after first run, and (c) used catalyst after third run in an autoclave reactor

4.2.4 Chemical states of surface functional groups

The XPS spectra of catalysts are depicted in Fig. 4.13. It is found that all XPS reveal peaks at 168 eV, 284 eV, and 530 eV, corresponding to the S2p, C1s, and O1s binding energy, respectively (Russo et al., 2014). In addition, it is found that, X-DS-SO₃H show higher S2p peak intensities compared to X-BCS-SO₃H, showing that direct sulfonation is effective compared to the sulfonation of pre-incompletely carbonized biomass during the activation. This confirms the possible higher degree of de-oxygenation during incomplete carbonization, resulting in the decrease in degree of sulfonation.

Since, these peaks are conspicuously shown in each spectrum, the details of S2p, C1s, and O1s peaks of X-DS-SO₃H are studied via de-convolution. The presence of S-C (168 eV) and S-O/S=O (169 eV) bonds at S2p band, the presence of C-O (286 eV) and C=O (287 eV) bonds at C1s band, and the presence of C-O/C-O-H (533 eV) bonds at the O1s band (Nakajima & Hara, 2012) can be seen in Fig. 4.14, 4.15, and 4.16 of PEFB-DS-SO₃H, CMR-DS-SO₃H, and CCH-DS-SO₃H catalysts, respectively. In addition, it is found that the peak intensity for S2p of CMR-DS-SO₃H catalysts is stronger than PEFB-DS-SO₃H and CCH-DS-SO₃H. In line with weight percentage of sulfur as found in elemental analysis, this confirms the CMR-DS-SO₃H catalysts bear a high density of sulfonic acid groups. Overall, these data are consistent with FT-IR data confirming the presence of chemically bound sulfonic, carboxylic, and phenolic groups on the surface of the catalysts.

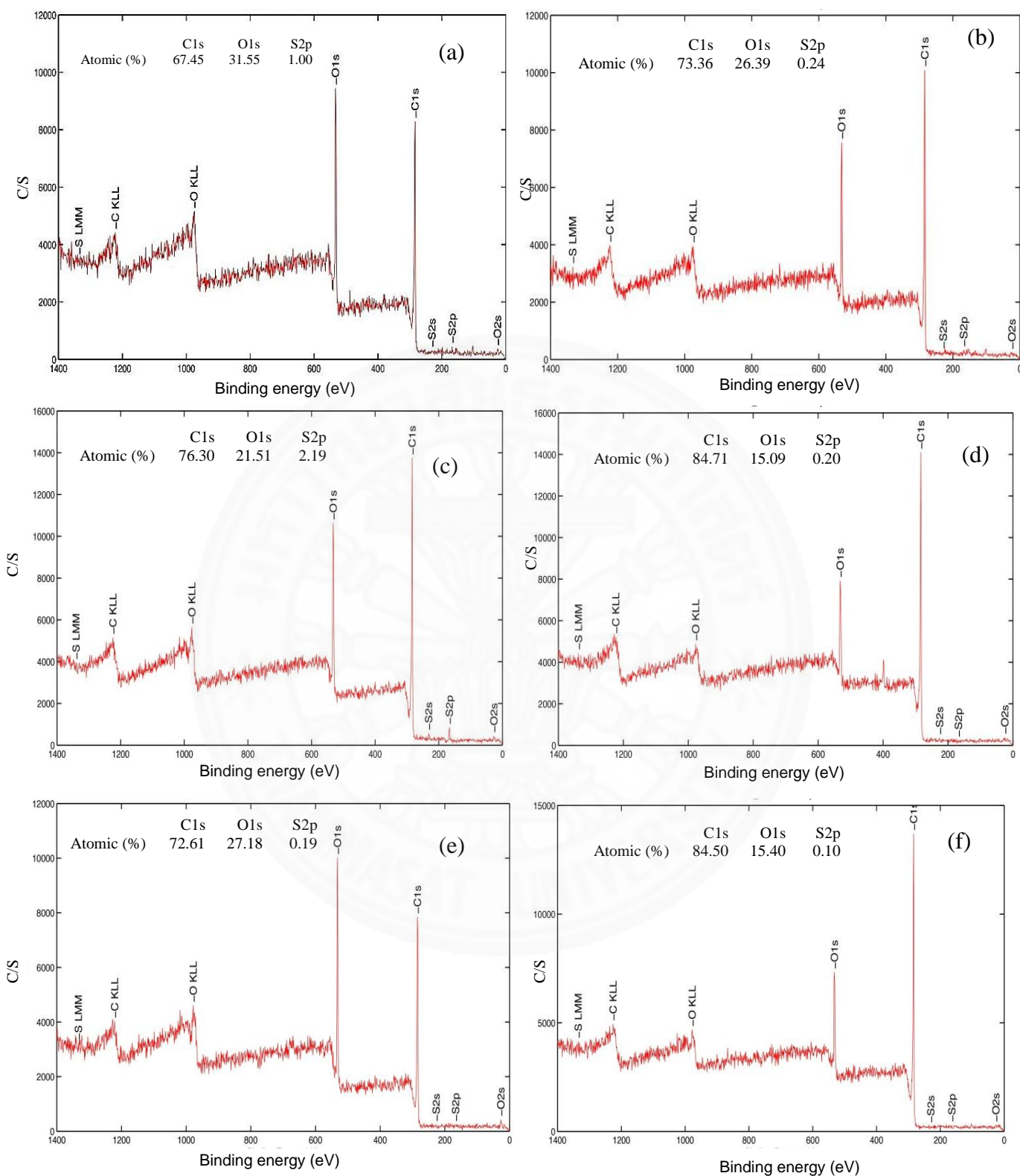


Fig. 4.13 XPS of (a) PEFB-DS-SO₃H, (b) PEFB-BCS-SO₃H, (c) CMR-DS-SO₃H, (d) CMR-BCS-SO₃H, (e) CCH-DS-SO₃H, and (f) CCH-BCS-SO₃H

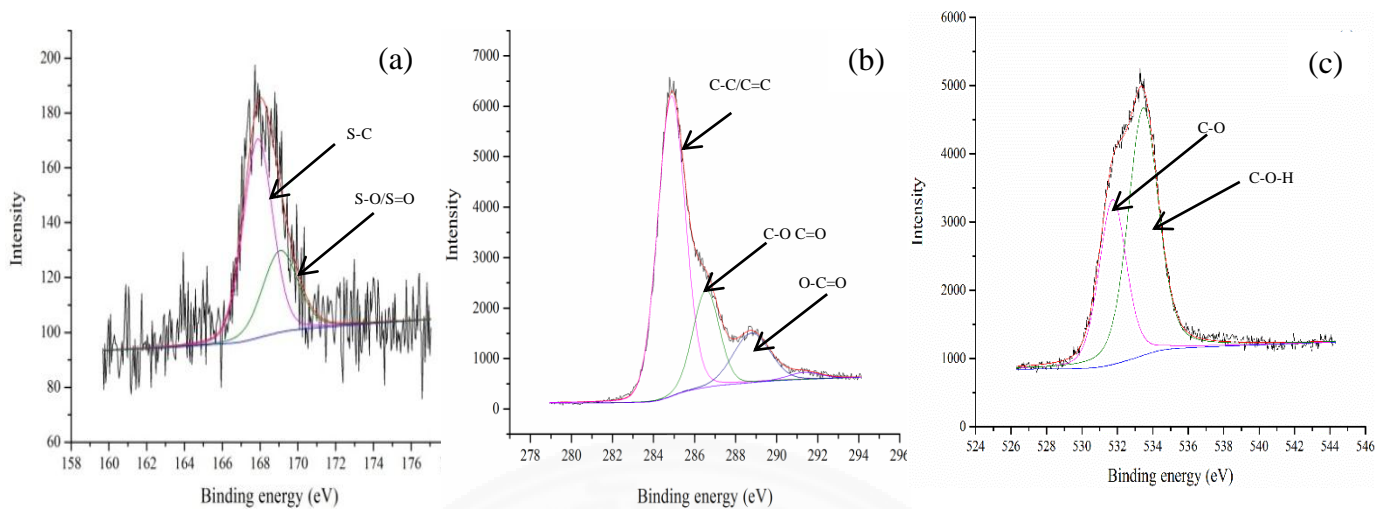


Fig. 4.14 De-convoluted spectra of (a) S2p, (b) C1s, and (c) O1s peaks of PEFB-DS-SO₃H

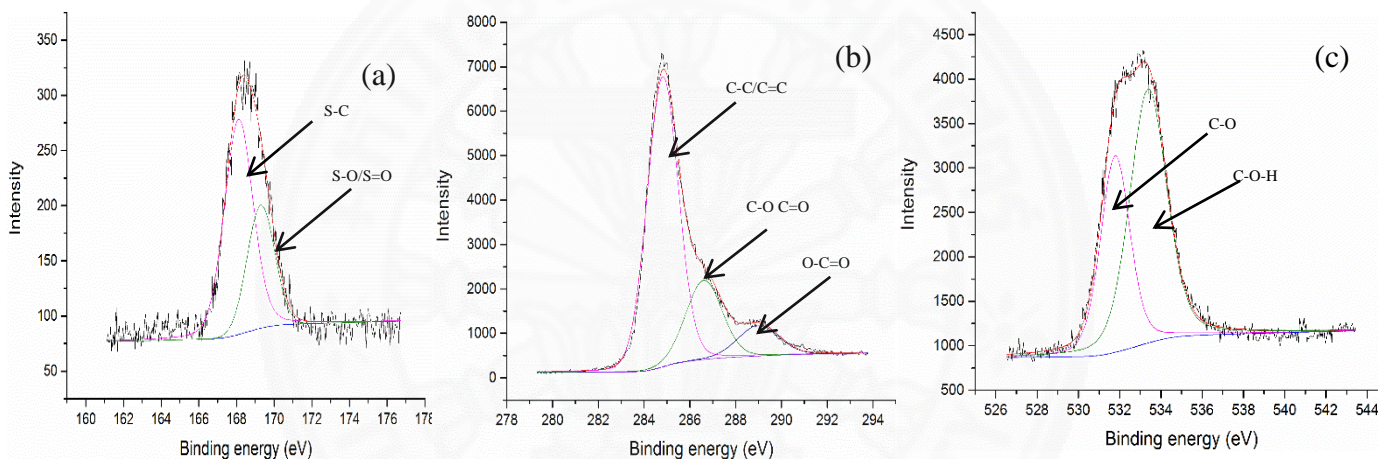


Fig. 4.15 De-convoluted spectra of (a) S2p, (b) C1s, and (c) O1s peaks of CMR-DS-SO₃H

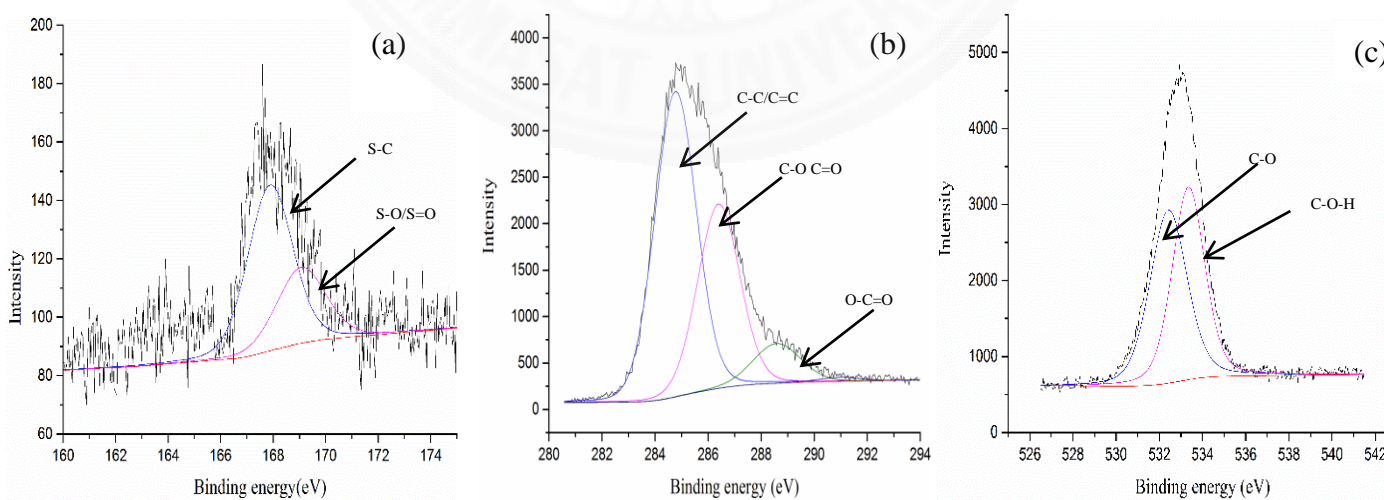


Fig. 4.16 De-convoluted spectra of (a) S2p, (b) C1s, and (c) O1s peaks of CCH-DS-SO₃H

The stability of functional groups of the catalysts (PEFB-DS-SO₃H and CMR-DS-SO₃H) used for biodiesel production from an open reflux reactor are investigated (Fig. 4.17). It is found that the intensity of the peak at S2p slightly declines for re-used catalysts, claiming to the possible deactivations during the reaction.

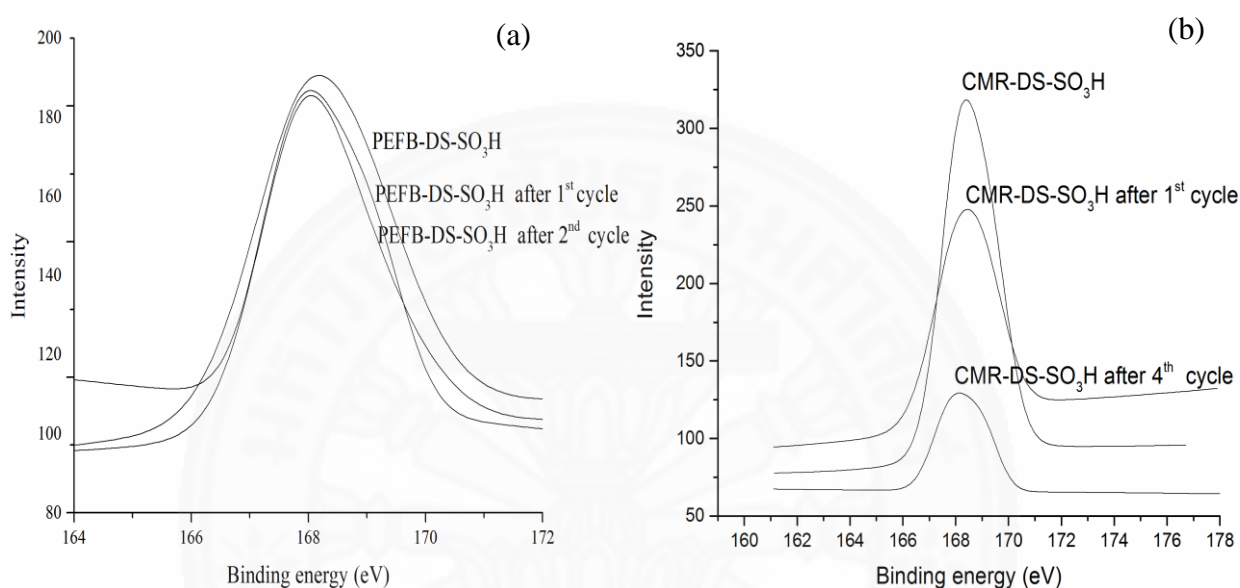


Fig. 4.17 S2p of used catalysts (a) PEFB-DS-SO₃H (b) CMR-DS-SO₃H

4.2.5 Thermal stability

The TGA of all the catalysts are shown in Fig. 4.18a-f. It is found that all the catalysts exhibit two main mass loss stages. The low temperature mass loss is below 150 and 200 °C for X-DS-SO₃H and X-BCS-SO₃H, respectively. The high temperature mass loss ranges between 200 °C and 800 °C. The small mass loss in the low temperature range is attributed to the evaporation of physisorbed water from the catalyst. Since the thermal degradation of the samples starts after 200 °C, the mass loss is relatively high. This is involved with thermal degradation of cellulose, hemicellulose, and lignin. Hemicellulose starts to decompose at around 250-275 °C and depletes at around 300 °C. Degradation of cellulose lies within

300-400 °C while lignin starts to decompose at around 200 °C and depletes at around 500 °C (Cabeza et al., 2015). In addition, as reported by several studies, the weight loss after 150 °C (Malins et al., 2015), and after 280 °C (Tamborini et al., 2016), is also attributed to the degradation of sulfonic acid groups of the carbon acid catalysts. Therefore, it can be concluded that all the catalyst samples are thermally stable until 200 °C despite the method of preparation. Thus, it is required to use the reaction temperature below 200 °C to achieve maximum catalytic activity. All the experiments in this study are conducted at a temperature below 200 °C. The thermal degradation of the catalysts with temperature is tabulated in Table 4.6.

Table 4.6 Thermal degradation of the catalysts

Catalysts	Thermal degradation (wt. %)	
	Below 150 °C	After 200-800 °C
PEFB-DS-SO ₃ H	18.38	47.12
CMR-DS-SO ₃ H	12.48	41.47
CCH-DS-SO ₃ H	10.66	46.69
PEFB-BCS-SO ₃ H	27.93	19.07
CMR-BCS-SO ₃ H	17.01	36.04
CCH-BCS-SO ₃ H	11.50	31.72

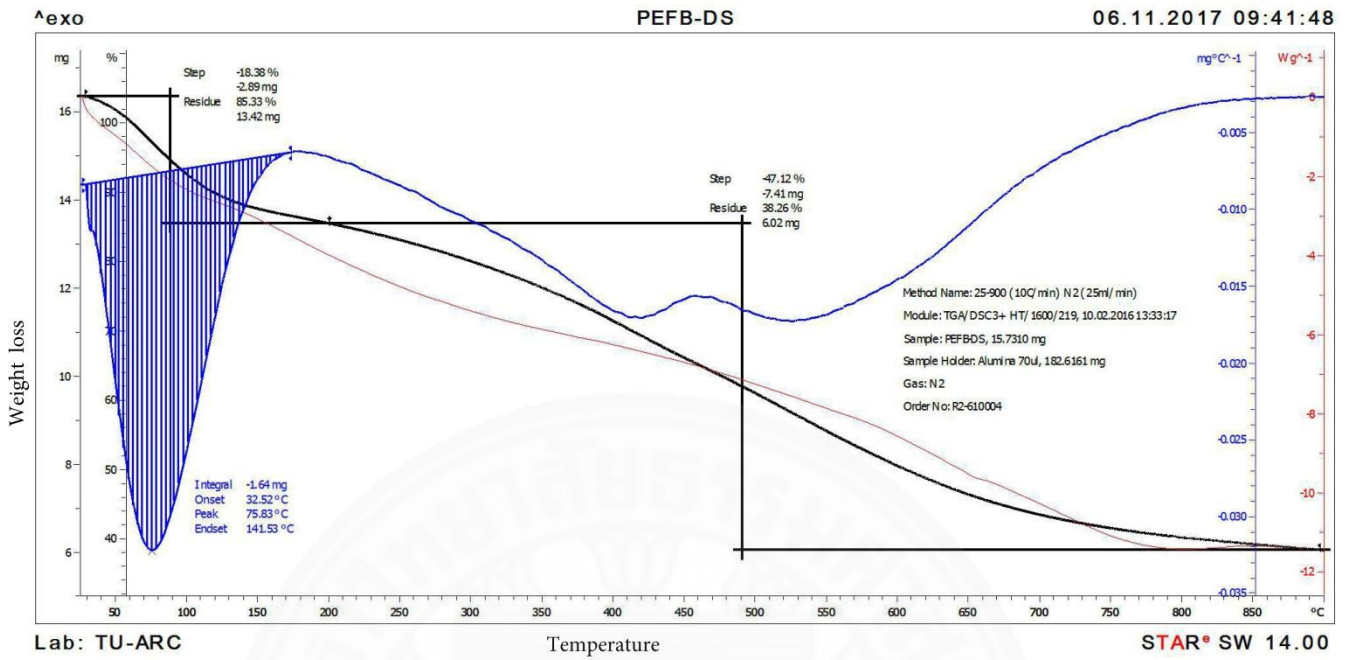


Fig. 4.18a TGA of PEFB-DS-SO₃H

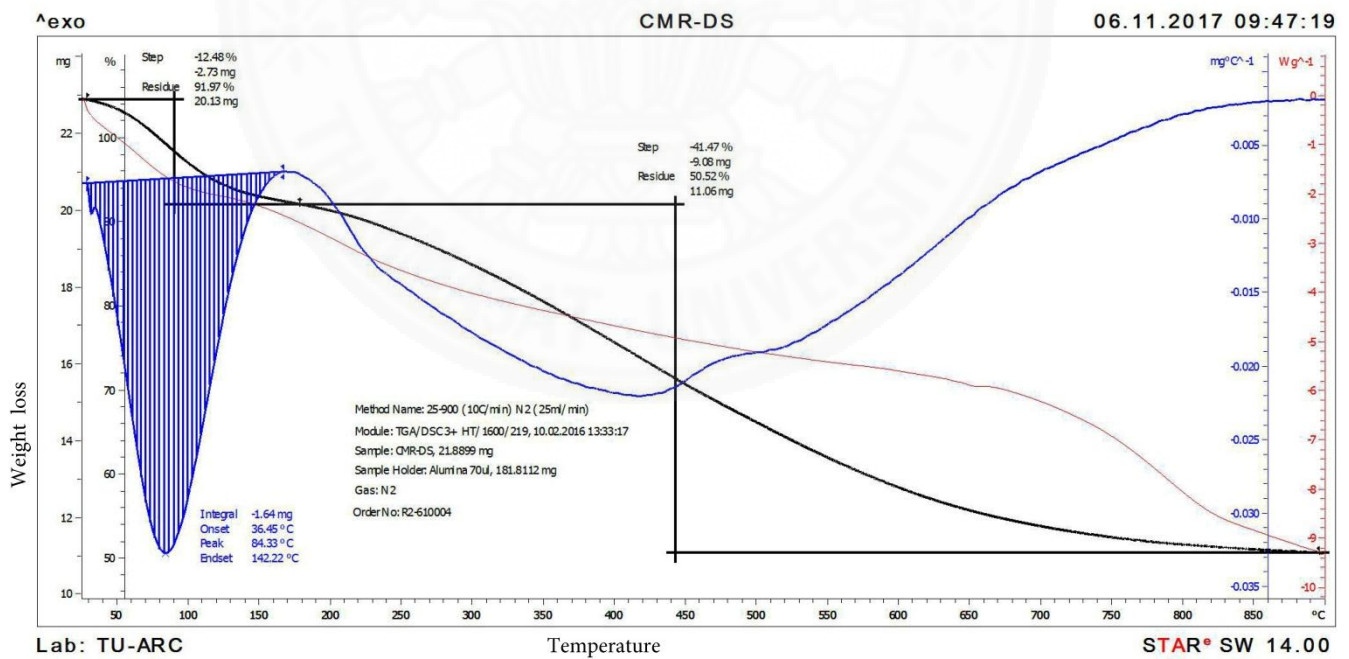


Fig. 4.18b TGA of CMR-DS-SO₃H

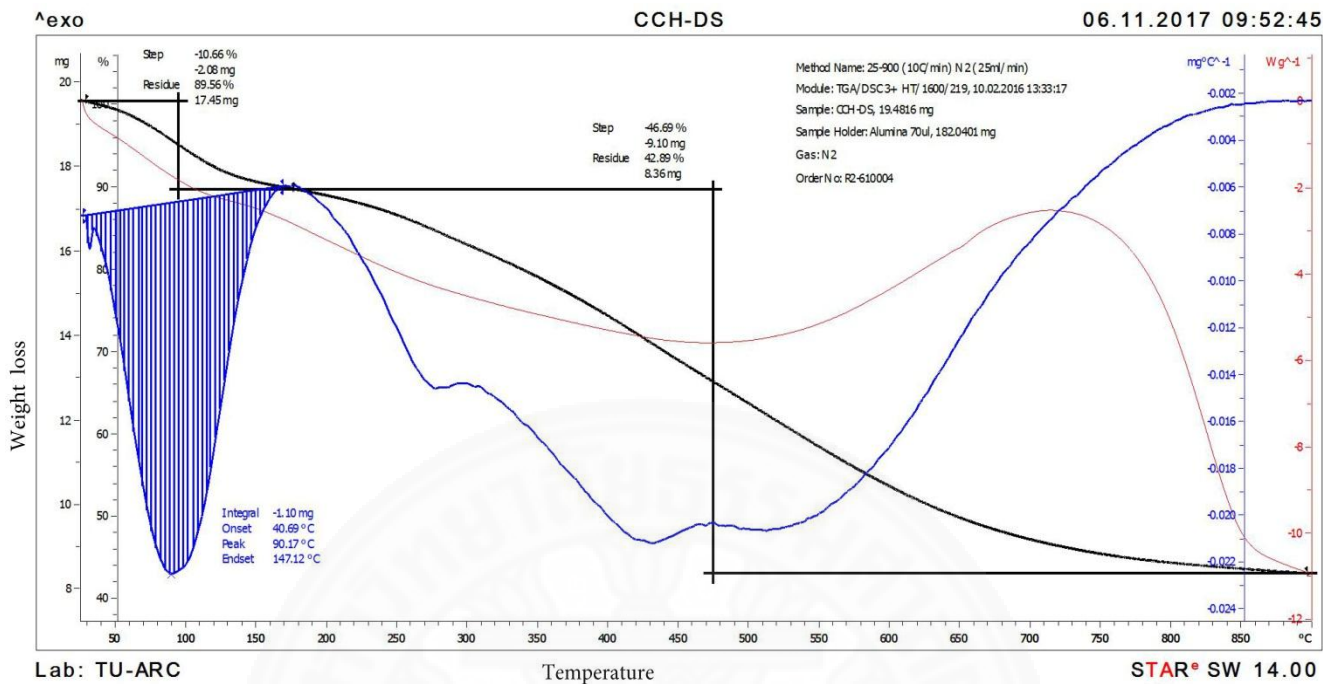


Fig. 4.18c TGA of CCH-DS-SO₃H

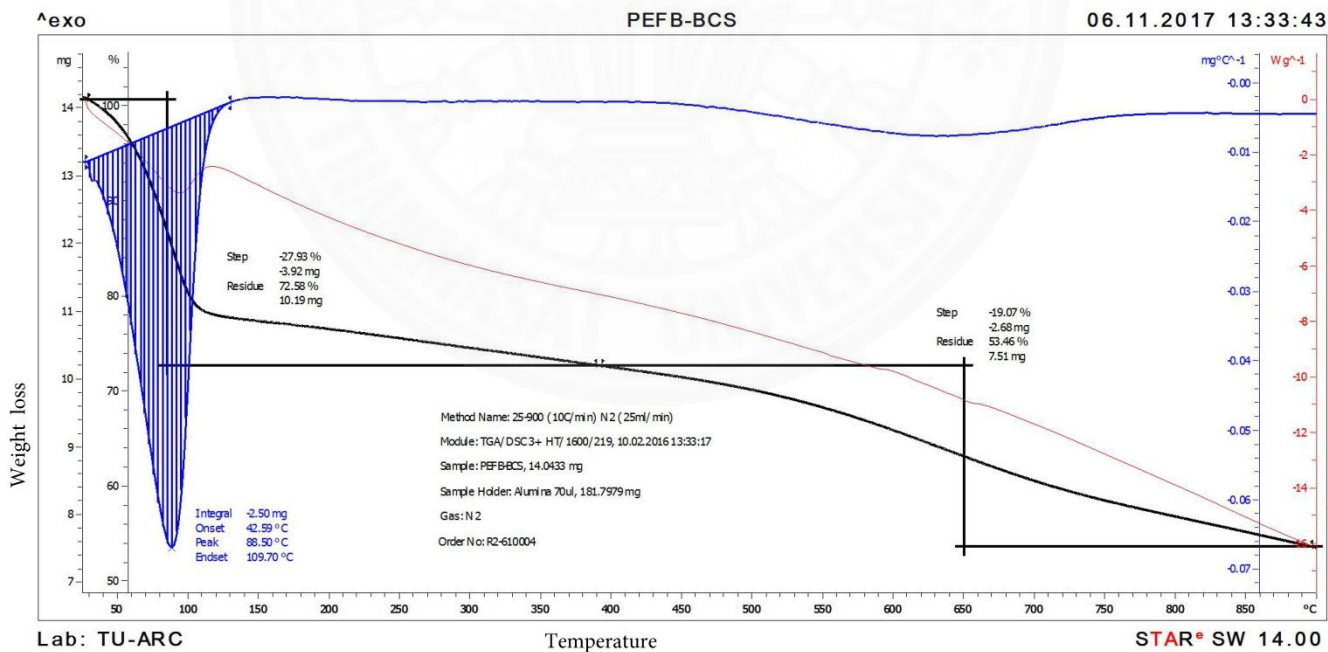


Fig. 4.18d TGA of PEFB-BCS-SO₃H

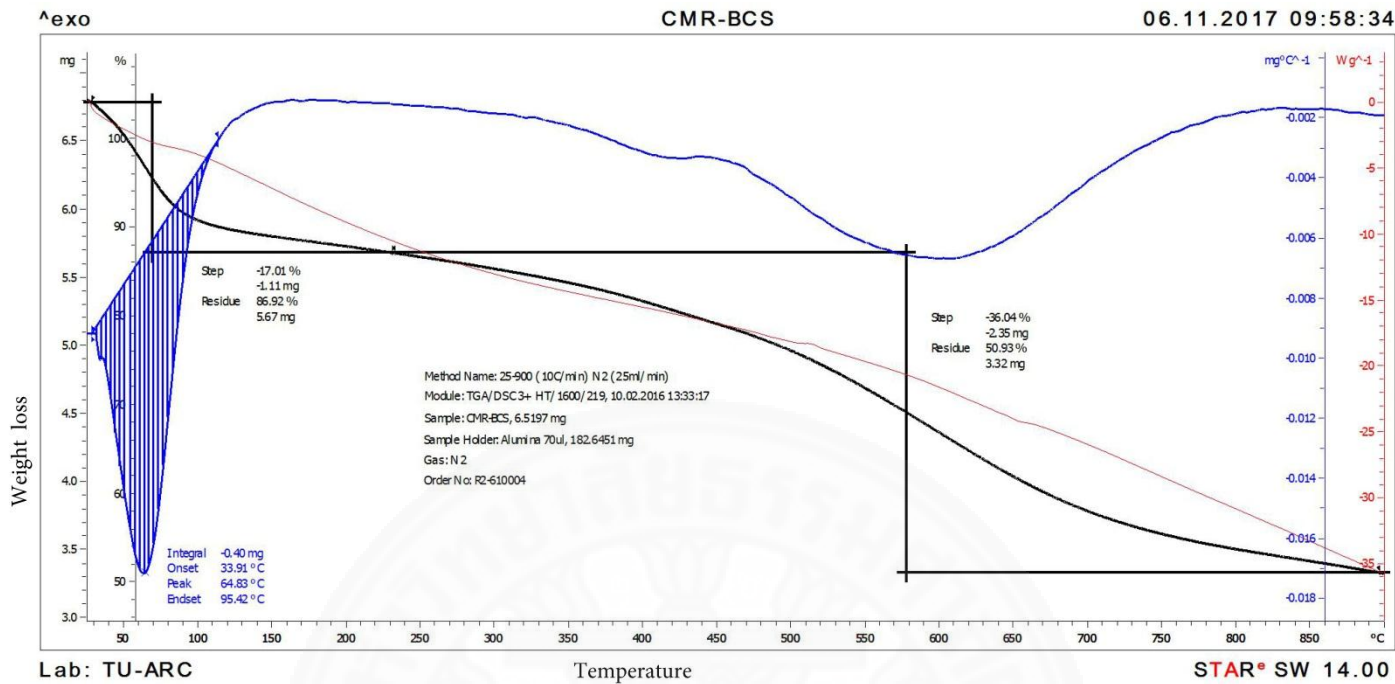


Fig. 4.18e TGA of CMR-BCS-SO₃H

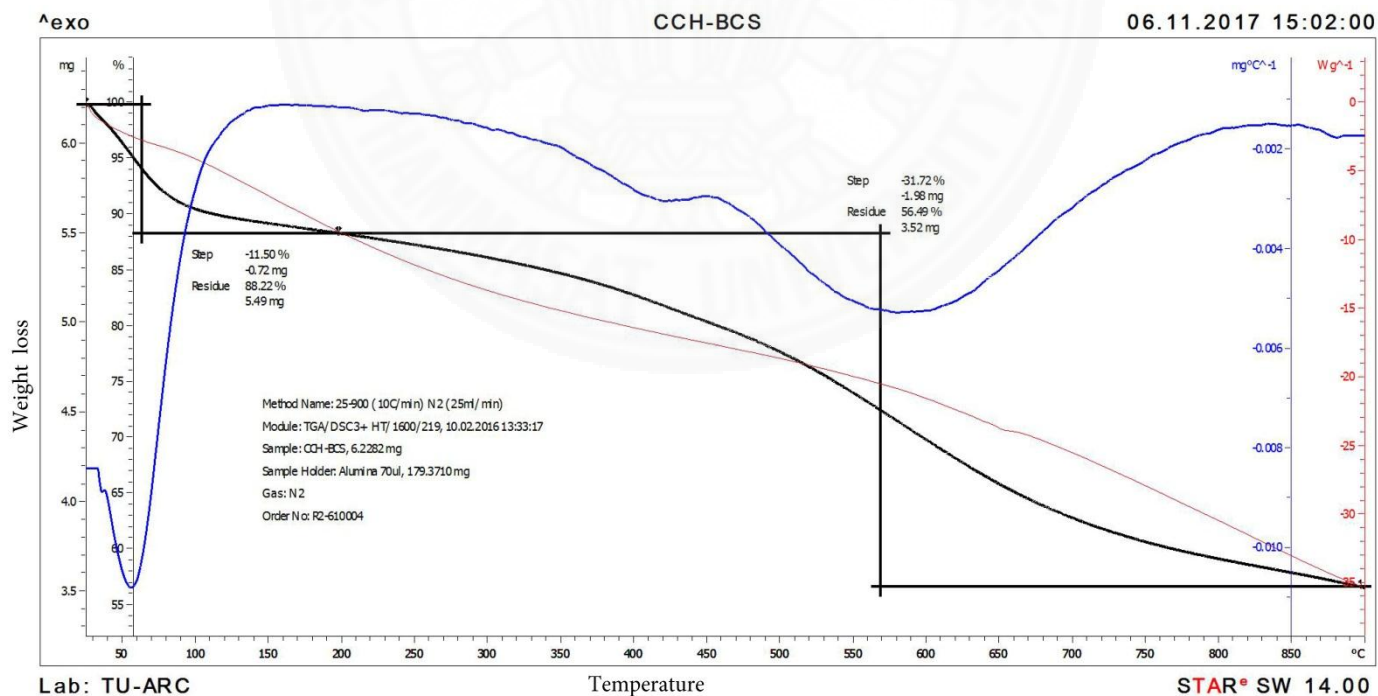


Fig. 4.18f TGA of CCH-BCS-SO₃H

4.3 Catalyst activity for esterification of palmitic acid

The activity of the PEFB-DS-SO₃H catalyst for esterification is investigated by decrease in acid value of the palmitic acid feedstock. The highest esterification efficiency of the catalyst is 98% at the optimum reaction conditions of 5% of catalyst (wt. %), 6:1 methanol:palmitic acid molar ratio, and at 80 °C after 5 h in a conventional open reflux reactor. Further, results reveal that the increase of reaction temperature and the reaction time increase the catalytic activity (Fig. 4.19). Among the three selected reaction temperatures used in this study, more than 70% of the esterification efficiency is observed at both 60 °C and 80 °C after 3 h.

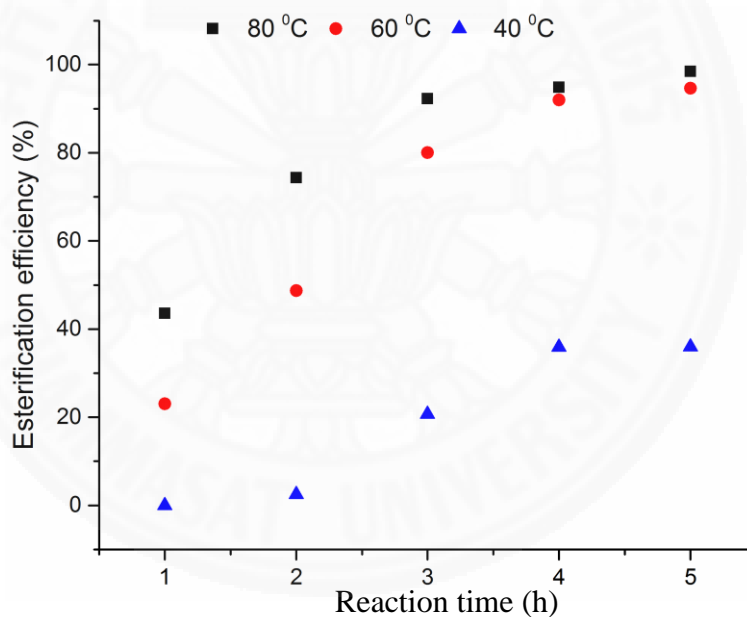


Fig. 4.19 Effect of reaction time and temperature on esterification efficiency of palmitic acid in an open reflux reactor with 5 wt. % PEFB-DS-SO₃H and 4:1 methanol to palmitic acid molar ratio

Even though, esterification reaction stoichiometrically requires 1:1 methanol:fatty acid molar ratio, it is found that an increase of methanol: palmitic acid molar ratio increases the esterification efficiency (Fig. 4.20). However, a further increase of

the methanol:palmitic acid molar ratio (>8:1) decreases the esterification efficiency. This is possibly due to the decrease of the rate of forward reaction according to the Le Chaterlier's principle. In addition, water produced during the reaction may poison the catalyst decreasing the esterification efficiency.

When investigating the reusability of the catalyst, it is found that the catalyst can be re-used for three consecutive runs without significant loss of the activity. The PEFB-DS-SO₃H catalyst obtains high esterification efficiencies of 98%, 93.3%, and 90.8% for the first, second, and third runs, respectively (Fig. 4.21).

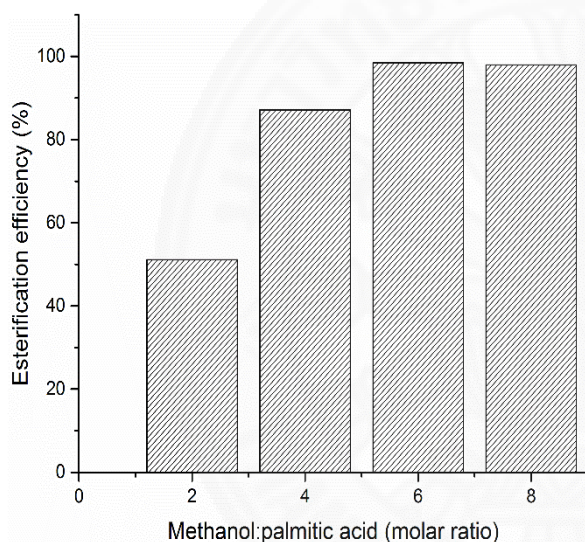


Fig. 4.20 Effect of methanol loading on esterification efficiency of palmitic acid in an open reflux reactor with 5 wt. % PEFB-DS-SO₃H at 80 °C for 5 h

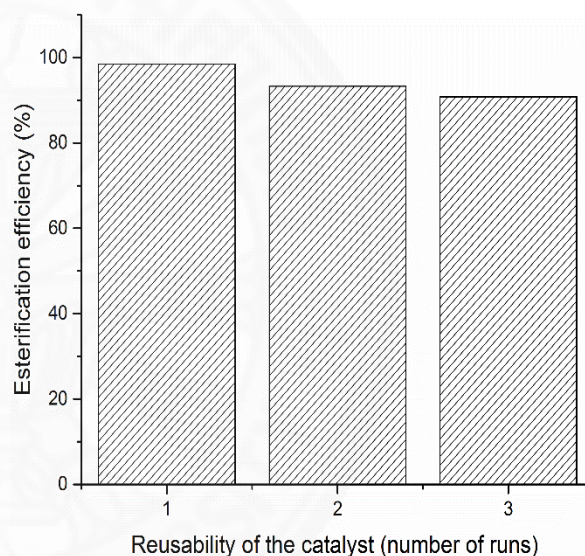


Fig. 4.21 Reusability of PEFB-DS-SO₃H for esterification of palmitic acid in an open reflux reactor with 5 wt. % catalyst and 6:1 methanol to oil molar ratio at 80 °C for 5 h

4.4 Catalyst activity for biodiesel production from WPO

4.4.1 Biodiesel production using an open reflux reactor

Preliminary experiments were carried out using 5 wt.% catalysts, at 65-70 °C, and 8 or 10 h reaction time using different methanol:oil (molar ratio) in order to screen the activity of all catalysts prepared in this study. For the catalysts which showed an acceptable activity during the screening experiments, optimum reaction conditions, such as methanol:oil (molar ratio), reaction time, and catalyst loading for biodiesel production from WPO were studied. Results are compared with control experiments which are conducted without using the catalysts, using raw biomass, and H₂SO₄ as catalyst at optimum conditions.

Even though, trans-esterification stoichiometrically requires 3:1 methanol: triglycerides molar ratio, it is required to have excess methanol for the esterification reaction to neutralize the excess FFA in the medium. Therefore, the effect of methanol for FAME yield (%) is studied using different methanol:oil (molar ratio) loading for each catalyst during the screening experiments. As shown in Fig. 4.22, it is found that FAME yield (%) increases with increasing methanol loading up to an optimum value. The highest FAME yield of 88.9% is shown by PEFB-DS-SO₃H at 14:1 methanol:oil (molar ratio) at 5 wt.% catalyst after 10 h. A further increase of methanol loading decreases the %FAME yield to 64.5%. However, it is found that FAME yield of CMR-DS-SO₃H catalyzed biodiesel production increases until 77.3% with increasing methanol loading to 12:1 methanol to oil molar ratio after 8 h reaction time. Even though, PEFB-BCS-SO₃H, CMR-BCS-SO₃H, CCH-BCS-SO₃H, and CCH-DS-SO₃H showed a similar trend of increase of FAME yield to an optimum value with increasing methanol:oil (molar ratio) after 8 h, their catalytic activity is relatively poor (<50%) compared to PEFB-DS-SO₃H and CMR-DS-SO₃H. Increase of methanol in the reaction medium increases the FAME yield due to increase rate of forward reaction. However, a further increase of the methanol:oil (molar ratio) after the

optimum value decreases the rate of forward reaction according to the Le Chatelier's principle.

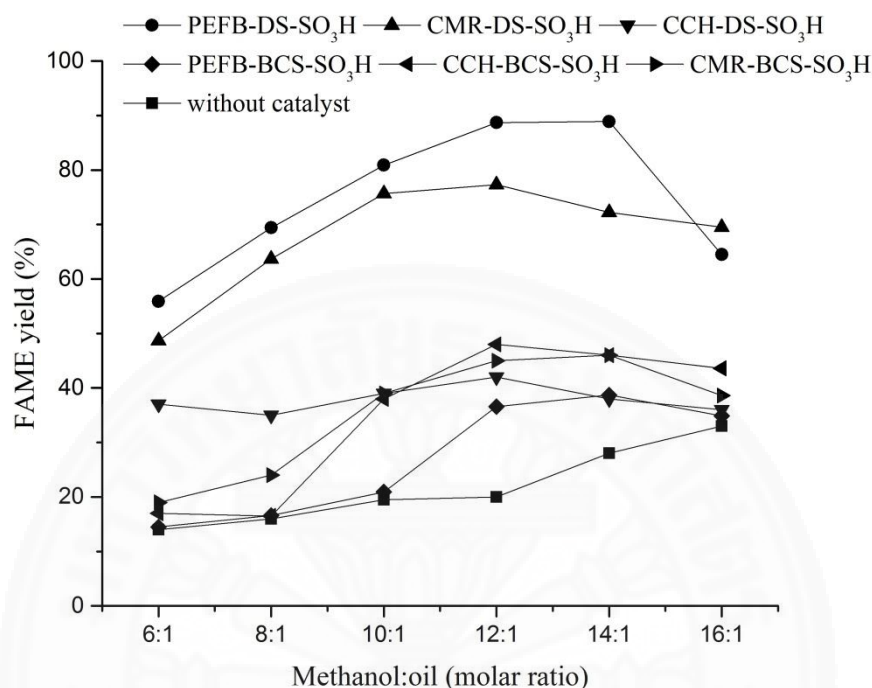


Fig. 4.22 Effect of methanol:oil (molar ratio) on FAME yield (%) in an open reflux reactor with 5 wt.% catalyst at 65-70 °C for 8 or 10 h

Results show that PEFB-DS-SO₃H and CMR-DS-SO₃H catalysts have higher activity compared to other catalysts during the screening experiments (Fig. 4.22). Therefore, PEFB-DS-SO₃H and CMR-DS-SO₃H catalysts are used for further investigations of biodiesel production using a conventional open reflux reactor.

As stated by Shu et al. (2010a) acid catalyzed ester production requires high reaction temperature to initialize the reaction. However, in this study, the experiments are carried out at 65-70 °C in a conventional open reflux reactor. Therefore, the reaction required longer reaction time when compared to the alkaline catalyzed trans-esterification reaction. Thus, the effects of reaction time for both PEFB-DS-SO₃H and CMR-DS-SO₃H catalyzed reactions are studied.

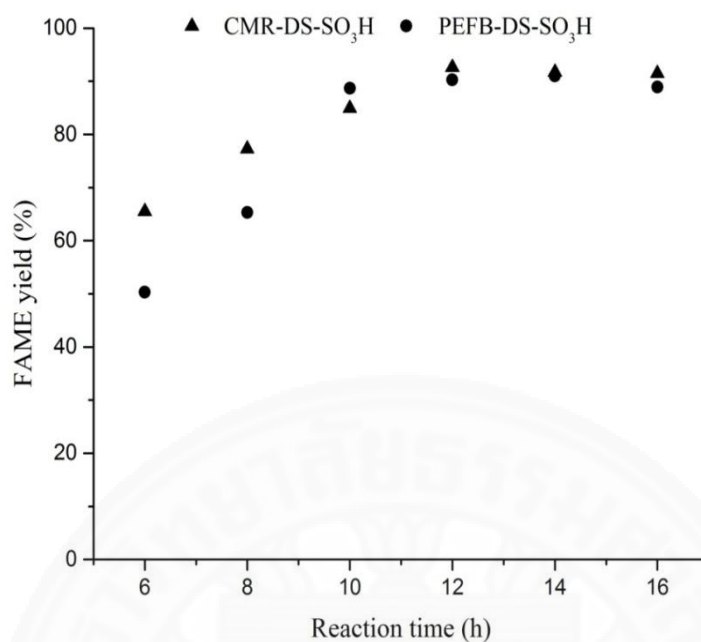


Fig. 4.23 Effect of reaction time on FAME yield (%) in an open reflux reactor (5 wt. % catalyst, 14:1 and 12:1 methanol to oil molar ratio) for PEFB-DS-SO₃H and CMR-DS-SO₃H, at 65-70 °C

As shown in Fig. 4.23, FAME yields for both PEFB-DS-SO₃H and CMR-DS-SO₃H catalyzed reactions increase until 91% and 92.7% after 14 h and 12 h, respectively. The low FAME yields at initial shorter reaction time may be possible because of the mass transfer resistance. As the reaction proceeds, the viscosity of the mixture decreases and the rate of the reaction increases, eventually. However, it is found that a further increase of the reaction time decreases the FAME yield. This can be explained as follows. Esterification is faster than trans-esterification. Water produced due to increase rate of esterification poisons the catalyst during a longer reaction time. In addition, deactivation of the catalyst is possible by the binding of polar molecules due to long time exposure in the reaction mixture (Lou et al., 2008). This may be identified as a disadvantage of conventional open reflux reactor assisted biodiesel production using SACs.

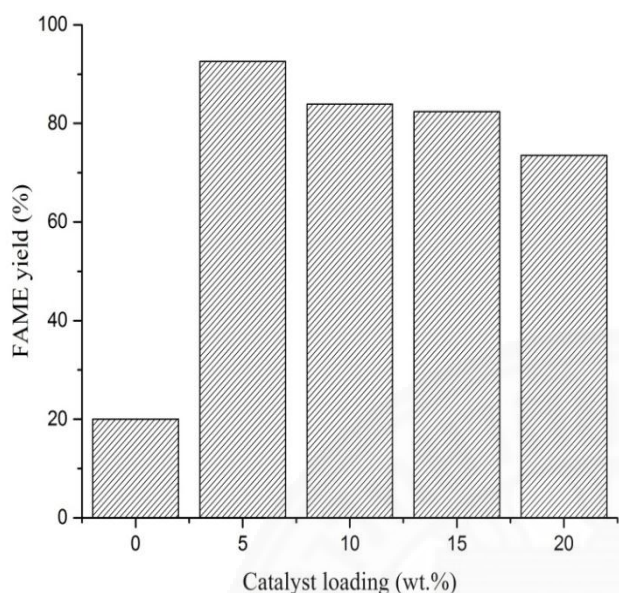


Fig. 4.24 Effect of CMR-DS-SO₃H loading on FAME yield (%) in an open reflux reactor with 12:1 methanol to oil molar ratio at 65-70 °C for 12 h

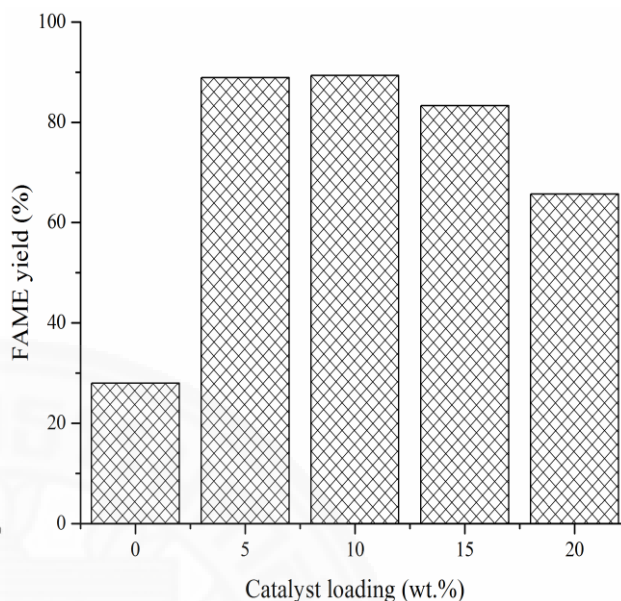


Fig. 4.25 Effect of PEFB-DS-SO₃H loading on FAME yield (%) in an open reflux reactor with 14:1 methanol to oil molar ratio at 65-70 °C for 10 h

An increase of catalyst loading increases the active acid sites available for catalyzing esterification and trans-esterification. A decrease in FAME yield with increasing catalyst loading after 5 wt. % is found, when investigating the effect of CMR-DS-SO₃H catalyst loading on FAME yield (Fig. 4.24). However, it is found that FAME yield increases to 89.3% when increasing PEFB-DS-SO₃H catalyst loading until 10 wt. % (Fig. 4.25). A further increase of catalyst loading decreases the FAME yield for both catalysts. These results are possible due to various reasons. Even though, increase of catalyst loading increases the active acid sites, this can decrease the rate of diffusion due to bulk mass in the reaction medium. In addition, as per the effect of reaction time, water accumulated due to increased rate of esterification can deactivate the catalyst reducing the FAME yield at higher catalyst concentrations. However, increase of FAME yield until 10 wt. % PEFB-DS-SO₃H may be attributed to the relatively high surface area and the pore

volume of the catalyst compared to CMR-DS-SO₃H which influence on the mass diffusion. The relatively higher surface area and pore diameter of PEFB-DS-SO₃H catalyst facilitate reactant to contact with more acid sites in the catalyst and increases the rate of the reaction.

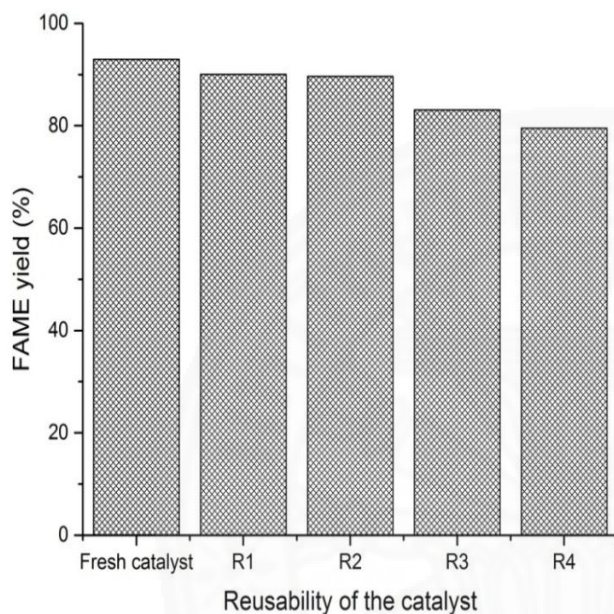


Fig. 4.26 Reusability of CMR-DS-SO₃H for FAME production from WPO in an open reflux reactor with 5 wt. % catalyst and 12:1 methanol to oil molar ratio at 65-70 °C for 12 h

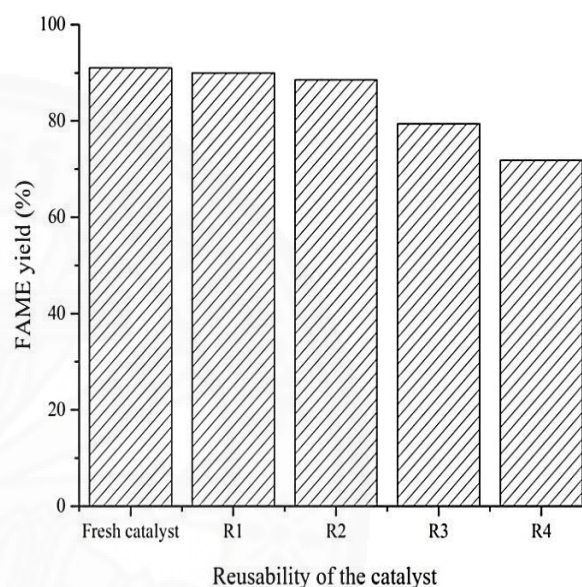


Fig. 4.27 Reusability of PEFB-DS-SO₃H for FAME production from WPO in an open reflux reactor with 5 wt. % catalyst and 14:1 methanol to oil molar ratio at 65-70 °C for 14 h

Further, low FAME yields of 12.3% and 15% were obtained in the control experiments using dry CMR and PEFB powder as the catalysts at optimum reaction conditions, while a FAME yield of 20% was obtained without the catalyst using 12:1 methanol to oil molar ratio at 65-70 °C and 8 h. This may be due to the reason that dry biomass powder can absorb methanol, which limits reactant diffusion resulting a low FAME yield. Thus, the results confirm that PEFB-DS-SO₃H and CMR-DS-SO₃H are successfully functionalized, and the

active sites of the catalyst are contributing to the reaction as can be seen by the higher FAME yield. In addition, a maximum FAME yield of >98% is given by concentrated H₂SO₄ catalyzed biodiesel production from WPO using 12:1 methanol to oil molar ratio at 65-70 °C and 8 h.

Besides preparation from inexpensive waste biomass following simple preparation steps, the main advantage of the use of carbon based SACs is their reusability (Savaliya & Dholakiya, 2015; Zheng et al., 2006). Therefore, reusability of the catalyst is studied under observed optimum reaction conditions with 5 wt. % of catalyst for all reactions. It is found that catalysts can be easily recovered by vacuum filtration. As shown in Fig. 4.26 and Fig. 4.27, fresh CMR-DS-SO₃H and PEFB-DS-SO₃H results maximum FAME yield of 92.6% and 91%, respectively. The FAME yields for CMR-DS-SO₃H (90%, 89.6%, 83% and 79.5% for consecutive runs) and PEFB-DS-SO₃H (90%, 88.5%, 79.4%, and 71.8% for consecutive runs) were >70% after fourth run with reused catalysts. It is found that the stability of CMR-DS-SO₃H is higher compared to the stability of PEFB-DS-SO₃H giving a higher FAME yield with reused catalysts. Relatively high stability of the carbon based SAC is mainly related with the presence of strongly attached sulfonic groups to the porous carbon structure (Liu et al., 2015). However, it is found that the total acid density of the catalyst decreases from 5.4 to 4.26 (PEFB-DS-SO₃H) and 3.80 to 3.25 mmolg⁻¹ (CMR-DS-SO₃H) after the first usage. In addition, it is found from elemental analysis that sulfur content of both catalysts decrease after the first run (3.89 to 1.74 and 1.10 to 0.98 wt.%, for CMR-DS-SO₃H and PEFB-DS-SO₃H catalysts, respectively) (Table 4.2). This is possibly due to the leaching of weakly attached sulfonic acid groups during the reaction (Konwar et al., 2016). In addition, leaching of active sites of both catalysts are confirmed by FT-IR (Fig. 4.9) and XPS (Fig. 4.17) analysis by declining the peak intensities.

4.4.2 Biodiesel production using an autoclave assisted reactor

Biodiesel production using a conventional open reflux reactor under atmospheric pressure requires a longer reaction time to complete the reaction. This increases the ultimate cost of the biodiesel production. The rate of the acid catalyzed ester production is slower than the alkaline catalyzed ester production. In addition, acid catalyzed ester production requires high reaction temperature in order to facilitates the methanol nucleophilic attack on the triglycerides (Shu et al., 2010a). The laboratory scale autoclave is able to maintain high reaction temperature and pressure. The use of high temperature for acid catalyzed ester production decreases the required reaction time. This may reduce the rate of catalyst degradation due to short time exposure to water and other reactants.

Use of CCH-DS-SO₃H for biodiesel production from an open reflux reactor was not successful. Therefore, the activity of the catalyst at high reaction temperature using an autoclave reactor is studied. The effects of reaction temperature, time, and catalyst loading on FAME yield and the reusability of the catalyst were studied using the optimum methanol:oil (12:1 molar ratio) as found in an open reflux reactor assisted biodiesel production.

It is found that the FAME yield increases to 87% with increasing reaction temperature until 130 °C (Fig 4.28). A slight decrease of FAME yield is observed when increasing the reaction temperature to 150 °C. Since, esterification and trans-esterification are endothermic reactions; an increase of reaction temperature increases the FAME yield. Also, an increase of reaction temperature facilitates molecular collision and decreases the viscosity of the oil. This reduces the mass transfer limitation, thus, increases the rate of reaction with increasing temperature. However, the reaction may reach to the equilibrium at 130 °C leading to a decrease in FAME yield after 130 °C. A laboratory scale autoclave can maintain a high reaction temperature and high pressure in a closed system. This prevents the methanol loss while forcing evaporated methanol back to the reaction phase. This may be the reason for the high FAME yield under a high

reaction temperature beyond the boiling point of methanol. As found by TGA, the catalysts are stable to be used below 200 °C without thermal degradation.

When investigating the effect of reaction time on FAME yield using a laboratory scale autoclave reactor, it is found that the FAME yield increases up to 87.6% with increasing reaction time until 3 h using 5 wt.% CCH-DS-SO₃H catalyst, 12:1 methanol:oil molar ratio, at 130 °C (Fig. 29). A further increase of the reaction time causes a slight decrease in the FAME yield. Therefore, 3 h is taken as the optimum reaction time and used for further investigations. A decrease of FAME yield after 3 h is possible due to various reasons. The catalyst can be deactivated by poisoning of water accumulated as a result of an increased rate of esterification. Also, various depositions on the catalyst surface during the reaction decreases the activity by blocking pores and hindering the active sites (Lou et al., 2008). However, the effect of reaction time on FAME yield relies on various factors, such as biodiesel production process, reaction temperature, methanol and catalyst loading.

The amount of active sites available for the reaction also affects the FAME yield. An increase of catalyst loading increases the available active acid sites for esterification and trans-esterification. As shown in Fig. 4.30, it is found that the FAME yield increases to 89.8% with increasing catalyst loading until 10 wt. %. A further increase causes a decrease in the FAME yield. Similar to results found in the conventional reflux reactor assisted biodiesel production, the results can be explained as follows. Since esterification is faster than trans-esterification, a high density of acid sites increases the rate of esterification, producing more water. Excess catalyst present in the system can be poisoned by water, resulting in a low FAME yield when increasing the catalyst loading. In addition, difficulty in reactant diffusion due to bulk mass (excess catalyst) in the reaction medium may decrease the final FAME yield. However, a low FAME yield of 25.4% is obtained in the control experiment carried out without using the catalyst at optimum reaction conditions. This confirms that CCH-DS-SO₃H is successfully

functionalized, and the active sites of the catalyst contribute to the reaction. It was also found that when biodiesel is produced without using the catalyst, the FAME yield in an autoclave reactor is higher than that of open reflux reactor.

The reusability of the catalyst is studied under the optimum reaction conditions for four cycles. It is found that the catalyst can be easily recovered by vacuum filtration. As shown in Fig. 4.31, the activity of the catalyst is slightly decreased from 89.8% to 77.5% from fresh catalyst to the recovered catalyst after fourth cycle. The relatively high stability of the catalyst is probably due to the presence of strongly attached sulfonic groups to a highly stable carbon structure (Liu et al., 2015). In addition, it is hypothesized that CCH-DS-SO₃H has high amount of COOH and OH due to its' high O:C ratio. These functional groups increase the rate of catalytic activity by anchoring the reactants and assisting them to easily reach to SO₃H groups (Hara, 2010). However, it is found that total acid density and the sulfur content of the catalyst decreases from 2.50 to 1.90 mmol g⁻¹ and 1.99 to 1.02 wt. %, respectively. As stated by Fraile et al. (2012), deactivation of the sulfonated carbon catalyst is possible after a long time with continued exposure to methanol due to the binding of methanol to sulfonic acid groups. In addition, leaching of active acid sites (especially SO₃H groups) is possible during the reaction.

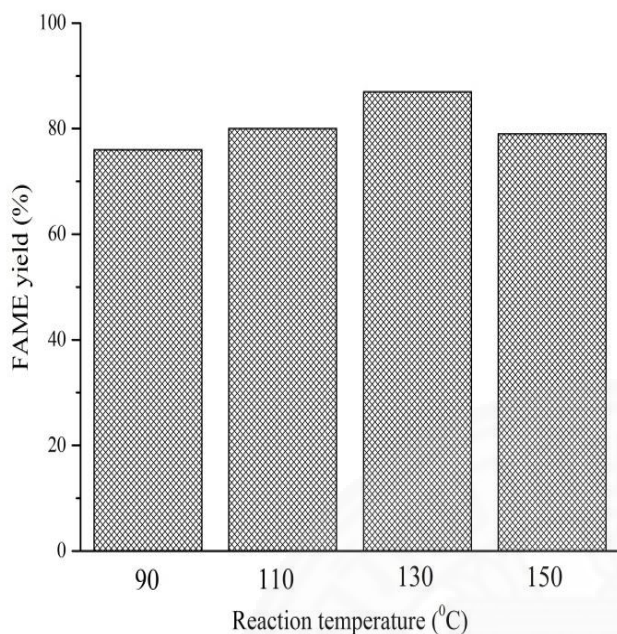


Fig. 4.28 Effect of reaction temperature on FAME yield (%) in an autoclave reactor with 5 wt. % CCH-DS-SO₃H and 12:1 methanol to oil molar ratio for 3 h

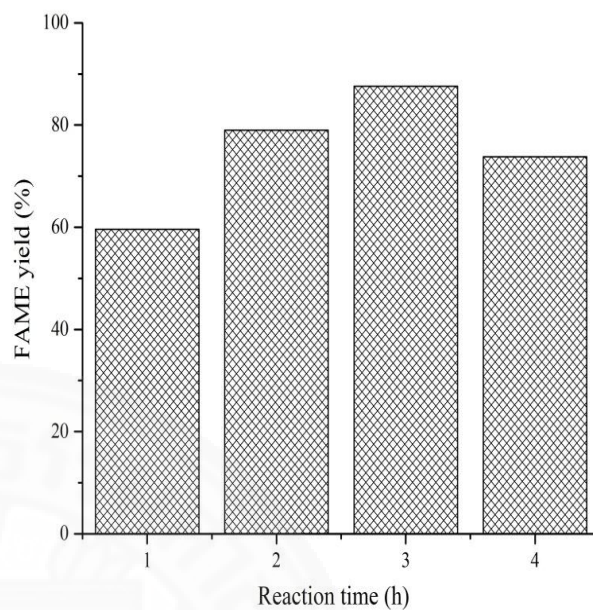


Fig. 4.29 Effect of reaction time on FAME yield (%) in an autoclave reactor with 5 wt. % CCH-DS-SO₃H and 12:1 methanol to oil molar ratio at 130 °C

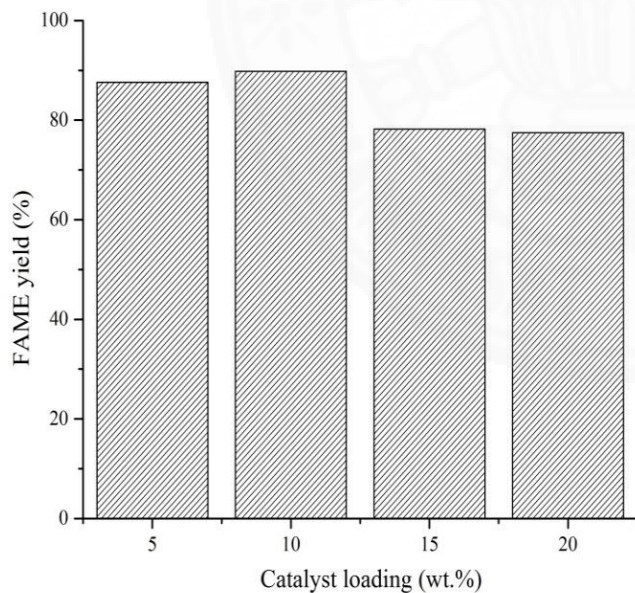


Fig. 4.30 Effect of CCH-DS-SO₃H loading on FAME yield (%) in an autoclave reactor with 12:1 methanol to oil molar ratio at 130 °C for 3 h

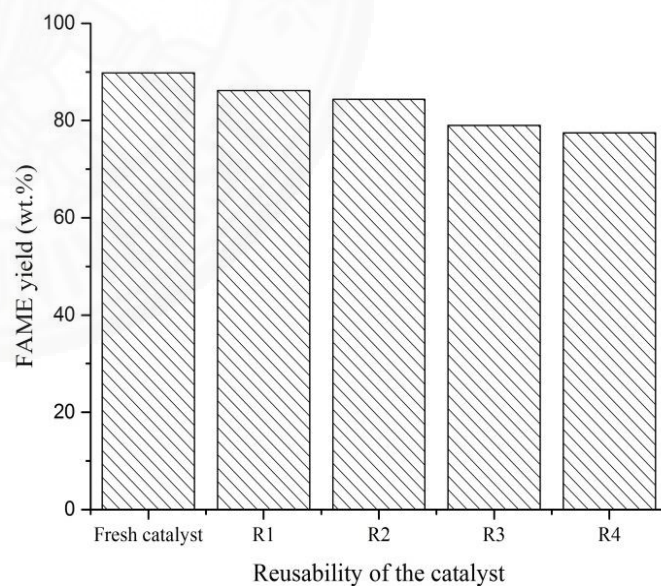


Fig. 4.31 Reusability of CCH-DS-SO₃H for FAME production from WPO in an autoclave reactor with 10 wt. % catalyst and 12:1 methanol to oil molar ratio at 130 °C for 3 h

It is found that CMR-DS-SO₃H is the most stable and active catalyst during biodiesel production using a conventional open reflux reactor. Therefore, the effects of the reaction temperature and time on the FAME yield were studied using the optimum methanol (12:1 methanol to oil molar ratio) and catalyst loading (5 wt. %) as found in an open reflux reactor.

A maximum FAME yield of 95.5% is obtained for CMR-DS-SO₃H catalyzed biodiesel production at 150 °C and 3 h (Fig. 4.32). A further increase of the reaction temperature decreases the FAME yield to 78%. These results are similar to the trend of CCH-DS-SO₃H catalyzed biodiesel production. CMR-DS-SO₃H catalyzed ester production may reach to the reaction equilibrium at around 150 °C, leading for a decrease of the FAME yield when increasing the reaction temperature after 150 °C.

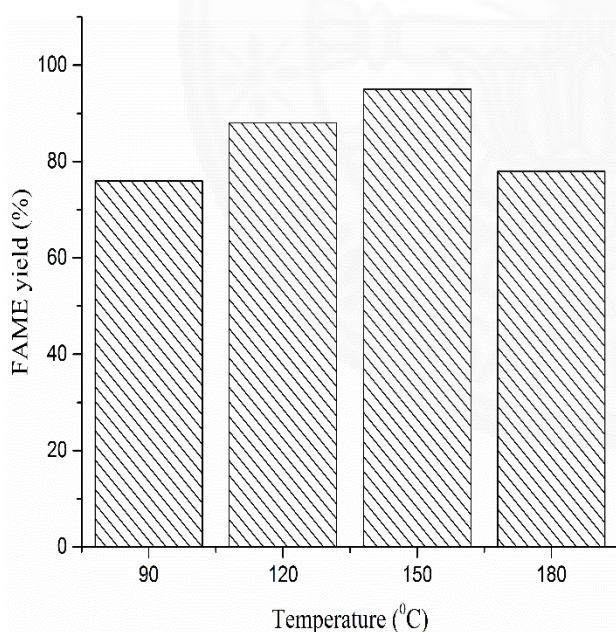


Fig. 4.32 Effect of reaction temperature on FAME yield (%) in an autoclave reactor with 5 wt. % CMR-DS-SO₃H and 12:1 methanol to oil molar ratio after 3 h

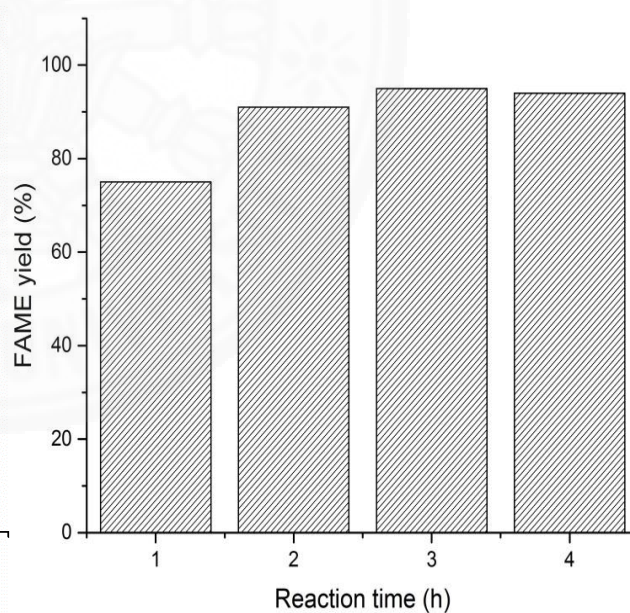


Fig. 4.33 Effect of reaction time on FAME yield (%) in an autoclave reactor with 5 wt. % CMR-DS-SO₃H and 12:1 methanol to oil molar ratio at 150 °C

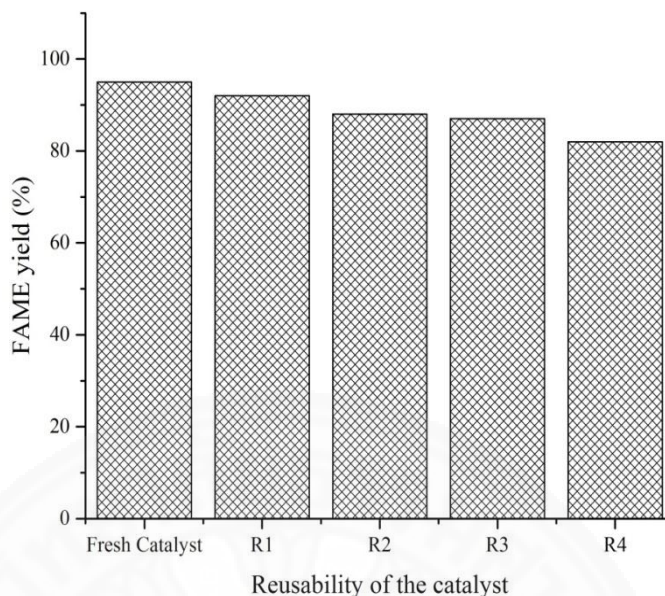


Fig. 4.34 Reusability of CMR-DS-SO₃H for FAME production from WPO in an autoclave reactor with 5 wt. % CMR-DS-SO₃H and 12:1 methanol to oil molar ratio at 150 °C for 3 h

The reaction time plays an important role and directly affects the cost of biodiesel production. It is found that 3 h reaction time gives the maximum FAME yield of 95.5% with 5 wt. % CMR-DS-SO₃H, 12:1 methanol:oil (molar ratio), at 150 °C (Fig. 4.33). This is a significantly lower reaction time compared to the biodiesel production using a conventional open reflux reactor (3 and 12 h for 95% and 92% FAME yield in autoclave and conventional reflux reactor assisted biodiesel production, respectively).

Reusability of the catalyst is very important. When investigating the reusability of CMR-DS-SO₃H in an autoclave reactor, it is found that the FAME yield slowly declines until 82% after fifth run (Fig. 4.34). In addition, it is found that the total acid density of the catalyst decreases from 3.80 to 3.15 mmolg⁻¹ after the first run, in an autoclave reactor assisted biodiesel production. This is attributed to the possible deactivation of the catalyst during the reaction. The % FAME yield after fifth run for biodiesel production using an open reflux reactor is 79.5%, which is

slightly lower than the autoclave assisted biodiesel production. Use of longer reaction time during biodiesel production in an open reflux reactor decreases the activity of the catalyst as it is more prone to deactivate during the long time exposure to water, methanol, and other substances in the medium. However, as can be seen in the FT-IR spectra, the functional groups are remaining unchanged after the second usage of the catalyst. Further, the results confirm CMR-DS-SO₃H is highly stable than CCH-DS-SO₃H for biodiesel production in an autoclave reactor.

Additionally, the effect of reaction temperature on FAME yield under low methanol loading (6:1 methanol:oil molar ratio) for biodiesel production from PEFB-DS-SO₃H is shown in Fig. 4.35. A higher FAME yield of 90.5% is obtained at 150 °C and 3 h. Results confirm that the rate in an autoclave reactor assisted biodiesel production is faster and the requirement of methanol is lower compared to a conventional open reflux reactor.

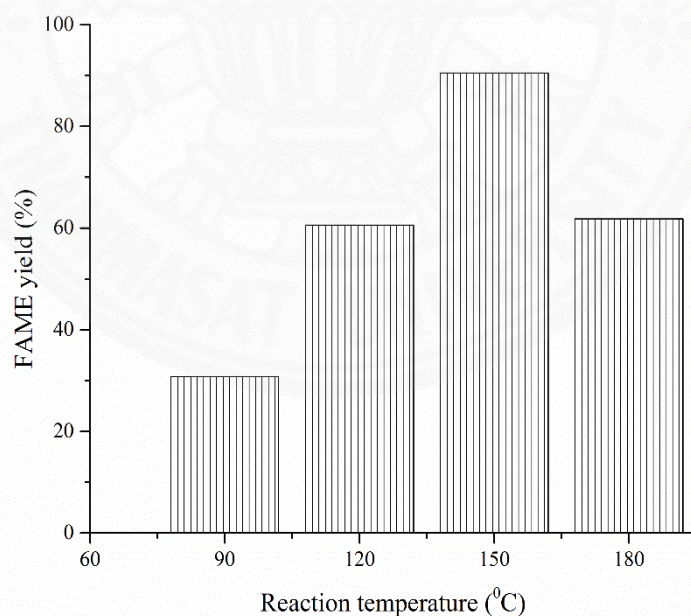


Fig. 4.35 Effect of reaction temperature on FAME yield (%) in an autoclave reactor with 5 wt. % PEFB-DS-SO₃H and 6:1 methanol to oil molar ratio for 3 h

4.4.3 Biodiesel production using a microwave assisted reactor

Microwave assisted biodiesel production has gained increased attention over conventional biodiesel production in terms of higher energy efficiency. Reduction of overall reaction time due to rapid, selective, and uniform heating, reduction of overall process steps and cleaner production during microwave assisted process have facilitated their use in biodiesel production (Gude et al., 2013).

Since the biodiesel production from WPO and using catalysts produced by two step protocol (X-BCS-SO₃H) in an open reflux reactor was not successful, the activity is investigated in a microwave assisted reactor. The effects of reaction time, methanol loading, and temperature on the % FAME yield are investigated.

Trans-esterification of TGs is a reversible and complex reaction with multiple steps, which produces mono and di-glycerides as intermediates. Therefore, finding a proper reaction time that can complete the overall reaction by giving 3 moles of esters is required. The effect of reaction time on FAME production using microwave assisted reactor is shown in Fig. 4.36. It is found that increasing the reaction time increases the %FAME yield. The highest FAME yield of 85.6% is obtained by PEFB-BCS-SO₃H after 60 min at 70 °C, which may be attributed to the high acid density of the catalyst. In addition, it is found that the reaction needs at least 60 min to reach > 60% FAME yield for each catalyst. Therefore, 60 min reaction time is used for further investigations.

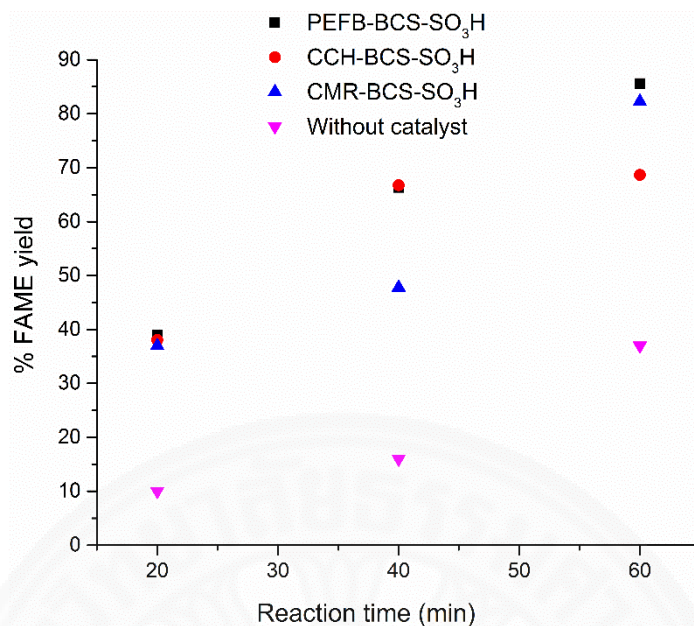


Fig. 4.36 Effect of reaction time on FAME yield (%) in a microwave assisted reactor with 5 wt. % catalyst and 12:1 methanol to oil molar ratio at 70 °C

Both esterification and trans-esterification reactions are reversible, and thus, an excess of methanol in the reaction medium is required to shift the reaction equilibrium. Therefore, experiments are carried out to find the optimum methanol:oil (molar ratio) for biodiesel production from WPO in a microwave assisted reactor. It is found that low methanol loadings, such as 3:1 and 6:1 gave very low %FAME yields during the preliminary experiments. As stated by Encinar et al. (2012), 65-90 °C is the best reaction temperature range for microwave assisted biodiesel production. Therefore, 70 °C is selected as the initial reaction temperature for the experiments. This is slightly beyond the boiling point of methanol, and therefore, a loss of methanol is possible during the reaction. As seen in Fig. 4.37, %FAME yield increases with increasing methanol to oil molar ratio for PEFB-BCS-SO₃H and CMR-BCS-SO₃H catalysts while %FAME yield of CCH-BCS-SO₃H catalyzed reaction decreases after 16:1 methanol to oil molar ratio. A higher methanol loading increases the rate of the reaction due to increase in the contact between alcohol and triglycerides (Tangy et al., 2017). However, it is found that PEFB-BCS-SO₃H and CMR-BCS-SO₃H gave

maximum of >95% and 89% FAME yield at 20:1 methanol to oil molar ratio while CH-BCS-SO₃H gave 84.5% FAME yield at 16:1 methanol to oil molar ratio.

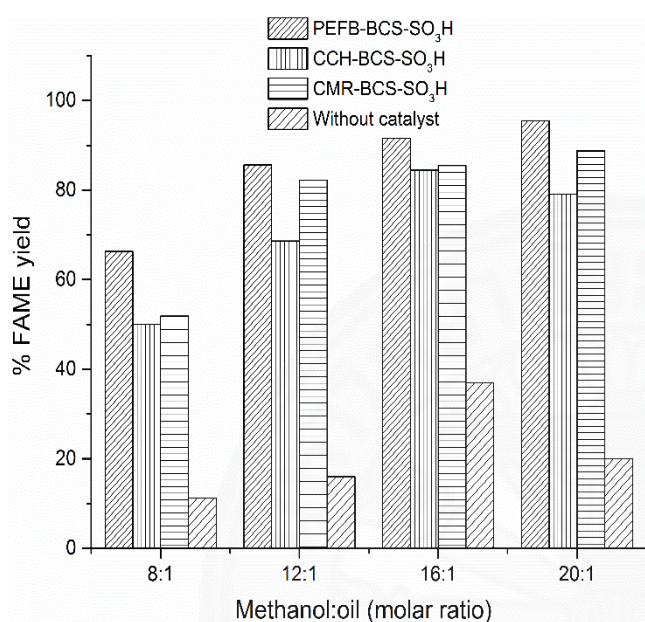


Fig. 4.37 Effect of methanol:oil molar ratio on FAME yield (%) in a microwave assisted reactor with 5 wt.% catalyst at 70 °C for 60 min

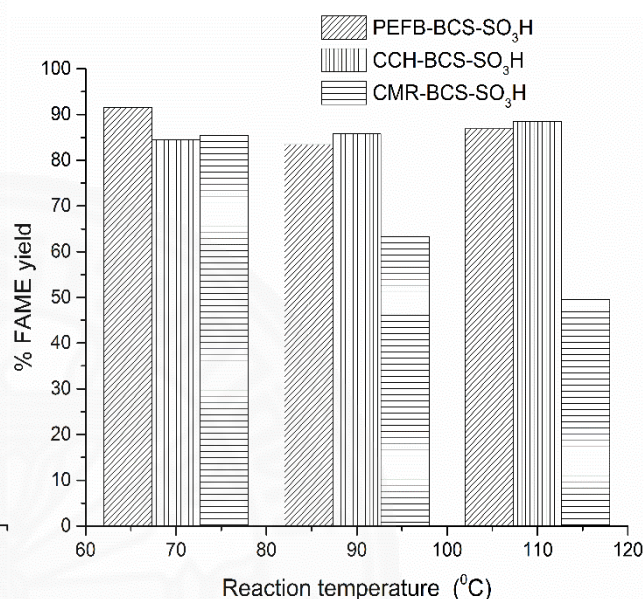


Fig. 4.38 Effect of reaction temperature on FAME yield (%) in a microwave assisted reactor with 5 wt. % catalyst and 16:1 methanol to oil molar ratio for 60 min

The effect of three different temperatures, such as 70, 90, and 110 °C on biodiesel production from WPO are investigated using 16:1 methanol:oil molar ratio. The results are shown in Fig. 4.38. The highest FAME yield of 91.6% and 85.5% are shown by PEFB-BCS-SO₃H and CMR-BCS-SO₃H catalysts at 70 °C, respectively, while the CCH-BCS-SO₃H catalyst shows its highest %FAME yield (88.5%) at 110 °C. As stated by Encinar et al. (2012), methanol starts to boil after the boiling point, and methanol vapor can effectively contact with oil, providing a higher conversion. This may be the reason for a higher biodiesel yield of >80% for each catalyst at 70 °C. However, a further increase of the reaction temperature increases the methanol evaporation, leading a complete separation of methanol in the vapor phase and oil at the liquid phase (Choedkiatsakul et al., 2015; Encinar et al., 2012). This may be the

reason that there is a low %FAME yield with high reaction temperatures after 70 °C. However, it is found that the activity of CCH-BCS-SO₃H catalyst slightly increases with increasing reaction temperature.

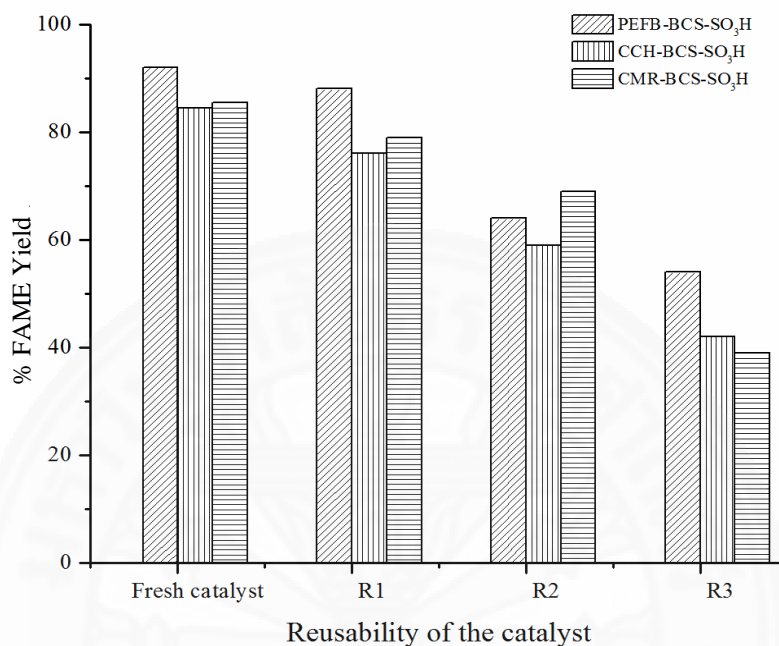


Fig. 4.39 Reusability of PEFB-BCS-SO₃H, CMR-BCS-SO₃H, and CCH-BCS-SO₃H for FAME production from WPO in a microwave assisted reactor with 5 wt. % catalyst and 16:1 methanol to oil molar ratio at 70 °C for 60 min

When investigating the reusability of the catalyst, it is found that the FAME yield decreases with each run (Fig.4.39). It is found that the FAME yield decreases significantly from 91.6 to 54 %, 85.5 to 39% and 84.5 to 42% for PEFB-BCS-SO₃H, CMR-BCS-SO₃H, and CCH-BCS-SO₃H, respectively, after third usage. Results reveal that PEFB-BCS-SO₃H, CMR-BCS-SO₃H, and CCH-BCS-SO₃H catalysts have very low stability. This is further confirmed by the decrease of total acid density of each catalyst after the reaction (Table 4.3). As reported in previous sections, the leaching of SO₃H groups is one of the main reasons for decrease in the activity, hence, measures should be taken in order to enhance the stability of SO₃H in catalysts.

In addition, CMR-DS-SO₃H which showed a higher catalytic activity during an open reflux reactor and an autoclave reactor assisted biodiesel production, is studied for a microwave reactor assisted biodiesel production. The effects of reaction time, temperature, and catalyst loading on FAME yield, and the reusability are investigated using the optimum methanol loading (12:1 methanol to oil molar ratio) as found from the open reflux reactor.

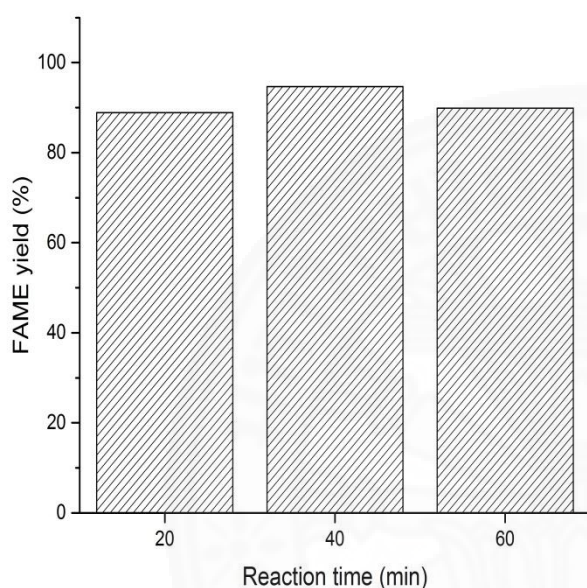


Fig. 4.40 Effect of reaction time on FAME yield (%) in a microwave assisted reactor with 5 wt. % CMR-DS-SO₃H and 12:1 methanol to oil molar ratio at 70 °C

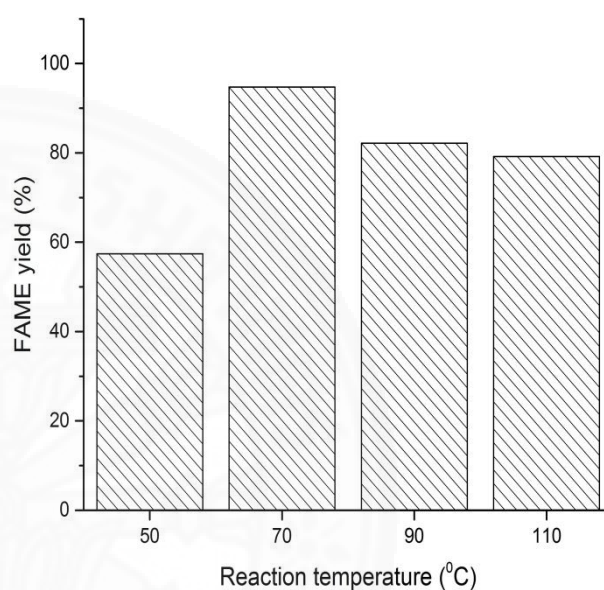


Fig. 4.41 Effect of reaction temperature on FAME yield (%) in a microwave assisted reactor with 5 wt. % CMR-DS-SO₃H and 12:1 methanol to oil molar ratio and 40 min

When investigating the reaction time on %FAME yield in a microwave reactor, it is found that CMR-DS-SO₃H gives maximum FAME yield of 94.7% using 5 wt. % catalyst, 12:1 methanol:oil (molar ratio) at 70 °C and 40 min (Fig. 4.40). This is very low reaction time compared to a conventional open reflux reactor and an autoclave assisted biodiesel production. As stated by Chen and Cui (2016), higher activity of the sulfonated catalyst in a microwave reactor is attributed to the special amorphous nature and the presence of polar functional groups (SO₃H and COOH) in the catalyst. These polar functional groups form local hot spots inside the catalysts by absorbing microwave power which triggers the rate of reaction. However, it is found that %FAME yield slightly decreases with increasing reaction time after 40 min. The reaction may reach to equilibrium at 40 min and a

further increase of the reaction time decreases the %FAME yield. A decrease of the %FAME yield after 40 min reaction time may also be possible due to the deactivation of the catalyst by accumulated water as a result of increase rate of esterification, as well as long time exposure to microwave power. Therefore, 40 min reaction time is used for further investigations.

The effect of reaction temperature on FAME yield is shown in Fig. 4.41. It is shown that an increase of reaction temperature after 70 °C decreases the %FAME yield. This may be attributed to the possible evaporation of methanol during the reaction as the temperature rises far beyond the boiling point.

Additionally, it is found that the catalyst loading after 5 wt. % decreases the %FAME yield for microwave assisted biodiesel production from CMR-DS-SO₃H (Fig. 4.42). An increase of catalyst loading increases the bulk mass fraction of the reaction, which decreases the reactant diffusion and the rate of the reaction. However, a 20% of FAME yield was obtained in the control experiment conducted without using the catalysts.

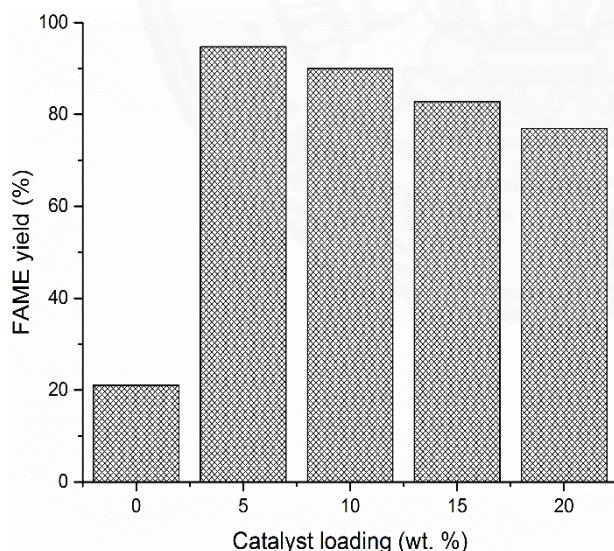


Fig. 4.42 Effect of CMR-DS-SO₃H loading on FAME yield (%) in a microwave assisted reactor with 12:1 methanol to oil molar ratio at 70 °C for 40 min

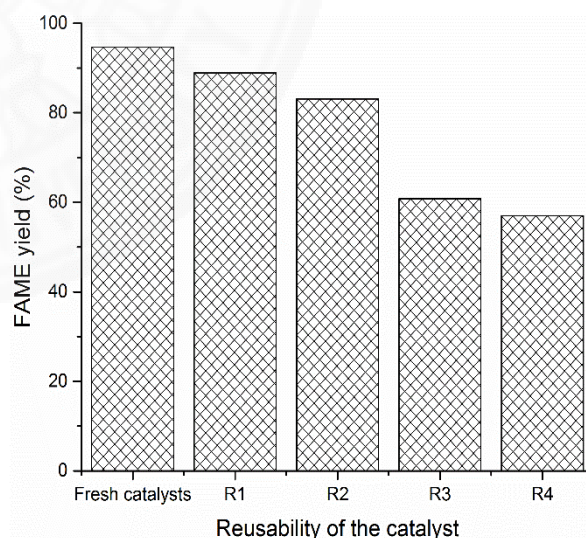


Fig. 4.43 Reusability of CMR-DS-SO₃H for FAME production in a microwave assisted reactor with 5 wt. % catalyst and 12:1 methanol to oil molar ratio at 70 °C for 40

Reusability of the catalyst is studied and results are shown in Fig. 4.43. A slight decline of the FAME yields for first and second run was observed with reused catalyst whereas a significant decrease of FAME yield resulted at third and fourth run. The decline of the catalytic activity is possible due to deactivation of functional groups. It is found that the total acid density of the catalyst decreases from 3.80 to 2.92 mmol g⁻¹ after first run claiming for a possible degradation during microwave assisted biodiesel production. However, these data reveals that degradation of the catalyst in microwave assisted biodiesel production is higher compared to a conventional open reflux reactor and an autoclave reactor assisted biodiesel production. The local hot spots formed inside the catalysts by absorbing strong microwave power, may lead to degradation of functional groups when exposed for long time.

4.4.4 Comparison of biodiesel production from WPO and CMR-DS-SO₃H using three different reactors

According to the results, it is found that CMR-DS-SO₃H is the most stable catalyst and it shows the highest activity for biodiesel production. The activity of the catalyst for biodiesel production in a conventional open reflux reactor, an autoclave reactor, and a microwave assisted reactor is summarized in Table 4.7. The energy requirement of the each reactor for production of 1 kg of biodiesel is tabulated in Table 4.8.

Table 4.7 Comparison of the activity of CMR-DS-SO₃H catalyst using different reactors

	Methanol:oil (molar ratio)	Catalyst loading (wt.%)	Reaction temperature (°C)	Reaction time (h)	FAME yield (%)	Reusability
Reflux reactor	12:1 (optimum)	5% (optimum)	65-70	12	92.7	>80, for 4 cycles
Autoclave reactor	12:1*	5%*	150	3	95.5	>80, for 4 cycles
Microwave reactor	12:1*	5% (optimum)	70	0.67	94.7	> 50, for 4 cycles

Remark:* Optimum condition from reflux reactor

Table 4.8 Comparison of energy consumption by three different methods

Reactor	Heating capacity (W)	Reaction time (h)	Energy requirement		
			kWh	kWhKg ⁻¹ (If 50 g of biodiesel produced per run)	kWhkg ⁻¹
Reflux reactor	500	12	6	(6/50)* 1000 g	120
Autoclave reactor	1073	3	3.22	(3.22/50)*1000 g	64.4
Microwave reactor	400	0.67	0.27	(0.27/50)* 1000 g	5.4

Remarks:* it is assumed that 50 g of biodiesel can be produced using the maximum volume of the reactor per each run

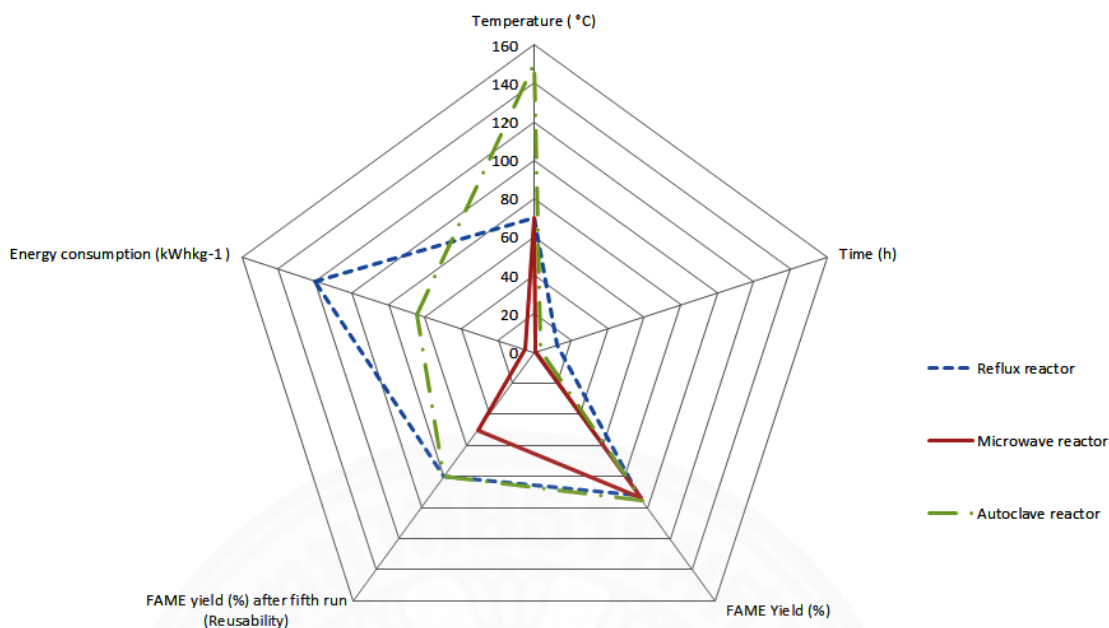


Fig. 4.44 Comparison of the activity of CMR-DS-SO₃H using different reactors

As depicted in Fig. 4.44, it is found that biodiesel production in each process reaches >90% FAME yield at optimum conditions. However, results show that an open reflux reactor requires longer reaction time (12 h) compare to the other reactors. This may affect to the stability of the catalyst as long time exposure to methanol and water can deactivate the catalyst. Also, an increase of the reaction time increases the required amount of energy for biodiesel production. Even though, microwave assisted reaction achieved >94% FAME yield at 70 °C within 40 min, the reusability of the catalysts is very low compared to the other methods. An autoclave assisted biodiesel production is capable of producing 95.5% high biodiesel production at 150 °C in 3 h and reusability of the catalyst is also high (>80% FAME yield), even after fifth run.

The economic viability of the each method is compared for 1 kg of biodiesel production, assuming that 50 g of biodiesel can be produced from each reactor per each run (Table 4.8). It is found that the energy requirement for microwave heating is much lower than the hot plate assisted heating in an open reflux reactor

and an autoclave reactor assisted heating. The conventional open reflux reactor requires the maximum 120 kWhkg^{-1} energy for production of 1 kg of biodiesel due to the requirement of a longer reaction time. However, the actual energy consumption may low in each reactor since the actual/average usage is lower than the maximum requirement. The total cost of 1 kg of biodiesel production from WPO using CMR-DS-SO₃H catalyst in each reactor is calculated in Appendix C. It is found that the cost of biodiesel produced in this study is about $\$2.5 \text{ kg}^{-1}$, which is a higher value compared to the price of biodiesel ($\$1.12 \text{ L}^{-1}$) and diesel ($\0.81 L^{-1}) in Thailand. Since, these calculations are based on the current study which was carried out in a lab scale, the actual energy consumption, and also the cost of raw materials may low when used in the large scale, decreasing the cost of biodiesel.

However, according to the results it can be concluded that even though each process has its own advantages and disadvantages, CMR-DS-SO₃H catalyst is successful in biodiesel production. The catalyst is used to produce >90% FAME yield at optimum reaction conditions. Therefore, it is required to conduct a life cycle analysis of entire biodiesel production to understand the affirmative cost effectiveness and sustainability of the process.

4.5 Fuel characteristics of produced biodiesel

The fuel properties of biodiesel depend on several factors, such as the type/composition of biodiesel feedstock, and the production process (Babaki et al., 2015). Therefore, biodiesel produced by using WPO and PEFB-DS-SO₃H (in an open reflux reactor), CMR-DS-SO₃H (in an open reflux reactor, an autoclave reactor, and a microwave assisted reactor), and CCH-DS-SO₃H (in an autoclave reactor), are analyzed in order to find that produced biodiesel meets international fuel standards. The fuel properties of produced biodiesel are tabulated in Table 4.10 along with a comparison to the international and Thailand biodiesel standards.

4.5.1 Acid value

Acid value of biodiesel is a measure of the residual FFA content and other mineral acids, thus a direct measure of the corrosiveness of the fuel. According to ASTM 6751 and EN 14214, maximum allowed acid value for biodiesel is $0.5 \text{ mg KOH g}^{-1}$. It is found that acid values of the biodiesel produced by using PEFB-DS-SO₃H (in an open reflux reactor), and CMR-DS-SO₃H (in an open reflux reactor and an autoclave reactor), are under the international standards. Sulfonic acid groups which are leaching out from the sulfonated SACs is the main reason for an increase of the acid value of biodiesel produced, in this study. Even though biodiesel cleaning by using hot water washing removes the residual sulfonic acids presented, the acid value of biodiesel produced using CCH-DS-SO₃H (in an autoclave reactor) and CMR-DS-SO₃H (in a microwave reactor) are slightly higher than the recommended value ($0.5 \text{ mg KOH g}^{-1}$). This is due to the possible leaching of active functional groups, such as sulfonic acid groups from the catalysts. Therefore, it is required to purify biodiesel more vigorously in order to remove all the sulfonic acid groups. In addition, it is necessary to take measures to enhance the stability of the functional groups of the catalysts.

4.5.2 Viscosity

Kinematic viscosity of biodiesel is a critical fuel property, since it affects the behavior of the fuel injection. The viscosity of biodiesel is generally higher than conventional diesel due to the presence of electronegative oxygen in biodiesel (Sarin, 2012). It is essential to have fuel viscosity under the recommended level as both higher and lower viscosity can disturb the engine in various ways. ASTM 6751 and EN 14214 standard specifications for viscosities are 1.9-6.0 and 3.5-5.0 mm^2s^{-1} , respectively, at 40 °C. It is found that viscosity values for produced biodiesel are under the recommended value for ASTM 6751. Therefore, no hardware modification is required in handling the biodiesel in existing engines. However, it is found that the biodiesel produced in an autoclave reactor using

CMR-DS-SO₃H and CCH-DS-SO₃H catalyst showed slightly lower viscosities of 2.7 and 2.9 C mm²s⁻¹, respectively. A low viscous biodiesel makes the black smoke during combustion due to formation of very fine spray with low mass which limits sufficient penetration (Barabás & Todoruț, 2011; Bățaș et al., 2003).

4.5.3 Density

Density of the biodiesel is another critical property since it directly affects the fuel performance as some of the engine properties, such as cetane number, heating value, and viscosity are strongly connected to the density. The density of biodiesel is generally higher than the diesel fuel. It relies on the fatty acid composition and purity of the biodiesel, and can be considered as an indicator of the contamination. However, the density values for biodiesel is slightly changed between the limits as the biodiesel is made up of a similar types of methyl esters (Barabás & Todoruț, 2011). It is found that densities of produced biodiesel are in the range of 830-840 kgm⁻³ at 30 °C. According to EN 14214, density is measured at 15 °C and the required specification is 860-900 kgm⁻³.

Table 4.9 Fuel properties of produced biodiesel

	Waste palm oil	PEFB-DS-SO ₃ H catalyzed biodiesel (Reflux)	CMR-DS-SO ₃ H catalyzed biodiesel (Reflux)	CMR-DS-SO ₃ H catalyzed biodiesel (Autoclave)	CMR-DS-SO ₃ H catalyzed biodiesel (Microwave)	CCH-DS-SO ₃ H catalyzed biodiesel (Autoclave)	Thailand standards	ASTM D 6751	EN 14214	Diesel
Acid value (mg KOH g ⁻¹) ASTM D664	10.3	0.43	0.5	0.48	0.6	0.51	0.5	0.5 max	0.5 max	-
Kinematic viscosity at 40 °C (mm ² s ⁻¹) ASTM D446	24.1	4.04	3.12	2.7	3.5	2.9	3.5	1.9-6.0	3.5-5.0	2.0-4.5
Density at 30 °C (kgm ⁻³)	970	834	840	838	836	830	860*	860-900*	860-900*	820-845
Heating value (MJkg ⁻¹) ASTM D240-2	-	39.1	34.72	37.8	39.0	39.1	-	37.27	-	45.5
Oxidation stability (h) EN 15751	-	66.7	30	9.9	9.9	4	10 min	3 min	8 min	-
Flash point (°C) ASTM-D92	300	260	260	230	246	-	120	> 93	> 120	55
Pour point (°C) ASTM-D97	-23	-8.5	-6.5	-7.3	-9.3	-6.8	-	-	-	-19
Ash content (wt.%) ASTM-D482-13	0.430	0.004	0.009	0.004	0.010	0.009	0.02	0.01	0.01	0.01
S content (wt. %)	0.0016	0.0038	0.0012	0.0001	0.1296	0.0039	0.0010	0.0015	0.001	0.001-0.005

Remark:* Biodiesel density at 15 °C.

4.5.4 Heating value

Heating value of biodiesel is different depending on the biodiesel feedstock and 10-15% lower than the conventional diesel (43-45 MJkg⁻¹) (Ali et al., 2015; Ghazali et al., 2015). This study found that the heating values of produced biodiesel are 39.1 (PEFB-DS-SO₃H, an open reflux reactor), 34.7 (CMR-DS-SO₃H, an open reflux reactor), 37.8 (CMR-DS-SO₃H, an autoclave reactor), 39.0 (CMR-DS-SO₃H, a microwave reactor), and 39.1 MJkg⁻¹ (CCH-DS-SO₃H, an autoclave reactor). The higher heating value (39.1 MJkg⁻¹) of biodiesel may be due to the presence of long carbon chains (Ghazali et al., 2015; Oliveira & Da Silva, 2013). However, as mentioned by Barabás and Todoruț (2011), oxidation of biodiesel during storage decreases the heating value. Also, the presence of high amounts of short carbon chains which are possible due to oxidation of biodiesel, decreases the heating value (Oliveira & Da Silva, 2013). Even though, the values are not so deviated from the reported higher heating values in the literature, these are the possible reasons for comparatively lower heating value of CMR-DS-SO₃H (an autoclave reactor), and CMR-DS-SO₃H (an open reflux reactor) produced biodiesel.

4.5.5 Oxidation stability

Biodiesel can be degraded during storage and handling, due to the presence of unsaturated compounds. Also, biodiesel are more prone to the oxidation when the feedstocks contain a high amount of oleic and linoleic acid contents (Agarwal et al., 2015). This is a major drawback of biodiesel compared to the conventional diesel fuel, since biodiesel has a poor oxidation stability (Kumar, 2017). Features, such as acid value, viscosity, and heating value are changed with the degradation of biodiesel (Barabás & Todoruț, 2011). It is found that oxidation stability of the biodiesel produced using an open reflux reactor (PEFB-DS-SO₃H and CMR-DS-SO₃H) is higher than the biodiesel produced from an autoclave reactor and a microwave reactor. They meet the minimum requirement according to ASTM D

6751. Biodiesel produced using PEFB-DS-SO₃H in an open reflux reactor showed a higher oxidation of 66.7 h. As reported by Han and May (2012), PEFB contains phenolic compounds which exhibits antioxidant property. The catalyst may still release some antioxidants during biodiesel production which increase the stability of the produced biodiesel.

4.5.6 Flash point

Flash point is the minimum temperature at which the fuel starts to ignite. Even though flash point does not affect the combustion directly, biodiesel is safe for storage and transportation when it has higher flash point value. The flash point is an indicator of the residual methanol in the biodiesel and decreases with the increase of residual methanol (Barabás & Todoruț, 2011). It is found that, flash points of biodiesel produced in this study are higher than the recommended specifications and satisfy both ASTM and EN standards.

4.5.7 Pour point

Pour point of a fuel is defined as the temperature at which fuel cease to flow. However, pour point of biodiesel is mainly related with the feedstock type. According to (Moser (2008)), the pour point of palm oil is 15 °C and it would be reduced for waste palm oil. It is found that pour point of waste palm oil used for this study -23 °C. Biodiesel produced in this study shows lower pour point values ranging from -9.3-(-6.5), confirming the ability of use of these biodiesel in cold climate conditions.

4.5.8 Ash content

Ash content of biodiesel is an indicator of the presence of impurities, such as inorganic metallic compounds, soaps, glycerides, and residuals of catalysts

(Barabás & Todoruț, 2011). As shown in Table 4.10, ash contents of the produced biodiesel are under the recommended values for biodiesel standards.

4.5.9 Sulfur content

Biodiesel is popular than conventional diesel fuels due to the presence of ultra-low sulfur composition. However, biodiesel can be contaminated from sulfur which may be from the feedstock, or from the catalysts. Sulfonic acid groups which are leaching out from the sulfonated SACs are a main source of sulfur in biodiesel. Therefore, it is vital to determine the sulfur content of biodiesel. It is found that sulfur contents of produced biodiesel are in the range of international standards except biodiesel produced by using CMR-DS-SO₃H in a microwave assisted reactor (0.1296 wt.%). This is due to the leaching of sulfonic acid groups from the catalyst during the reaction. Therefore, it is important to take measures to increase the stability of the catalyst during the microwave assisted biodiesel production. This helps to increase the yield while increasing the quality of the biodiesel.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

Both WPO and biomass, such as PEFB, CMR, and CCH as waste were used for economical and sustainable biodiesel production. Six types of promising SACs were successfully prepared from three different waste biomass using two methods (DS and BCS), and employed for biodiesel production from WPO with 5.2% FFA. XPS, FT-IR, acid value, and the elemental analysis confirmed the activation of the catalysts with main functional groups, such as SO_3H , COOH , and OH . Results show that the DS protocol is more efficient in catalyst preparation and provides high sulfonic acid groups compared to the BCS protocol and they showed a higher acid density despite a low surface area. Thermal stability of all the catalysts was found below 200 °C.

It was found that PEFB-DS- SO_3H and CMR-DS- SO_3H show a higher catalytic activity compared to other catalysts for biodiesel production from WPO in an open reflux reactor. PEFB-DS- SO_3H and CMR-DS- SO_3H obtained maximum FAME yields of 91% and 92.7% using the optimum reaction conditions of 5 wt.% catalyst, 14:1 and 12:1 methanol to oil (molar ratio), after 14 h and 12 h, respectively, at 65-70 °C. Even though the activity of the catalysts slightly decreases after reuse, both catalysts were able to achieve >70% FAME yield, after fifth run. CMR-DS- SO_3H obtained a maximum biodiesel yield of 95.5% at 150 °C after 3 h using 5 wt.% catalyst, a 12:1 methanol:oil (molar ratio) in an autoclave reactor. CCH-DS- SO_3H also showed an excellent activity in an autoclave reactor. It can be concluded that the biodiesel production in an autoclave reactor is efficient and required relatively shorter reaction time compared to an open reflux reactor. Nevertheless, when investigating on the catalytic activity for biodiesel production in microwave assisted reactor, CMR-DS- SO_3H obtained a maximum FAME yield of 94.7% using 5 wt. % catalysts and a 12:1 methanol:oil molar ratio at 70 °C and 40 min. Similarly high FAME yields

were shown by PEFB-BCS-SO₃H and CMR-BCS-SO₃H using microwave assisted reactor. However, results reveal that catalysts were considerably degraded in microwave assisted reactor compared to an open reflux reactor and an autoclave reactor assisted biodiesel production. Deactivation of the catalyst during the reaction over the time is challenging for a large scale biodiesel production. In general, increasing methanol loading, reaction time, and temperature up to an optimum value, increases the FAME yield in each reactor. Based on the results, it can be concluded that catalysts prepared for direct in-situ sulfuric carbonization showed relatively high catalytic activity compared to the catalysts prepared from sulfonation of incompletely carbonized biomass despite of the relatively small surface area. Oxygen rich functional groups in biomass may support for a greater degree of sulfonation in this method as compared to the sulfonation of incompletely carbonized biomass. Relatively higher activity of the catalysts may also be attributed to the presence of large number of strong (SO₃H) and weak (COOH, OH) acid groups bonded to the hydrophobic carbon frame. In addition, it is found that a conventional open reflux reactor assisted biodiesel production has the highest energy consumption, among the three different reactors used.

Fuel properties, such as kinematic viscosity, density, flash point, pour point, heating value, oxidation stability, and ash content of produced biodiesel were according to the international standards. Therefore, prepared biodiesel can be used. Leaching of some active sulfonic groups from the catalysts increases the acid value of the produced biodiesel during the reaction causing loss of the activity over time and contaminating the final product. Therefore, it is required to take measures to improve the stability of the catalysts and to control the quality of the biodiesel.

Results conclude that the prepared SACs can be successfully used in one-step lab scale biodiesel production from WPO with high FFAs content. Fuel properties of the prepared biodiesel were found to meet the international standards. Therefore, these catalysts are promising alternatives for conventional catalysts used in industrial

biodiesel production. The use of recyclable SACs which are not sensitive to the FFAs eliminates unnecessary side reactions, decreasing the complicated downstream processes. One-step direct biodiesel production avoids costly pre-treatment of acidic feedstocks and increases the product yield. This improves the economy and the sustainability of the biodiesel industry.

5.2 Recommendations for future work

The results of the experimental work indicate a number of areas that would be interesting for further research and are discussed below.

This study focused on the experimental and technical aspects of biodiesel production from WPO using carbon based SACs. Use of waste biomass for biodiesel production is sustainable approach. However, a detailed analysis is required to understand the economic and environmental viability. Therefore, a life cycle analysis of use of waste biomass derived SACs for biodiesel production is required. Since it is found that different biodiesel production processes affect differently to biodiesel production for different catalysts, it is required to analyze the entire biodiesel production process via life cycle analysis.

Additionally, it can be recommended that an investigation of kinetic mechanism of biodiesel production from WPO and waste biomass derived SACs would be important.

Since, it is found that catalysts are degraded during the reaction, it is very important to study on possible catalyst deactivation mechanism.

It was found that biodiesel produced using PEFB-DS-SO₃H in a reflux reactor shows the highest oxidation stability. This may be due to possible release of antioxidants from the catalyst during biodiesel production. Therefore, it is recommended to investigate the phenomena behind this as this increases the quality of the biodiesel.

In addition, even though this study investigated about some of the important fuel properties of produced biodiesel, it is required to understand the engine performance and the emission profiles of biodiesel. Therefore, it is required a life cycle evaluation of biodiesel produced in this study in order to understand the overall cost and benefits compared to the conventional diesel fuel. This study was a laboratory scale project which evaluated feasibility of use of waste biomass for carbon based SACs preparation. Since, the biodiesel produced in this study is according to the international fuel standards, a pilot scale biodiesel production is recommended.



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Appendices

Appendix A

Experimental data

1. XPS spectra of raw biomass, fresh catalyst, and used catalysts

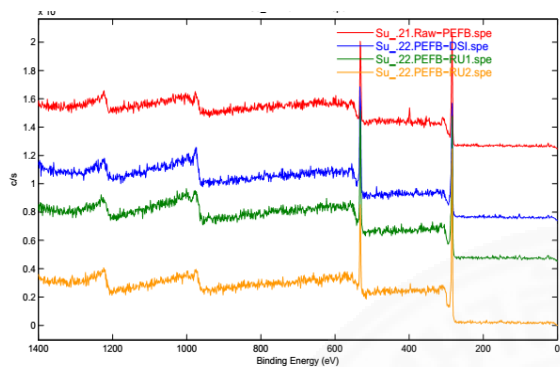


Fig. 1A Raw PEFB, PEFB-DS-SO₃H, used catalysts in reflux reactor

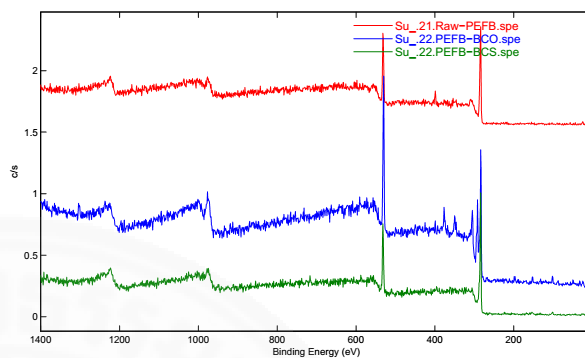


Fig. 2A Raw PEFB, carbonized PEFB PEFB-BCS-SO₃H

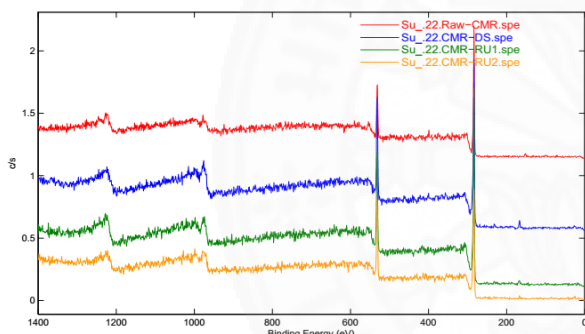


Fig. 3A Raw CMR, CMR-DS-SO₃H, used catalysts in reflux reactor

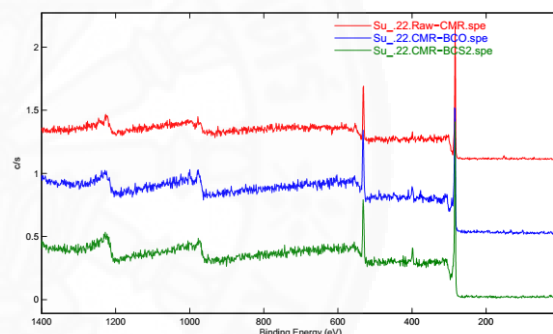


Fig. 4A Raw CMR, carbonized CMR, CMR-BCS-SO₃H

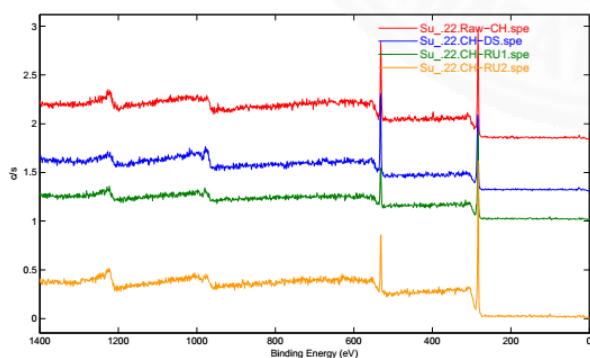


Fig. 5A Raw CCH, CCH-DS-SO₃H, used catalysts in reflux reactor

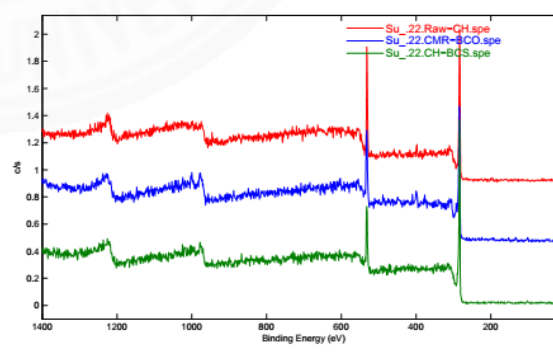


Fig. 6A Raw CCH, carbonized CCH, CCH-BCS-SO₃H

2 Chromatogram of few selected ester yield using different catalysts

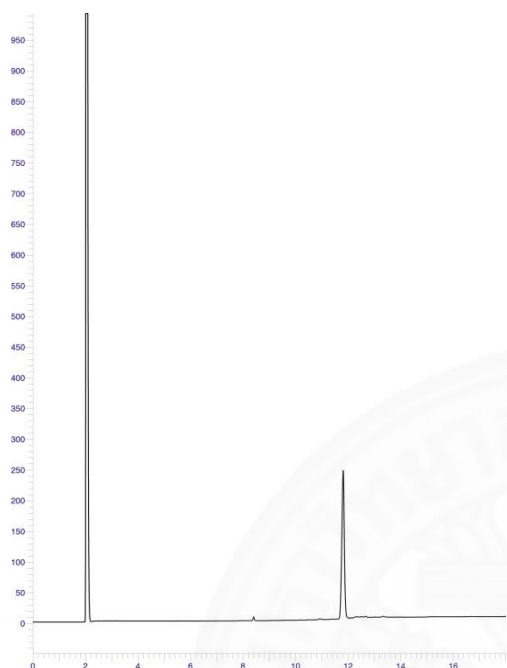


Fig. 1A Chromatogram with Standard (C17)

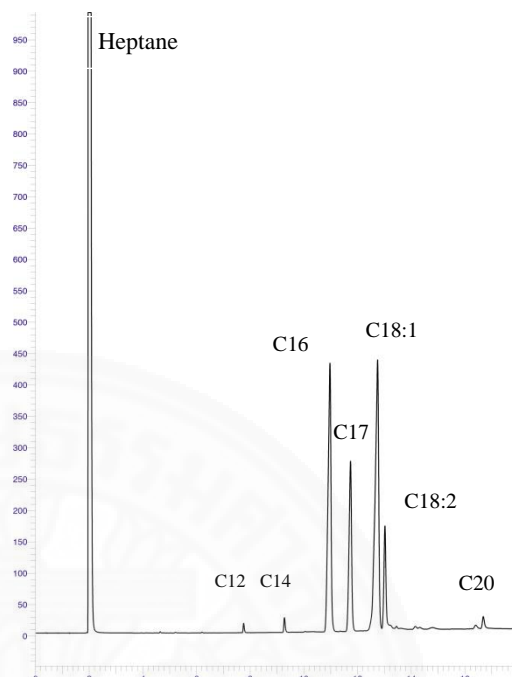


Fig. 2A Chromatogram of H₂SO₄ catalyzed biodiesel produced in an open reflux reactor

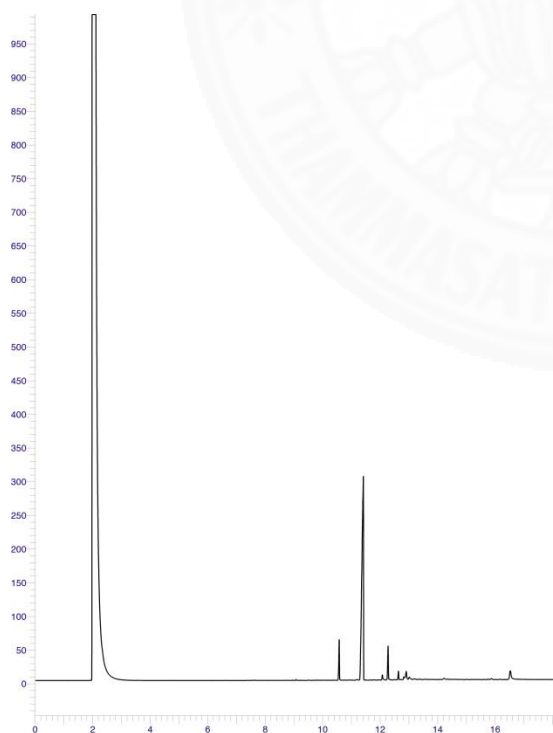


Fig. 3A Chromatogram of control experiment (without catalyst) in an autoclave reactor

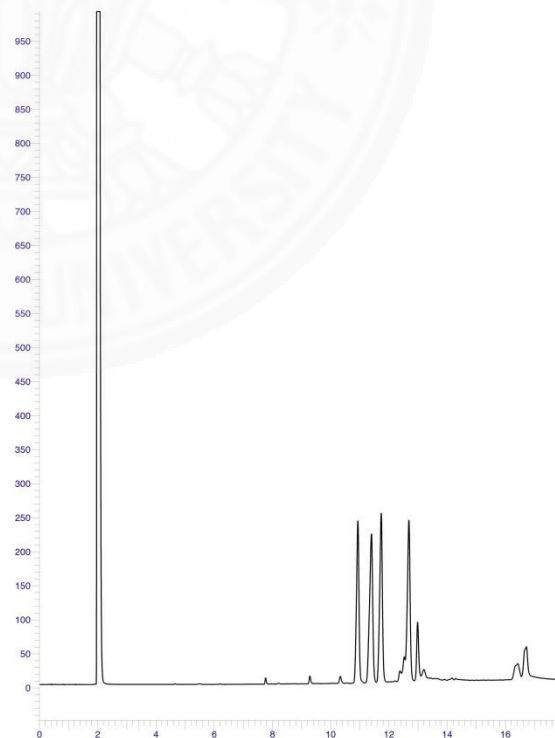


Fig. 4A Chromatogram of PEFB-DS-SO₃H catalyzed biodiesel produced in an open reflux reactor

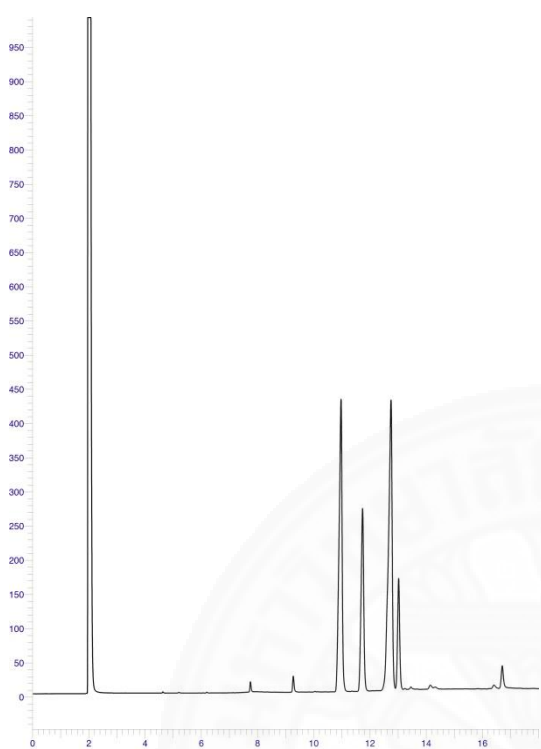


Fig. 5A Chromatogram of CMR-DS-SO₃H catalyzed biodiesel produced in an autoclave reactor

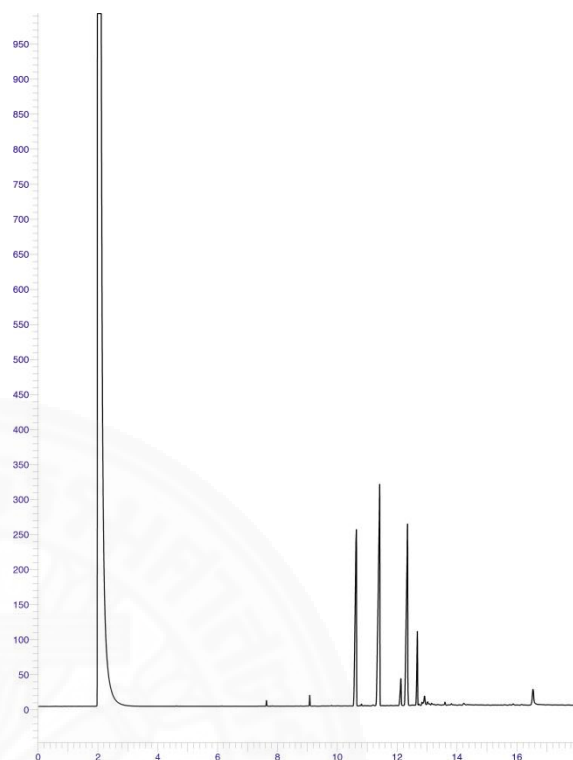


Fig. 6A Chromatogram of CCH-DS-SO₃H catalyzed biodiesel produced in an autoclave reactor

3. Analysis condition according to standard method of EN 14103

1. Capillary column - HP-INNOWAX
 - Length: 30 m
 - Internal diameter: 0.25 mm
 - Film thickness: 0.25 μm

Table 1A Column temperature programme

	Temperature °C	Rate/min
Initial	80	15
2	200	10
3	250	end

2. Variable flow split injector
 - Split flow rate: 27 mlmin^{-1}
 - Temperature: 250 °C
3. Carrier gas: Helium
 - Pressure: 14.9 psi
 - Flow: 1 mlmin^{-1}
4. Flame ionization detector
 - Temperature: 250 °C
5. Reagents
 - Heptane
 - Methyl heptadecanoate (C 17, 99% minimum)
6. Preparation of internal standard
 - Methyl heptadecanoate 10 mgml^{-1} solution
 - 100 mg of methyl heptadecanoate was dissolved with heptane in a 10 ml volumetric flask.
7. Preparation of sample (FAME)
 - 50 mg of sample was dissolved with 1 ml of methyl heptadecanoate solution in vial.
8. Injection of sample to GC
 - 1 μL of prepared sample will be injected at GC injection port by using auto sampler

4 Preliminary experiment for microwave assisted biodiesel production

- Effect of reaction time on FAME yield (%) using 5 wt. % catalyst, 6:1 methanol: oil (molar ratio) at 60 °C.

Table 2A Biodiesel yield during preliminary experiments using microwave reactor

Reaction time (min)	FAME yield (%)	
	PEFB-DS-SO ₃ H	PEFB-BCS-SO ₃ H
5	9.23	8.7
10	16.1	21.5
15	32.0	28.5

- Effect of reaction time on FAME yield (%) using 5 wt. % catalyst, 6:1 methanol: oil (molar ratio) at 80 °C.

Table 3A Biodiesel yield during preliminary experiments using microwave reactor

Reaction time (min)	PEFB-DS- SO ₃ H	CMR-DS- SO ₃ H	CCH-DS- SO ₃ H	PEFB-BCS- SO ₃ H
5	19.5	15.9	9.6	20.6
10	17.5	29.5	12.5	21.7
15	30.2	39	32	25.5

Appendix B

Experimental setups

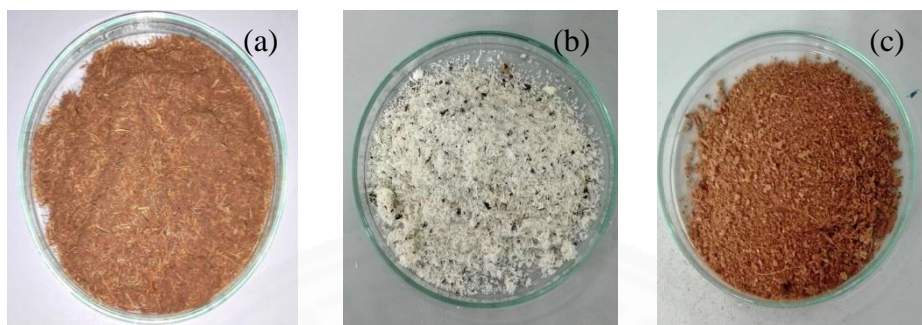


Fig. 1B carbon precursors (a) PEFB, (b) CMR, and (c) CCH

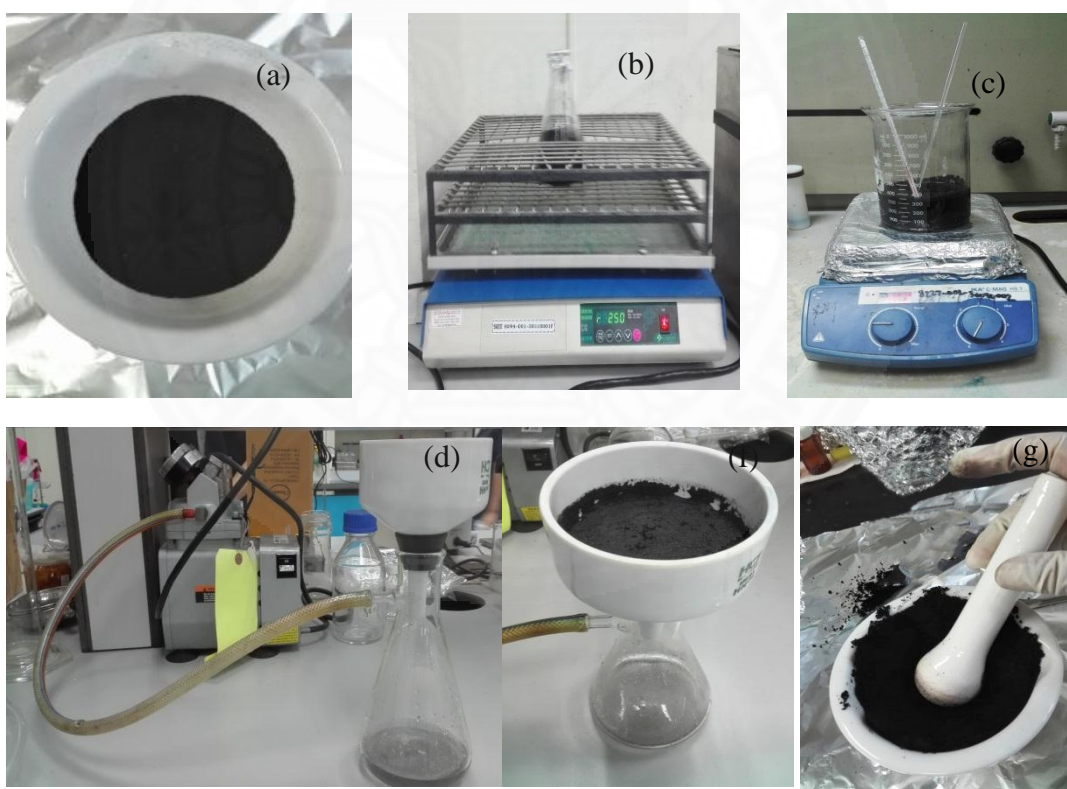


Fig. 2B Catalysts preparation (a) incompletely carbonized biomass, (b) sulfonation (c) direct in-situ sulfuric carbonization, (d and f) Vacuum filtered catalyst, and (g) powdered DS catalyst



Fig. 3B Biodiesel production (a) conventional open reflux reactor, (b) microwave reactor, (c) autoclave reactor, and (d) phase separation of biodiesel produced in (d1) autoclave reactor, (d2) microwave reactor, and (d3) autoclave reactor



Fig. 4B Experimental setups used for biodiesel characterization (a) viscometer, (b) pour point tester, (c) bomb calorimeter, (d) open-cup flash point tester

Appendix C

Cost of Biodiesel Production

The cost of catalyst preparation from CMR by DS protocol, and 1 kg of biodiesel production from WPO using the prepared catalyst was calculated. Results are presented in Table 1C and 2C.

Table 1C The cost of catalyst preparation

	Mass (kg)	Volume (L)	Energy (kWh)	Unit price (\$)	Price (\$)
CMR	1.5				-
H ₂ SO ₄	7.5	4.1		12.41L ⁻¹	50.88
Electricity for Grinding			0.16*0.55 =0.09		
Biomass drying in oven			5*1.6 =8		
Treatment using a hot plate			1*0.5 =0.5		
Vacuum filtration			0.25*0.1 =0.025		
Catalysts drying in oven			2*1.6 =3.2		
Total electricity			11.81	0.006kWh ⁻¹	0.07
Wash Water	400	400		2.7x10 ⁻⁴ L ⁻¹	0.10
Total cost for 1 kg of CMR-DS-SO₃H catalyst					51.05

Table 2C The cost of biodiesel production from WPO using CMR-DS-SO₃H catalyst

Cost of biodiesel production	Mass (kg)	Volume (L)	Energy (kWh)	Unit price (\$)	Biodiesel production cost for 5 kg		
					An open reflux reactor	An autoclave reactor	A microwave reactor
WCO	1.11*5			-	-	-	-
Methanol	0.456*5	0.57*5		1.6L ⁻¹	4.56	4.56	4.56
CMR catalyst	0.05+(0.0025*4)=0.06 0.05+(0.0025*4)=0.06 0.05+(0.0025*2)+0.05+0.0025=0.10			51.05kg ⁻¹	3.06	3.06	5.10
Acetone		0.25*4 0.25*4 0.25*3		4.24L ⁻¹	4.25	4.25	3.18
Electricity for 1Catalyst separation			0.1*0.25*4=0.1 0.1*0.25*4=0.1 0.1*0.25*3=0.075		0.0006	0.0006	0.00045
2 Catalyst drying			1.6*2*4=12.6 1.6*2*3=9.6 0.5*12*4=24	0.006kWh ⁻¹	0.00756	0.00756	0.00576
3Biodiesel production			1.073*3*4=12.87 0.4*0.67*4=1.072		0.144	0.077256	0.006432
Total cost for 5 kg of biodiesel					12.022	11.955	12.85

WCO and CMR were obtained free of charge. Purchasing prices of the chemicals for this study were considered. The maximum energy requirement for each reactor was considered for the calculations. The cost of energy (per kWh) was used as reported by Sakdasri et. al. (Sakdasri et al., 2018). The use of catalyst was considered for consecutive five runs, in an open reflux reactor and an autoclave reactor while that was considered for only three consecutive runs in a microwave assisted reactor. However, the capital cost, the cost of transportation of raw materials, human labor expenses, and the cost of downstream processes including waste treatment were excluded. Added values of byproducts, such as glycerol, and also methanol recycling were not accounted into the calculations.

It was found that the cost of biodiesel production is about \$2.40, 2.39, and 2.57 per kilogram in an open reflux reactor, an autoclave reactor, and a microwave reactor, respectively. As reported in Thailand industry outlook 2017-19, the average price of biodiesel is \$1.12 L⁻¹ (Krungsri, 2017), while diesel is \$0.81 L⁻¹ (Ministry of Energy, 2018). It should be noted that these calculations are based on the current study which was carried out in a lab scale. The actual energy consumption, and also the cost of raw materials may change when used in the large scale biodiesel production. Therefore, a fair comparison is not possible with the existing diesel or biodiesel price in Thailand.