EnvironmentAsia
The international journal by the Thai Society of Higher Education Institutes on Environment

EnvironmentAsia 14(1) 2021 23-32
DOI 10.14456/ea.2021.3
ISSN 1906-1714; ONLINE ISSN: 2586-8861

Production of Biodiesel from Low-Grade Crude Palm Oil Using Hydrochloric Acid

Nichmon Puagsang[1], Issara Chanakeawsomboon[2*], Suchada Chantrapromma[3] and Arkom Palamanit[4,5]

[1] *Sustainable Energy Management Program, Faculty of Environmental Management, Prince of Songkla University, Thailand*
[2] *Sustainable Innovation Center, Faculty of Environmental Management, Prince of Songkla University, Thailand*
[3] *Devision of Physical Science, Faculty of Science, Prince of Songkla University, Thailand*
[4] *Interdisciplinary Graduate School of Energy Systems, Prince of Songkla University, Thailand*
[5] *Energy Technology Program, Department of Specialized Engineering, Faculty of Engineering, Prince of Songkla University, Thailand*

* Corresponding Author: issara.c@psu.ac.th
Received: August 30, 2020; Revised: November 10, 2020; Accepted: November 21, 2020

Abstract

In this study, low-grade crude palm oil (LGCPO) containing 13.81 wt.% free fatty acid (FFA) was used as raw material. This study aimed to investigate the effects of LGCPO preparation methods on biodiesel basic properties, easing environmental impacts from sulfur emissions, and getting to zero-sulfur biodiesel. Hence, hydrochloric acid, which is an effective and environmentally friendly homogeneous acid catalyst, was selected as the catalyst to reduce FFA in pretreatment and to produce green biodiesel. The results indicate that the use 0.25 wt.% of hydrochloric acid as a catalyst in biodiesel production could efficiently reduce the FFA content to a standard level (< 2.00 wt.%) at 0.56 wt.% (FFA conversion 95.95%). The final ester contents were 98.05 and 97.31 wt.% for washed esterified palm oil (EPO) and for rinsed EPO without washing, respectively. Consequently, hydrochloric acid is a suitable catalyst and could replace the conventional sulfuric acid in biodiesel production from low quality crude palm oil. This would reduce the environmental impacts, especially sulfur emissions. High FFA leads to soap formation in fatty acid methyl ester (FAME) saponification causing problems in phase separation and emulsion formation during the purification stage, so catalytic preprocessing is a necessity.

Keywords: Biodiesel; Free fatty acid; Hydrochloric acid; Low-grade crude palm oil; Sulfuric acid

1. Introduction

Biodiesel is an alternative fuel generally made from used vegetable oil and/or animal fats. Currently, the environmental impacts and climate change caused by fossil energy utilization are driving many countries to apply renewable and alternative energy resources, especially "biodiesel" (Nikhom *et al.,* 2019).

The highest oil yield productivity per land requirement, compared with other bio-resources, is from biodiesel production from palm oil. In this present era, most people have awareness of the environment, and of renewable alternative energy sources. Biodiesel is among the main options for sheltering the environment. Furthermore, there are important advantages to producing biodiesel from palm oil, particularly in comparatively clean emissions, and engines can run smoothly with less noise due to the high cetane number (Wan *et al.,* 2015).

Additionally, many industrialists are considering bio-resources as renewable sources for biodiesel production with zero-emission net goals. Palm oil is an outstanding candidate among the types of bio-resources to meet the increasing demands for greener and cleaner energy (Kerschbaum *et al.,* 2008).

Crude off-grade palm oil or low-grade crude palm oil (LGCPO) has potential as a low-cost feedstock for biodiesel production, with 5-20% of free fatty acids (Supardan and Satriana, 2009). In general, biodiesel can be produced commercially by homogenous alkaline catalysts in the transesterification process, but a high free fatty acid (FFA) content in the feedstock (especially CPO) would cause soap and emulsion formation in the final product, incurring biodiesel yield losses along with processing problems (Anastopoulos *et al.,* 2009). Therefore, reducing the free fatty acids of the raw material by a pretreatment is needed to avoid soap forming and yield losses. Moreover, LGCPO with high FFA was processed in a two-step "trans-esterification reaction" via using an acidic catalyst in the pretreatment step, as opposed to directly applying alkaline catalysis (this was done in the second step) (Soon *et al.,* 2013). Hence, such two-step process is appropriate for improving the biodiesel yield over the one-step process (transesterification) (Nurhayati *et al.,* 2017; Prateepchaikul *et al.,* 2007).

A raw material with high FFA content should be subjected to esterification with acid catalyst, such as concentrated sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), or hydrochloric acid (HCl). Various studies have shown good catalytic performance in CPO pretreatment with sulfuric acid, normally used at 2.00 to 3.00 wt.%, and giving FFAs reduction from 5.60- 20.00 wt.% to less than 2.00 wt.%, with a high biodiesel yield exceeding 87.00 wt.%. (Prateepchaikul *et al.,* 2007; Somnuk and Prateepchaikul; 2013; Worapun *et al.,* 2011; Nurhayati *et al.,* 2017 Hayyan *et al.,* 2014; Sungnat and Wongwuttanasatian, 2018). Due to its high catalytic capability and low cost, sulfuric acid is an appropriate catalyst choice for the reaction (Somnuk *et al.,* 2019). However, sulfuric acid use causes sulfur dioxide emissions that will cause acid rain that is very corrosive, and will badly burn plants, buildings, or even humans. Moreover, emissions of sulfur incur long-term environmental toxicity. Su (2013) reported that the only reusable homogeneous acid catalyst for the esterification process was hydrochloric acid, and it was completely reserved for reactant used before the actual production phase after esterification. Furthermore, hydrochloric acid retained in the reactant phase could be recovered and recycled multiple times. Hence, hydrochloric acid can reduce the processing costs in biodiesel purification and production. Therefore, to obtain high-quality biodiesel with use of a low-cost catalyst, hydrochloric acid could serve as an effective catalyst in the esterification reaction that is non-toxic to the environment.

The main aim of this study was to facilitate the use LGCPO as an inexpensive raw material, focusing on wt.% FFA conversion to reduce the level of FFA to acceptable levels (below 2%). Different acid catalysts have been used in the esterification reaction, such as HCl and H_2SO_4, normally used as homogeneous acid catalysts. Optimization of various parameters will be conducted to find the optimum conditions for the pretreatment and biodiesel production from LGCPO via using homogeneous acid catalysts: HCl or H_2SO_4. Additionally, in biodiesel production, esterification reaction is the reaction between a fatty acid and alcohol using an acid catalyst. Moreover, the effect of free fatty acid and catalyst concentration on soap formation or the saponification reaction of FAME at a low moisture content is another important point to consider, in the context of producing biodiesel. To reach high-level purification and yield of biodiesel with high FFA, the esterification reaction will convert free fatty acids to alkyl eaters with acidic catalysts.

2.Materials and Methods

2.1 Materials

Low-grade crude palm oil with 13.81 wt.% FFA and 1 wt.% water was obtained from Roongreungkit Ltd. company located in Songkhla province, Thailand. The commercial-

grade methanol (MeOH, 99.8 wt.% purity) was purchased from P-General Co. Ltd. A commercial potassium methoxide (CH_3KO) in methanol solution with a concentration of 32 wt.% was ordered from Jebsen & Jessen Chemicals, Thailand. Poffassium hydroxide (KOH) 85 wt.% was purchased from Rci Labscan Chemicals, Thailand. Refined palm oil (RPO) was dewatered by heating at 105 °C for 3 h, and then analyzed, to control its moisture level to < 0.05 wt.%.

2.2 Pretreatment of low-grade crude palm oil

The esterification reaction was conducted in a 1-liter 3-necked flat-bottomed flask equipped with a condenser and a 400-rpm magnetic stirrer. The reaction procedure was as follows: 100 g of raw material was poured into the reactor and heated up to a reaction temperature of 60 °C. Hydrochloric (MeOH/HCl), or sulfuric ($MeOH/H_2SO_4$) solution had been prepared earlier from hydrochloric acid (37% purity) or sulfuric acid (98% purity) by dissolving in methanol.

The mixture was then poured into the oil and stirred for the next 60 min. After the reaction, the mixture was allowed to settle for 2 h for phase separation, and was then washed and dried with a 400-rpm heater-stirrer at 105 °C for 2 h. The ester content was determined following Thailand Petty Patent 5060.

2.3 The 2nd step transesterification of esterified palm oil (EPO)

The transesterification reaction was conducted in a 1-liter 3-necked flat-bottomed flask equipped with a condenser and a 400-rpm magnetic stirrer. The reaction procedure was as follows: 100 g of raw material was poured into the reactor and heated up to a reaction temperature of 50 °C. The potassium hydroxide (MeOH/KOH) solution was earlier prepared by dissolving KOH in methanol.

The mixture was then poured into oil and stirred for the next 60 min. After the reaction, the mixture was allowed to settle for 2 h for phase separation, and was then washed and dried with a 400-rpm heater-stirrer at 105°C for 2 h. The ester content was determined following Thailand petty patent 5060.

2.4 Study on effects of FFA content and catalyst amount on the FAME saponification reactions

All experiments studying the saponification reaction of FAME were conducted in a 1-liter 3-necked flat-bottomed flask equipped with a condenser and a 400 rpm magnetic stirrer. The experimental conditions are presented in Table 4. The reaction procedure was as follows: 150 g of FAME was poured into the reactor and heated up to a reaction temperature of 60 °C. The alkaline catalyst-methanol mix was earlier prepared with KOH dissolved in methanol, at a molar ratio of methanol/FAME of 6:1. The mixture was poured into biodiesel reactor and stirred at 400 rpm for 30 min and was then collected using a volumetric pipette.

The catalyst and soap contents were analyzed using an acid-base titration method (AOCS Official Method Cc 17-79). The mixture was then stirred for 30 min, and three approximately 3mL samples were taken at the end of reaction time (at 30 min) using a volumetric pipette. Each sample was transferred into a pre-weighed 250 ml Erlenmeyer flask containing 50 ml of isopropanol to immediately halt the reaction and was then analyzed for catalyst and soap contents.

2.5 Free fatty acid content analysis

The FFA content in crude oil, esterified palm oil, and ester was evaluated by the AOAC official method No.940.28 (Helrich, 1990).

2.6 Catalyst and soap contents analyses

After the transesterification reaction was complete, the small amount of catalyst remaining and the soap tended to concentrate in the glycerol phase. Then the remaining catalyst and soap contents were analyzed by AOCS official method Cc 17-79 (Gerpen, 2005).

2.7 FFA content and catalyst amount effects on the FAME saponification reactions

The water content of raw materials and methanol was analyzed by Karl Fischer method (ISO 12937). FFA content was analyzed by titration (Method AOAC 940.28). Ester content was analyzed by a chemical method (Thoai *et al.,* 2017). The catalyst and soap contents in samples were tested using an acid-base titration method (AOCS Official Method Cc 17-79).

2.8 Determination of ester content by proximate analysis for total glycerides and ester content (Thailand Petty Patent 5060)

Ruamporn and Tongurai (2014) demonstrated that the total glyceride content in FAME could be determined by transesterification with microwave irradiation. The remaining glycerides in the biodiesel sample were reacted with the mixed solutions of methanol and KOH to produce the final products.

3. Results and Discussion

3.1 Effects of acid catalysts in pretreatment of low-grade crude palm oil

In the biodiesel production process from raw materials with a high FFA content, especially LGCPO, homogeneous acid catalysts are preferred in the pretreatment. The FFA can respond with alcohol (MeOH) to form ester bonds (biodiesel) in an acid-catalyzed esterification reaction. This reaction is very useful for treating raw materials with high FFA content, and is shown below (Leung *et al.,* 2010):

$$RCOOH+R'OH \xleftrightarrow{H^+} RCOOR'+H_2O \quad (1)$$

Due to their strong acidic characteristic and low cost, sulfuric acid and hydrochloric acid are the most extensively used. This study revealed the results of esterification with methanol and using a homogeneous catalyst (hydrochloric or sulfuric acid) under the same conditions: 60 °C, at methanol to oil ratio of 10:1, reaction time 120 min, and stirrer speed at 400 rpm. The catalyst performances are summarized in Table 2. and Figures 1, 2, and 3 show that 0.25 HCl wt.% per LGCPO gave optimum reduction of the FFA content in LGCPO, reaching the target level (less than 2 wt.%) by reduction from 13.81 wt.% to 0.56 wt.% (FFA conversion 95.95%), and this was more effective than H_2SO_4 at the same proportion of catalyst for which the results showed a reduction of FFA content in LGCPO from 13.81 wt.% to 1.0113 wt.% (FFA conversion 92.70%).

Table 1. The reaction conditions for all experiments

Parameter	Unit	Exp.1	Exp.2	Exp.3	Exp.4
Raw materials	-	LGCPO	LGCPO	EPO (without washing EPO)	EPO (with washing EPO)
FFA	wt.%	13.81	13.81	<2.00	<2.00
Moisture content	wt.%	0.14 to 0.15	0.04 to 0.05, (0.09 to 0.10)	0.10 to 0.14	0.10 to 0.14
Catalyst types	-	HCl (37%)	H_2SO_4 (98%)	KOH	KOH
Catalyst amount	wt.%	0.25, 0.50, 1.00, 1.50, 2.00, 4.00	0.25, 0.50, 1.00, 1.50, 2.00, 4.00	1.00	1.00
MeOH/oil molar ratio	mol: mol	10:1	10:1	6:1	6:1
Reaction temp	°C	60	60	60	60
Reaction time	min	120, 400 rpm	120, 400 rpm	60, 400 rpm	60, 400 rpm

Table 2. The results for esterification process, summary

Feedstock	FFA content (wt.%)	Esterification: Catalysts	FFA final (wt.%)	FFAs conversion (%)
Low-grade crude palm oil	13.81	HCl	0.56	95.95
Low-grade crude palm oil	13.81	H_2SO_4	1.01	92.70

The FFA conversion experiments in esterification reaction with alternative catalysts (HCl and H_2SO_4) are summarized in Table 1. Mostly a catalyst is used at more than 2.00 wt.% and could get FFA reduction to the standard target (< 2.00 wt.%), suitable for the two-step method. However, the aim of this study was to use the smallest amount of catalyst possible for reducing the FFA content, with the least impact on the environment. Therefore, 0.25 wt.% is an optimal content, and this is a much smaller amount than in previous research by about tenfold, while it gets the FFA reduction to standard target.

Furthermore, Hayyan *et al.* (2012) reported similar results on the catalytic performance of hydrochloric acid, with better performance than for sulfuric acid and being suitable to treat CPO with ultrasonic assist, which could give a high conversion of FAME and decrease the FFA content in CPO from 8.70% to less than 1.00% (which is acceptable point in FFA for continued action in the transesterification reaction). Sulfuric acid is the most commonly use as a pretreatment catalyst in esterification of the FFA with methanol, in various prior studies. However, concentrated sulfuric acid causes corrosion, and waste from neutralization. Moreover, Su (2013) reported on advantages of hydrochloric acid. The main aim of this research was to examine the recoverability and reusability of homogeneous acid catalysts, such as phosphoric, nitric, sulfuric, and hydrochloric acid, when used to catalyze esterification reaction. Hydrochloric acid is the only catalyst among these that is recoverable and reusable. Besides, Chiu *et al.* (2005) assessed the remaining acid catalysts (sulfuric acid or hydrochloric acid) in the biodiesel phase, by adding calcium chloride and silver nitrate to the biodiesel phase since these chemicals could react with the anions forming insoluble sulfate and chloride salts. In biodiesel production via using sulfuric acid, calcium sulfate silt ($CaSO_4$) was found in the biodiesel phase, while silver chloride silt (AgCl) was not observed for biodiesel treated with hydrochloric acid.

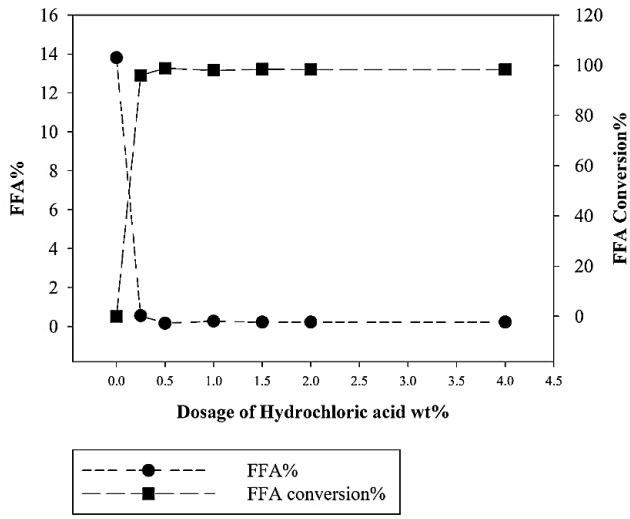

Figure 1. Effect of hydrochloric acid dose on the reduction of FFA and conversion of FFA to FAME

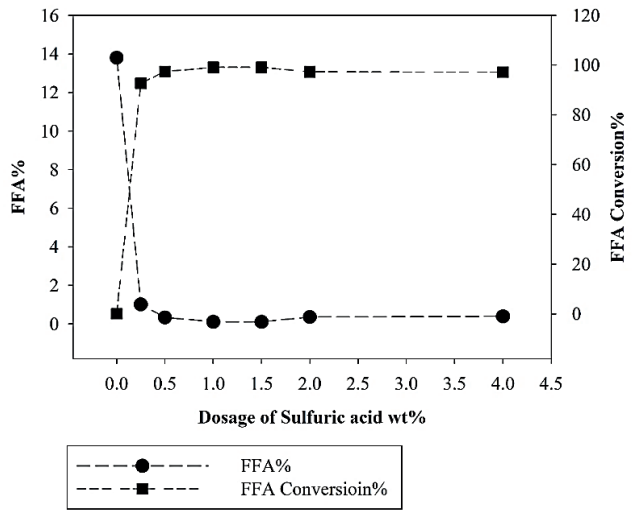

Figure 2. Effect of sulfuric acid dose on the reduction of FFA and conversion of FFA to FAME

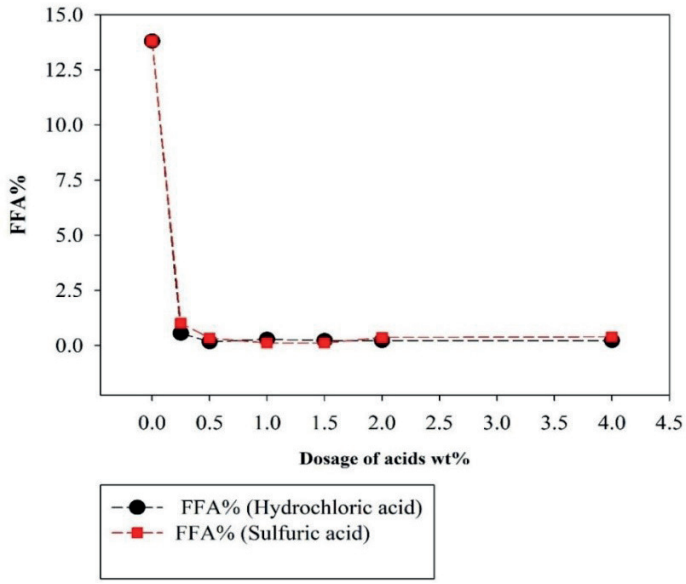

Figure 3. Effects of the alternative acids: comparison between HCl and H_2SO_4 in reduction of FFA content of LGCPO

Consequently, we target clean biodiesel with zero-emissions from sulfur. Additionally, the residue in the biodiesel phase may result in emissions of SO_2 on combustion of the fuel, causing harm to the environment downstream of biodiesel production (Shin *et al.,* 2018). A greener biodiesel production from LGCPO is achieved by replacing H_2SO_4 with a lesser volume of HCl as the acid catalyst for reducing FFA.

3.2 The 2nd Step transesterification of esterified palm oil (EPO)

Transesterification is the second conventional conversion process in biodiesel making (also called alcoholysis). This reaction acts with an alcohol producing esters and glycerol from vegetable oils or animal fats. The conventional catalysts used in biodiesel production are homogeneous

alkaline catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), that can give a very high yield in esters and are usually used to increase the reaction rate and biodiesel yield (Leung *et al.,* 2010), and the esters that remain are called biodiesel. However, these catalysts need a large amount of water in the washing step to remove the remaining catalyst from biodiesel, and this causes environmental problems (Ritprasert *et al.,* 2019). Additionally, washing is needed for biodiesel purification, and the FAME phase was washed by warm water (45-50 °C) to remove impurities including alcohol, remaining catalyst, and soap (Thoai *et al.,* 2019). However, the neutralization produces a large amount of wastewater from the hot water used in purification (Bashir *et al.,* 2018). This needed treatment before release to the environment to avoid pollution (Obanla *et al.,* 2018).

The results in Table 3 show that with or without washing the EPO for use as feedstock in the transesterification process, biodiesel and ester contents do not significantly differ, and FFA can be reduced to the same final level (0.05%). Hence, our study suggests that producing a high yield of biodiesel and ester in the transesterification process without washing EPO is the appropriate option. Moreover, biodiesel production that uses less hydrochloric acid is non-toxic with reduced emissions, not only in terms of contaminated wastewater but also from absence of sulfur dioxide, as mentioned before.

3.3 Effect of FFA content on FAME saponification with methanol and KOH

In saponification reaction triglycerides in fat/oil are reformed into soap and glycerol (called alkaline hydrolysis of ester) by reacting with base catalyst KOH as shown here.

$$\underset{\text{FFA}}{R'COOH} + \underset{\text{Potassium hydroxide}}{KOH} \longrightarrow \underset{\text{Soap}}{R'COOK} + \underset{\text{Water}}{H_2O} \quad (2)$$

To evaluate the effect of FFA content on soap formation from FAME, by the saponification reaction, experiments were done with varied FFA content in FAME from 0.20 to 1.14 wt.%.

Table 3. The 2nd transesterification esterified palm oil (EPO)

Feedstock	Catalyst	Transesterification reaction: initial catalyst content (wt.%), MeOH: oil (ratio), Time (min) Temp. (°C)	Yield (wt.%)	Ester content (wt.%)	FFA final (%)
Esterified palm oil (EPO) (0.5 wt.% FFA) without washing EPO	KOH	1.2, 6:1, 60, 60	82	97.31	0.05
Esterified palm oil (EPO) (0.5 wt.% FFA) with washing EPO	KOH	1.2, 6:1, 60, 60	85	98.05	0.05

Table 4. Experimental conditions for assessing effect of FFA content on FAME saponification

Run#	FAME		MeOH		KOH			%FFA	%Water	FFA+ Water	Excess catalyst	
	g	mol	g	mol	wt.%	g	mol	wt.%	wt.%	mol	mol	%
1	150.0	0.528	101.408	3.169	1.00	1.50	0.027	0.20	0.12	0.011	0.016	59.8
2	150.0	0.528	101.408	3.169	1.00	1.50	0.027	0.50	0.12	0.012	0.014	53.7
3	150.0	0.528	101.408	3.169	1.00	1.50	0.027	0.70	0.12	0.013	0.013	49.6
4	150.0	0.528	101.408	3.169	1.00	1.50	0.027	1.14	0.12	0.016	0.011	40.4

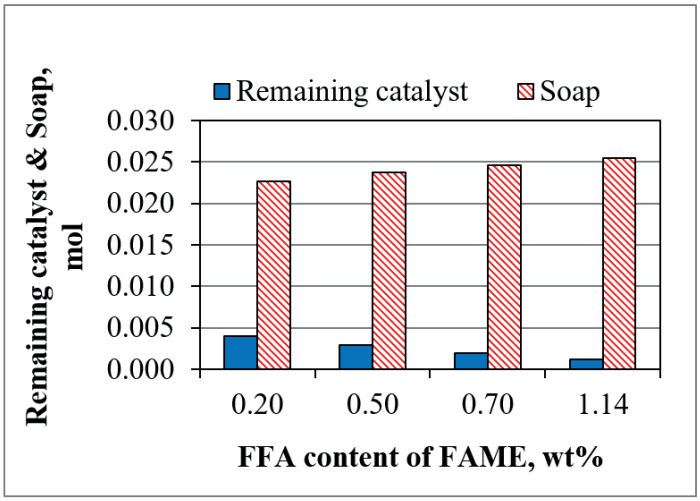

Figure 4. Influence of catalyst amount on the saponification reaction: FAME (0.2-1.14 wt.% FFA), total moisture content (0.12 wt.% of FAME), KOH concentration (1.0 wt.% of FAME), 6:1 molar ratio of MeOH/FAME, 30 min reaction time, 60 °C, and 400 rpm.

In Figure 4 the soap formation rapidly increased as the amount of catalyst decreased, because potassium ions bound to the FFA remaining in FAME and formed soap as in Eqn. 2. Also, the head of the chain (potassium ion) is hydrophilic while the tail (FFA) is hydrophobic. In the case of FFA produced in large quantities, soap formation will also increase and bind to FAME resulting in loss of biodiesel yield.

Also, KOH contributes to the saponification of FAME. The saponification reaction is highly undesirable because soap not only consumes the catalyst but also causes a problem in phase separation by emulsion formation, during the purification stage. The soap formation is also the main reason for biodiesel yield loss (Anastopoulos *et al.,* 2009). Additionally, the presence of free fatty acids and moisture in these oils leads to serious soap formation. Some studies have demonstrated the influence of FFA on transesterification using an alkaline catalyst to determine the optimal conditions (Cai *et al.,* 2015; Atadashi *et al.,* 2013). Moreover, the FFA content affects biodiesel yield and purity (Bouaid *et al.,* 2016). 70% of the initial base catalyst amount, especially sodium hydroxide, was converted into soap after reaction of acidity oil (0.41%). However, potassium methoxide created a lesser amount of soap than sodium methoxide catalyst.

4. Conclusions

Appropriate techniques to convert low-grade crude palm oil (LGCPO) containing 13.81 wt.% free fatty acid (FFA) into zero-sulfur biodiesel have been examined and demonstrated. Alternative homogeneous acid catalysts, namely sulfuric acid (H_2SO_4) and hydrochloric acid (HCl), were used in the esterification reaction. Hydrochloric acid with 0.25 wt.% was selected as a suitable catalyst to reduce FFA, with 95.95% FFA conversion (0.56 wt.%) in pretreatment, and to produce green biodiesel. The final ester contents were 98.05 and 97.31 wt.% for washed esterified palm oil (EPO) and for rinsed EPO without washing, respectively. Regarding soap formation in biodiesel production, high FFA leads to soap formation in fatty acid methyl ester (FAME) saponification resulting in phase separation and emulsion formation during the purification stage. The acid catalytic preprocessing of low-grade crude palm oil is an important procedure to avoid such problems.

Acknowledgements

The authors would like to express thanks to the Faculty of Environmental Management, Department of Chemistry (Faculty of Science),

Interdisciplinary Graduate School of Nutraceutical and Functional Food Center, Crop-Biotech Laboratory (Faculty of Natural Resources), the Specialized R & D Center for Alternative Energy from Palm Oil and Oil Crops and Sustainable Innovation Center, Prince of Songkla University for providing facility assistance and supporting our work. And also, special appreciation goes to the Mechanical Department of Krabi Technical College for instructive extraction of low-grade crude palm oil. The authors would like to acknowledge the PSU Research and Development Office (RDO) and Dr. Seppo Karrila for editing the manuscript.

References

Anastopoulos G, Zannikou Y, Stournas S, Kalligeros S. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. Energies 2009; 2: 362-376.

Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. The effects of catalysts in biodiesel production: A review. Journal of Industrial and Engineering Chemistry 2013; 19: 14-26.

Bashir MA, Thiri M, Yang X, Yang Y, Safdar A. Purification of biodiesel via pre-washing of transesterified waste oil to produce less contaminated wastewater. Journal of Cleaner Production 2018; 180: 466-471.

Bouaid A, Vázquez R, Martinez M, Aracil J. Effect of free fatty acids contents on biodiesel quality: Pilot plant studies. Fuel 2016; 174: 54-62.

Cai ZZ, Wang Y, Teng YL, Chong KM, Wang JW, Zhang JW, Yang DP. A two-step biodiesel production process from waste cooking oil via recycling crude glycerol esterification catalyzed by alkali catalyst. Fuel Processing Technology 2015; 137: 186-193.

Chiu CW, Goff MJ, Suppes GJ. Distribution of methanol and catalysts between biodiesel and glycerin phases. Aiche Journal 2005; 51(4): 1274-1278.

Gerpen JHV. Biodiesel processing and production. Fuel Processing Technology 2005; 86: 1097-1107.

Hayyan A, Hashim MA, Mirghani MES, Hayyan M, AlNashef IM. Treatment of industrial low-grade palm oil via esterification reaction using sonoreactor. Journal of Industrial and Engineering Chemistry 2014; 20(4): 2066-2070.

Hayyan A, Mjalli SF, Hayyan M, Alnashef I. Utilizing ultrasonic energy for reduction of free fatty acids in crude palm oil. African Journal of Biotechnology 2012; 11(61): 12510-12517.

Helrich K. Official methods of analysis of the association of official analytical chemists: agricultural chemicals; contaminants; drug.15th ed (2). Association of analytical chemists, Inc. Publishing, Arlington, Virginia, USA. 1990.

Kerschbaum S, Rinke G, Schubert K. Winterization of biodiesel by micro process engineering. Fuel 2008; 88(12): 2590-2597.

Leung DYC, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. Applied Energy 2010; 87(4): 1083-1095.

Nikhom R, Mueanmas C, Suppalakpanya K. Enhancement of biodiesel production from palm fatty acid distillate using methyl t-butyl ether co-solvent: process optimization. International Journal of Renewable Energy Research 2019; 9: 1319-1327.

Nurhayati N, Anita S, Amri TA, Linggawati A. Esterification of crude palm oil using H_2SO_4 and transesterification using CaO catalyst derived from Anadara granosa. Indonesian Journal of Chemistry 2017; 17(2): 309-315.

Obanla OR, Bababtunde DE, Ogunbiyi TA, Oladimeji TE, Ifepe MI. Biodiesel washing water treatment using zeolite and activated carbon as adsorbents. International Journal of Engineering and Applied Sciences (IJEAS) 2018; 5(3): 124-126.

Prateepchaikul G, Michael LA, Leevijit T, Thaveesinsopha K. Methyl ester production from high free fatty acid mixed crude palm oil. Songklanakarin Journal of Science and Technology 2007; 29(6): 1551-1561.

Ritprasert P, Ngaosuwan K, Assabumrungrat S. Application of co-solvent for improving biodiesel production in an ultrasound-assisted reactor. Proceeding of AASE International Conference 2019; 28-19 May 2019: 46-55.

Ruamporn N, Tongurai C. Production development of ethyl ester biodiesel from palm oil using a continuous deglycerolisation process. Fuel 2014; 117: 926-931.

Shin D, Kim Y, Moon HS. Fate and toxicity of spilled chemicals in groundwater and soil environment I: strong acids. Environmental Health and Toxicology 2018; 33(4): 1-5.

Somnuk K, Prateepchaikul G. Effects of acid catalyst types and concentrations on free fatty acid reduction in mixed crude palm oil using continuous static mixer. Applied Mechanics and Materials 2013; 446-447: 1523-1527.

Somnuk K, Soysuwan N, Prateepchaikul G. Continuous process for biodiesel production from palm fatty acid distillate (PFAD) using helical static mixers as reactors. Renewable Energy 2019; 131: 100-110.

Soon LB, Zafiah MRA, Hasan S, Daim AD. The novel continues biodiesel proses using ultrasonic clamp on tubular reactor. Applied Mechanics and Materials 2013; 315: 691-694.

Su CH. Recoverable and reusable hydrochloric acid used as a homogeneous catalyst for biodiesel production. Applied Energy 2013; 104: 503-509.

Sungnat C., Wongwuttanasatian T. Esterification of crude palm oil with low ultrasonic intensity. International Conference on Energy and Power Engineering (EPE June 2018) 2018; 75-81.

Supardan MD, Satriana S. Esterification of free fatty acid in crude palm oil off grade. Jurnal Rekayasa Kimia and Lingkungan 2009; 7(2): 70-74.

Thoai DN, Chanakaewsomboon I, Prasertsit K, Photaworn S, Tongurai C. A novel inspection of mechanisms in conversion of refined palm oil to biodiesel with alkaline catalyst. Fuel 2019; 256(115831): 1-9.

Thoai DN, Photaworn S, Kumar A, Prasertsit K, Tongurai C. A novel chemical method for determining ester content in biodiesel. Energy Procedia 2017; 138: 536-543.

Wan Ghazali WNM, Mamat R, Masjuki HH, Najafi G. Effects of biodiesel from different feedstocks on engine performance and emissions: A review. Renewable and Sustainable Energy Reviews 2015; 51: 585-602.

Worapun I, Pianthong K and Thaiyasui, P. Optimization of biodiesel production from crude palm oil using ultrasonic irradiation assistance and response surface methodology. Journal of Chemical Technology and Biotechnology 2011; 87(2): 189-197.