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Continuous Double-Step Esterification Production of Palm Fatty Acid Distillate Methyl Ester Using Ultrasonic Tubular Reactor

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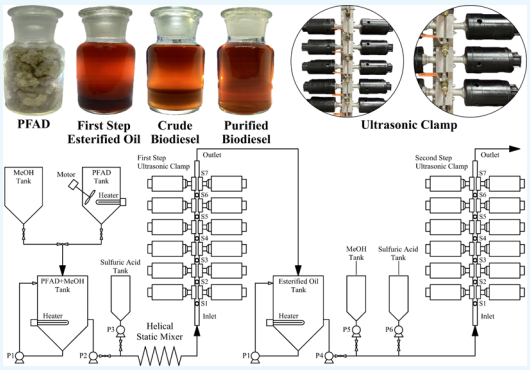
ABSTRACT: Double-step esterification to produce biodiesel from palm fatty acid distillate (PFAD) was performed by utilizing an ultrasound clamp reactor. Six pairs of ultrasonic clamps were attached to the left and right sides of the stainless-steel tube, and each pair was separated 100 mm apart from each other. Therefore, a total of 12 units of ultrasound clamps distributed 4800 W maximum power (12 × 400 W) throughout the continuous reactor by an ultrasonic generator. To optimize each step of the continuous esterification process for producing methyl ester from PFAD, a response surface methodology was used. The final 93.32 wt % methyl ester purity was attained under a double-step esterification process. For the first step, a 3.75:1 molar ratio of methanol to PFAD (46.4 vol % methanol), 6.6 vol % sulfuric acid, and 400 mm length of ultrasound clamp at 25 L/h PFAD flow rate for converting the PFAD to 60.24 wt % methyl ester were recommended. For the second step, the esterification was repeated under a molar ratio of methanol to the first esterified oil of 2.87:1 (61.6 vol % methanol), 5.6 vol % of sulfuric acid, and 400 mm length of ultrasound clamp at 25 L/h esterified oil flow rate. The ultrasonic clamp reactor achieved high yields of esterified oil and the crude biodiesel in a relatively short residence period of 32 s. To determine the product yields of a double-step esterification process, the maximum yields were 103.9 wt % first esterified oil, 107.6% crude biodiesel, and 98 wt % purified biodiesel when calculated on the basis of 100 vol % initial PFAD. The average energy consumed in the production of double-step esterification biodiesel was 0.05796 kWh/L. Therefore, this current approach has a high potential for producing biodiesel with less energy and requires less time to convert the PFAD to a high purity of methyl ester.



1. INTRODUCTION

A byproduct from the refining process of producing refined palm oil (RPO) from raw crude palm oil (CPO) is the palm fatty acid distillate (PFAD).[1,2] Normally, PFAD is used for the formulation of soap, animal feed, and the oleochemical industry. Because of the involvement of vitamin E in PFAD, it can also be applied as a feedstock in the food production and pharmaceutical industries.[3,4] PFAD mainly consists of FFA, and it is a potential resource for biofuels.[5,6] PFAD can be available at a very low price in the market, whereas it cannot be used in edible grade approaches. Furthermore, PFAD is promising a second-generation feedstock for the production of biofuels.[7] Second-generation feedstock biofuel is a nonedible substance derived from waste and byproducts of the palm oil refining plant. These raw materials can be used effectively to produce biodiesel because they can supply a greater amount of biofuel sustainably and at a cheaper cost than crude palm oil, which is the main raw material used to produce biodiesel in Thailand and Asian countries.[8,9] According to a global report on the estimated amount of crude palm oil (CPO) production, worldwide CPO production in 2021 was approximately 75.45 million tons. It is difficult to find an official production rate of PFAD. However, the concentration of free fatty acid in palm oil was approximately 4%.[10] Therefore, the estimated production of PFAD was 3.018 million tons in 2021. The three largest CPO production countries in Asia are Indonesia, Malaysia, and Thailand. In these countries, CPO production was 48.5, 18.8, and 3.8 million tons, and the estimated production of PFAD was 1.94, 0.752, and 0.152 million tons in 2021, respectively.[11] Moreover, for the key application of biodiesel production, ultrasound was applied to convert the high free fatty acid (FFA) in PFAD to a high-quality methyl ester within a short reaction time.[12] An advantage of ultrasound in biodiesel production is the sonochemical impacts on the reaction that assist in the mixing of immiscible liquid for biodiesel production.[13] By applying ultrasound in biodiesel

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Table 1. Summary of Reviews for Biodiesel Production Process Using an Ultrasonic Reactor[a]

author	process	reaction	type of reactor	raw material	molar ratio of MeOH to oil	type of catalyst	T (°C)	time (min)	yield (%)	ester (wt %)
Choedkiatsakul et al.[22]	continuous	transesterification	mechanical stirrer (160 rpm), ultrasound probe (800 W, 20 and 50 kHz)	palm oil	6:1	NaOH = 1 wt %	45	5		93.78
Delavari et al.[23]	continuous	transesterification	helicoidal reactor, ultrasonic probe (1500 W, 20 kHz)	waste cooking oil	8.6:1	NaOH = 0.5 wt %	60	2.5	>90	
Manickam et al.[24]	batch	transesterification	ultrasonic probe (300 W, 70 kHz)	palm oil	3:1	KOH = 1 wt %	60	15	93	
Abulizi et al.[25]	batch	transesterification	ultrasonic probe (260 W, 20 kHz)	waste cooking oil	6:1	KOH = 3 wt %	55	120	91.5	
Thangarasu et al.[26]	batch	esterification and transesterification	microchannel, ultrasonic probe (315 W)	*Aegle marmelos* Correa seed oil	1.6:1	HCL = 0.5 wt %	60	1.383	98	
					9:1	NaOH = 1.3 wt %	48			
Dubey et al.[27]	batch	esterification and transesterification	ultrasonic probe (120 W, 20 kHz)	nagchampa oil	12:1	H_2SO_4 = 2.5 wt %	60	150	79	
					4:1	CaO = 1 wt %	60			
Maghami et al.[28]	batch	esterification and transesterification	ultrasonic probe (400 W, 24 kHz)	waste fish oil	12:1	H_2SO_4 = 1 wt %	60	90	79.6	87
					6:1	KOH = 1 wt %	55			
Saha and Gound[29]	batch	esterification and transesterification	ultrasonic probe (100 W, 30 kHz)	karanja oil	9:1	H_2SO_4 = 0.5 wt %	30	150		84
					9:1	$Ba(OH)_2$ = 5 wt %	30			
Sarve et al.[30]	batch	esterification and transesterification	ultrasonic probe (250 W, 20 kHz)	*Schleichera triguga* oil	4:1	H_2SO_4 = 1 wt %	40	100		96.8
					9:1	$Ba(OH)_2$ = 3 wt %	50			
this study	continuous	esterification and esterification	ultrasonic clamps (4800 W, 20 kHz)	palm fatty acid distillate	3.75:1	H_2SO_4 = 6.6 wt %	50	0.533	98	60.34
					2.87:1	H_2SO_4 = 5.6 wt %	50			93.22

[a]Note: MeOH is methanol, NaOH is sodium hydroxide, KOH is potassium hydroxide, HCl is hydrochloric acid, and H_2SO_4 is sulfuric acid.

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production, the benefits of reducing the reaction time, consuming fewer chemical reactants, and enhancement of the product yield were achieved.[14] For the fundamentals and application of ultrasound in chemical processes, the main function of using ultrasound is to intensify the chemical reaction and process. In the ultrasonic cavitation process, the formation, growth, and collapse of vapor bubbles occurred in the liquid due to the transmission of high-frequency ultrasonic waves in the range of 20−1000 kHz, which were generated by acoustic pressure variation from an ultrasonic source.[12] High pressure and temperature can be created when vapor collapses due to high energy release. Mass transfer can be improved in the process by using ultrasonic cavitation, which minimizes the reaction time, improves mixing intensity, and increases product yield.[13,14]

Regarding the use of ultrasound in the homogeneous esterification reaction for producing the biodiesel from high FFA feedstock, Deshmane et al.[15] reported an esterification process to deliver the esters from PFAD which was operated with 25 kHz ultrasonic frequency and 1000 W ultrasonic power. To obtain the optimal conditions, the operating parameters of the molar ratio of isopropanol to oil, catalyst, and reaction temperature were examined. The results showed that under the recommended conditions of a 2-propanol to PFAD molar ratio of 5:1, H_2SO_4 5%, at a 60 °C reaction temperature during 6 h reaction time, 80% ester conversion was obtained. Hayyan et al.[16] researched the pretreatment of low-grade palm oil (LGPO) using ultrasound. In their study, LGPO was sonicated using an esterification reaction. It is an impressive and appropriate approach for the biodiesel synthesizing process. The optimal conditions of 2% sulfuric acid, 10:1 methanol to oil molar ratio, 50 °C reaction temperature, and 300 min reaction time were used. These optimized conditions have the potential to reduce the FFA concentration in LGPO from 20% to less than 3% under optimal conditions.[9] Mohod et al.[17] also reported that biodiesel could be synthesized from karanja oil using acoustic cavitation. The acid value of 14.15 mgKOH/g of karanja oil was reduced to less than 2.7 mgKOH/g at the optimal condition of 5:1 methanol to oil ratio and 2% H_2SO_4 concentration at ambient temperature. Sarve et al.[18] studied biodiesel manufacturing from the high acid value of kusum (*Schleichera triguga*) oil with a two-step esterification process using ultrasonic irradiation. The sulfuric acid was used as an acid catalyst in this study, while barium hydroxide ($Ba(OH)_2$) was used as an alkaline catalyst in the transesterification reaction. For the first step, the initial acid value in kusum oil was decreased from 21.65 to less than 0.84 mgKOH/g under the conditions of 4:1 methanol to oil molar ratio, 1 vol % H_2SO_4, and 20 min ultrasonic irradiation time at 40 °C. Then the optimal conditions of the second step, 3 wt % $Ba(OH)_2$ concentration, 9:1 molar ratio of methanol to oil, and 80 min ultrasonic irradiation time at 50 °C, converted the first esterified oil to 96.8 wt %. The ultrasonic aided esterification reaction to reduce FFA from high FFA rubber seed oil (RSO) was studied by Trinh et al.[19] Their experiment was performed with a 500 W and 20 Hz ultrasonic homogenizer. The diameter of the ultrasonic probe was 13 mm. The FFA value of RSO was reduced from 40.14 to less than 0.75 wt % under the optimal conditions of a 23:1 molar ratio of methanol to oil and a 7.5 wt % of sulfuric acid at 50 °C reaction temperature. They concluded that the ultrasonic approach was working well and was more effective than the traditional method with an esterification reaction. Tan et al.[20] conducted another study on the two-step esterification followed by a transesterification process with the oil from jatropha seeds using an ultrasonic enhancement approach to synthesize biodiesel. In the esterification process, when the optimal conditions for esterification were used, the acid value of jatropha oil was reduced from 18.2 to 5.3 mg KOH/g, which was achieved at a 3:1 molar ratio of methanol to oil, 5 vol % sulfuric acid, 60% ultrasonic amplitude, and 150 min reaction time. Subsequently, the esterified jatropha oil ws used in the transesterification step to produce biodiesel. In this step, the four independent variables were varied such as KOH concentration (0.5−2.0 wt %), molar ratio of methanol to esterified oil (9:1−18:1), ultrasonic amplitude (50−70%), and reaction time (10−20 min). The highest methyl ester amounts of 99 and 85.5 wt % of biodiesel yield were attained under the optimized conditions of 1.5 wt % of KOH loading, 12:1 molar ratio of methanol to esterified oil, and 60% ultrasonic amplitude within a short period around 15 min. In addition, Gandhi and Gogate[21] have reported methyl ester production from high FFA raw materials of mahua oil by esterification and transesterification processing with an ultrasonic horn. The esterification step was performed by varying the molar ratio of methanol to oil (6:1−15:1), H_2SO_4 (1−5 wt %), and reaction temperature (30−60 °C). The FFA value of 18.27 wt % was reduced to 0.875 wt % at a 9:1 molar ratio of methanol to oil and 3 wt % of H_2SO_4 concentration. The ultrasonic horn specification was 150 W power and a 20 kHz frequency. In the transesterification step, the molar ratio and reaction temperature were varied as in the esterification step at a constant KOH concentration of 0.5 wt %. The ultrasonic power was varied from 20 to 150 W with the range of the duty cycle being 30−70%. The maximum yield of 93 wt % was attained at a 9:1 molar ratio of methanol to esterified oil, an ultrasonic power of 120 W with a 50% duty cycle, 0.5 wt % KOH, and 45 min reaction time at 45 °C reaction temperature. They confirmed that the properties of biodiesel met the standards of ASTM.

In a summary, ultrasonic clamps were used in a few studies to study methyl ester synthesis using a double-step esterification process from high FFA feedstock (PFAD). The main focus in this operating process was the ultrasound clamp which was used as a continuous reactor. The raw materials and chemical solutions of each step were integrated with the ultrasound clamp reactor to enhance the esterification integrations by acoustic cavitation for both the first and second esterification processes, allowing optimization of three parameters such as methanol, sulfuric acid concentration, and length of ultrasonic clamp. According to the above-mentioned summary studies, most biodiesel research has been performed using the ultrasonic probe batch approach. As listed in Table 1, there are no studies that have produced biodiesel using ultrasonic clamps for a continuous double-esterification process from high FFA feedstock of PFAD. To fill the knowledge gap for this issue, the main focus of this study is use of the ultrasound clamps, which are performed as a continuous reactor to produce biodiesel by a double-step esterification continuous process from the high FFA feedstock of PFAD. Moreover, important parameters such as methanol, sulfuric acid concentration, and length of ultrasonic clamp were optimized to produce biodiesel for both the first and second esterification processes using a response surface methodology (RSM). As a benefit of using ultrasound clamp, it can minimize the working space for apparatus setup than a continuous stirred

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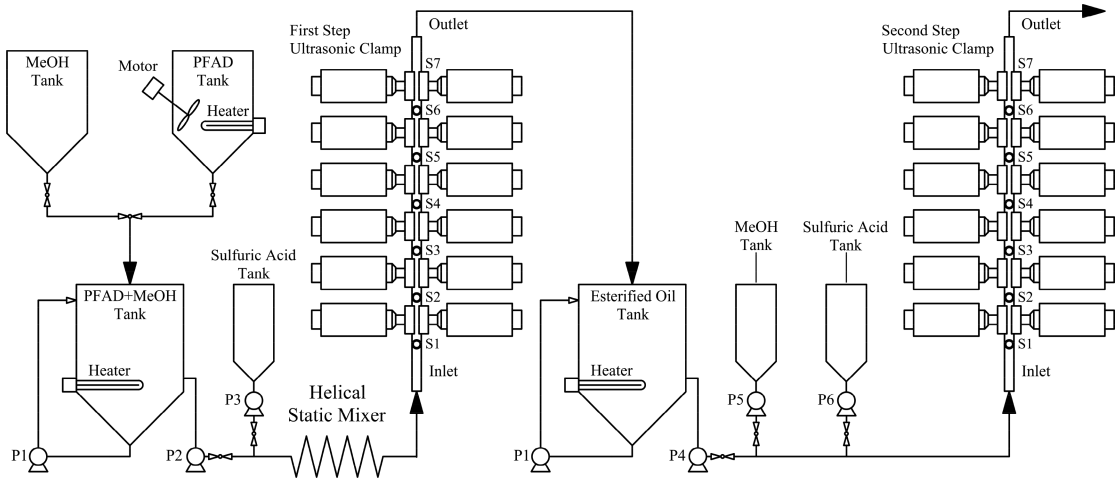

Figure 1. Schematic diagram of a double-step esterification continuous production of biodiesel from palm fatty acid distillate (PFAD) utilizing an ultrasound clamp.

tank reactor (CSTR). Moreover, many researchers have indicated that using ultrasound in biodiesel synthesis leads to an increase in the yield, decreased reaction time, and reduced chemical demanding.[18,31] Therefore, the results from this study can be efficiently used for continuous biodiesel production with less energy and time demanding than the traditional method of biodiesel production.

2. MATERIALS AND METHODS

2.1. Materials. The palm fatty acid distillate (PFAD) was used as the primary source for producing biodiesel in this study. At 30 °C, the phase condition of PFAD was a solid wax with light-yellow color. At 43 °C, the solid wax condition changed to a liquid state.[32,33] Therefore, the PFAD was warmed to transform the liquid phase and blend it homogeneously with methanol for the first-stage esterification procedure. The compositions of PFAD were 90.61 wt % free fatty acid (FFA), 1.31 wt % triglyceride (TG), 2.33 wt % diglyceride (DG), 4.79 wt % monoglyceride (MG), and 0.96 wt % methyl ester (ME). The viscosity and density of PFAD at 50 °C were 12.68 cSt and 0.869 kg/L, respectively. The average molecular weight of PFAD was 284.14 g/mol, and the first esterified oil was 163.31 g/mol. In this study, commercial-grade chemical solutions were employed for both steps of continuous esterification: 99.7% methanol and 99% sulfuric acid.

2.2. Equipment. The experimental setup of this study was illustrated in Figure 1. Twelve ultrasound clamps were located on the left- and right-side stainless steel (SUS304) tube for double-step esterification continuous processing of biodiesel from PFAD according to Figure 1. The stainless-steel tube dimensions were designed as 13 mm inside diameter of the tube, 1000 mm in length, and 3.5 mm wall thickness for taking place both in the first- and second-step continuous reaction with ultrasonic clamps on tubular reactor. Each ultrasound clamp was run at a frequency of 20 kHz and 400 W maximum power of the ultrasound device. Therefore, a total of 12 units of ultrasound clamps distributed 4800 W maximum power (12 × 400 W) throughout the continuous reactor by an ultrasonic generator.[34] The ultrasonic power is used to transmit energy to the flowing mixtures in the tube. A pair of ultrasonic clamps were attached to the left and right sides of the tube, and each pair was separated 100 mm apart from each other. The function of the clamps was to enhance the power of ultrasound from the tip of the ultrasonic horn. The ultrasonic clamps were made of aluminum alloy, and the dimensions were 3 mm in width, 65 mm in length, and 20 mm in height.[34] The acoustic energy density (AED) is directly proportional to the ultrasonic power (P_{US}) and inversely proportional to the total volume of the liquid (V_{total}), as mentioned in eq 1.[34,35] The estimated AED in ultrasonic clamp is equal to 25.6 W/mL at the maximum power condition for the 187.5 mL volume of the mixture inside the reactor. Therefore, the AED will be maintained at 25.6 W/mL for further scaling up conditions.

$$\mathrm{AED} = \frac{P_{US}}{V_{total}} \tag{1}$$

where AED is the acoustic energy density, V_{total} is the total volume of the liquid (mL), and P_{US} is the ultrasonic power (W).

2.3. Experimental Procedure. Referring to Figure 1, to prepare the continuous first-step esterification, the tank was prepared for raw material PFAD and heated to 50 °C with a heater in the tank. The PFAD in the tank was stirred regularly by a mechanical stirrer to control the temperature inside the tank. When the temperature of PFAD was ready, the PFAD from the tank and the methanol in the tank flowed into the mixing tank and homogenized the two liquids by a chemical circulation pump (P1, Sanso, model PMD-371). The PFAD and methanol blends in the mixing tank were also heated by a heater and blended by a chemical circulation pump to control the temperature at 50 °C during the continuous process. Subsequently, the mixture from the tank was pumped continuously to the 5 m length of a helical static mixer (HSM) using the digital dosing pump (P2). At the same time, H_2SO_4 in the tank was pumped into the same line to the HSM using the chemical resistant pump (P3). The mixture of these three solutions was passed through the HSM and flowed into the ultrasonic clamp on a tubular reactor for the first step. The outcome from the outlet port of the first-step ultrasonic clamp was collected in the first-step separator tank to separate the generated water from the first-step process esterification. After the wastewater was removed from the continuous separator tank, the first-step esterified oil was then overflowed to the esterified oil tank, which is the tank used for preparing raw material (first step esterified oil) for the second-step

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continuous esterification process. The first esterified oil in the tank was heated to a temperature 50 °C by an immersion heater. The MeOH tank and H_2SO_4 tank were arranged on the same pipeline of the flowing line of the first esterified oil in the tank. All these solutions from esterified oil, methanol, and sulfuric acid tanks were pumped into the ultrasonic clamp of the second step using digital dosing pumps P4, P5, and P6, respectively. The final product from the outlet port of the second step was collected at the outlet port of second stage. After completion of reaction, the crude biodiesel and wastewater were separated. After the crude biodiesel was separated from the separator tank, the pure crude biodiesel was moved into the new tank. To analyze the methyl ester from the first and second steps, the samples were collected with a 30 mL glass bottle along the length of 100−700 mm from sampling ports S1−S7 for both ultrasonic clamp reactors of the first and second step, as described in Figure 1. After collecting the samples from every sampling port, they were immediately put into the 0 °C ice cabinet to end the reaction. After that, all of the obtained samples were cleaned with warm water to eliminate contaminants and impurities from the crude biodiesel. The experiment of GC analysis was performed to determine the composition of methyl ester, linoleic acid ester, MG, DG, TG, free glycerin, and total glycerin of commercial biodiesel standards using a gas chromatograph flame ionization detector (GC−FID, GC 6890; Agilent Technologies, USA). The experimental GC result of methyl ester for this study was 94.22 wt %. Finally, the methyl ester of esterified oil after the first step and purified biodiesel after the second step were analyzed using the Fourier transform nuclear magnetic resonance (FT−NMR) analyzer. The purity of the ester was determined on a ^{1}H NMR spectrometer (Unity Inova, Varian, Germany) operating at 500 MHz and using $CDCl_3$ as the solvent. Subsequently, the purity of the methyl ester in the final product was detected to confirm the quality of biodiesel utilizing a gas chromatograph flame ionization detector (GC−FID, GC 6890; Agilent Technologies, USA). Moreover, the compositions of MG, DG, TG, free glycerin, and total glycerin in purified biodiesel were measured to compare the compositions of esters for the specifications of commercial-based biodiesel and the biodiesel for using in agricultural diesel engines.

2.4. Experimental Design. The optimization of methyl ester values from the experimental results of both the first and second processing steps of esterification was executed with the RSM method. For the central composite design, the RSM comprised five levels and three factors (CCD). The five-level coding factors such as $-\alpha_x$, −1, 0, +1, and $+\alpha_x$ were applied to spin the values of independent variables in CCD.[36] The calculation of the axial point (α_x) of rotatable CCD was based on the number of variables (k). The experimental results were performed by varying three independent variables. Therefore, the number of variables (k) in this study was 3. For this experiment, this value was used in eq 2 to generate five independent variables, including −1.682, −1, 0, +1, and +1.682 coded levels. Table 2 lists the values of independent variables in the ranges of the coded factor level for each independent variable. The experimental design and results of methyl ester values from both the first and second esterification processes are described in Table 3. The second-order polynomial model (eq 3) for multiple regression analysis was adapted to determine the methyl ester purity from each continuous operation step.[37] The three independent variables in this experimental study were methanol (M), sulfuric acid concentration (S), and length of ultrasonic clamp (L). These three independent variables affected the achievement of high methyl ester purity (ME_1 and ME_2 for the first step and second step, respectively), which was the dependent variable in this optimization. There are two steps; the first and second steps of continuous processes; therefore, the variables M_1, S_1, and L_1 represented the first step and the variables M_2, S_2, and L_2 represented the second step. The experimental analysis of methyl ester values was performed with a nuclear magnetic resonance (NMR) analyzer. The final experimental results after analysis with NMR were run with the Microsoft Excel Solver, which is available in the add-in tool.

Table 2. Experimental Ranges of the Independent Variables

		coded level				
process	independent variable	−1.682	−1	0	+1	+1.682
first step	M_1: methanol (vol %)	19.8	30.0	45.0	60.0	70.2
	S_1: sulfuric acid (vol %)	0.8	2.5	5	7.5	9.2
	L_1: length of ultrasound clamp (mm)	100	200	400	600	700
second step	M_2: methanol (vol %)	26.4	40	60	80	93.6
	S_2: sulfuric acid (vol %)	0.6	2	4	6	7.4
	L_2: length of ultrasound clamp (mm)	100	200	400	600	700

$$\alpha_x = \sqrt[4]{2^k} \tag{2}$$

where α_x is the rotatability axial point and k is the variable numbers

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} x_i x_j + \varepsilon \tag{3}$$

where Y is the response variable (methyl ester purity), x_i and x_j are the independent variables (methanol, sulfuric acid, and length of ultrasound clamp), β_0, β_i, β_{ii}, and β_{ij} are coefficients of intercept term, linear term, quadratic term and interaction term, respectively, k is the number of variables, and ε is the error.

3. RESULTS AND DISCUSSION

3.1. Experimental Results. The experimental conditions and results from both first- and second-step esterification are described in Table 3. There were 18 experimental conditions from each step according to the experimental design of RSM. The range of methyl esters converting from FFA in PFAD was between 20.73 to 79.52 wt % of methyl ester for the first stage, according to the data summarized in Table 3. For the second step, the methyl ester converting range was between 83.34 and 93.17 wt %. These highest methyl ester values were determined by the multiple regression of RSM. The final results of 18 experimental conditions from both the first and second steps were run in Microsoft Excel Solver to obtain the multivariate second-order polynomials predictive model which was described as eq 4 for the first step and eq 5 for the second step. Table 4 described the precise analysis of p-values for every coefficient of individual terms, determination coefficient

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Table 3. Design of Experimental Conditions and Methyl Ester Results[a]

	first-step esterification				second-step esterification			
run	M_1 (vol %)	S_1 (vol %)	L_1 (mm)	ME_1 (wt %)	M_2 (vol %)	S_2 (vol %)	L_2 (mm)	ME_2 (wt %)
1	19.8	5.0	400	33.74	26.4	4.0	400	85.11
2	30.0	2.5	200	27.68	40.0	2.0	200	83.34
3	30.0	2.5	600	30.35	40.0	2.0	600	87.96
4	30.0	7.5	200	48.81	40.0	6.0	200	88.34
5	30.0	7.5	600	53.05	40.0	6.0	600	89.11
6	45.0	0.8	400	20.73	60.0	0.6	400	88.50
7	45.0	5.0	100	55.62	60.0	4.0	100	90.50
8	45.0	5.0	400	55.79	60.0	4.0	400	92.59
9	45.0	5.0	400	55.85	60.0	4.0	400	92.29
10	45.0	5.0	400	55.55	60.0	4.0	400	92.34
11	45.0	5.0	400	55.40	60.0	4.0	400	92.39
12	45.0	5.0	700	65.91	60.0	4.0	700	90.91
13	45.0	9.2	400	52.49	60.0	7.4	400	92.59
14	60.0	2.5	200	60.80	80.0	2.0	200	91.46
15	60.0	2.5	600	65.07	80.0	2.0	600	92.17
16	60.0	7.5	200	67.07	80.0	6.0	200	93.17
17	60.0	7.5	600	75.43	80.0	6.0	600	92.17
18	70.2	5.0	400	79.52	93.6	4.0	400	93.02

[a]Note: For both the first and second steps: M_1, M_2 are methanol, S_1, S_2 are sulfuric acid, L_1, L_2 are length of ultrasound clamp, and ME_1, ME_2 are purity of methyl ester

Table 4. Coefficients in the Fitted Response Surface Models[a]

	first step (eq 4)		second step (eq 5)	
coefficient	value	p-value	value	p-value
β_0	−41.8704	0.00001184	54.9424	0.00000000
β_1	1.3587	0.00000003	0.6110	0.00000078
β_2	17.7393	0.00000002	3.3948	0.00002174
$\beta 3$	−0.0416	0.00923838	0.0357	0.00002943
β_4			−0.0030	0.00001211
β_5	−0.0907	0.00047824	−0.0139	0.00850943
β_6			−0.0002	0.00219043
β_7	−1.0324	0.00000011	−0.1662	0.00067564
β_8			−0.0017	0.00248302
β_9	0.0001	0.00124239	0.0000	0.00078349
R^2	0.990		0.988	
$R^2_{adjusted}$	0.985		0.974	

[a]Note: R^2 is the determination coefficient, $R^2_{adjusted}$ is the adjusted coefficient of determination, and the p-value is a symbol of statistical significance.

(R^2), and determination for the adjusted coefficient ($R^2_{adjusted}$). Moreover, the analysis of variance (ANOVA) for all response surface model terms was represented for the double-step esterification as shown in Table 5.

$$ME_1 = \beta_0 + \beta_1 M_1 + \beta_2 S_1 + \beta_3 L_1 + \beta_5 M_1 S_1 + \beta_7 S_1^2 + \beta_9 L_1^2 \quad (4)$$

$$ME_2 = \beta_0 + \beta_1 M_2 + \beta_2 S_2 + \beta_3 L_2 + \beta_4 M_2^2 + \beta_5 M_2 S_2 + \beta_6 M_2 L_2 + \beta_7 S_2^2 + \beta_8 S_2 L_2 + \beta_9 L_2^2 \quad (5)$$

where ME is methyl ester (ME_1 for the first step, ME_2 for the second step, vol%), M is methanol (M_1 for the first step, M_2 for the second step, vol %), S is sulfuric acid (S_1 for the first step, S_2 for the second step, vol %), and L is the length of ultrasound clamp (L_1 for the first step, L_2 for the second step, mm), and β is a fixed coefficient.

3.2. Statistical Analysis of Predictive Model. According to Table 4, the statistical analysis, the significant parameter evaluation of the linear terms for all models, was done with the fewest p-values. For eq 4 of the first-stage esterification, the smallest p-values or most significant coefficients were found in

Table 5. ANOVA of Response Surface Models

source	SS[a]	MS[b]	F_0	F_{crit}	DOF[c]
first step					
regression	4353.0	725.50	187.69	3.09 ($F_{0.05,6,11}$)	6
residual	42.52	3.866			11
lack-of-fit error	42.39	5.299	120.3544	0.00113	8
pure error	0.132	0.04403			3
total	4395.5				17
second step					
regression	134.71	14.97	72.91	3.39 ($F_{0.05,9,8}$)	9
residual	1.642	0.205			8
lack-of-fit error	1.590	0.318	18.3951	0.01852	5
pure error	0.05187	0.01729			3
total	136.35				17

[a]SS = sum of squares. [b]MS = mean squares. [c]DOF = degrees of freedom.

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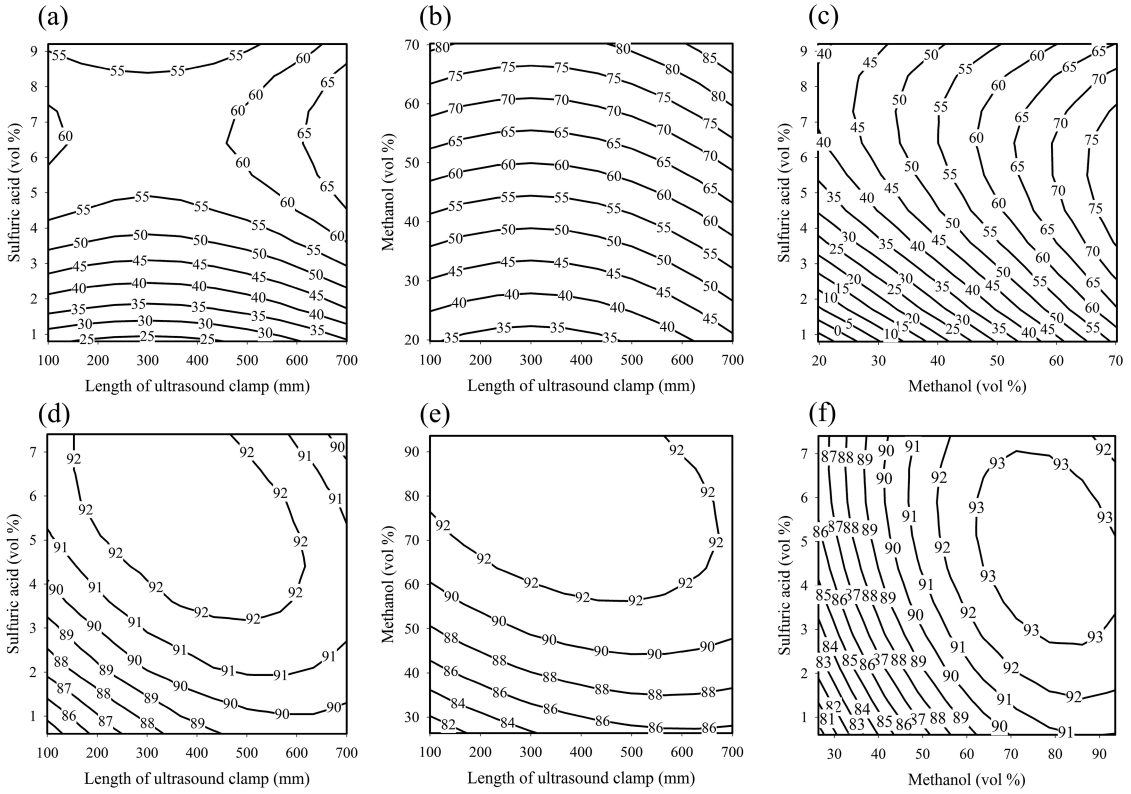

Figure 2. Contour plots of continuous methyl ester production using an ultrasound clamp. For the first and second processing steps, (a) and (d) present the relationship between the length of the ultrasound clamp and sulfuric acid concentration, (b) and (e) present the relationship between the length of ultrasound clamp and methanol concentration, and (c) and (f) present the relationship between the methanol concentration and sulfuric acid concentration on the purity of methyl ester.

β_2S_1 followed by the term of β_1M_1. Therefore, the sulfuric acid content is the strongest significant independent variable for the first step followed by the methanol concentration. Increasing the sulfuric acid and methanol contents in the first step process highly impacted the conversion of methyl ester purity from the FFA in PFAD. Thus, the sulfuric acid and methanol contents were mostly influenced on the first step for reducing FFA in PFAD using an ultrasound clamp. For the second stage, the lowest *p*-value in eq 5 was detected in the term of β_1M_2, which means that the linear term for the second step was dependent on the methanol concentration. Therefore, methanol is the most important variable in the second step of esterification procedure. The second priority of significance in the second step was found for the term $\beta_4M_2^2$. Hence, the concentration of the methanol amount was an important parameter in the second step for generating a methyl ester from the first-step esterified oil using an ultrasound clamp. The predictive equation's coefficient of multiple determination (R^2) and adjusted coefficient of multiple determination (R^2_{adjusted}) were 0.990 and 0.985 for the first step and 0.998 and 0.974 for the second step, respectively. Both the R^2 and R^2_{adjusted} values for the first and second steps were close to 1, indicating that the parameters and predicted results were substantially related. In addition, the analysis of variance (ANOVA) as shown in Table 5 was performed for the consideration of the significance of the predictive models. In the ANOVA analysis, the lack of fit test was considered to prove the represented model was performed well or not with the experimental data. So that the obtaining results will be a well-fitting model, the lack of fit value should be insignificant. In this analysis, the lack of fit of test statistic (F_0) is determined by dividing the lack of fit mean square (MSLF) by the pure error mean square (MSPE). The calculated lack of fit values for the first and second steps were 120.354 and 18.391 as described in Table 5. For this study, the calculated lack of fit values were not significant as pure errors when compared to the experimental data. This means that the proposed models were well-fitted to the data. In other words, these independent variables were shown to have a considerable impact on methyl ester production. Furthermore, the *F*-test analysis was also applied to detect the significance of the model. By checking whether the calculated F_0 value is greater than the critical value (F_{crit}), it is possible to detect whether the predictive model was significant or not. The critical value (F_{crit}) is interpreted as $F_{\alpha,i,n-1-i}$. The critical value can be available in an *F*-distribution table at a 95% confidence level or α is equal to 0.05. According to Table 5 and the *F*-distribution table, F_0 values of 187.69 and 72.91 were greater than the F_{crit} values of 3.09 $F_{(0.05,6,11)}$ and 3.39 $F_{(0.05,9,8)}$. Therefore, the significance of the predictive model in this study was statistically agreed upon for the production of methyl ester from both the first step and the second step of acid-catalyzed esterification.

3.3. Response Surface Plots. Figure 2 shows the contour plot illustration for the relations between the dependent and the independent variables (methanol, sulfuric acid, and length of ultrasound clamp) of both first and second steps. These plots represent the first processing step (Figure 2a–c) and the second processing step (Figure 2d–f). The purities of methyl esters were the dependent variables for both the first and second steps. In the first-stage esterification, the most

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significance coefficient was found in the term of β_2S_1 followed by the term of β_1M_1. Thus, sulfuric acid is the most important parameter for the first step of the esterification stage, and second important priority parameter was methanol concentration. In the contour plot of Figure 2a, the effect of methyl ester purities on sulfuric acid and the length of the ultrasonic clamp was demonstrated. At a length of ultrasonic clamp approximately 650 mm, high methyl ester values of around 65 wt % were achieved in the range of sulfuric acid concentrations between 4 and 9 wt %. In Figure 2c, a methyl ester value of 75 wt % was achieved in the range of 3−8 wt % H_2SO_4 at nearly 70 vol % methanol concentration. The methyl ester values were decreased beyond 8 vol % and below 3 vol % of the sulfuric acid concentration. In a related study regarding the esterification of *Jatropha curcas* seed oil (CJCO), Tan et al.[38] used an ultrasonic probe to study the esterification production from CJCO. In their study, the various sulfuric concentrations were varied from 5 to 30 mL. The ester conversion results approximately 70, 40, 50, 60, 40, and 40 wt % were attained at 5, 10, 15, 20, 25, and 30 mL of sulfuric acid content. In their results, the highest ester value was found at 5 mL of sulfuric acid, and the ester efficiency decreased when the acid catalyst concentration increased because of the formation of wastewater in the reacted mixture at a high concentration of sulfuric acid. According to the statistical analysis for first step, methanol is also second priority significant parameter. Therefore, the high methyl ester value 75 wt % was found since from 100 mm length of ultrasound clamp, as shown in Figure 2b. The methyl ester values increased when the methanol concentration increased. Moreover, in Figure 2c, the highest methyl ester value of 75 wt % was observed at around 70 vol % of methanol concentration. The methyl ester value was getting decreased when the methanol volume percent decreased. For the second step, the statistical analysis of response surface model described in the earlier session, the methanol concentration had a significant influence on the generation of high methyl ester values in the second step. The contour plots relating to methanol with the length of ultrasonic clamp and sulfuric acid, which impacted on the methyl ester purities, are shown in Figure 2e,f. In Figure 2e, the highest methyl ester value of 92 wt % was gained in the condition above 60 vol % of methanol since from a 100 mm length of ultrasound clamp within a very short reaction time. The ester values decreased by less than 90 wt % when the methanol concentration was lower than 50 vol %. In Figure 2f, the highest methyl ester purity of 93 wt % was attained in the range of methanol concentrations of 60−95 vol % and sulfuric acid 2−7 vol %. As shown in Figure 2e, less than 90 wt % of ester values were observed below 50 vol % of methanol concentration. A similar research report, methyl ester synthesized from buriti oil with an esterification analysis, was reported by Pantoja et al.[39] The esterification analysis was performed by varying the methanol to oil ratio (9:1−27:1), acid catalyst (2−6 vol %), and reaction time (1−14 h). The highest ester value of more than 99 wt % was obtained with an oil to methanol ratio of 1:18, 4 vol % sulfuric acid, and a 14 h reaction time. They found that the concentration of methanol was the most important element in ester conversion. The methyl ester values were 77.3, 83.9, and 72.4 wt % at methanol to oil 9:1, 18:1, and 27:1, respectively. The ester conversion was low over the condition of methanol to oil of 18:1 because the excess methanol was formed in the wastewater and diluted the reaction.

3.4. Optimum Conditions of Double-Step Esterification Continuous Production. According to the design of experimental results, the predictive model's equations as described in eqs 4 and 5 examine the optimal conditions of methyl ester values from double steps continuous esterification process. The optimal conditions of maximum methyl ester values for each step are described in Table 6. For the first step, the maximum methyl ester value of 89.79 wt % was attained with the conditions of 70.2 vol % methanol, 5.5 vol % sulfuric acid, and 700 mm length of ultrasound clamp (approximately 27 s of retention time in the ultrasound clamp). Nonetheless, the methanol consumption was high for this condition and affected the cost of chemical consumption. Therefore, Excel Solver was used to solve the dependent variable (ME_1) and independent variables (the length of ultrasound clamp, methanol, and sulfuric acid) by exchanging the various values of methyl ester purities in eq 4. As a result, the methyl ester conversion sharply increased by 19.8 vol % methanol content and 60 wt % ester purity reached equilibrium after 46.4 vol % methanol was used. Thus, over 46.4 vol % methanol content is

Table 6. Results of Optimal and Suggested Conditions from Models, Real Tests, and Retention Time for Double-Step Esterification[a]

	condition	
	optimized	recommended
first step (continuous esterification)		
condition		
methanol (vol %)	70.2	46.4
sulfuric acid (vol %)	5.5	6.6
length of US reactor (mm)	700	400
residence time in US reactor (s)	≈27	≈16
purity of methyl ester purity		
predictive model (wt %)	89.79	60.00
actual experiment (wt %)	88.89	60.24
second step (continuous esterification)		
condition		
methanol (vol %)	80.0	61.6
sulfuric acid (vol %)	5.2	5.6
length of US reactor (mm)	300	400
residence time in US reactor (s)	≈12	≈16
purity of methyl ester purity		
predictive model (wt %)	93.88	93.00
actual experiment (wt %)	90.91	93.32
total		
methanol consumption (vol %)	150.2	108
sulfuric acid consumption (vol %)	10.7	12.2
total length of US reactor (mm)	1000	800
total retention time in US reactor (s)	≈39	≈32
chemical cost		
methanol cost[b] (USD/h)	12.84	9.24
sulfuric acid cost[c] (USD/h)	0.58	0.66
total chemical cost	14.76	10.88
ultrasonic power[d]	6400 (16 × 400W)	4800 (12 × 400W)

[a]Exchange rate from 1 RMB = 0.15 USD at 10 February 2022[40] [b]The methanol cost referred 1 kg = 0.432 USD[41] [c]The sulfuric acid cost referred 1 kg = 0.118 USD[42] [d]The electricity consuming was calculated based on the total units ultrasound clamps under optimal and recommended conditions for whole process.

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not necessary to dose into the process to improve the slight increase in methyl ester purity. Thus, the recommended conditions for the first step were 46.4 vol % methanol, 6.6 vol % sulfuric acid, and 400 mm length of ultrasound clamp (approximately 16 s residence time in the ultrasound clamp) and delivered 60 wt % of methyl ester by the predictive model equation. Finally, in the second step following the predictive model of eq 5, a highest 93.88 wt % methyl ester was attained at the optimal conditions 80.0 vol % MeOH, 5.2 vol % H_2SO_4, and 300 mm length of ultrasound clamp. However, methanol consumption under these condition was high, resulting in a high cost for chemical consumption; therefore, an estimated methyl ester purity of 93 wt % was required to fit as the value of the dependent variable (ME_2) and searched to consider the new recommended methanol content, as in the first step. Therefore, the new recommended conditions of the second step, 61.6 vol % methanol, 5.6 vol % sulfuric acid, and 400 mm length of ultrasound clamp (approximately 16 s residence time in the ultrasound clamp), gave 93.0 wt % methyl ester purity in the prediction model. For the whole process, total methanol consumption at a recommended condition was reduced significantly when compared to that of the optimum conditions. The optimal and recommended conditions differed by 42.2 vol % in methanol consumption. 3.61 USD/h could be saved on methanol costs if the recommended condition was operated under this condition of the whole process, resulting in a lower cost of biodiesel production. In a related study regarding the cost of methanol consumption in biodiesel production, Karmakar et al.[43] described that low demand for the methanol is one the requirement for the production process. In their study, the methanol to oil ratio was varied in the range between 3:1 and 12:1 to produce methyl ester from *Madhuca indica* oil. Their result showed that the maximum methyl ester was achieved at a methanol to oil ratio of 6:1. The methyl ester conversion did not increase when the methanol to oil ratio was over 6:1 because a large excess of methanol was diluted and became diffusional resistance for mass transfer in the product. Therefore, the adjustment of methanol consumption is important not only for improving biodiesel yields but also for reducing the production cost. After the recommended conditions of the predictive model were considered, these conditions were proved with experimental studies. Biodiesel compositions, yields, and residual methanol from the double-step esterification process are given in Table 7 and discussed in the next section.

3.5. Compositions and Yields of Biodiesel from Double-Step Esterification. The details of the optimum and selected conditions and the occurrence of residence time for double-step esterification to prepare the biodiesel from PFAD is shown in Table 6. Two recommended operating conditions are corroborated by analyzing the purities of the ester with an NMR analyzer. Ester purities of 60.24 wt % and 93.32 wt % from NMR analysis were achieved in real tests at 25 L/h PFAD flow rate of both first and second steps, receptively. The ester purification results in Table 6 are close to the model-predicted ester purities. The second step's final sample was reevaluated to ensure the purity of methyl ester. As shown in Table 8, 94.22 wt % ester was obtained using GC−FID in accordance with the EN 14103 test standard. According to Table 7, the yields of 103.9 vol % in the first step esterified oil, 107.6 vol % biodiesel (no washing), and 98 vol % purified biodiesel (after washing) were attained. The percentage of yield for first-step esterified oil and crude biodiesel was

Table 7. Compositions, Yields, Residual Methanol of Biodiesel from Double-Step Esterification

composition,[a] yield,[b] and residual methanol	content
first step esterification	
composition of first esterified oil	
ester content (wt %)	60.24
yield[b]	
first esterified oil (vol %)	103.9
first step wastewater (vol %)	48.8
residual methanol	
residual methanol in the first esterified oil (vol %)	1.5
residual methanol in the first step wastewater (vol %)	42.0
second step esterification	
composition of biodiesel	
ester content (wt %)	93.32
yield[b]	
crude biodiesel (vol %)	107.6
second wastewater (vol %)	59
residual methanol	
residual methanol in the crude biodiesel (vol %)	6.2
residual methanol in the second wastewater (vol %)	40.8
purification	
yield[b]	
purified biodiesel (vol %)	98.0

[a]The results from an actual experiments. [b]The yield results given are related to 100 vol % initial PFAD.

obtained within 10 s in the ultrasound clamp for both the first and second steps. The average yield of 98 vol % purified biodiesel from the double esterification process was attained after the purification process of the biodiesel, with 100 vol % relating to the volume of PFAD. The residual sulfuric acid and methanol in crude biodiesel were eliminated by washing. An excess of methanol was employed to perform the two-step esterification in order to produce biodiesel with a high purity and yield. The unreacted methanol contents were found in the crude biodiesel phase and generated wastewater. The residual methanol result was examined using a GC analyzer in accordance with the EN 14110 standard test procedure, as indicated in Table 6. The methanol involvement in generated wastewater was high at 42.0 and 40.8 vol % in the first and second steps. Thus, the industrial-scale operation needs retrieval of the extra methanol from formed wastewater. Nonetheless, the residual methanol at 1.5 vol % in the first esterified oil does not need to be recovered because this methanol content could be used as a forward reaction in the second step of esterification. Furthermore, 6.2 vol % of residual methanol remained in the crude biodiesel, which does not need to be recovered. Because, the reverse reaction may occur when the process is repeatedly heated to recover the residual methanol. The properties of methyl ester from biodiesel production from PFAD using a double-step esterification process in comparison to the community and commercial standards in Thailand, the USA, and Europe are listed in Table 8.

3.6. Time Consumption for Double-Step Esterification. The overall duration for the double-step esterification procedure took approximately 193 min when using empty ultrasonic clamps and continuous separators. For the first operating process, the 58 s of residence time took in 5 m of HSM, 16 s for the ultrasound clamp, and 150 min in the separator tank. For the second step, the reaction time in the

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Table 8. Physical Properties of the Biodiesel Product Using a Double-Step Esterification Process

			biodiesel standard		biodiesel standard in Thailand[a]		
property	method	diesel	EU	USA	for agricultural engine	for commercial-based biodiesel	result[b]
ester (wt %)	EN 14103		96.5 min			96.5 min	94.22[c]
density at 15 °C (kg/m^3)	ASTM D1298	810−870	860−900		860−900	860−900	870
viscosity at 40 °C (cSt)	ASTM D445	1.8−4.1	3.5−5.0	1.9−6.0	1.9−8	3.5−5	5.36
flash point (°C)	ASTM D 93	52	101 min	130 min	120 min	120 min	168
copper strip corrosion	ASTM D 130	no. 1 max	no. 1 max	no. 3 max	no. 3 max	no. 1 max	no. 1a
acid value (mgKOH/g)	ASTM D664		0.5 max	0.5 max	0.8 max	0.5 max	11.78
methanol (wt %)	EN 14110		0.2 max	0.2 max		0.2 max	<0.01
monoglyceride (wt %)	EN 14105		0.8 max			0.7 max	0.69
diglyceride (wt %)	EN 14105		0.2 max			0.2 max	1.32
triglyceride (wt %)	EN 14105		0.2 max			0.2 max	0.56
free glyceride (wt %)	EN 14105		0.02 max	0.02 max	0.02 max	0.02 max	0.00
total glyceride (wt %)	EN 14105		0.25 max	0.24 max	1.5 max	0.25 max	0.25

[a]Refer to Thawornprasert et al.[33] [b]Results of biodiesel production from the recommended conditions. [c]Purity of ester from the GC−FID analysis method.

ultrasonic clamp was approximately 16 s and the duration time for separation in the second step separator tank was 42 min. The most time-consuming part of this whole process was separation time after the first- and second-step esterification process. In the generated wastewater, some amounts of sulfuric acid and methanol remain. A specially designed gravity separation method for the separator tank was used to separate esterified oil and formed wastewater. The time to settle time in the separation funnel was accurately observed. However, it was tested to ensure that the gravity separation could work well with generating wastewater in the continuous process. To separate these produced wastewaters under total flow rate of the reaction of mixtures, 50 L of the first separator and 30 L of the second separator were specially constructed.

3.7. Electricity Consumption in the Double-Step Esterification Continuous Process. An electric power meter was applied to determine the consumption of average electricity for the whole process. First, 25 L of PFAD was warmed from 30 °C and kept constant at 50 °C for 40 min by a heater. For the first step in the continuous process, PFAD was homogenized with methanol, the mixture was heated to 50 °C within 40 min using a mixing pump and heater ,and the total electricity demand of the start-up conditions was 1.48 kWh. In the first-step process, total electricity consumed was 0.91 kWh including electricity for pumping the mixture of PFAD blended with MeOH and H_2SO_4 into HSM and the first-step ultrasound clamp applying two chemical-resistant dosing pumps and controlling the first esterified oil temperature at 50 °C during the first step. For the second step, total electricity demand was 0.51 kWh for pumping three mixtures, such as the first-step esterified oil, the methanol, and the sulfuric acid constantly into the ultrasound clamp, which was performed by three manual dosing pumps. Therefore, the overall total energy usage of the whole process was 1.42 kWh for producing around 24.5 L of purified biodiesel, which was calculated based on 25 L of PFAD, and did not include the electricity used during startup and the purification process of the crude biodiesel. The moderate amount of energy usage for crude biodiesel output was 0.05796 kWh/L. Furthermore, when the average energy consumed while considering the length of ultrasound clamps at optimal and recommended conditions is examined, the length of the ultrasound clamp and the average energy consumed for the ultrasound clamp are related. When the ultrasonic clamp length is lowered, the average energy consumed decreases as well. Under optimal conditions, the total length of the e ultrasonic reactor for the whole processing step was 1000 mm, as listed the total length of the ultrasonic reactor in Table 6. This meant that the entire ultrasonic power (6400 W) had to be operated. However, when the recommended conditions were employed in the process, the total ultrasonic power was lowered to 4800 W for the whole process. As a result, the total electricity demand for the optimal condition is greater than the recommended condition.

4. CONCLUSIONS

In this study, methyl ester production from high FFA feedstock (PFAD) was investigated using ultrasound clamps with the double-step esterification process. The optimum conditions such as methanol, sulfuric acid concentration, and length of ultrasonic clamp for both the first and second steps were considered using response surface methodology. For the first step, purity of methyl ester value of 60.24 wt % was achieved under the recommendation condition of 3.75:1 molar ratio of methanol to PFAD (46.4 vol % methanol), 6.6 vol % sulfuric acid, and 400 mm length of ultrasound clamp at 25 L/h PFAD flow rate. For the second step, a purity of methyl ester value of 93.32 wt % was obtained under the recommended conditions of 2.87:1 molar ratio of methanol to the first esterified oil (61.6 vol % methanol), 5.6 vol % of sulfuric acid, and 400 mm length of ultrasound clamp at 25 L/h esterified oil flow rate. The maximum yields of recommended conditions were 103.9 wt % of the first esterified oil, 107.6 wt % of the crude biodiesel, and 98 wt % of the purified biodiesel which were calculated based on 100 wt % of initial PFAD. The energy demand for the whole process to obtain high purity of crude biodiesel was 0.05796 kWh/L. According to the current study, ultrasonic clamps may provide high yield results in a short residence time of 32 s. As a result, ultrasonic clamps may be efficiently used as a potentially promising technology to create biodiesel and increase biodiesel productivity from second-generation biodiesel feedstock (PFAD), thereby minimizing biodiesel production costs. For further research and development, a solid catalyst has been focused on the production of biodiesel from high FFA oils using ultrasonic cavitation to decrease environmental impacts as compared to employing a homogeneous acid catalyst in the esterification process.

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Notes

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