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Research paper

A one-pot synthesis of biodiesel from leather tanning waste using supercritical ethanol: Process optimization

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ABSTRACT

Due to its substantial lipid content, leather tanning waste (LTW) is regarded as a potential feedstock for the waste-derived biodiesel. To promote the valorization of LTW, one-pot synthesis of biodiesel via supercritical ethanol method was investigated. The influence of the three independent reaction variables, namely reaction time t (10, 20, 30, 40, 50 min), temperature T (300, 350, 400 °C) and ethanol to LTW molar ratio r_{eo} (35, 40, 45), on the yield of fatty acid ethyl ester (FAEE) Y_F was studied. The multilevel factorial design combined with the response surface methodology and three-way analysis of variance was employed to design and optimize the experiment in regards to the three independent variables. Based on the optimization results, the highest FAEE yield was predicted at 99.68% when t = 47.4 min, T = 374.6 °C, and r_{eo} = 40.02. The actual FAEE yield was experimentally obtained at 98.91 ± 0.31% using the optimized reaction conditions. A deviation of 0.77% in the experimental verification shows a satisfactory agreement between the actual and predicted Y_F. All reaction variables were also found to give a significant effect on the yield of FAEE.

1. Introduction

The depletion of global petroleum reserves, the rising market price of crude oil, and the increased environmental concerns have stimulated recent interest in alternative sources to replace fossil fuels. Among the alternatives for fossil diesel, biodiesel has been widely investigated due to its renewability. Biodiesel is also characterized by low particulate matter and carbon monoxide emissions, and the absence of sulfur in the exhaust emission [1]. Due to its benefits, biodiesel consumption in Indonesia has significantly escalated in the past 9 years, while its annual production has increased exponentially from 44,000 tons in 2006 to 2.5 million tons in 2016 [2]. Currently, Indonesia blends a 20% volume of biodiesel with the petrodiesel [3] for direct use in the existing diesel engines. Vegetable oils derived from diverse sources, e.g., soybean oil [4], sunflower oil [5,6], and palm oil [7] were actively screened as raw materials for the production of the second-generation biodiesel. Moreover, many recent studies also use a wide variety of non-edible oils, e.g., Karanja oil, jatropha oil, industrial waste fat, oil and grease (FOG), and animal tallow [8–12], as the raw material for biodiesel production. Non-edible oils, specifically FOG and animal tallow, are currently the best alternative for biodiesel feedstock compared to the others due to its lower price. Their valorization will also prominently reduce the waste and turn a waste problem into an asset, in-country.

The leather industry is one of the national outstanding sectors in Indonesia. Based on the data released by Statistics Indonesia, the export value of leather products from Indonesia to the global market has recorded the transaction of more than US$ 500 million [13]. However, leather tanneries are known to produce a higher amount of waste than products, as 80% of the rawhide is discharged as waste in leather processing [14,15]. Approximately 0.15 million tons of leather tanning waste (LTW) is generated in Indonesia each year. LTW contains a high amount of water, free fatty acids (FFA), acyl glycerides, and many other organic compounds, which can be converted to biodiesel. For this reason, it is of great interest to valorize this particular FOG into a high value-added product, which in this case is biodiesel.

The valorization of LTW to biodiesel encounters several challenges, generally due to the presence of water and FFA. The high water content

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Abbreviation

FOG	Fat, oil and grease
LTW	Leather tanning waste
FFA	Free fatty acid
SpCE	Supercritical ethanol
RSM	Response Surface Methodology
FAEE	Fatty acid ethyl ester
IS	Internal standard
GC-FID	Gas chromatography-Flame Ionization Detector
MLFD	Multilevel Factorial Design

promotes the hydrolysis of acyl glycerides to FFA, while a substantial amount of FFA (>0.1%) drives the occurrence of the saponification reaction between FFA and the basic catalyst during the transesterification step, which results in a reduced yield of biodiesel. Several techniques have been investigated to convert this type of waste-originated lipid to biodiesel. Idowu et al. (2019) proposed a combination technique of thermal pre-treatment, microwave-assisted esterification, and alkaline transesterification to improve the yield of animal fat-based biodiesel [16]. Meanwhile, Wang et al. (2017) used a bifunctional magnetic solid catalyst to produce biodiesel from soybean oil and jatropha oil with high acid value [17]. Another route extensively studied to transform the low-quality oils to biodiesel is the one-pot transesterification using subcritical [12,18] and supercritical [19–21] alcohol. Compared with the above methods, the subcritical and supercritical alcohol techniques have the advantage of faster reaction rates and simpler separation since there is no catalyst involved. The supercritical alcohol technique even offers a shorter reaction time than the subcritical one, which is favorable to further improve the process efficiency. Moreover, this catalyst-free technique is tolerant of FFA and water content in the raw feedstock [22]. The major shortcomings of this route come from the extreme operating temperature and pressure, as well as the considerably high alcohol to lipid molar ratio, which certainly increases the operating cost and hinders its industrial scale-up. Several innovations have been conducted by Sawangkeaw et al. (2010) to find milder conditions for the supercritical alcohol technique, including the use of co-solvent (CO_2 or propane), the addition of base or acid catalyst, and the combination of subcritical hydrolysis and supercritical alcohol transesterification [23]. However, the addition of more chemicals or processing steps would have once again posed an economical constraint as it increases the material costs.

The present investigation aims to produce LTW-based biodiesel with commercial purity and yield using a single-step catalyst-free supercritical ethanol (SpCE) technique, which has never been explored in this field. Ethanol is selected instead of methanol, due to its abundant availability, sustainability, and less toxicity which made it safer to use. The optimum operating condition (reaction time t, temperature T, and ethanol to LTW molar ratio r_{eo}) of this SpCE technique is also investigated using the response surface methodology (RSM) approach to maximize the process performance, and at the same time, minimize the energy and material consumptions.

2. Materials and methods

2.1. Materials

LTW was collected from a leather tanning factory in Bogor, Indonesia. Prior use, LTW was repeatedly washed with deionized water to remove the unwanted components (i.e., dirt, gangue, and other impurities). The washed LTW was then heated at 120 °C to remove the water and subsequently filtered to obtain the purified LTW. The analysis of fat and FFA content, as well as the fatty acid composition of LTW, were carried out according to the standard methods of AOAC 991.36, ASTM D5555-95, and ISO 12,966, respectively. The fatty acid profile of LTW was identified with GC-2014 (Shimadzu Ltd., Japan), using Restek Rtx-65TG (30 m × 0.25 mm ID x 0.10 μm film thickness, Restek, USA) as the fused silica capillary column. Meanwhile, the molecular weight of LTW was calculated using the equation below:

$$\text{Molecular weight of LTW}\left(MW_{LTW}, \frac{g}{g\ mol}\right) = 56.1\ x\ 1000\ x\ \frac{3}{(SV - AV)} \quad (1)$$

where SV is the saponification value of LTW $\left(\frac{mg_{KOH}}{g_{oil}}\right)$ and AV is the acid value of LTW $\left(\frac{mg_{KOH}}{g_{oil}}\right)$ [24–26]. The characteristics of LTW are presented in Table 1.

Absolute ethanol and technical hexane were purchased from Sigma-Aldrich and Merck (Germany), respectively. All chemicals used for the analysis were of high purity grade and require no further purification. The fatty acid ethyl esters (FAEE) standard pack (10008188) was purchased from Cayman Chemicals (Ann-Arbor, MI, USA). Methyl heptadecanoate was used as an internal standard (IS) in the analysis of FAEE purity. Ultra-high purity-grade nitrogen (99.99%) and helium (99.9%) for the gas chromatography-flame ionization detector (GC-FID) analysis were provided by Aneka Gas Industry Pty. Ltd., Surabaya.

2.2. SpCE transesterification of LTW

The reaction system for the SpCE transesterification of LTW consists of a 50 cm^3 cylindrical reactor, made from SS-316 grade stainless steel, and is completed with a pressure indicator, a thermocouple, and an external heater. This high-pressure reactor is also connected to a nitrogen gas cylinder. Fig. 1 depicts the schematic diagram of SpCE transesterification apparatus arrangement.

A certain proportion of ethanol and LTW were introduced to the vessel to achieve the intended molar ratio of ethanol to LTW (r_{eo} = 35, 40, 45). The molar weight of LTW was determined by dividing the mass of LTW to its average molecular weight that was previously measured using equation (1). After the vessel was properly tightened, nitrogen was purged into the reactor to remove air from the system. The reactor was then rapidly heated from room temperature to the desired reaction temperature (T = 300, 350, 400 °C). To reach the required pressure P (15 MPa), the nitrogen gas at the specified rate of 3 ml/min was once again injected into the reactor. The reaction begins after it reached the intended pressure and temperature. Both pressure and temperature were monitored throughout the reaction course using pressure gauge and thermocouple installed in the system to maintain the system isobaric and isothermal.

The reactor vessel was then immediately cooled down in a water bath right after it reached the specified reaction time (t = 10, 20, 30, 40,

Table 1
The characteristics of LTW.

Parameters	Result
Water content, %	12.37
FFA, %	15.24
Crude fat, %	62.61
Fatty acid profile, %	
C14:0	3.01
C16:0	26.83
C16:1	3.99
C17:0	0.42
C18:0	14.34
C18:1	43.32
C18:2	5.95
C18:3	2.03
C20:0	0.11

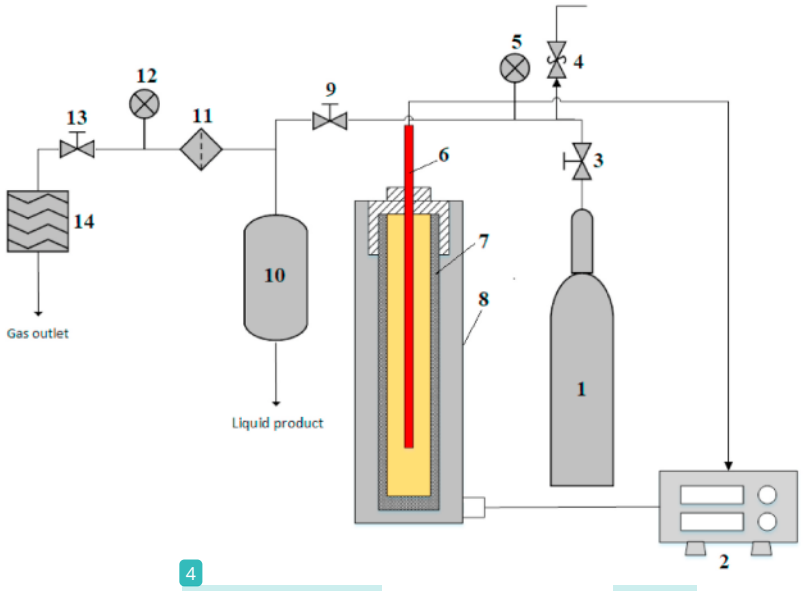

Fig. 1. Schematic diagram of the SpCE apparatus: (1) nitrogen gas cylinder, (2) Temperature control system, (3) valve, (4) pressure relief valve, (5) pressure gauge, (6) thermocouple, (7) Supercritical reactor, (8) electric heater, (9) valve, (10) gas-liquid flash separator, (11) 1 μm filter, (12) pressure gauge, (13) valve, (14) moisture trap.

50 min) to terminate the reaction. The liquid-liquid separation was performed to separate FAEE from its by-product. A given amount of hexane was mixed with the product mixture to extract FAEE, and the mixture was allowed to settle overnight. The FAEE-rich layer was retrieved and subsequently subjected to the vacuum evaporation (IKA RV 10B) to obtain the final FAEE product.

2.3. Compositional assay of FAEEs using GC-FID

The purity and compositional assay of FAEE was conducted using Shimadzu GC-2014 with the split/splitless injector and a flame ionized detector (FID). The narrow bore DB-WAX capillary column (30 m × 0.25 mm ID x 0.25 μm film thickness, Agilent Technology, CA) was used as the stationary silica phase in the analysis. A 100 mg of FAEE sample was properly dissolved in 2 ml of 10 μg/ml IS solution. The sample was then injected into the GC using a split ratio of 1:50. The temperature profile for the analysis was in accordance with the study conducted by Harijaya et al. (2019), where the column temperature was initially set at 50 °C and maintained at the same temperature for 15 min. The temperature was then raised to 220 °C at the heating rate of 4 °C/min, and held constant for another 15 min. Both split/splitless injector and FID was set isothermal at 250 °C and 260 °C, respectively. The flowrate of helium (99.9%) as the carrier gas was adjusted at a constant velocity of 30 cm/s [12].

The peaks in the final FAEE product were identified using the FAEE standard pack (10008188), while the IS solution acted as the calibration solution to precisely calculate the purity of FAEE in the product:

$$FAEE\ Purity\ (F_p,\ \%) = \left(\frac{\sum A_{FAEE} - A_{IS}}{A_{IS}} \times \frac{V_{IS} C_{IS}}{m_{FAEE}}\right) \times 100\% \quad (2)$$

where $\sum A_{FAEE}$ is the total area of FAEE peaks, A_{IS} is the corresponding area of the IS peak, V_{IS} is the volume of the IS solution (ml), C_{IS} is the concentration of the IS solution (g/ml), m_{FAEE} is the actual weight of the final FAEE product (g). Meanwhile, the yield of FAEE was determined by the following equation (3):

$$FAEE\ Yield\ (\%) = \left(\frac{m_{FAEE}}{m_{LTW}} x\ F_p\right) \times 100\% \quad (3)$$

where m_{FAEE} is the weight of final FAEE product (g), m_{LTW} is the initial weight of LTW (g), and F_p is the FAEE purity obtained from equation (2).

2.4. Statistical analysis: experimental design and process optimization

RSM method coupled with the multilevel factorial design (MLFD) was employed to statistically determine the optimum point of the SpCE technique for the LTW conversion to biodiesel. Three important parameters, reaction time t (min), temperature T (°C), and the molar ratio of ethanol to LTW r_{eo}, were selected based on the study conducted by Ong et al. (2013) and their relevance to the industrial feasibility. Ong et al. (2013) mentioned that exposure time takes a crucial role in the thermal degradation of alkyl ester, particularly in extreme temperature and pressure [1]. Therefore, while temperature and molar ratio of ethanol to LTW are classified into three different levels: low (1), center point (2) and high (3), reaction time is encoded into five different levels with 1 as the lowest level and 5 as the highest one to closely monitor its influence on the yield of FAEE. The encoded variables and their corresponding values are summarized in Table 2.

Table 3 lists the MLFP-based design of experiment (DOE), along with the experimental and predicted responses. All experiments were conducted in replicates to obtain a good data reproducibility. A total of 45 experiments were completely performed in a randomized order to

Table 2
The encoded levels of the transesterification condition.

Variables	Encoded factor	Factor level				
		1	2	3	4	5
Time (min)	T	10	20	30	40	50
		1		**2**		**3**
Temperature (°C)	T	300		350		400
Molar ratio of ethanol to LTW	r_{eo}	35		40		45

Table 3
Statistical MLFD-based design of experiment, generated by Minitab (version 18.1).

Run	Input variables			Response (FAEE yield, %)		
	T	T	r_{eo}	Experimental[a]	Predicted (Y_F)[a]	Standard deviation[b]
1	5	1	1	17.2	17.8	0.42
2	5	2	1	88.6	84.9	2.62
3	2	2	2	68.1	71.7	2.55
4	1	2	1	46.2	52.6	4.53
5	3	3	1	72.4	74.1	1.20
6	1	1	3	9.4	5.9	2.47
7	2	3	2	72.1	67.7	3.11
8	4	2	1	88.1	81.7	4.53
9	5	2	3	92.8	90.2	1.84
10	3	1	3	19.3	20.6	0.92
11	4	1	3	21.2	23.0	1.27
12	5	1	2	20.2	22.5	1.63
13	3	1	1	15.3	14.7	0.42
14	1	3	3	52.9	53.8	0.64
15	1	2	2	56.3	59.1	1.98
16	2	3	3	70.8	69.4	0.99
17	3	2	1	73.6	75.3	1.20
18	5	1	3	22.8	22.3	0.35
19	5	3	2	92.3	95.8	2.47
20	4	3	3	90.7	90.7	0.00
21	2	1	1	8.6	8.3	0.21
22	4	3	2	91.4	89.7	1.20
23	2	1	3	11.8	14.8	2.12
24	2	3	1	64.3	61.2	2.19
25	1	2	3	57.9	60.7	1.98
26	1	1	2	8.9	4.7	2.97
27	5	3	1	86.3	90.3	2.83
28	1	1	1	5.8	1.4	3.11
29	5	3	3	91.2	96.5	3.75
30	4	3	1	85.8	83.9	1.34
31	4	1	2	19.8	22.9	2.19
32	3	2	2	82.4	81.0	0.99
33	3	2	3	83.4	81.9	1.06
34	4	2	2	94.2	87.1	5.02
35	3	1	2	18.2	20.1	1.34
36	4	2	3	93.9	87.7	4.38
37	2	1	2	12.7	14.0	0.92
38	3	3	3	81.6	81.6	0.00
39	3	3	2	78.6	80.3	1.20
40	1	3	2	51.9	51.8	0.07
41	2	2	3	71.6	72.9	0.92
42	1	3	1	48.9	45.0	2.76
43	4	1	1	16.4	17.9	1.06
44	2	2	1	54.1	65.6	8.13
45	5	2	2	90.7	90.0	0.49

[a] The overall standard error of estimate (SEE) between the experimental and its corresponding predicted responses was 3.30%.
[b] Standard deviation between the experimental and predicted responses for each run.

eliminate any systematic errors. The responses obtained from the experiments were then fitted into a second-order polynomial equation, generated by analysis of variance (ANOVA) using Minitab (ver.18.1) with a 95% confidence interval. The developed mathematical regression model was statistically evaluated for its goodness-of-fit by using the values of the coefficient of determination (R-squared). The response surface plots were developed by holding one variable constant in the middle level while manipulated the other two variables.

The correlation between the predicted response (FAEE yield, %) and the three independent parameters are expressed by equation (4), where Y_F is the predicted FAEE yield (%); q_0, q_i, q_{ii}, q_{ij} are the regression coefficients for the intercept, linear, quadratic and interactions of the two independent variables, respectively; X_i and X_j are the coded parameters (t, T, r_{eo}). The value of i ranges from 1 to 3 for temperature and molar ratio of ethanol to LTW, while it spreads from 1 to 5 for reaction time.

$$Y_F = q_0 + \sum_{i=1}^{3} q_i X_i + \sum_{i=1}^{3} q_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} q_{ij} X_i X_j \quad (4)$$

3. Results and discussions

3.1. Specification of LTW

As seen in Table 1, LTW contains a substantial amount of FFA and moisture content, with the respective value of 15.24% and 12.37%. A large amount of fat (i.e., acyl glycerides and minor lipid components) are observed in LTW, which covers 62.61% of the total mass. According to the fatty acid profile, three major fatty acids that compose LTW are palmitic acid (C16:0), stearic acid (C18:0), and oleic acid (C18:1).

Several studies reported that a feedstock with the above characteristics requires at least three steps (i.e., pre-treatment for the impurities removal, esterification for the FFA reduction, and transesterification) to produce biodiesel with commercial yield and purity [27,28]. The high content of FFA in a feedstock induces the reaction between FFA and basic catalyst to form soap. Moreover, a significant amount of moisture in the raw material promotes the hydrolysis of acyl glycerides into FFA, which then again triggers the soap formation [29]. The presence of soap in the reaction system (1) tends to shift the transesterification to the reactant side, lowering the yield of biodiesel, and (2) induces the formation of emulsified products, causing difficulties in the purification process. SpCE technique, however, facilitates both esterification and transesterification to run simultaneously in a one-pot system, negates the requirement to pretreat the FFA or moisture content in raw lipids, and subsequently simplifies the complicated separation steps [30,31]. The conversion of the lipid material to biodiesel using supercritical alcohol also offers a high reaction rate, hence, requiring only a relatively short time to achieve a high production yield [31,32].

3.2. Process optimization using RSM

RSM combined with MLFD was employed to determine the optimum operating conditions for the production of LTW-based biodiesel by simultaneously integrating the three independent processing variables (e.g., reaction time t, temperature T, and the molar ratio of ethanol to LTW r_{eo}). Table 3 summarizes the correlation between the series of encoded input variables and the experimental yield of FAEE as the response. Subsequently, these results were statistically analyzed and found to fit into a polynomial quadratic model. Using the coded values presented in Table 2, the model derived to predict the biodiesel production is expressed by the following equation:

$$\begin{aligned} Y_F\,(\%) = &-137.5 + 11.62(t) + 142.8(T) + 13.23(r_{eo}) - 1.624\left(t^2\right) \\ &- 30.83\left(T^2\right) - 2.42\left(r_{eo}{}^2\right) + 3.273(t)(T) - 0.348(t)(r_{eo}) \\ &+ 0.415(T)(r_{eo}) \end{aligned} \quad (5)$$

where Y_F is the predicted FAEE yield (%); t, T, r_{eo} are the encoded level of the independent variables (1, 2, 3, 4, 5 for t and 1, 2, 3 for T and r_{eo}). All values of Y_F are also presented in Table 3.

The positive sign indicates a synergistic effect given by the factor to the increase of FAEE yield, while the negative sign implies that the factor possesses an antagonistic effect on the response. The mathematical model above showed that t, T, r_{eo}, (t) (T), (T) (r_{eo}) provide a linear effect on the increase of FAEE yield, while the negative coefficients of the intercept, t^2 T^2 $r_{eo}{}^2$, and (t) (r_{eo}) indicate that these variables decrease the FAEE yield.

Referring to the ANOVA results (Table 4), the regressed model shows that all terms except that of $r_{eo}{}^2$, (t) (r_{eo}), and (T) (r_{eo}) (p-value > 0.05) are significant. The Pareto chart (Fig. 2) also presents that all linear terms are found to be prominent with the significance order of $t > T > r_{eo}$. The notable quadratic terms were t^2 and T^2, with T^2 gives the highest

Table 4
The significance study of the tested variables, performed by three-way ANOVA.

Term	Coefficient	SE Coefficient	T-Value	*P*-Value
Constant	67.65	1.58	42.79	<0.0001
t	14.25	1.01	14.15	<0.0001
T	−69.64	5.54	−12.58	<0.0001
r_{eo}	4.09	1.30	3.13	0.003
t^2	−1.624	0.368	−4.42	<0.0001
T^2	−123.33	5.22	−23.63	<0.0001
r_{eo}^2	−2.42	1.30	−1.86	0.072
(t) (T)	6.55	1.07	6.15	<0.0001
(t) (r_{eo})	−0.348	0.533	−0.65	0.517
(T) (r_{eo})	0.83	1.85	0.45	0.656
R-squared (R^2)			0.9865	
Adjusted R^2			0.9830	
Predicted R^2			09770	

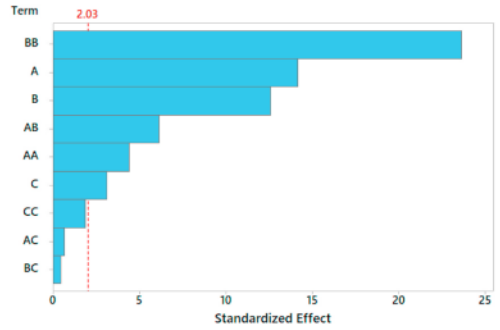

Fig. 2. Pareto chart of the standardized effect, generated by Minitab (version 18.1), for the LTW-based biodiesel preparation via the SpCE technique, using the yield of FAEE as the response at a 95% confidence level where A = t, B = T, C = r_{eo}.

effect on the FAEE yield. The only two-ways interaction that was found to be significant to the process is the interaction between reaction time and temperature ((t) (T)).

As seen in Table 4, the coefficient of determination (R^2) value of the mathematical model (Equation (5)) is 0.9865, implying that 98.65% of the variance results are attributed by the three investigated parameters. This R^2 value also points out that this quadratic equation can reasonably interpret the experimental data. The value of both adjusted and predicted R^2 (0.9830 and 0.9770, respectively) shows a good agreement between the predicted and experimental data of FAEE yield. Thus, the fitted regression model is considered sufficient to describe the behavior of all the independent input variance.

The two-way interaction effect on the predicted response is depicted in Fig. 3 (a) – (c) as the 3D surface plots. Fig. 3 (a) describes the effect of reaction time and temperature on the yield of FAEE. It can be seen from the curvature lines, the enhancement of reaction time and temperature from the bottom level to the highest one gives a favorable influence on the yield of FAEE. While the FAEE yield rapidly escalates along with the temperature rise from T = 300 °C to T = 350 °C at a constant reaction time, it reaches a plateau point and then gradually decreases when the temperature approaches 400 °C. A similar trend is also observed for reaction time where the response rapidly escalates from t = 10 min to t = 30 min. The further extent of reaction time gives only a slight increase of FAEE yield. Imahara et a. (2008) reported that the decomposition of biodiesel occurs dominantly at a temperature above 350 °C over a prolonged reaction time [33].

Fig. 3 (b) represents the two-ways interaction between reaction time and the molar ratio of ethanol to LTW on the FAEE yield. It is evident that reaction time has the most significant influence on the yield of FAEE as it tends to have a steeper slope than the other factors. Meanwhile, the

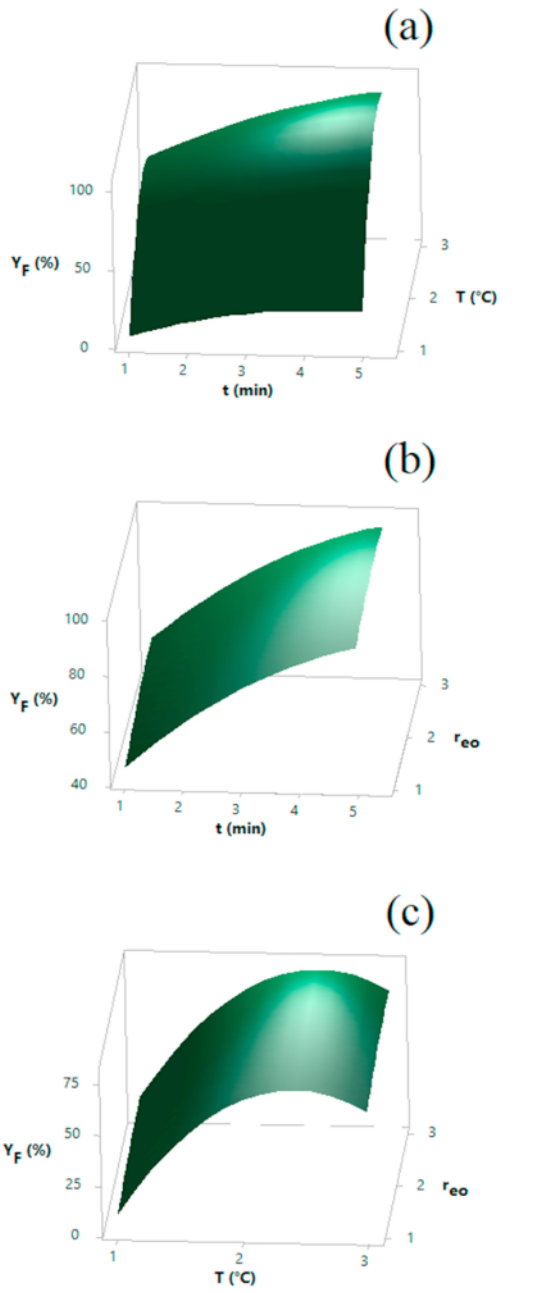

Fig. 3. The 3D response surface plot of the FAEE yield, generated by Minitab (version 18.1) at various (a) t and T, (b) t and r_{eo}, (c) T and r_{eo}.

enhancement of the molar ratio of ethanol to LTW from r_{eo} = 35 to r_{eo} = 45 at a constant reaction time causes a slight increase in the FAEE yield. A consistent trend is also monitored in Fig. 3 (c), where the elevation of ethanol to LTW molar ratio at a constant temperature induces only a minor increase of FAEE yield. It can be seen from Fig. 3 (a) and (c) that the optimum yield of FAEE is obtained at the middle level of temperature. A further rise in temperature results in a lower FAEE yield.

The optimum operating variables for the SpCE technique were generated by Minitab (version 18.1), based on the developed

mathematical equation and the experimental data. The resulting optimum point for the SpCE process is as shown in Fig. 4: t = 47.4 min (4.7395), T = 374.6 °C (2.4918), and r_{eo} = 40.02 (2.0046). The optimum FAEE yield Y_F was predicted at 99.68% with the model desirability of 1.00. To verify the reliability of the model, three replicated experiments were performed under these optimum variables. The average optimum yield of FAEE was experimentally obtained at 98.91 ± 0.31% with a purity of 97.55%. With the error between the experimental and predicted values of only 0.77%, it can be concluded that the developed mathematical equation provides excellent accuracy for the prediction of FAEE yield using the operating parameters within the tested levels. The optimized FAEE yield is comparable, if not higher, than that reported in the literature, indicating that this SpCE technique is compatible to convert LTW to biodiesel. Tan et al. (2010) and Gui et al. (2009) mentioned that the transesterification of the refined palm oil using ethanol under supercritical conditions can achieve the optimum yield of 79.2% at T = 349 °C, t = 29–30 min, and the molar ratio of ethanol to RPO r_{ep} = 33 [20,21]. Bunyakiat et al. (2006) reported a 95% FAME yield was produced from the conversion of coconut oil at T = 350 °C, t = 6.7 min, and methanol to coconut oil molar ratio r_{mc} = 42 [34]. Meanwhile, Reddy et al. (2014) stated that only 67% conversion of FAEE was obtained from dry algae via SpCE method at T = 265 °C, t = 20 min, and 1:9 dry algae to ethanol (w/v) ratio [35].

In this study, the optimum molar ratio of ethanol to LTW (r_{eo} = 40.02) is also found within the range reported by previous studies [20,21,34,36]. Although in most cases the high molar ratio of ethanol to LTW is unfavorable in the industries, the excess ethanol can be recovered through the rectification system and recycled back to the reactor. Moreover, a short reaction time (t = 47.4 min) definitely provides a benefit in production efficiency.

3.3. The effect of the reaction parameters on the FAEE yield

The effect of the reaction parameters on the FAEE yield is illustrated in Fig. 5 (a) – (c). Fig. 5 (a)–(b) show that in both constant temperature and molar ratio of ethanol to LTW, a sharp hike in the yield of FAEE is monitored by lengthening reaction time from the lowest to the highest level. Extending the duration of transesterification allows longer contact between the supercritical alcohol, oil, and water phase, ensuring a higher conversion of acyl glycerides and FFA into FAEE [19]. A major increase in the FAEE yield is also observed by prolonging reaction time at a higher temperature level (T = 350–400 °C). This is likely due to the increased miscibility among ethanol, water, and LTW at a higher temperature, creating a more homogenous system and promoting intensive contact between the reactants. The results are in agreement with the study conducted by Maaira et al. (2011), which stated that the yield of biodiesel is affected by the residence time. The study also mentioned that a higher conversion rate is also monitored at a higher temperature because the collision between particles intensifies along with the escalation of temperature; thus, the activation energy of the reaction is easier to achieve [37].

Temperature is usually considered as the critical parameter in the supercritical transesterification because this parameter affects the density, viscosity, and miscibility of the reactants. Moreover, it is a known fact that both esterification and transesterification are endothermic and reversible. As seen in Fig. 5 (a) and (c), increasing the temperature from T = 300 °C to T = 350 °C improves the FAEE yield remarkably in all levels of reaction time and the molar ratio of ethanol to LTW. This is attributed to the change of reactant properties in the supercritical state. Both water and ethanol have low miscibility with LTW at the standard room temperature. However, a great enhancement of temperature to the supercritical condition reduces their dielectric constant and viscosity. The weakened hydrogen bonding between water and the hydroxyl group in ethanol caused by the temperature increase also magnifies their miscibility in the non-polar LTW phase [38] and subsequently increases the mass transfer and reaction rate between the reactants [39]. Moreover, based on the kinetic Arrhenius law, the temperature increment plays a significant role in the improvement of the reaction rate constant

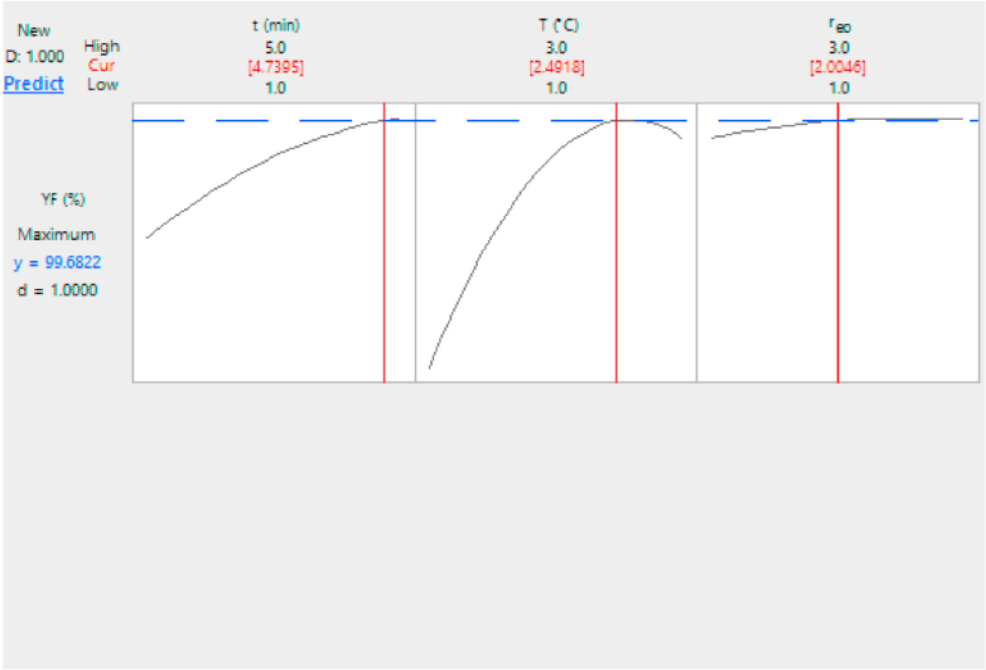

Fig. 4. The response optimization plot of the three independent reaction variables (D = composite desirability, y = predicted response, d = desirability), generated by Minitab (version 18.1).

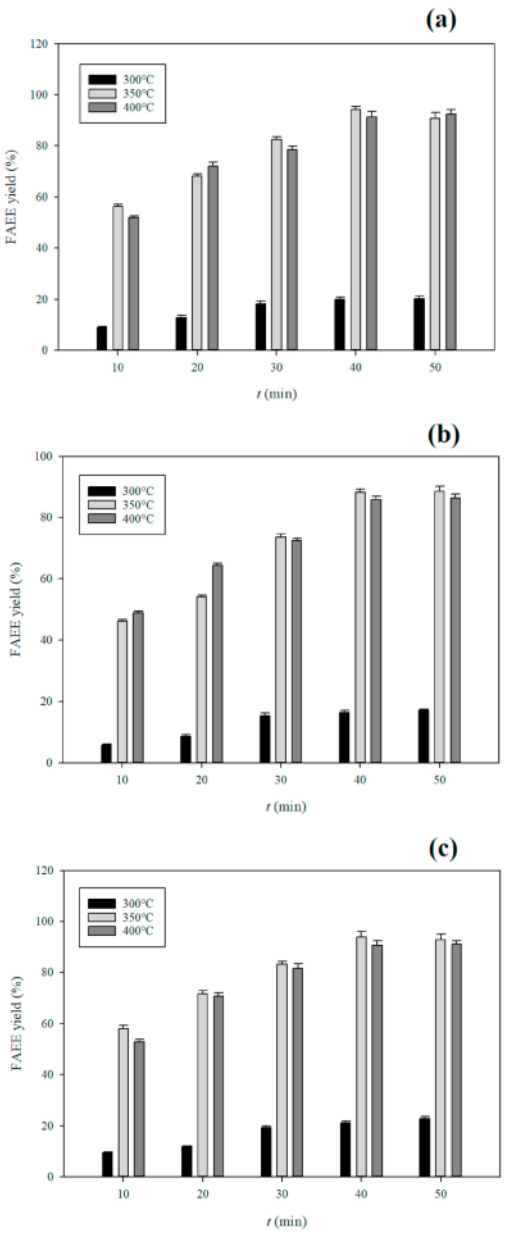

Fig. 5. The variation of the experimental FAEE yield with time t (min) at different temperatures (T = 300, 350, 400 °C) and a constant molar ratio of ethanol to LTW (a) r_{eo} = 35, (b) r_{eo} = 40, (c) r_{eo} = 45 (plotted by SigmaPlot version 14).

and shifts the equilibrium to the right (product side).

From another viewpoint, temperature greatly affects the hydrolysis of the lipids into FFA in the presence of water. This reaction is desirable in the SpCE technique since a high FFA content increases the miscibility between water and lipid, and promotes a faster diffusion rate. Unlike the traditional technique, Gunawan et al. (2014) mentioned that high water content may encourage the occurrence of the in-situ esterification/transesterification reaction to form biodiesel, as the number of the dissociated ions in water (i.e., H_3O^+ and OH^-) significantly escalates along with the increase of temperature and behaves as a bifunctional catalyst to induce the in-situ esterification/transesterification, leading to higher recovery of FAEE [18].

Fig. 5 (a) and (c) also show that the yield of FAEE reaches a stagnant phase (even slightly decreases in some points) when the temperature is further escalated to the highest level (T = 400 °C). This phenomenon indicates that the reaction has reached equilibrium conditions and further escalation may lead to a reverse reaction to the reactant side [40]. The results are also in agreement with several works conducted by Wang et al. (2018), Shin et al. (2011) and Ortiz-Martinez et al. (2019), where a further temperature rise above 350 °C does not give a major increase on the recovery of biodiesel, and instead, thermally degrades the unsaturated carbon-chain in the product [41–43].

The influence of the molar ratio of ethanol to LTW on the FAEE yield is shown in Fig. 5 (b) and (c). Although the addition of excess alcohol, theoretically, should improve the interaction between the lipid and ethanol and promote the conversion of LTW to biodiesel, only a mild increase in the yield of FAEE is observed when the molar ratio of ethanol to LTW was enhanced from the lowest to the highest level. As explained above, alcohol under the supercritical condition is able to dissolve the lipid largely, and therefore, changing the reaction from the heterogeneous system to a homogenous one. However, since the mixture has already been in a homogenous state, further increasing the molar ratio of alcohol to oil will not increase the biodiesel yield significantly. Gunawan et al. (2014) and He et al. (2007) mentioned that excess alcohol seems to have a favorable effect on the biodiesel yield only to a certain extent due to equilibrium constraint [18,44], while Thoai et al. (2017) stated that high alcohol content in the system causes a lower concentration of acyl glycerides which is disadvantageous for the transesterification reaction since both alcohol and acyl glycerides are required to stimulate the reaction [45]. Moreover, further addition of excess ethanol tends to negate the product recovery because a higher glycerol content will lead the reaction to the reactant side, resulting in the lower biodiesel yield [46].

3.4. Composition profile of LTW-based biodiesel

The purity and FAEE profile of LTW-based biodiesel obtained at the optimum operating condition (t = 47.4 min, T = 374.6 °C, and r_{eo} = 40.02) was analyzed by using GC-FID. The FAEE purity in the LTW-based biodiesel is obtained at 97.55%. Ten peaks are identified using the external FAEE standard pack (10008188), with the profile as follows: 4.19% C14:0, 25.71% C16:0, 4.55% C16:1, 1.02% C16:2, 0.69% C17:0, 15.21% C18:0, 41.51% C18:1, 4.76% C18:2, 2.19% C18:3 and 0.17% C20:0. A minor change of fatty acid composition in the raw material (LTW) and final FAEE product (LTW-based biodiesel) is monitored, with the peak of C16:2 detected only in the final product. The occurrence of this C16:2 peak in the LTW-based biodiesel is likely due to the decomposition of long carbon-chain to shorter ones in the high-temperature process [42,43,47].

3.5. Fuel properties of LTW-based biodiesel

Table 5 lists the fuel characteristics of LTW-based biodiesel along with their corresponding ASTM standard method. The results are also compared to the standard requirement of biodiesel (ASTM D6751) and diesel fuel (ASTM D975-08). With the value of 2.36 mm^2/s, the viscosity of the final FAEE product obtained in this study is comparable with the specification of the regular diesel fuel, indicating that it can be widely used as a diesel fuel blend and there is no particular hardware modification required [48]. The flashpoint and cetane number of LTW-based biodiesel are measured at 98.4 and 51.2, slightly higher than the minimum value of ASTM D6751, emphasizing a good fuel ignition. A high calorific value (43.451 MJ kg^{-1}) is also comparable to that in the common petrodiesel (42–46 MJ kg^{-1}) [49]. The cloud point, which is obtained at 9.8 °C, indicates a good flowability. Both acid value and density of the fuel are also within the range required by ASTM D6751.

Table 5
The fuel characteristics of LTW-based biodiesel obtained via the SpCE technique.

Properties	Methods	Unit	LTW-based biodiesel	ASTM D6751	Diesel fuel (ASTM D975-08)
Kinematic viscosity (at 40 °C)	ASTM D445	$mm^2 s^{-1}$	2.36	1.9–6.0	1D: 1.3–2.4 2D: 1.9–4.1
Flashpoint	ASTM D93	°C	98.4	93 min	1D: 38 min 2D: 52 min
Cetane number	ASTM D613	–	51.2	47 min	46 min
Calorific value	ASTM D240	$MJ kg^{-1}$	43.451	–	–
Cloud point	ASTM D2500	°C	9.8	Location and season dependent	–
Density (at 15 °C)	ASTM D4052	$g cm^{-3}$	0.857	–	–
Acid value	ASTM D664	mg KOH/g	0.31	0.50 max	–

Based on the results, it can be concluded that the LTW-based biodiesel is a potential replacement for diesel fuel.

4. Conclusions

A one-pot synthesis of biodiesel using SpCE has been successfully conducted to produce LTW-based biodiesel. RSM, in conjunction with ANOVA, has been applied to design the experiment, predict the response, and maximize the result by optimizing the tested variables (reaction time t, temperature T, and ethanol to LTW molar ratio r_{eo}). The optimum operating conditions are at $t = 47.4$ min, $T = 374.6$ °C, and $r_{eo} = 40.02$. The optimum FAEE yield was experimentally obtained at 98.91 ± 0.31%, with the product purity (97.55%) reached the commercial requirement (higher than 96.5%), meanwhile, the predicted FAEE yield Y_F was calculated at 99.68%. The experimental and predicted responses have a proportional output, with an error of only 0.77%. A consistent result is also observed from the adjusted coefficient of determination which is close to unity (0.9830), indicating that the quadratic regression is in conform with the experimental results. The fuel properties of LTW-based biodiesel are in accordance with ASTM D6751 and ASTM D975-08. The results described in this study show that the SpCE technique is compatible to valorize LTW to biodiesel. Therefore, future studies should expand to the techno-economic and scalability analysis to create a plausible pathway between the outcomes of this research and its implementation in the industries.

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