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MULTILEVEL FACTORIAL DESIGN - BASED RESPONSE SURFACE METHODOLOGY FOR PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION FROM LEATHER TANNING WASTE USING NON-CATALYTIC SUPERCRITICAL ETHANOL

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December 18, 2019

Professor Patricia Thornley
Editor
Biomass & Bioenergy

Dear Professor Thornley,

On behalf of my co-author, I am writing to submit the manuscript for publication consideration in *Biomass & Bioenergy*. The details of the manuscript are as follows:

Title of Manuscript: **MULTILEVEL FACTORIAL DESIGN - BASED RESPONSE SURFACE METHODOLOGY FOR THE PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION FROM LEATHER TANNING WASTE USING NON-CATALYTIC SUPERCRITICAL ETHANOL**

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Keywords: *waste-derived biodiesel; leather tanning waste; supercritical ethanol; noncatalytic process; optimization study; renewable energy*

Statement of novelty :

Supercritical ethanol has been successfully employed to convert LTW into biodiesel and its operating condition optimization was conducted using multilevel factorial design-based response surface methodology and 3-way analysis of variance. 98.91% of FAEE recovery with 97.55% purity was obtained in the non-catalytic process with the newly found optimum conditions as follows: 47.4 min, 374.6^{o}C, and ethanol to LTW molar ratio of 40.02. The fuel properties of LTW-based biodiesel conform to ASTM D6751.

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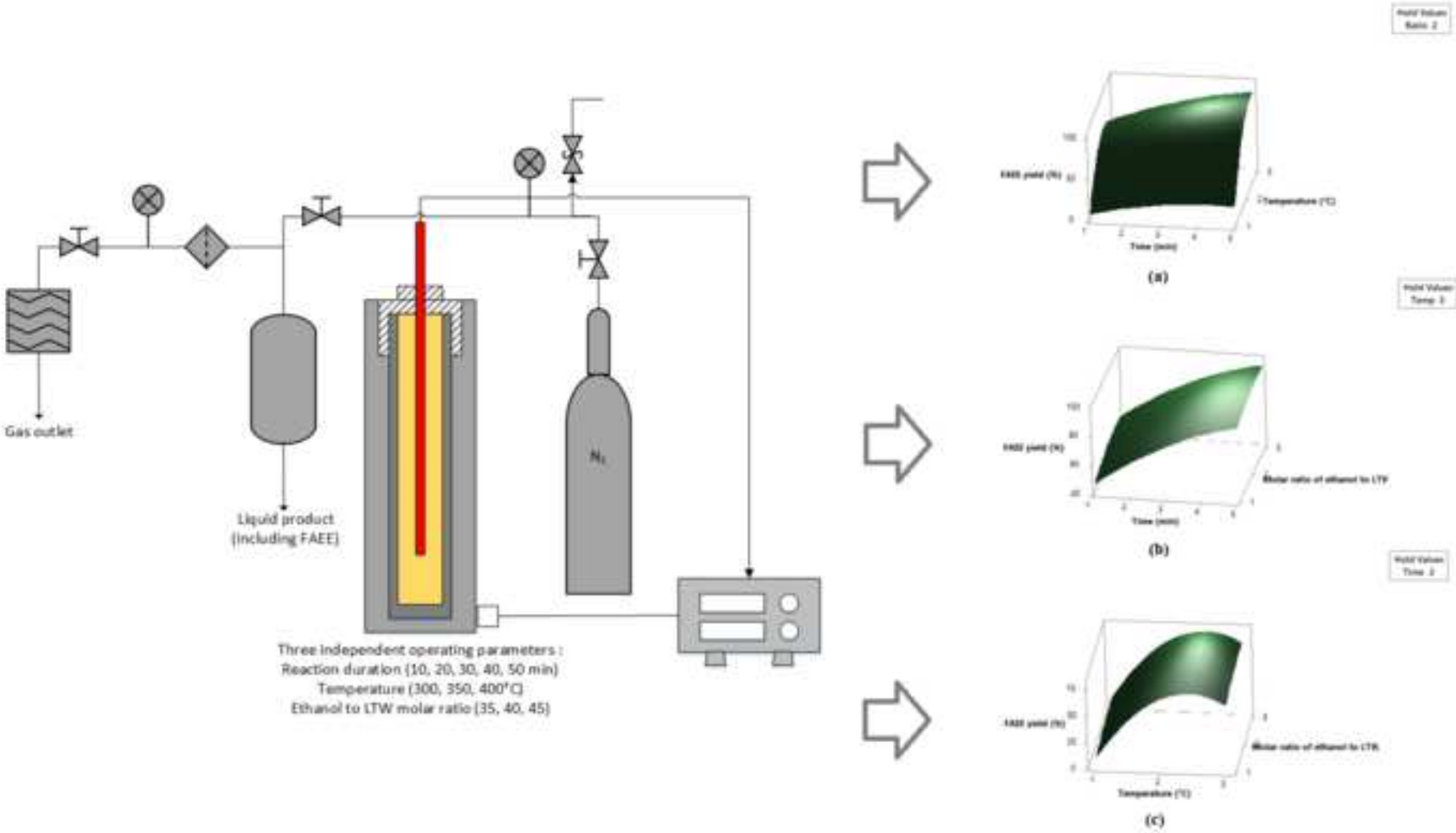
We ensure that the submitted manuscript is entirely original work of the authors. We have never previously submitted the manuscript to *Biomass & Bioenergy* and mutually agree that this manuscript should be submitted to the journal. Furthermore, we have read, understood and adhered to the Ethical Guidelines, and we have strictly prepared the manuscript in accordance with the journal guidelines.

Thank you for your consideration. I am looking forward to hearing from your positive response.

Sincerely yours,

Maria Yuliana

Graphical Abstract



Highlights:

- Supercritical ethanol has been successfully employed to convert LTW into biodiesel
- Optimization study was conducted using MLFD-based RSM and 3-way ANOVA
- 98.91% of FAEE recovery with 97.55% purity was obtained in the non-catalytic process
- Optimum conditions: 47.4 min, 374.6^{o}C, and ethanol to LTW molar ratio of 40.02
- The fuel properties of LTW-based biodiesel conform to ASTM D6751

MULTILEVEL FACTORIAL DESIGN - BASED RESPONSE SURFACE METHODOLOGY FOR PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION FROM LEATHER TANNING WASTE USING NON-CATALYTIC SUPERCRITICAL ETHANOL

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ABSTRACT

Currently, waste-derived biodiesel is drawing attention as an alternative fuel for its use shall not result in the competition of the edible source and is able to help in reducing the amount of waste produced. Leather tanning waste (LTW) is regarded as a highly potential feedstock for a waste-origin biodiesel since its annual production reaches 150,000 tons and creates harmful impacts on the environment. The utilization of LTW as a biodiesel feedstock can be one promising solution to both environmental dan energy problems. In this work, the conversion of LTW into biodiesel was investigated in supercritical ethanol (SpCE) condition with various reaction time (10 – 50 min), temperature (300 – 400°C) and ethanol to LTW molar ratio (35, 40 and 45). Multilevel factorial design (MLFD) in compliance with response surface methodology (RSM) and three-way ANOVA were employed to design and optimize the experiment in regards of the three independent variables. The FAEE yield as the response was fitted into a second-order polynomial regression model using the least-square analysis. It was found that all the independent variables gave significant effect on the FAEE recovery. The optimized operating conditions are as follows: reaction time of 47.4 min, temperature of 374.6°C and molar ratio of ethanol to LTW of 40.02, with the experimental and predicted FAEE yield of 98.91 ± 0.31% and 99.68%, respectively. This incredible high yield proves the compatibility of SpCE technique for the conversion of LTW to biodiesel.

Keyword: waste-derived biodiesel; leather tanning waste; supercritical ethanol; noncatalytic process; optimization study; renewable energy

1. Introduction[1]

The increase in the use of biodiesel in recent decades is a result of rising market prices of crude oil and the depletion of world oil reserves. This has led to the interest of researchers to be able to increase the use of alternative fuels, particularly for transportation and industrial purposes. Of the several types of alternative fuels available, biodiesel is considered as the most renewable fuel used as a substitute for diesel fuel. Currently Indonesia blends 20% volume of biodiesel with the petrodiesel for direct use in the existing engines without extensive modifications. Biodiesel is characterized by low particulate matter emissions, carbon monoxide and the absence of sulfur in exhaust emissions [1]. Due to this benefit, the growth of annual biodiesel production in Indonesia increased exponentially by almost 60 folds in a period of 10 years, while its consumption escalated more than a hundred times in the past 9 years [2].

Various types of vegetable oils have been studied as raw materials for the production of second generation biodiesel, such as soybean oil [3], sunflower oil [4,5] and palm oil [6], although currently the latest trend uses a lot of non-edible oils, such as karanja and jatropha

[1] **Abbreviation**

LTW	Leather tanning waste
FFA	Free fatty acid
FAEE(s)	Fatty acid ethyl ester(s)
RSM	Response Surface Methodology
SpCE	Supercritical ethanol
SCE	Subcritical ethanol
GC-FID	Gas chromatography-Flame Ionization Detector
MLFD	Multilevel Factorial Design

oil, waste fat, oil and grease (FOGs) from industrial origin and sewers as well as animal tallow [7–11]. These non-edible lipids, particularly FOGs and animal tallow are difficult to handle since they are rapidly degraded and possesses high content of free fatty acids (FFA) and moisture, which require pre-treatment before being subjected into the biodiesel conversion step.

In Indonesia, the availability of leather tanning waste (LTW), one of the FOGs produced from the leather industry, is quite substantial with the annual production of 0.15 million tons. Direct discharge of LTW into the environment creates unpleasant odor and harmful impacts on the fertility of soil and quality of water [1]. However, LTW possesses high amount of FFA and triglycerides (TG) which can be reacted with ethanol to produce biodiesel. Therefore, it is of great interest to positively utilize this particular FOGs into a higher value product such as biodiesel.

Valorization of LTW to biodiesel encounters several challenges, generally due to the presence of water and FFA. High content of water promotes the hydrolysis of TG to FFA, while substantial content of FFA (more than 0.1%) drives the occurrence of soap formation with the basic catalyst in the transesterification step, resulting in low biodiesel yield. Several conversion techniques have been investigated for this type of waste-originated lipid to biodiesel. Idowu et al. (2019) studied the yield improvement of biodiesel from waste animal fat through the combination of acidic esterification followed by alkaline transesterification and microwave technique [12]. Wang et al. (2017) proposed the use of bifunctional magnetic solid acid catalysts with both Lewis and Brondsted acid sites to produce biodiesel from soybean oil and jatropha oil with high acid value [13].

Another route extensively studied to transform low quality oils to biodiesel is the non-catalytic transesterification using subcritical [11,14] and supercritical [15] alcohol. This method offers short reaction time and simple product separation since no catalyst involved.

Moreover, these catalyst-free techniques are able to tolerate high FFA and water contents in the raw feedstock up to 30% and 36% (w/w), respectively [16]. It is likely attributed to their significant amount of hydrogen bond and ion solvation/association capability [17,18]. The major shortcomings of this route come from the extreme operating temperatures and pressures, leading to the requirement of certain reactor design, considerable high alcohol to lipid molar ratio used in the process, which certainly increase the operating cost and hinder its industrial scale-up application. In order to make it feasible for the industrial practice, several innovations have been conducted by Sawangkeaw et al. (2010) to find milder conditions for the supercritical alcohol technique, namely using co-solvent (CO_2 or propane), base or acid catalyst; or optimizing the transesterification yield using two-step subcritical hydrolysis-supercritical alcohol transesterification [19]. However, addition of more chemicals or processing steps would have once again pose economical constraints as it increases the material costs.

The objective of this study, therefore, is to perform the optimization analysis to discover the optimum operating condition (reaction time, temperature and alcofol to fats molar ratio) of the single-step catalyst-free supercritical ethanol (SpCE) technique, without co-solvent or catalyst addition and intricate process, using response surface methodology (RSM) approach. Ethanol was selected instead of methanol, due to its abundant availability, sustainability, and less toxicity which made it safer to use. The obtained optimum condition of SpCE technique will definitely contribute to the improvement of this particular process and cost efficiency. This study focuses as well on the LTW valorization ability as raw material to produce biodiesel with high purity and recovery under SpCE condition.

2. Materials and methods

2.1 Materials

LTW was originated from a leather tanning factory in Bogor, Indonesia. The pretreatment of waste prior to use was conducted by the following steps: (1) LTW was repeatedly washed with deionized water to remove the unwanted components, namely dirt, gangue and other impurities. The washed LTW was then heated at constant temperature of 120°C for the water removal and subsequently filtered to obtain the ready-to-use LTW. The fatty acid profile of LTW was measured with GC-2014 (Shimadzu Ltd., Japan), using Restek Rtx-65TG (30 m x 0.25 mm ID x 0.10 µm film thickness, Restek, USA) as the fused silica capillary column.

The analysis of LTW as raw materials was conducted to determine the fat and FFA content as well as its fatty acid composition using the standard methods of AOAC 991.36, ASTM D5555-95 and ISO 12966, respectively. The characteristics of LTW are presented in Table 1.

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 standard of fatty acid ethyl esters (FAEEs) 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. UHP-grade nitrogen (99.99%) and helium gases (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, thermocouple and external heater. The high-pressure reactor is also connected to a nitrogen gas cylinder. Figure 1 depicted the schematic diagram of SpCE transesterification apparatus arrangement. Certain proportion of ethanol and LTW were introduced to the vessel in order to achieve the intended ethanol to LTW molar ratio. The molar weight of LTW was determined by dividing the mass of LTW to its average molecular weight that is calculated using the equation below.

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

where SV is the saponification value of LTW ($\frac{mg\ KOH}{g\ oil}$) and AV is the acid value of LTW ($\frac{mg\ KOH}{g\ oil}$) [20–22]. After properly tightened, gaseous nitrogen was purged into the reactor to remove air from the system. The reactor was then rapidly heated from room temperature to the desired temperature. To reach the required pressure (15 MPa), the N_2 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 for a specified duration in an isobaric and isothermal condition. The pressure and temperature were monitored throughout the reaction course using pressure gauge and thermocouple installed in the system.

The reactor vessel was then immediately cooled down in a water bath right after the reaction duration reached the prescribed time to terminate the reaction. Liquid-liquid separation was performed to separate FAEE from its by-product. A given amount of hexane were mixed with the product mixture to extract FAEE and allowed to settle overnight. The FAEE-rich layer was retrieved and subsequently subjected to the vacuum evaporation (IKA RV 10B).

Figure 1

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 x 0.25 mm ID x 0.25 µm film thickness, Agilent Technology, CA) was used as the stationary silica phase in the analysis. A specified amount of FAEE sample (100 mg) was properly dissolved in 2 ml of 10 µg/ml IS solution. The sample was then injected to the GC using a split ratio of 1:50. The temperature program for the chromatography analysis was following the study conducted by Harijaya et al. (2019), where the column temperature was initially set at 50°C and maintained for 15 mins. The heat rate was then raised at the rate of 4°C/min to increase the temperature up to 220°C and held constant for another 15 mins. 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 constant velocity of 30 cm/s [11].

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

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

Where $\sum A_{FAEE}$ is the total area of FAEE peaks, A_{IS} is the corresponding area of IS peak, V_{IS} is the volume of IS solution (ml), C_{IS} is the concentration of IS solution (g/ml), m is the actual weight of the FAEE sample (g). Based on the F_p obtained from equation (2), the determination of FAEE yield can be performed using equation (3):

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

Where m_{FAEE} is the final FAEE weight obtained (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. Reaction time (min), temperature (°C) and the molar ratio of ethanol to LTW (mol/mol) were selected as the important parameters based on the study conducted by Ong et al. (2013) and their relevance to the industrial feasibility, both in processing and economic viewpoint. Ong et al. (2013) mentioned that exposure time takes crucial role in the thermal degradation of alkyl ester, particularly in the extreme temperature and pressure [1]. Therefore, while reaction 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 the effect of time to the yield of FAEE. The encoded variables and their corresponding values were summarized in Table 2.

Table 2

Table 3 listed the matrix of design of experiment (DOE) based on MLFD, along with the experimental and predicted response (FAEE yield, %). All experiments were conducted in replicates to obtain reliable data reproducibility and performed in a randomized order. The responses obtained from the experiments were then fitted into a second-order polynomial equation, generated using analysis of variance (ANOVA) by Minitab (ver.18.1) with 95% confidence interval.

The developed mathematical regression model was statistically evaluated for its goodness-of-fit by using the values of coefficient of determination (R-square). The response surface plots were developed from the mathematical regression analysis of experimental

responses by holding one variable constant in the middle level while manipulated the other two variables.

Table 3

The correlation between the predicted response parameter (FAEE yield, %) and the three independent parameters are expressed by equation (4), where Y 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 independent variables, respectively; X_i and X_j are the coded parameters (A, B, C). The value of *i* ranges from 1 to 3 for reaction temperature and ethanol to LTW molar ratio, while it spreads from 1 to 5 for reaction time.

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

3. Results and Discussions

3.1 Specification of raw materials (LTW)

As seen in Table 1, LTW contains large amount of FFA and moisture content, with the respective value of 15.24% and 12.37%. Substantial amount of fat (including TG, other acylglycerides and minor components) are observed in LTW, which covers 62.61% of the total mass. According to the fatty acid profile, three major fatty acids that composes LTW are palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1).

Several studies reported that with these particular characteristics of raw materials, at least one single pre-treatment and two-step esterification and transesterification process are required to produce biodiesel with commercial yield and purity [23,24]. High FFA content in raw materials induces the soap formation via saponification reaction with basic catalyst in the classical transesterification technique. Significant amount of moisture in the raw feedstock promotes the hydrolysis of lipids into FFA, which then again triggers the soap

formation [25]. The formation of soap tends to shift the transesterification to the reactant side, lowering the yield of biodiesel and as well induces the formation of emulsified products, causing difficulties in purification process.

SpCE technique, however, provides in-situ esterification/transesterification reaction, negates the requirement to pretreat the FFA or moisture content in raw lipids, which is, as well, able to subsequently omit the complicated separation steps [26,27]. Another advantage is that the conversion of vegetable oils to biodiesel using supercritical alcohol possesses high reaction rates and requires a relatively short time to achieve high production yield [27,28].

3.2 Process Optimization using RSM

Currently, SpCE process is still at the pilot-research stage, with extreme temperature and pressure as well as the enormous amount of alcohol become the main drawback in the implementation of this process to the industrial scale, because these factors result in high energy consumption that has to be minimalized. However, on the other hand, many studies reported that SpCE technique possesses many advantages, particularly in the time consumption and process simplicity. Therefore, simulating a model for the process is important to investigate the feasibility and limitation of SpCE from both economic and technological viewpoints. Furthermore, study on the behavior of processing variables in the reaction system such as operating temperature, time and molar ratio of ethanol to LTW needs to be done to find the optimal point of this promising SpCE technique.

RSM combined with MLFD was selected to conduct the determination of optimal parameters for the FAEE production by simultaneously integrating the three independent processing variables (reaction temperature, time and molar ratio of ethanol to LTW). The correlation between the FAEE yield as the response and the series of encoded input variables was summarized in Table 3.

The polynomial quadratic model was selected as the best-fitted model by RSM using the least square analysis, performed by Minitab (ver.18.1), due to its significance terms and the model was not alienated. The equation derived for the biodiesel production was expressed by Eq. 5, based on the coded values presented in Table 2.

$$FAEE\ yield\ (wt\%), Y = -137.5 + 11.62(A) + 142.8(B) + 13.23(C) - 1.624(A^2) - 30.83(B^2) - 2.42(C^2) + 3.273(A)(B) - 0.348(A)(C) + 0.415(B)(C) \quad (5)$$

where Y is the FAEE yield (wt%); A, B, C are the encoded value of the independent variable levels (1, 2, 3, 4, 5 for *A* and 1, 2, 3 for *B* and *C*).

Positive sign indicates synergistic effect in the increase of FAEE yield, while negative sign indicates that the factor possesses antagonistic effect on the response. The mathematic model (Eq. 5) ahowed that the linear coefficient (*A, B, C*) and two-ways interaction variables between time and temperature as well as between temperature and molar ratio of ethanol to oil ((*A*)(*B*), (*B*)(*C*)) provides linear effect on the increase of FAEE yield, while the negative coefficient of intercept, quadratic variables (A^2, B^2, C^2) and the other two-ways interaction between time and molar ratio of ethanol to oil indicated that these variables decrease the FAEE yield.

Table 4 presented the result of the significance study of the independent variable individually, quadratically as well as their interactions performed by statistical ANOVA. Referring to the ANOVA results, the regressed model showed that all terms except that of quadratic term of ethanol to oil molar ratio and two-ways interaction between the molar ratio of ethanol to LTW and both time and temperature (p-value > 0.05) were significant. The pareto chart of standardized effects (**Figure 2**) presented that all linear terms were found to be prominent with the significance order of reaction time > temperature > molar ratio of

ethanol to oil, while the notable quadratic terms were reaction time (A^2) and temperature (B^2), with quadratic term of temperature gives the highest effect to the SpCE process. The only two-ways interaction that was found to be significant to the process is the interaction between reaction time and temperature (A)(B).

Table 4

Figure 2

As also seen in Table 4, the coefficient of determination (R^2) value of the mathematical model (Eq. 5) was 0.9865, ascribing that 98.65% of the variance results was attributed by the three investigated parameters. This R^2 value also points out that this quadratic equation is able to reasonably interpret the experimental data. A good agreement between the predicted and experimental data of FAEE yield was monitored from the value of adjusted and predicted R^2 (0.9830 and 0.9770, respectively). From the results of ANOVA, the fitted regression model is considered sufficient to describe the behavior of all the independent input variance.

The profile of predicted response (FAEE yield) with the interactions between two design variables are depicted as the 3D surface plots in Figure 3 (a) – (c). Figure 3 (a) described the effect of temperature and reaction time to maximizing the yield of FAEE. It can be seen from the curvature lines of temperature vs FAEE and reaction time vs FAEE that the enhancement of temperature and reaction time from the bottom level to the highest one gave a favorable influence on the yield of FAEE. While the FAEE yield escalated rapidly along with the temperature rise from 300°C (1) to 350°C (2) at constant reaction time, it reaches plateau point and then gradually decrease when it is closer to the temperature of 400°C. A similar trend was observed for the reaction time where the response rapidly escalated from the 10 min (1) to the 30 min (3). Further extent on reaction time leads to a slight increase of FAEE yield.

Figure 3 (b) represents the two-ways interaction between reaction time and molar ratio of ethanol to LTW on the FAEE yield. As depicted in the pareto chart, it is also evident that the reaction time gives the most significant influence on the yield of FAEE as reaction time tends to have steeper slope than the other factors, while the enchancement of molar ratio of ethanol to LTW from 35 to 45 at the constant reaction time causes only insignificant increase the FAEE yield. A consistent trend was also monitored in Figure 3 (c), where the elevation of ethanol to LTW molar ratio gave only minor increase at the constant reaction temperature. It can be seen that the optimum yield of FAEE was obtained at the middle level of temperature. Further rise in the temperature resulted in lower FAEE yield.

Figure 3

The optimal levels of process variables for SpCE technique were generated by Minitab (ver.18.1) based on the developed mathematical equation and the experimental data. The resulting optimal point for SpCE process are as shown in Figure 4: reaction time of 47.4 min (4.7395), temperature of 374.6°C (2.4918) and ethanol to LTW molar ratio of 40.02 (2.0046), with the predicted optimum FAEE yield of 99.68% and model desirability of 1.00. To verify the reliability of the model, three replicated experiments were performed under these optimal variables and it was found that the average optimal yield of FAEE was 98.91 ± 0.31% with the 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. Low molar ratio of ethanol to LTW (40.02) is in most cases favorable for the industries since the cost of materials usually pose as the major operating expenditures (38, Felix), while short time requirement (47.4 min) provides benefit in the production efficiency.

Figure 4

3.3 The effect of reaction paramaters on FAEE yield

The effect of reaction parameters on the FAEE yield is illustrated in Figure 5 (a) – (c). Based on the statistical ANOVA, time was the second most significant variable affecting the FAEE yield following the quadratic temperature interaction. Figure 5 (a) – (b) showed that in both constant temperature and ethanol to LTW molar ratio, a sharp hike in FAEE yield was monitored by lengthening the reaction time from the lowest to the highest level. Extending the duration of transesterification reaction allows longer contact between the supercritical alcohol, oil and water phase, ensuring higher conversion of TG and FFA into FAEE [15]. The interaction effect between reaction time and temperature was also revealed where major increase of FAEE yield occurred by prolonged the reaction time at the higher temperature level (350 - 400°C). It was likely due to the miscibility of ethanol and water in LTW that increases along with the temperature, forming a more homogenous system in higher temperature and promoting an intensive contact between the reactants. The results were in agreement with the study conducted by Maaira et al (2011), which stated that the yield of biodiesel is affected by resident time. The study also mentioned that higher conversion and reaction rate was also monitored in higher temperature, due to the collision between particles intensifies along with the escalation of temperature so that the activation energy of the reaction is easier to achieve [29].

Temperature is usually considered as the critical parameter in the supercritical transesterification, because this parameter affects the density, viscosity and miscibility of the reactants at the supercritical state. Moreover, it is a known fact that both processes of esterification and transesterification are endothermic and reversible. Therefore, based on Figure 5 (a) – (c), the increase of temperature from 300°C to 350°C improves the FAEE yield remarkably in all levels of time and molar ratio of ethanol to LTW. This is likely due to the

change of reactant properties in the supercritical state. Both water and ethanol has low miscibility with LTW at the standard room temperature. However, great enhancement of temperature to the supercritical condition reduced their dielectric constant and viscosity, leading to a more homogenous mixture system and induces intense contact among the reactants. The weakened hydrogen bonding between water and hydroxyl group in ethanol caused by the temperature increase magnifies their miscibility in the non-polar LTW phase [30], and subsequently increase the mass transfer and reaction rate between the reactants [31]. Moreover, based on the kinetic Arrhenius law, temperature increment plays significant role in the improvement of the reaction rate constant and shift the equilibrium to the right (product side).

From another point of view, in the presence of water, temperature greatly affects the hydrolysis of the lipids into FFA. Higher rate of hydrolysis reaction in the system was highly attributed by the increase of temperature, which in this SpCE technique, is desirable since high FFA content increases the miscibility of water and lipid, and promotes faster diffusion rate. While Kusdiana and Saka (2004) also agrees that the presence of water has no effects on the conversion in the supercritical alcohol technique [32] unlike the traditional techniques, Gunawan et al. (2014) mentioned that high water content may encourage the simultaneous esterification/transesterification reaction to form biodiesel. The numbers of dissociated ions in water, H_3O^+ and OH^-, significantly escalates along with the increase of temperature and behave as bifunctional catalyst to induce the in-situ esterification/transesterification processes, leading to higher recovery of FAEE [14].

As seen on Figure 5 (a) and (c), yield of FAEE reached stagnant phase (even slightly decrease in some tested points) when the temperature was further escalated to the highest level (400°C). This might indicates that the reaction has reached equilibrium condition and further escalation may lead to reverse reaction to the reactant side [33] . This result is also in

agreement with several works conducted by Wang et al. (2018), Shin et al. (2011) and Ortiz-Martinez et al. (2019), where further temperature rise did not give a major increase on the recovery of biodiesel, instead the chance of the thermal degradation of product to occur might improve, particularly for the unsaturated carbon-chain in the mixture [34–36].

Figure 5 (b) and (c) shows the influence of molar ratio of ethanol to LTW on the FAEE yield. It can be seen clearly that the tendency of FAEE yield to increase when the molar ratio of ethanol to LTW was enhanced from the lowest to the highest level is mild, eventhough theoretically the addition of excess alcohol should improve the interaction between the lipid and ethanol, promoting the conversion of LTW to biodiesel. On supercritical condition, alcohol is able to dissolve the lipid largely and therefore, it changes the heterogenous reaction to a homogenous one. As a result, the reaction rate increases greatly. However, since the mixture has already been in a homogenous state, continuing increasing the molar ratio of alcohol to oil cannot help to increase the biodiesel yield significantly. The reaction migh as well be constrained by the equilibrium, which makes the addition of alcohol to the system do not give any major effect on the yield after a certain value of molar ratio [37]. Gunawan et al. (2014) also mentioned that excess alcohol seems to have a favorable effect on the biodiesel yield only to a certain extent, while Thoai et. al. (2017) stated that high alcohol content in the mixture system causes a lower concentration of acylglycerides which is disadvantageous for the transesterification reaction since the two reactants are required to stimulate the reaction [14,39]. Another reason is that further addition of excess ethanol inclines to negate the product recovery since higher glycerol content will lead the reaction to the reactant side, resulting in the lower biodiesel yield [40].

Figure 5

3.4 Composition profile of LTW-based biodiesel

The purity and FAEE profile of LTW-based biodiesel obtained at the optimum operating condition (reaction time of 47.4 min, temperature of 374.6°C, and molar ratio of ethanol to LTW of 40.02) was analyzed by using GC-FID. It was found that the FAEE content in the LTW-based biodiesel was 97.55%. Ten FAEE peaks were identified using the external FAEE standard pack (10008188), with the carbon-chain 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. Minor change of fatty acid composition in the raw material (LTW) and final product (LTW-based biodiesel) was 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 was likely due to the decomposition of long carbon-chain to shorter ones in the high temperature process [35,36,41].

3.5 Fuel properties of LTW-based biodiesel

Table 5 listed the fuel characteristics of LTW-based ethyl esters with the corresponding ASTM standard testing method. The results were compared to the standard requirement of biodiesel (ASTM D6751) and diesel fuel (ASTM D975-08). The viscosity of FAEE obtained from LTW were comparable to the specification of regular diesel fuel, with the value of 2.36 mm^2/s, indicating that no particular hardware modification are required for handling this fuel [42] and it can be widely used as diesel fuel blend. The flash point and cetane number of LTW-based ethyl esters were estimated as 98.4 and 51.2, slightly higher than the minimum value of ASTM D6751, emphasizing the good ignition of fuel. High calorific value was observed in LTW-based biodiesel, with the value of 43.451 MJ kg^{-1}, comparable to the usual petrodiesel (42-46 MJ/kg) [43]. This goes as well for the cloud point of this fuel which was found to be 9.8°C, indicating a good flow ability of this fuel in the

cold season. Both acid value and density of the fuel are also within the range required by ASTM biodiesel standard. Based on the results, it can be concluded that the LTW-based ethyl esters is a potential replacement for diesel fuel.

Table 5

4. Conclusions

Supercritical ethanol has been successfully conducted to produce LTW-based biodiesel. RSM in conjuction with ANOVA have been applied to design the experiment, predict the response and maximize the result by optimizing the tested variables (reaction time, temperature and ethanol to LTW molar ratio). The maximum FAEE recovery obtained from this optimization was 98.91 ± 0.31% with the product purity (97.55%) reached the commercial requirement (higher than 96.5%). The optimal operating conditions were 47.4 min, 374.6^{o}C and molar ratio of ethanol to LTW of 40.02, with the predicted FAEE yield of 99.68%. The experimental and predicted response have a proportional output, with an error of only 0.77%. Consistent result can be 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 ethyl esters are also in accordance with ASTM D6751 and ASTM D975-08. Therefore, it can be concluded that SpCE is a promising method to substitute the traditional technique, particularly for the utilization of raw materials originated from waste because it is more straightforward, sustainable and clean compared to the latter.

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Table 1. The characteristics of LTW

Parameters	Result
Water content, % (w/w)	12.37
FFA, % (w/w)	15.24
Crude fat, % (w/w)	62.61
Fatty acid profile, % (w/w)	
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

Table 2. The encoded levels of the transesterification condition

Variables	Encoded factor	Factor level				
		1	**2**	**3**	**4**	**5**
Time (min)	A	10	20	30	40	50
		1		**2**		**3**
Temperature (°C)	B	300		350		400
Molar ratio of ethanol to LTW (mol/mol)	C	35		40		45

Table 3. Statistical design of experiment based on MLFD

Run	Input variables			Response (FAEE yield, wt%)	
	A	B	C	Actual[a]	Predicted[a]
1	5	1	1	17.2	17.8
2	5	2	1	88.6	84.9
3	2	2	2	68.1	71.7
4	1	2	1	46.2	52.6
5	3	3	1	72.4	74.1
6	1	1	3	9.4	5.9
7	2	3	2	72.1	67.7
8	4	2	1	88.1	81.7
9	5	2	3	92.8	90.2
10	3	1	3	19.3	20.6
11	4	1	3	21.2	23.0
12	5	1	2	20.2	22.5
13	3	1	1	15.3	14.7
14	1	3	3	52.9	53.8
15	1	2	2	56.3	59.1
16	2	3	3	70.8	69.4
17	3	2	1	73.6	75.3
18	5	1	3	22.8	22.3
19	5	3	2	92.3	95.8
20	4	3	3	90.7	90.7
21	2	1	1	8.6	8.3
22	4	3	2	91.4	89.7
23	2	1	3	11.8	14.8
24	2	3	1	64.3	61.2
25	1	2	3	57.9	60.7
26	1	1	2	8.9	4.7
27	5	3	1	86.3	90.3
28	1	1	1	5.8	1.4
29	5	3	3	91.2	96.5
30	4	3	1	85.8	83.9
31	4	1	2	19.8	22.9
32	3	2	2	82.4	81.0
33	3	2	3	83.4	81.9
34	4	2	2	94.2	87.1
35	3	1	2	18.2	20.1
36	4	2	3	93.9	87.7
37	2	1	2	12.7	14.0
38	3	3	3	81.6	81.6
39	3	3	2	78.6	80.3
40	1	3	2	51.9	51.8
41	2	2	3	71.6	72.9
42	1	3	1	48.9	45.0
43	4	1	1	16.4	17.9

44	2	2	1	54.1	65.6
45	5	2	2	90.7	90.0

[a] The overall standard error of estimate (SEE) between the actual and its corresponding predicted responses was 3.30%.

Table 4. The significance study of the tested variables performed by ANOVA

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

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

Properties	Methods	Unit	LTW-based ethyl ester	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
Flash point	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	-

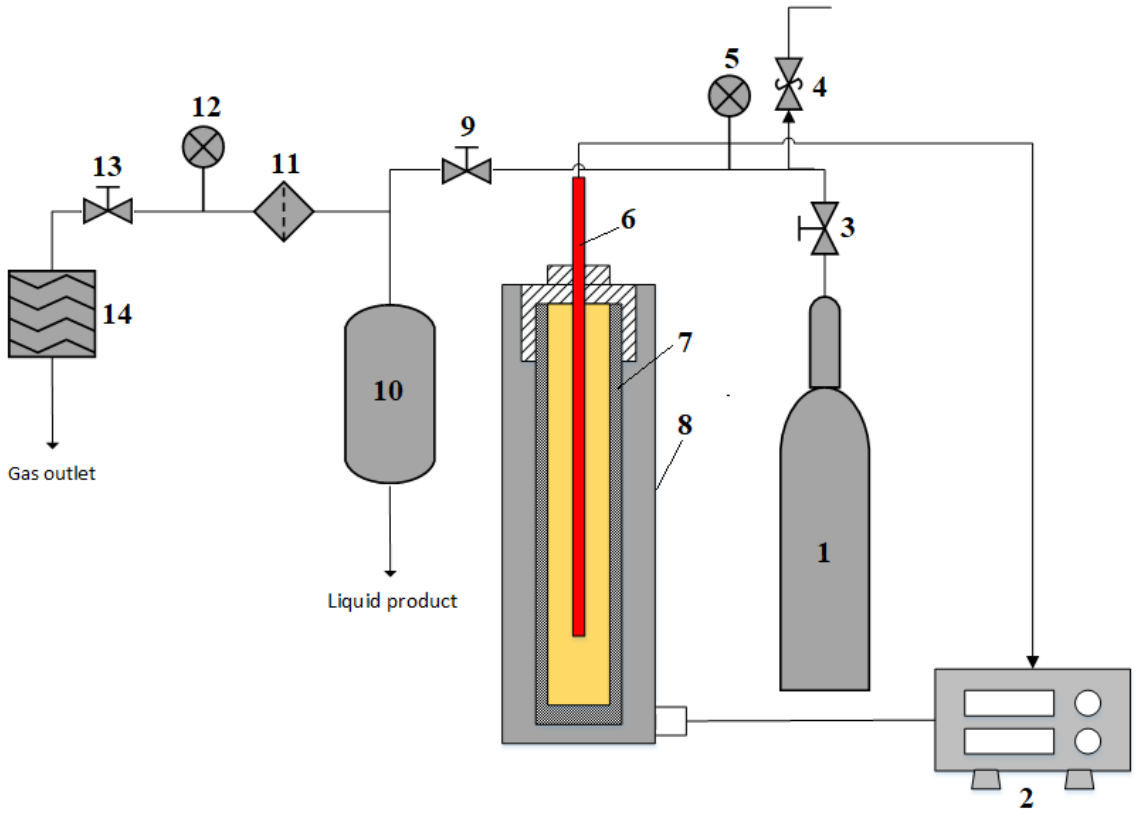

Figure 1. Schematic diagram of SpCE apparatus: (1) nitrogen gas cylinder, (2) Temperature control system, (3) valve, (4) pressure relief valve, (5) pressure gauge, (6) thermocouple, (7) Supercritical reactor, (8) electric heater, (9) valve, (10) gas-liquid flash separator, (11) 1 μm filter, (12) pressure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

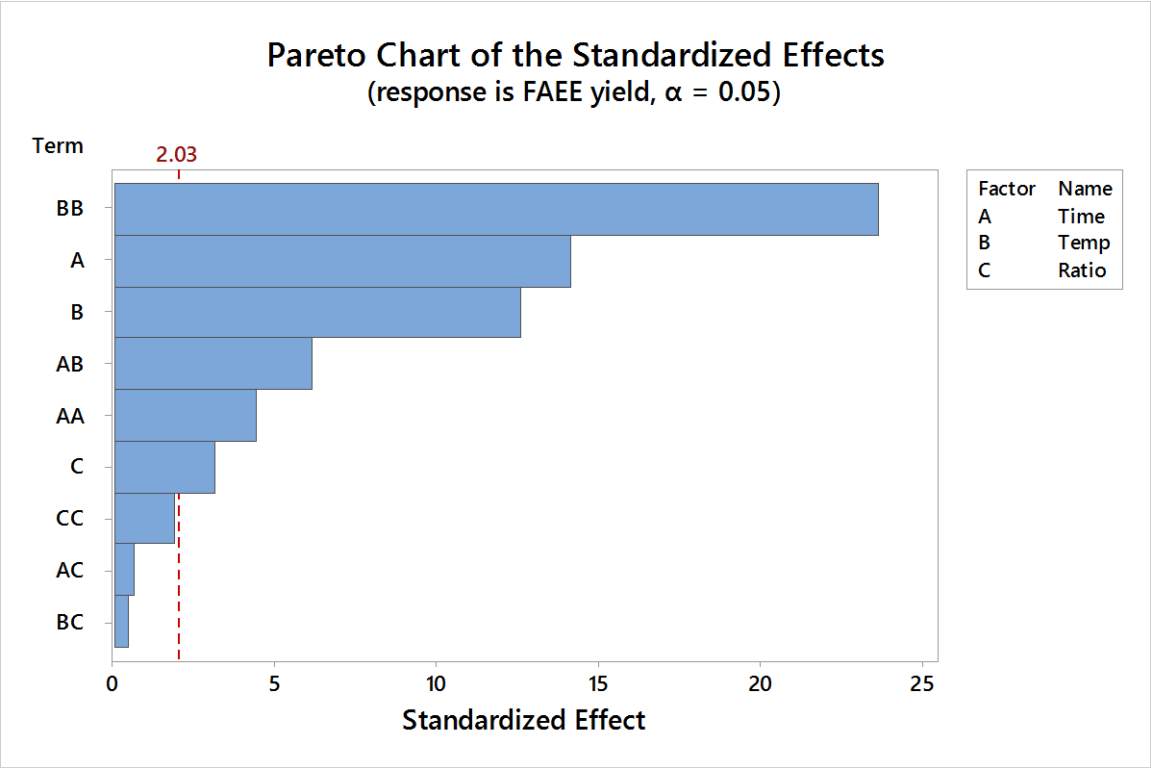

Figure 2. The significance order of the three independent variables (reaction time, temperature and molar ratio of LTW) on the FAEE yield, generated by ANOVA

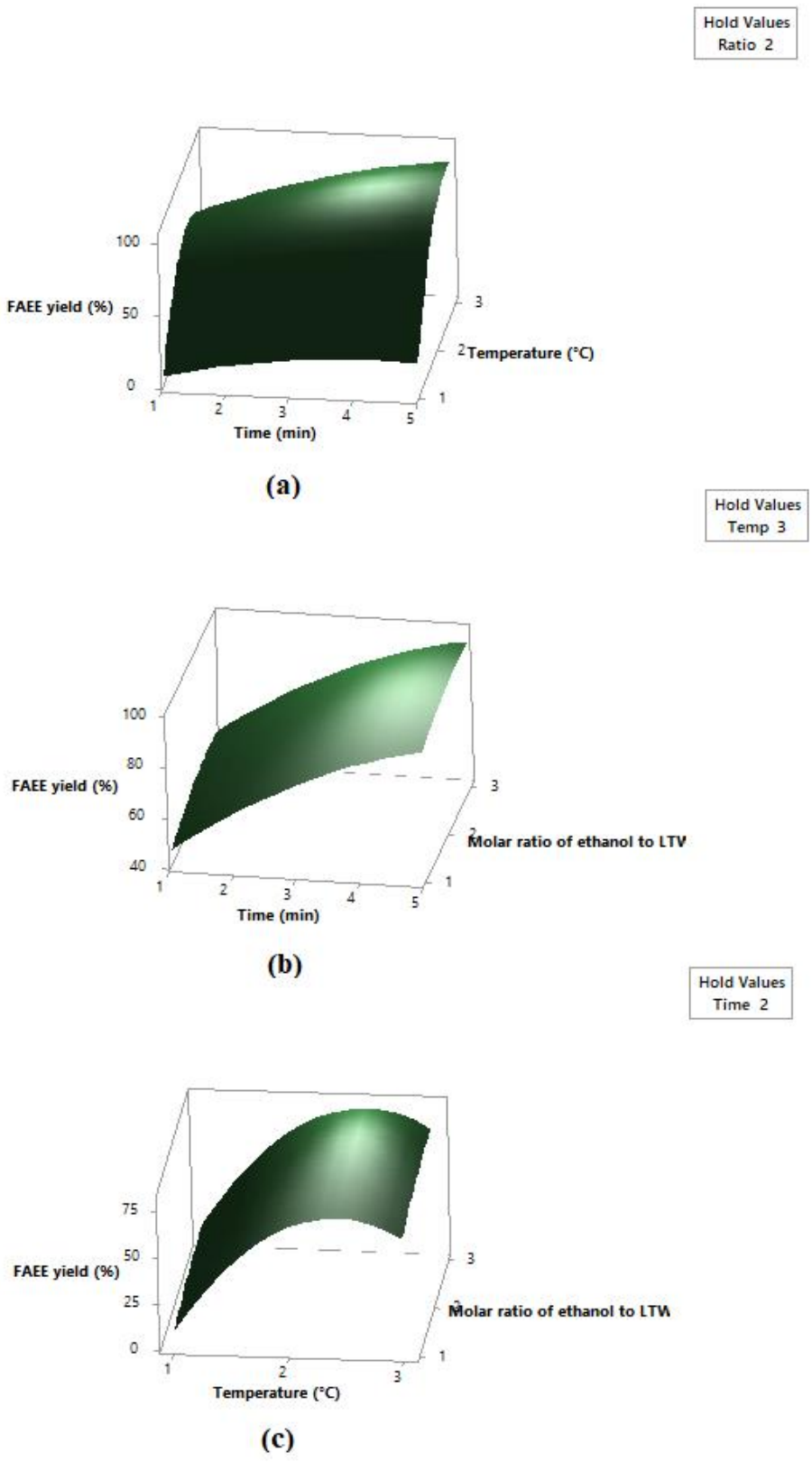

Figure 3. The 3D response surface plot of FAEE yield for the interaction between (a) time and temperature, (b) time and molar ratio of ethanol to LTW, (c) temperature and molar ratio of ethanol to LTW

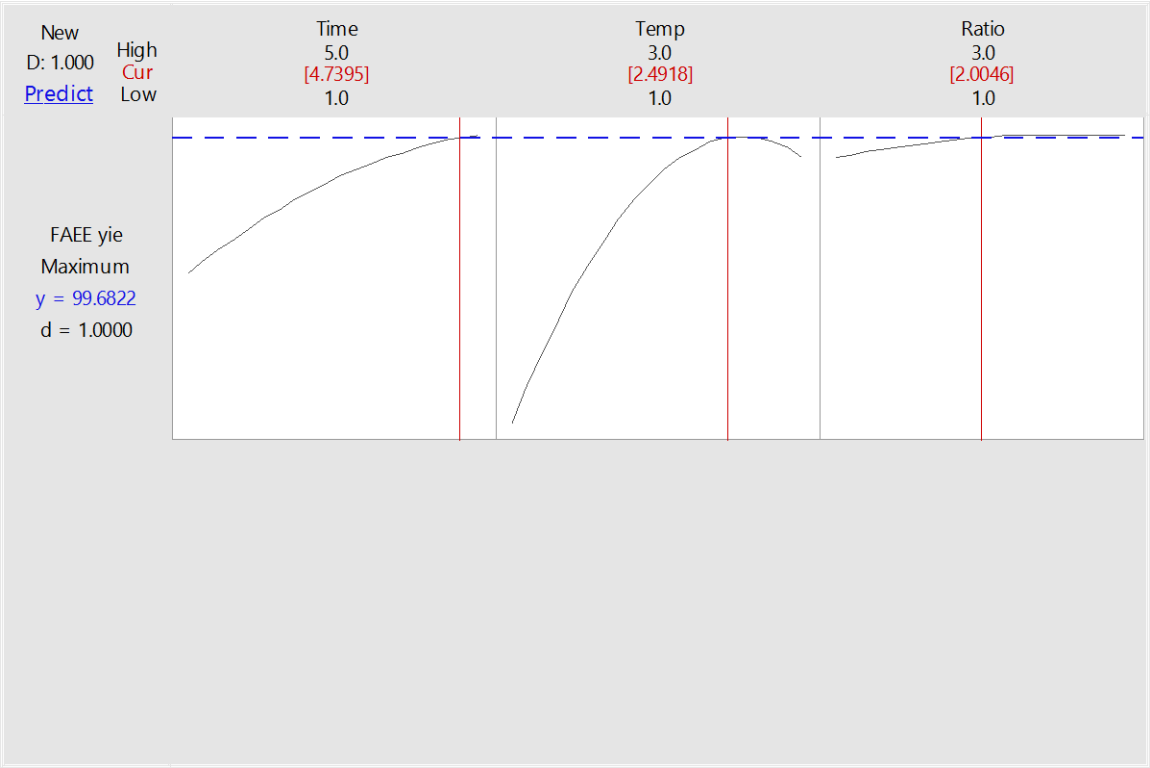

Figure 4. The optimization plot of the tested variables

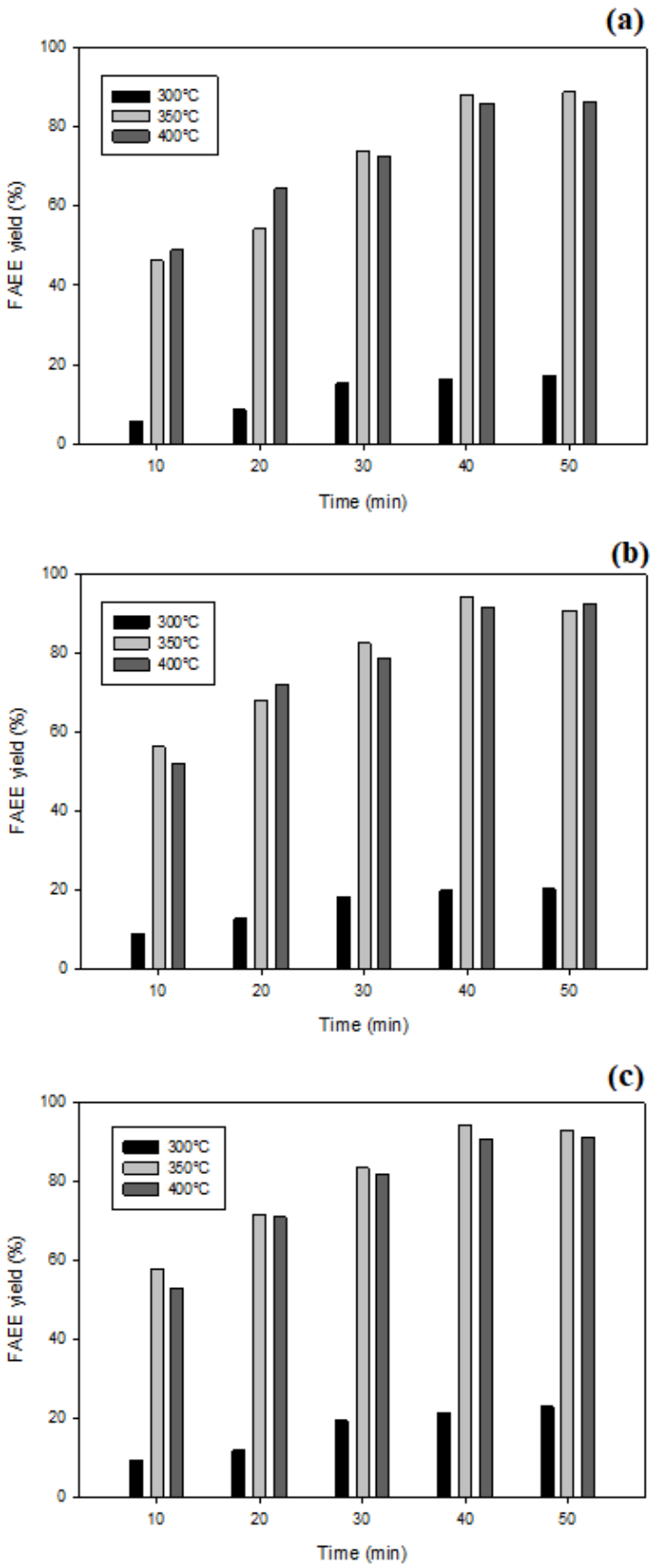

Figure 5. The experimental results of FAEE yield varied with time at different temperatures (300°C, 350°C, 400°C) at constant molar ratio of (a) 35 (b) 40 (c) 45

Your Submission

Dari: Abdelrahman Zaky (em@editorialmanager.com)

Kepada: maria_yuliana_liauw@yahoo.com

Tanggal: Jumat, 24 Juli 2020 pukul 01.53 GMT+7

Ms. Ref. No.: JBAB-D-19-01462
Title: MULTILEVEL FACTORIAL DESIGN - BASED RESPONSE SURFACE METHODOLOGY FOR PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION FROM LEATHER TANNING WASTE USING NON-CATALYTIC SUPERCRITICAL ETHANOL
Biomass and Bioenergy

Dear Dr. Maria Yuliana,

The editor and reviewers have commented on your above paper. They indicated that it is not ready for publication in its present form. However, if you feel that you can suitably address the comments (included below), I invite you to revise and resubmit your manuscript within 60 days, by Sep 21, 2020.

If you are submitting a revised manuscript, please do the following:

a) Carefully address the issues raised in the comments in your revised manuscript.
b) Outline each change made (point by point) as raised in the comments AND/OR provide a suitable rebuttal to each comment not addressed

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Please contact the Data in Brief editorial office at dib-me@elsevier.com or visit the Data in Brief homepage (www.journals.elsevier.com/data-in-brief/) if you have questions or need further information.

I look forward to receiving your revised manuscript.

Yours sincerely,

Abdelrahman Zaky, PhD
Managing Editor
Biomass and Bioenergy

Editor's and Reviewers' comments:

Editor: Thank you for your submission. The reviewer comments are below and attached. In addition to the reviewer comments please address the following
A complete overhaul of English language is needed. Note that only one revision is permitted and so if this is not addressed in the revision the paper may be rejected.

Reviewer #1:
Review of manuscript CARBPOL-D-19-05343

Title: MULTILEVEL FACTORIAL DESIGN - BASED RESPONSE SURFACE METHODOLOGY FOR PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION FROM LEATHER TANNING WASTE USING NON-CATALYTIC SUPERCRITICAL ETHANOL

The manuscript deals with utilizing leather tanning waste for producing bio-diesel. The authors describe that 150 thousand tons of this LTW is available annually in Indonesia and that it poses an environmental problem being not always disposed of adequately. The basic idea of the work complies well with circular and sustainable economy and the described overall process is both important and interesting. It also gives incentive to properly manage this waste stream as value could be obtained from it. Using widely available well-tolerated ethanol for the supercritical processing is also well justified. The authorshave made considerable effort in the experimental work and analysis and a fair amount of data has been generated to support the modelling efforts. The authors stress that the process does not employ a catalyst and of course it simplifies things, however, using catalysts is often beneficial from e.g. energy and efficiency point of view. Having a non-catalytic process
should not be an aim in itself. Aiming at production in a single step is good. I have some concerns and questions about the experimental work and the modeling of the process as well as the way the results are presented, which I hope that the authors could address and clarify.
1. The image quality of the graphical abstract is very poor. In its current for it does not actually provide any added value and I suggest the authors revisit their suggestion.

2. The Highlights are filled with abbreviations that many readers have no chance of understanding considering that they read the Highlights before the manuscript. I suggest the authors also to revisit the Highlights section.

3. Why is the term "non-catalytic" mentioned in the title and even more precisely "non-catalytic supercritical ethanol"? Is it in contrast to catalytic supercritical ethanol?

4. In the abstract, it is mentioned that 150000 tons of the waste is availably annually even though it is specified in the introduction that this applies to Indonesia and not globally. The authors should be careful in expressing the context in their discussion. This applies generally to the whole work. Moreover, the abstract again contains some abbreviations which are not explained and are not clear for all readers prior to reading the manuscript.

5. One of the major concern I have concerning the entire work is the general applicability of the results. It appears that no mixing of the reaction mixture is performed in the rector. However, e.g. solubility issues are mentioned as relevant for the reaction rates. How have the authors verified that mass transfer is not the rate determining step in the overall reaction rate? If the results reflect more the mass transfer rates than intrinsic kinetics, then the results are system specific and of little use for simulating and designing other systems.

6. It was concluded that the molar ratio of ethanol to LTW was the least significant parameter. However, the lowest molar ratio was 35, which is already extremely high. Lower molar ratios would have brought forth the impact of the parameter more clearly and it is not really justified to perform experiments at such high ratios and conclude that the parameter lacks relevance. The lack of correlation actually reduces the model to be dependent of two variables. One of the is temperature, for which good correlations exist if the reactions are performed in the domain of intrinsic kinetics e.g. the Arrhenius equation. Why is a polynomial equation with linear and second order dependence on temperature used instead?

7. What would be the basis for having partly a quadratic time dependence? This seems conceptually peculiar.

The authors have a nice collection of data, which is relevant and deserves to be published in the open literature. However, the I am not convinced that the model developed here is of relevance for further development, as it is not clear that it would be applicable in other than the specific reactor system that the authors have used, due to mass transfer issues. Besides mass transfer issues, more rigorous data interpretation would be beneficial overall e.g. in the form of evaluating solubility. A limited amount of additional experiments e.g. in temperatures between 300-350C and with lower ethanol LTW rations would add considerably to the data and to the modeling effort as data on both variables is not well suited for modelling in their current range.
The manuscript would benefit from one round more of language checking.

Reviewer #2: The manuscript entitled MULTILEVEL FACTORIAL DESIGN - BASED RESPONSE SURFACE METHODOLOGY FOR PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION FROM LEATHER TANNING WASTE USING NON-CATALYTIC SUPERCRITICAL ETHANOL, does not present a new approach in relation to the surface response methodology for optimization of biodiesel production.
The work is well configured and is interesting in the use of waste from the leather industry and in the use of ethanol instead of methanol as a reagent to form FAEEs. I suggest for future work to make an approach that allows working in wet subcritical conditions that would allow working with a less costly system in the treatment of LTW.

Reviewer #3: GENERAL OBSERVATION: The manuscript is focused on the biodiesel production from the leather tanning waste using super critical ethanol. The overall manuscript should have been written in a better way and too lengthy . Moreover, the language and grammar are not up to the mark needed in scientific writing.
* Authors have presented the optimization conditions (3 factors, namely, reaction time (10, 20, 30, 40, & 50 min), temperature (300, 350 & 400 C) & alcohol-to-fat ratio (35, 40 & 45), and 1 response, namely, FAEE yield) of biodiesel production from leather tanning waste through a single step non-catalytic transesterification using supercritical alcohol (ethanol, in this case).
* From the ANOVA and RSM, the reaction time of 47.4 min, temperature of 374.6 C and ethanol-to-fat ratio of 40.02 were found to be optimum to produce the predicted FAEE yield of 99.68% (98.91% actual yield). From the observations made, the manuscript is written well and almost all the elements are available.
Following are the suggestions , which can be incorporated by the authors in the manuscript to make it more effective.
* INTRODUCTION: The introduction section could be improved by including relevant works in this field using this RSM methodology, which could be compared.
* The novelty in the manuscript is not clearly explained. There are plenty of works available on non-catalytic transesterification using supercritical ethanol from oils. Below are mentioned previous articles published in this field, which are strongly recommended for additional literature study and references, which would improve the continuity and correlation and give the reader a better understanding.
1. Gui, M. M., Lee, K. T., & Bhatia, S. (2009). Supercritical ethanol technology for the production of biodiesel: process optimization studies -- The Journal of Supercritical Fluids, 49(2), 286-292.
2. Tan, K. T., Gui, M. M., Lee, K. T., & Mohamed, A. R. (2010). An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production. The Journal of Supercritical Fluids, 53(1-3), 82-87.
3. Muppaneni, T., Reddy, H. K., Ponnusamy, S., Patil, P. D., Sun, Y., Dailey, P., & Deng, S. (2013). Optimization of biodiesel production from palm oil under supercritical ethanol conditions using hexane as co-solvent: A response surface methodology approach. Fuel, 107, 633-640.

4. Reddy, H. K., Muppaneni, T., Patil, P. D., Ponnusamy, S., Cooke, P., Schaub, T., & Deng, S. (2014). Direct conversion of wet algae to crude biodiesel under supercritical ethanol conditions. Fuel, 115, 720-726.

* Most of the authors in the above mentioned papers, used the same three factors and responses in their experimental design. Then, what is the originality or variation in this manuscript? Is it just the use of leather tanning waste? If so, the Introduction has to be oriented towards this.

* -P6 Abbreviation : Following to be added in abbreviations of FOGs, TG, AOAC, ASTM, ISO, FAEE, UHP, GC-FID, AV, etc. are not present. Please include.
* -P1L1-4: The title of the manuscript seems to be lengthy and needs to be Precise for wide readership.
* -P2 Graphical Abstract: The graphical abstract seems to be blurred. Need to modify with higher resolution for better view.
* -P5L26-30: These sentences are not required in the abstract. Abstract should be focused more on the aim and outcome of the research in a crisp form. Try to modify it.
* -P5L31: The sentence, "In this work" should be "In this present research".
* -P5L40-42: These sentences are too lucid, try to rewrite with more focus on the present outcome of the study.
* -P5L43-44: In Abstract Keywords, Use single keyword which is not used in the abstract. For example. Use either Leather or Tanning waste and not the both.
* -P6L55-56: The sentence "Currently Indonesia blends 20% ….." needs citation.
* -P6L58-61: The sentence "by almost 60 folds in a period of 10 years" is too confusing need proper justification.
* -P6L62: The line "Various types of vegetable oils have been studied" should be "Vegetable oils derived from diverse source were actively screened".
* -P8L103: The line "The objective of this study" should be "The present investigation aims to".
* -P8 L104: "alcohol" is mispelled as "alcofol". Please correct.
* -P8L110-111: The present aim of the study needs to be explained better.
* -P14L241: Under the section 3.2. Process Optimization using RSM. Optimization using different methods needs to discuss properly. Cite references under this section is low. Need better discussion with the relevant literature.
* -P22L433-448: In Conclusion, the Future perspective and present research gap needs to be addressed properly.
* -P31-Table 3: The legend of the table needs to be elaborated with the statistical software's used for the study and also mention significance error in both Actual and predicted.
* -P33-Table 4: Which ANOVA analysis was performed "one way" or "two way" assay needs better explanation.
* -P36-Figure 2: Statistical error bar between the individual treatments needs to be included and software used for plotting the graph needs to be included in the figure legends.
* -P37L691: In figure 4, the legends needs to be explained in detail by including statistical data used and software used for plotting the graph.
* -P38-Figure 4: Statistical data for plotting the graph needs to be discussed whether it is plotted using Sigma or excel needs to be explained in detail in the figure legends.
* -P39-Figure 5: Similarly, the significant error bar between the individual treatments needs to be included and mention the statistical software used for plotting the graph needs to be included in the figure legends.
* The materials, methods, results and discussion have been written well.
* Overall, it is observed that the results are promising with about 98% yield, which is relatively high compared to other manuscripts. It would be more effective for better understanding , when a comparison of other papers results with your result could be presented. This can be included in the discussion part.

FINAL IMPRESSION OF THE REVIEWER: Overall, the manuscript requires major language and Grammar correction with native speaker. This Manuscript in its present form clearly fails to make a clear distinction about its Novelty , when there are similar papers published earlier. This comparison and discussion of Results of papers published using this technology should have been done with valid scientific rationale. Therefore, I do not find this manuscript suitable for publication in Biomass and Bioenergy Journal, without a major revision.

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Submission Confirmation for JBAB-D-19-01462R1

Dari: Biomass and Bioenergy (em@editorialmanager.com)

Kepada: maria_yuliana_liauw@yahoo.com

Tanggal: Senin, 10 Agustus 2020 pukul 18.16 GMT+7

Ms. Ref. No.: JBAB-D-19-01462R1
Title: A one-pot synthesis of biodiesel from leather tanning waste using supercritical ethanol: Process Optimization
Research paper
Biomass and Bioenergy

Dear Dr. Maria Yuliana,

This message is to acknowledge that we have received your revised manuscript for reconsideration for publication in Biomass and Bioenergy.

You may check the status of your manuscript by logging into the Editorial Manager as an author at https://www.editorialmanager.com/JBAB/.

Thank you for submitting your work to Biomass and Bioenergy.

Kind regards,

Editorial Manager
Biomass and Bioenergy

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Biomass and Bioenergy

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

--Manuscript Draft--

Manuscript Number:	JBAB-D-19-01462R1
Article Type:	Research paper
Keywords:	waste-derived biodiesel; tannery waste; supercritical ethanol; catalyst-free; optimization study; renewable energy
Corresponding Author:	Maria Yuliana Universitas Katolik Widya Mandala Surabaya INDONESIA
First Author:	Maria Yuliana
Order of Authors:	Maria Yuliana
	Shella Permatasari Santoso
	Felycia Edi Soetaredjo
	Suryadi Ismadji
	Aning Ayucitra
	Artik Elisa Angkawijaya
	Yi-Hsu Ju
	Phuong Lan Tran-Nguyen
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 reo (35, 40, 45), on the yield of fatty acid ethyl ester (FAEE) YF 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 reo = 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 YF. All reaction variables were also found to give a significant effect on the yield of FAEE.
Response to Reviewers:	We appreciate your useful comments and suggestions on our manuscript. We have modified the manuscript accordingly, and detailed corrections are listed in the "Detailed response to reviewers".

Widya Mandala Catholic University Surabaya
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August 10, 2020

Professor Patricia Thornley
Editor
Biomass & Bioenergy

Dear Professor Thornley,

On behalf of my co-author, I am writing to submit the revised manuscript for publication consideration in *Biomass & Bioenergy*. The details of the manuscript are as follows:

Title of Manuscript: **A ONE-POT SYNTHESIS OF BIODIESEL FROM LEATHER TANNING WASTE USING SUPERCRITICAL ETHANOL: PROCESS OPTIMIZATION**

Authors: Maria Yuliana, Shella Permatasari Santoso (shella_p5@yahoo.com), Felycia Edi Soetaredjo (felyciae@yahoo.com), Suryadi Ismadji (suryadiismadji@yahoo.com), Aning Ayucitra (aayucitra@yahoo.com), Artik Elisa Angkawijaya (artikelisa@mail.ntust.edu.tw), Yi-Hsu Ju (yhju@mail.ntust.edu.tw), Phuong Lan Tran-Nguyen (tnplan@ctu.edu.vn)
Corresponding author:
Maria Yuliana; Department of Chemical Engineering; Widya Mandala Catholic University Surabaya; Kalijudan 37, Surabaya 60114, Indonesia
Tel: (62) 31 3891264; Fax. (62) 31 3891267;
E-mail: maria_yuliana_liauw@yahoo.com

Keywords: *waste-derived biodiesel; tannery waste; supercritical ethanol; catalyst-free; optimization study; renewable energy*

Statement of novelty :

A one-pot synthesis of biodiesel via supercritical ethanol method has been successfully employed to valorize LTW. The optimization study was conducted using a multilevel factorial design-based response surface methodology and a three-way analysis of variance. The FAEE yield of 98.91 ± 0.31% with a commercial purity (97.55%) is obtained in this single-step catalyst-free process when reaction time t = 47.4 min, temperature T = 374.6^{o}C, and molar ratio of ethanol to LTW r_{eo} = 40.02. The fuel properties of LTW-based biodiesel conform to ASTM D6751.

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Website: http://www.ukwms.ac.id

We greatly appreciate the constructive comments and suggestions given by the editor and reviewers. We have addressed the major concerns of the reviewers and revised the manuscript accordingly. We also know of no conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome. Furthermore, we have strictly prepared the manuscript in accordance with the journal and ethical guidelines.

Thank you for your consideration. I am looking forward to hearing from your positive response.

Sincerely yours,

Maria Yuliana

Widya Mandala Catholic University Surabaya
Engineering Faculty
CHEMICAL ENGINEERING DEPARTMENT
Jl. Kalijudan 37 Surabaya 60114; Phone: +62 313893933 Fax: +62 31 3891267
Website: http://www.ukwms.ac.id

Journal: *Biomass and Bioenergy*

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

Dear Editor,

We appreciate your useful comments and suggestions on our manuscript. We have modified the manuscript accordingly, and detailed corrections are listed below:

Editor

1) Thank you for your submission. The reviewer comments are below and attached. In addition to the reviewer comments please address the following: A complete overhaul of English language is needed. Note that only one revision is permitted and so if this is not addressed in the revision the paper may be rejected.
Response: We are grateful for the reviews provided by the editor and reviewers. The comments are especially encouraging for the authors. The paper has been carefully revised by a native English speaker to improve the grammar and readability. Meanwhile, the detailed responses to the comments are provided below.

Reviewer #1

1) The manuscript deals with utilizing leather tanning waste for producing bio-diesel. The authors describe that 150 thousand tons of this LTW is available annually in Indonesia and that it poses an environmental problem being not always disposed of adequately. The basic idea of the work complies well with circular and sustainable economy and the described overall process is both important and interesting. It also gives incentive to properly manage this waste stream as value could be obtained from it. Using widely available well-tolerated ethanol for the supercritical processing is also well justified. The authorshave made considerable effort in the experimental work and analysis and a fair amount of data has been generated to support the modelling efforts. The authors stress that the process does not employ a catalyst and of course it simplifies things, however, using catalysts is often beneficial from e.g. energy and efficiency point of view. Having a non-catalytic process should not be an aim in itself. Aiming at production in a single step is good. I have some concerns

and questions about the experimental work and the modeling of the process as well as the way the results are presented, which I hope that the authors could address and clarify.

Response: The authors appreciate the reviewer's comments and have incorporated much of the feedback into the manuscript. As seen from the revised title, the authors have agreed to shift the main focus of the manuscript. Instead of focusing on its non-catalytic system, we emphasize our aim to produce biodiesel in one single-step via supercritical ethanol method. We also give a point-by-point reply to your comments below.

2) The image quality of the graphical abstract is very poor. In its current for it does not actually provide any added value and I suggest the authors revisit their suggestion.

   Response: We have improved the image quality of the graphical abstract for a better view.

3) The Highlights are filled with abbreviations that many readers have no chance of understanding considering that they read the Highlights before the manuscript. I suggest the authors also to revisit the Highlights section.

   Response: The authors have rewritten the Highlights to reduce the number of abbreviations. However, we did not change the term "FAEE" and "ASTM" because they are a common abbreviation for biodiesel-related studies.

4) Why is the term "non-catalytic" mentioned in the title and even more precisely "non-catalytic supercritical ethanol"? Is it in contrast to catalytic supercritical ethanol?

   Response: The authors have rewritten the title to "A one-pot synthesis of biodiesel from leather tanning waste using supercritical ethanol: Process Optimization".

   In regards to the second question, the non-catalytic supercritical ethanol is clearly different from the catalytic one. In the system proposed by the authors, the reaction occurs without any distinct catalyst. We also want to stress that the alcohol in the supercritical condition, alone, is able to dissolve the feedstock; hence, inducing the intense contact among the reactants, and magnifying the mass transfer and reaction rate between the reactants to produce biodiesel.

5) In the abstract, it is mentioned that 150000 tons of the waste is availably annually even though it is specified in the introduction that this applies to Indonesia and not globally. The authors should be careful in expressing the

context in their discussion. This applies generally to the whole work. Moreover, the abstract again contains some abbreviations which are not explained and are not clear for all readers prior to reading the manuscript.

Response: To avoid misinterpretation, we have removed the data related to the annual production of LTW from the abstract, and placed them only in the introduction section, in order to keep the consistency of the context. We have also revised the abstract according to the input from the reviewer in p.2 line 23-35.

6) One of the major concern I have concerning the entire work is the general applicability of the results. It appears that no mixing of the reaction mixture is performed in the rector. However, e.g. solubility issues are mentioned as relevant for the reaction rates. How have the authors verified that mass transfer is not the rate determining step in the overall reaction rate? If the results reflect more the mass transfer rates than intrinsic kinetics, then the results are system specific and of little use for simulating and designing other systems.

Response: Above the critical condition, gas and liquid ethanol become the same density and indistinguishable. As a liquid, supercritical ethanol dissolves the leather tanning waste (LTW), and at the same time, bubbles are also created in this state, eliminating the need for recirculating pumps or agitator, as the bubbles are randomly distributed within the reactants and act as the mixing system.

Chemical reactions, including transesterification, are always coupled with mass transfer, as the reactants have to travel to the reaction site, while the products have to travel away. Supercritical ethanol (SpCE) has high mobility, diffusivity, and solubility behavior which can improve the mass transfer rate. At the same time, the hydrogen bonding, ion cluster, and ion association occur to induce the intrinsic reaction between the reactants. However, in this study, we only evaluate the overall reaction as the focus of this research is (1) to produce LTW-based biodiesel with the commercial yield and purity via a single step SpCE transesterification, and (2) to determine the optimum conditions of the operating system. The authors will consider conducting a future study on the intrinsic kinetic and thermodynamic behavior of this SpCE transesterification system.

7) It was concluded that the molar ratio of ethanol to LTW was the least significant parameter. However, the lowest molar ratio was 35, which is already extremely

high. Lower molar ratios would have brought forth the impact of the parameter more clearly and it is not really justified to perform experiments at such high ratios and conclude that the parameter lacks relevance. The lack of correlation actually reduces the model to be dependent of two variables. One of the is temperature, for which good correlations exist if the reactions are performed in the domain of intrinsic kinetics e.g. the Arrhenius equation. Why is a polynomial equation with linear and second order dependence on temperature used instead?

Response: As presented in the introduction, one of the aims of this study is to produce LTW-based biodiesel with commercial yield using a one-pot catalyst-free supercritical ethanol technique (the current mass production of biodiesel via base-catalyzed transesterification generally yields >95% of biodiesel). Meanwhile, the existing studies reported that the molar ratio of alcohol to oil used in the supercritical alcohol technique ranges from 24 to 42, with the corresponding biodiesel yield spreads from a value as low as 70% to more than 90%. Therefore, to achieve a similar response (yield of biodiesel), we selected three values close to the one giving a biodiesel yield around 90%, e.g., 35, 40, and 45, as our molar ratios. The authors also wish to emphasize that the molar ratio is still a significant parameter in the reaction system, as seen in Figure 2 (p.33).

Another objective of this study is to find the optimum operating conditions using response surface methodology (RSM), where we investigate the interaction among variables on the response, which is vital and important for a comprehensive understanding of the whole process. However, RSM does not segregate the overall reaction that happened in the system to (1) mass transfer and (2) intrinsic kinetics. It only explores the complex relationship between the tested variables and the response, without further evaluating the reaction mechanism. Therefore, the authors do not use the Arrhenius equation or other intrinsic kinetic models to simulate the process. Instead, we employ the least square analysis performed by Minitab (version 18.1) to find the polynomial equation as the best-fitted model.

As mentioned above, the authors will consider performing an in-depth evaluation of the intrinsic kinetic and thermodynamic behavior of this reaction system.

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8) What would be the basis for having partly a quadratic time dependence? This seems conceptually peculiar?

Response: In the process optimization and evaluation, one would like to know the complete picture of the relationship between the tested variables and their response. A strong quadratic effect of a particular variable, e.g., reaction time, implies that the optimum level of that variable is not in the extremes of the experimental region, but within the region. This agrees with the results obtained in the study, where the optimum reaction time lies within the tested region (47.4 min). The quadratic effect also helps to test whether the relation is a complex surface or just a hyperplane. Based on the result presented in Figure 2 (p.33), it can be concluded that the relationship between the tested variables (temperature, time and molar ratio of ethanol to LTW) and the response is a complex surface, as many factors, including the quadratic time, quadratic temperature, and two-way interaction between reaction time and temperature, significantly affect the response.

9) The authors have a nice collection of data, which is relevant and deserves to be published in the open literature. However, the I am not convinced that the model developed here is of relevance for further development, as it is not clear that it would be applicable in other than the specific reactor system that the authors have used, due to mass transfer issues. Besides mass transfer issues, more rigorous data interpretation would be beneficial overall e.g. in the form of evaluating solubility. A limited amount of additional experiments e.g. in temperatures between 300-350C and with lower ethanol LTW rations would add considerably to the data and to the modeling effort as data on both variables is not well suited for modelling in their current range.

Response: As previously mentioned, the three values of molar ratio (35, 40, 45) were selected based on our literature review in order to achieve a commercial yield of biodiesel. Meanwhile, a prominent increase in FAEE yield was monitored when the temperature increases from 300°C to 350°C. Judging from the results, level addition of reaction temperature between 300°C and 350°C would not alter the FAEE yield significantly, or give much information either. Moreover, the optimum reaction temperature is not found in the range of 300-350°C. Therefore, the authors chose to investigate only three value points (300, 350, and 400°C).

10) The manuscript would benefit from one round more of language checking.

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Response: To improve the grammar and readability of the manuscript, the manuscript has been edited by an English-speaking native.

Reviewer #2

1) The manuscript entitled MULTILEVEL FACTORIAL DESIGN - BASED R ESPONSE SURFACE METHODOLOGY FOR PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION FROM LEATHER TANNING WASTE USING NON-CATALYTIC SUPERCRITICAL ETHANOL, does not present a new approach in relation to the surface response methodology for optimization of biodiesel production.

   Response: We agree with the reviewer that the optimization of biodiesel production using Response Surface Methodology has been widely reported. However, the main issue the authors want to raise is the valorization of leather tanning waste (LTW) to biodiesel using a single step and catalyst-free process, which in this case is supercritical ethanol (SpCE)method. LTW is selected due to its high amount of production in Indonesia (150,000 tons/year), which renders it an abundant raw material to prepare biodiesel. This valorization of LTW will prominently reduce the waste and at the same time, offers a cost-effective and environmentally benign route to produce high value-added biodiesel. Meanwhile, despite its extreme processing conditions (such as high temperature and pressure), SpCE is chosen because it has the advantage of easier separation, much shorter reaction time, and tolerance to impurities (i.e., FFA, water, and other minor components). Simulating a model for this process is important to investigate the feasibility and limitation of SpCE from both economic and technological viewpoints.

2) The work is well configured and is interesting in the use of waste from the leather industry and in the use of ethanol instead of methanol as a reagent to form FAEEs. I suggest for future work to make an approach that allows working in wet subcritical conditions that would allow working with a less costly system in the treatment of LTW.

   Response: We thank the reviewer for the thoughtful comments of our manuscript. We will consider conducting the transesterification of LTW using ethanol under its subcritical condition to create a less costly system.

Reviewer #3

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1) GENERAL OBSERVATION: The manuscript is focused on the biodiesel production from the leather tanning waste using supercritical ethanol. The overall manuscript should have been written in a better way and too lengthy. Moreover, the language and grammar are not up to the mark needed in scientific writing. Authors have presented the optimization conditions (3 factors, namely, reaction time (10, 20, 30, 40, & 50 min), temperature (300, 350 & 400 C) & alcohol-to-fat ratio (35, 40 & 45), and 1 response, namely, FAEE yield) of biodiesel production from leather tanning waste through a single step non-catalytic transesterification using supercritical alcohol (ethanol, in this case). From the ANOVA and RSM, the reaction time of 47.4 min, temperature of 374.6 C and ethanol-to-fat ratio of 40.02 were found to be optimum to produce the predicted FAEE yield of 99.68% (98.91% actual yield). From the observations made, the manuscript is written well and almost all the elements are available. Following are the suggestions , which can be incorporated by the authors in the manuscript to make it more effective.

   Response: We appreciate the suggested modifications and have carefully revised the manuscript in view of the constructive reviewer's comments as outlined in detail below.

2) INTRODUCTION: The introduction section could be improved by including relevant works in this field using this RSM methodology, which could be compared. The novelty in the manuscript is not clearly explained. There are plenty of works available on non-catalytic transesterification using supercritical ethanol from oils. Below are mentioned previous articles published in this field, which are strongly recommended for additional literature study and references, which would improve the continuity and correlation and give the reader a better understanding.

   (i) Gui, M. M., Lee, K. T., & Bhatia, S. (2009). Supercritical ethanol technology for the production of biodiesel: process optimization studies -- The Journal of Supercritical Fluids, 49(2), 286-292.

   (ii) Tan, K. T., Gui, M. M., Lee, K. T., & Mohamed, A. R. (2010). An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production. The Journal of Supercritical Fluids, 53(1-3), 82-87.

   (iii) Muppaneni, T., Reddy, H. K., Ponnusamy, S., Patil, P. D., Sun, Y., Dailey, P., & Deng, S. (2013). Optimization of biodiesel production

from palm oil under supercritical ethanol conditions using hexane as co-solvent: A response surface methodology approach. Fuel, 107, 633-640.

(iv) Reddy, H. K., Muppaneni, T., Patil, P. D., Ponnusamy, S., Cooke, P., Schaub, T., & Deng, S. (2014). Direct conversion of wet algae to crude biodiesel under supercritical ethanol conditions. Fuel, 115, 720-726.

Most of the authors in the above mentioned papers, used the same three factors and responses in their experimental design. Then, what is the originality or variation in this manuscript? Is it just the use of leather tanning waste? If so, the Introduction has to be oriented towards this.

Response:We have modified the introduction part according to the suggestion from the reviewer in p.3 line 47 – p.6 line 105.

3) P6 Abbreviation : Following to be added in abbreviations of FOGs, TG, AOAC, ASTM, ISO, FAEE, UHP, GC-FID, AV, etc. are not present. Please include.

Response: We have added all the abbreviations in p.3, according to the reviewer's suggestion. However, we did not add "ASTM", "AOAC", and "ISO" on the list as they are a well-known international standards organization that develops and publishes many technical standards.

4) P1L1-4: The title of the manuscript seems to be lengthy and needs to be Precise for wide readership.

Response: We have revised the title of the manuscript to "A one-pot synthesis of biodiesel from leather tanning waste using supercritical ethanol: Process Optimization".

5) P2 Graphical Abstract: The graphical abstract seems to be blurred. Need to modify with higher resolution for better view.

Response: We have improved the quality of the graphical abstract for a better view.

6) P5L26-30: These sentences are not required in the abstract. Abstract should be focused more on the aim and outcome of the research in a crisp form. Try to modify it.

Response: We have modified the abstract according to the reviewer's suggestions in p.2 line 23-35.

7) P5L31: The sentence, "In this work" should be "In this present research".

Response: We have rewritten this sentence in p.2 line 25-28.

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8) P5L40-42: These sentences are too lucid, try to rewrite with more focus on the present outcome of the study.
Response: We have rewritten the abstract in p.2 line 23-35.
9) P5L43-44: In Abstract Keywords, Use single keyword which is not used in the abstract. For example. Use either Leather or Tanning waste and not the both.
Response: We have rewritten one keyword in p.2 line 36-37 to "tannery waste", which is not used in the abstract.
10) P6L55-56: The sentence "Currently Indonesia blends 20% ….." needs citation.
Response: We have cited a reference for this specific statement in p.3 line 55.
11) P6L58-61: The sentence "by almost 60 folds in a period of 10 years" is too confusing need proper justification.
Response: We have rewritten the sentence in p.3 line 51-54.
12) P6L62: The line "Various types of vegetable oils have been studied" should be "Vegetable oils derived from diverse source were actively screened".
Response: We have rewritten the line "Various types of vegetable oils have been studied" to "Vegetable oils derived from diverse sources were actively screened" in p.3 line 55-57.
13) P8L103: The line "The objective of this study" should be "The present investigation aims to".
Response: We have rephrased the line to "The present investigation aims to" in p.5 line 98.
14) P8 L104: "alcohol" is mispelled as "alcofol". Please correct.
Response: We have revised the term "alcohol to fats molar ratio" to "ethanol to LTW molar ratio" in p.5 line 102.
15) P8L110-111: The present aim of the study needs to be explained better.
Response: We have explained the aim of the study in p.5 line 98-105.
16) P14L241: Under the section 3.2. Process Optimization using RSM. Optimization using different methods needs to discuss properly. Cite references under this section is low. Need better discussion with the relevant literature.
Response: We have added relevant references in section 3.2 (p.13 line 275-276, p.13 line 298 – p.14 line 307) to compare the results obtained in this study with the other literature.
17) P22L433-448: In Conclusion, the Future perspective and present research gap needs to be addressed properly.

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Response: We have addressed the research gap in p.5 line 98-100 and the future perspective in p.18 line 420-422.

18) P31-Table 3: The legend of the table needs to be elaborated with the statistical software's used for the study and also mention significance error in both Actual and predicted.

Response: We have revised the captions for Table 3 in p.28 line 614-615. The standard deviation between the actual and predicted responses has been added as well in the last column of Table 3 in p.28-29.

19) P33-Table 4: Which ANOVA analysis was performed "one way" or "two way" assay needs better explanation.

Response: We have added the captions for Table 4 in p.30 line 629-630.

20) P36-Figure 2: Statistical error bar between the individual treatments needs to be included and software used for plotting the graph needs to be included in the figure legends.

Response: The Pareto chart of the standardized effects is generated automatically by Minitab version 18.1 during the analysis of variance (ANOVA); therefore the authors can't include the error bar on the graph. We have mentioned the software used to generate Figure 2 in figure captions (p.33 line 669-671).

21) P37L691: In figure 4, the legends needs to be explained in detail by including statistical data used and software used for plotting the graph.

Response: We have added the details in figure captions (p.35 line 677-679).

22) P38-Figure 4: Statistical data for plotting the graph needs to be discussed whether it is plotted using Sigma or excel needs to be explained in detail in the figure legends.

Response: The response optimization plot is generated by the RSM optimizer (Minitab version 18.1). We have added the details in the figure captions (p.35 line 677-679).

23) P39-Figure 5: Similarly, the significant error bar between the individual treatments needs to be included and mention the statistical software used for plotting the graph needs to be included in the figure legends.

Response: We have added the error bars in Figure 5 (p.36). The software used for plotting the graph has also been mentioned in figure captions (p.36 line 682-684).

24) The materials, methods, results and discussion have been written well.

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Response: We appreciate the constructive comments given by the reviewer.

25) Overall, it is observed that the results are promising with about 98% yield, which is relatively high compared to other manuscripts. It would be more effective for better understanding , when a comparison of other papers results with your result could be presented. This can be included in the discussion part.
Response: We have added several references to compare our results to the other research studies (p.13 line 298 – p.14 line 305).

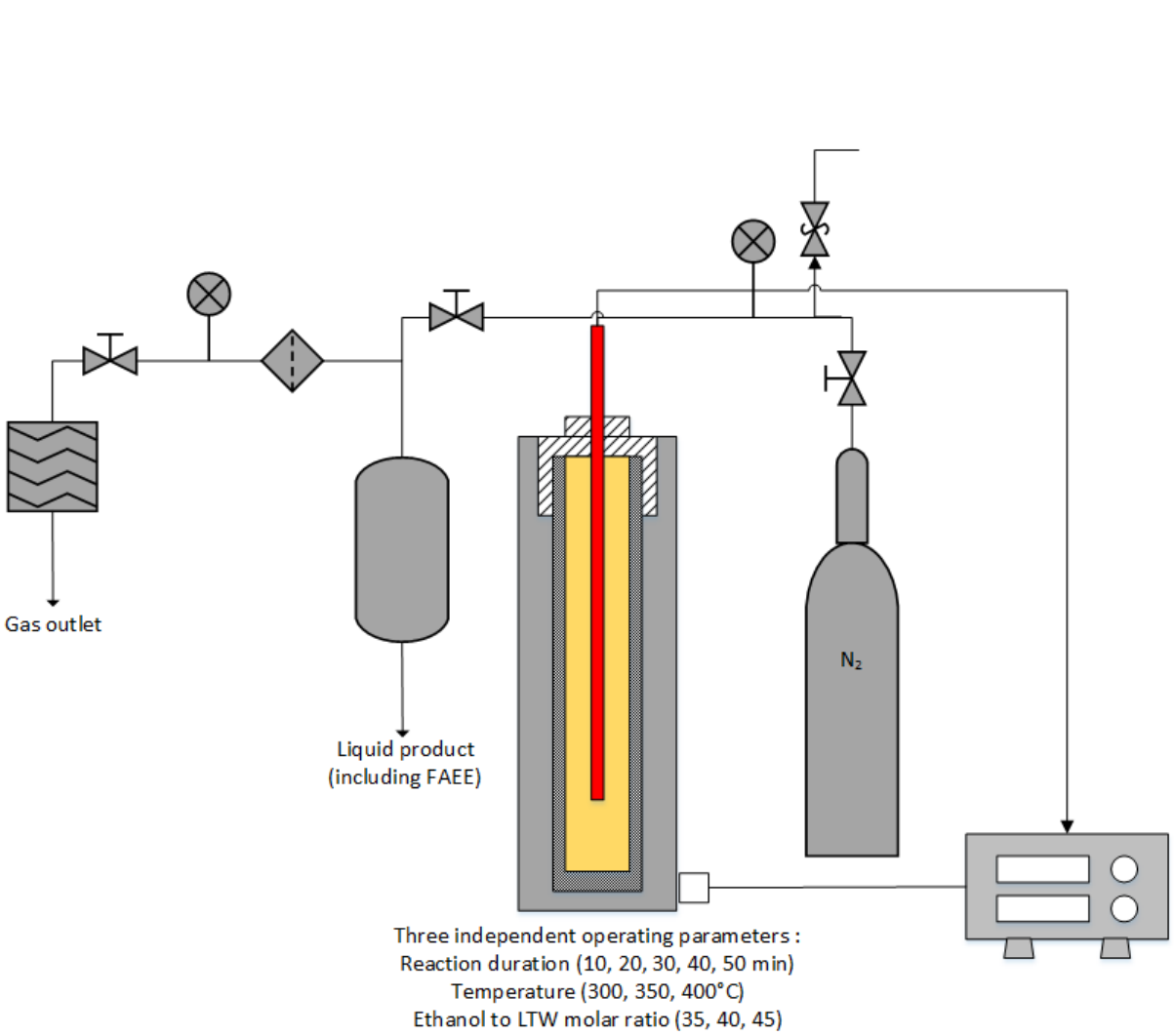
26) FINAL IMPRESSION OF THE REVIEWER: Overall, the manuscript requires major language and Grammar correction with native speaker. This Manuscript in its present form clearly fails to make a clear distinction about its Novelty , when there are similar papers published earlier. This comparison and discussion of Results of papers published using this technology should have been done with valid scientific rationale. Therefore, I do not find this manuscript suitable for publication in Biomass and Bioenergy Journal, without a major revision.
Response: We have modified the manuscript according to the comments given by the reviewer. The paper has been carefully revised by a native English speaker to improve the grammar and readability.

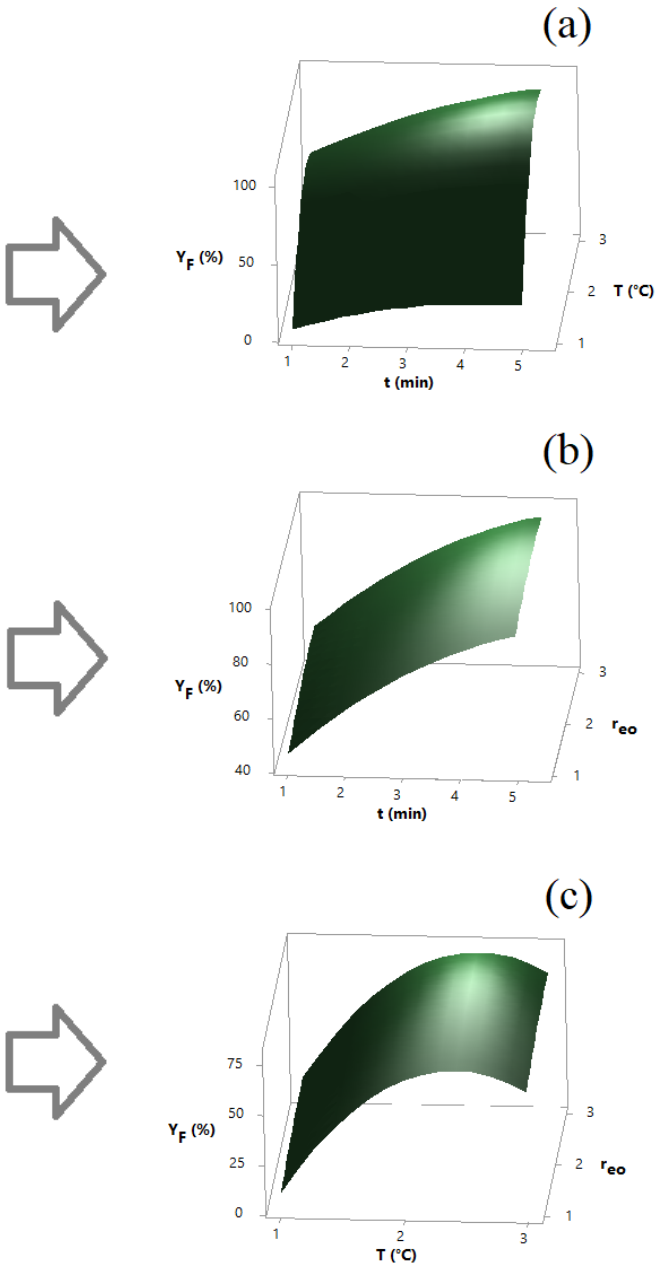
The manuscript has been resubmitted to your journal. We look forward to your positive response.

Sincerely yours,

Maria Yuliana

Graphical Abstract





Highlights:

- Tannery waste has been successfully converted to FAEE via supercritical ethanol
- The optimum FAEE yield was obtained at 98.91 ± 0.31%, with a purity of 97.55%
- The optimum operating condition is at t = 47.4 min, T = 374.6°C, r_{eo} = 40.02
- The fuel properties of leather tanning waste-based FAEE conform to ASTM D6751

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.

Keywords: waste-derived biodiesel; tannery waste; supercritical ethanol; catalyst-free; optimization study; renewable energy

1. Introduction[1]

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

[1] **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

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 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 12966, respectively. The fatty acid profile of LTW was identified with GC-2014 (Shimadzu Ltd., Japan), using Restek Rtx-65TG (30 m x 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:

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

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

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. Figure 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, 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.

Figure 1

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 x 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 a 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:

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

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):

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

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 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 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.

Table 3

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:

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

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 (Figure 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 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)).

Table 4

Figure 2

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 Figure 3 (a) – (c) as the 3D surface plots. Figure 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].

Figure 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 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 Figure 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 Figure 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.

Figure 3

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 Figure 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.

Figure 4

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 Figure 5 (a) – (c). Figure 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 Figure 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 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].

Figure 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 Figure 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].

Figure 5

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

Table 5

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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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

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.

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	

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	-

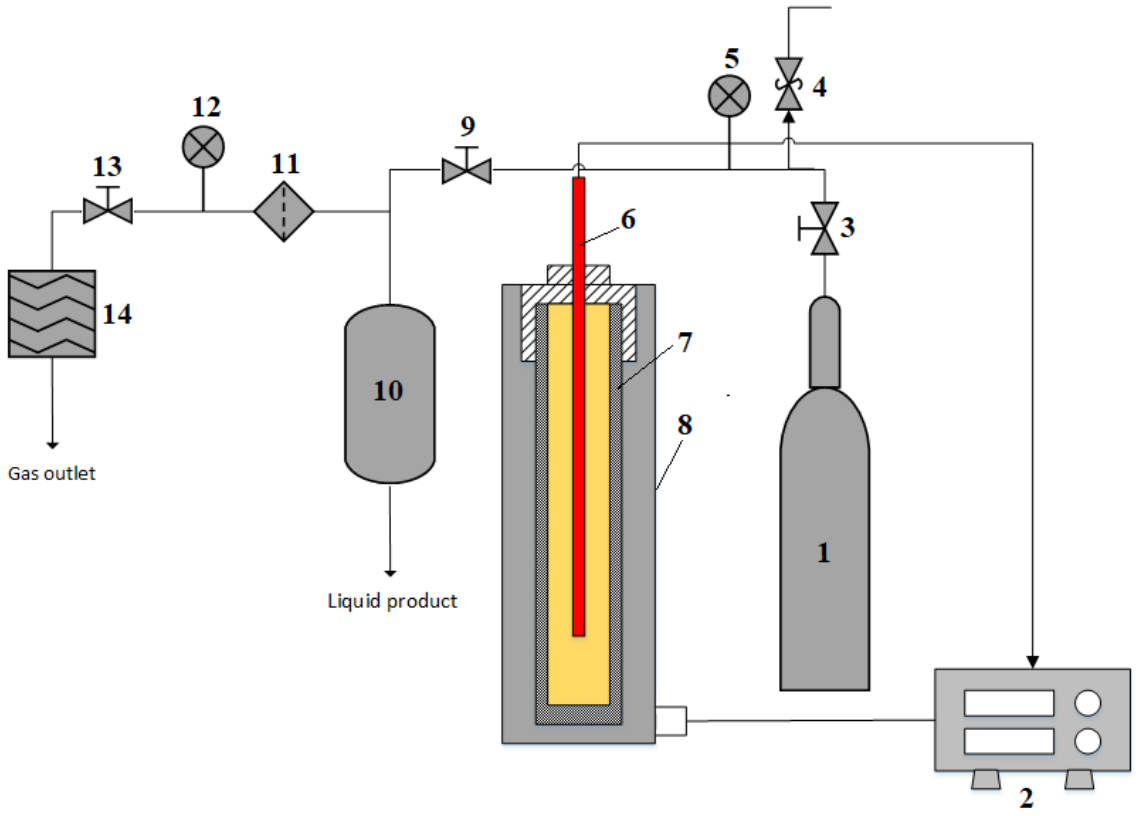

Figure 1. Schematic diagram of the SpCE apparatus: (1) nitrogen gas cylinder, (2) Temperature control system, (3) valve, (4) pressure relief valve, (5) pressure gauge, (6) thermocouple, (7) Supercritical reactor, (8) electric heater, (9) valve, (10) gas-liquid flash separator, (11) 1 μm filter, (12)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

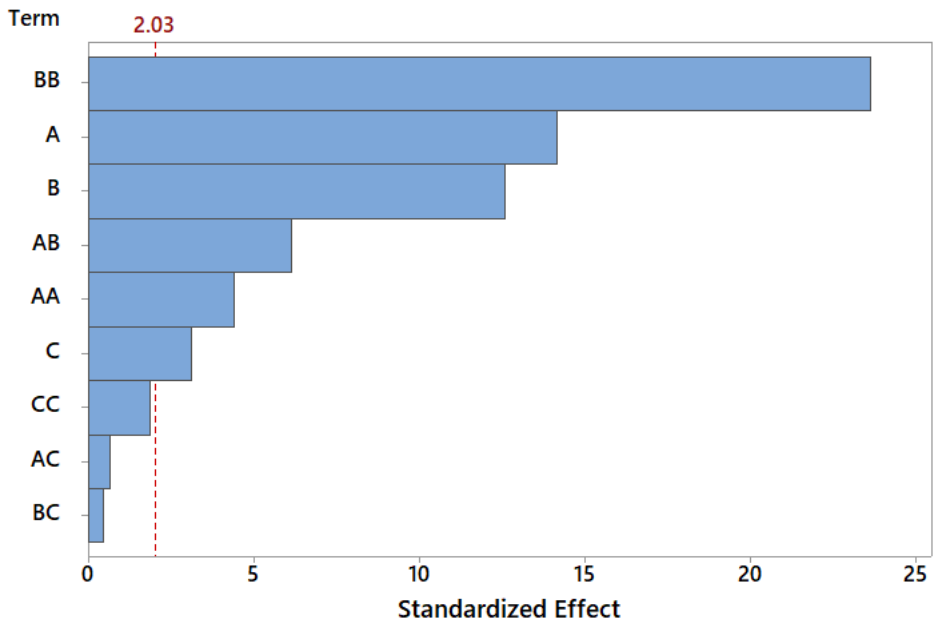

Figure 2. Pareto chart of the standardized effect, generated by Minitab (version 18.1), for the LTW-based biodiesel preparation via the SpCE technique, using the yield of FAEE as the response at a 95% confidence level where A = *t*, B = *T*, C = r_{eo}.

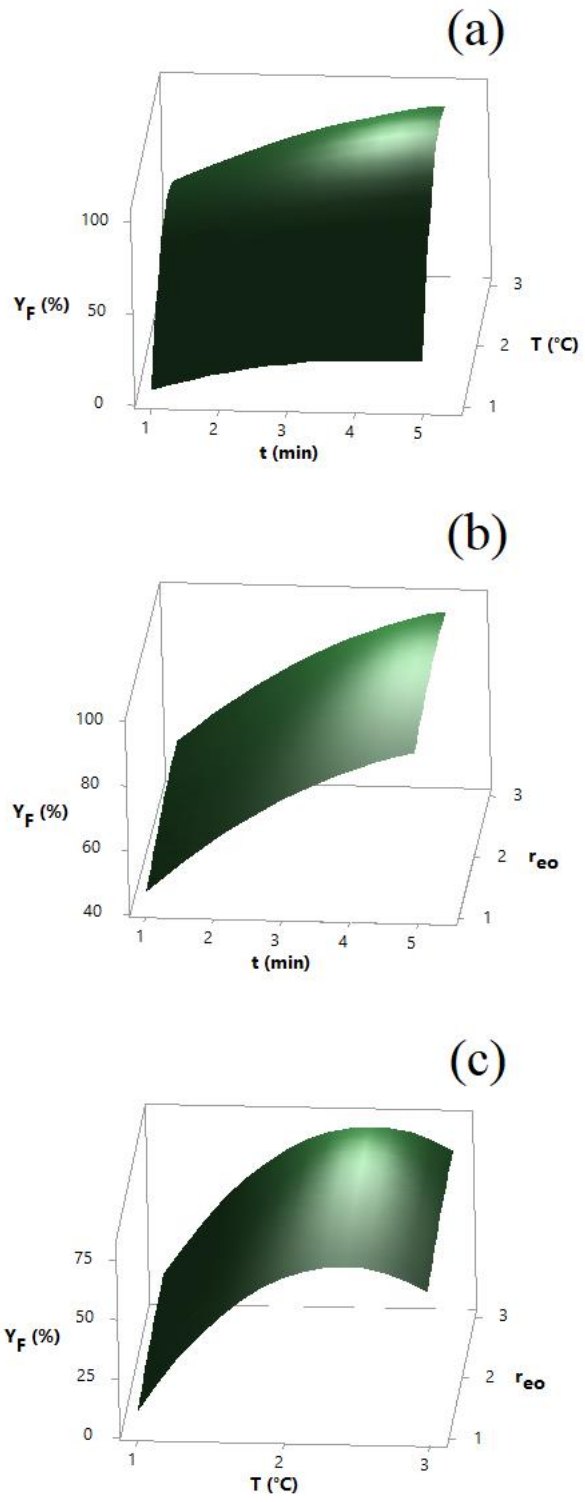

Figure 3. The 3D response surface plot of the FAEE yield, generated by Minitab (version 18.1) at various (a) *t* and *T*, (b) *t* and r_{eo}, (c) *T* and r_{eo}

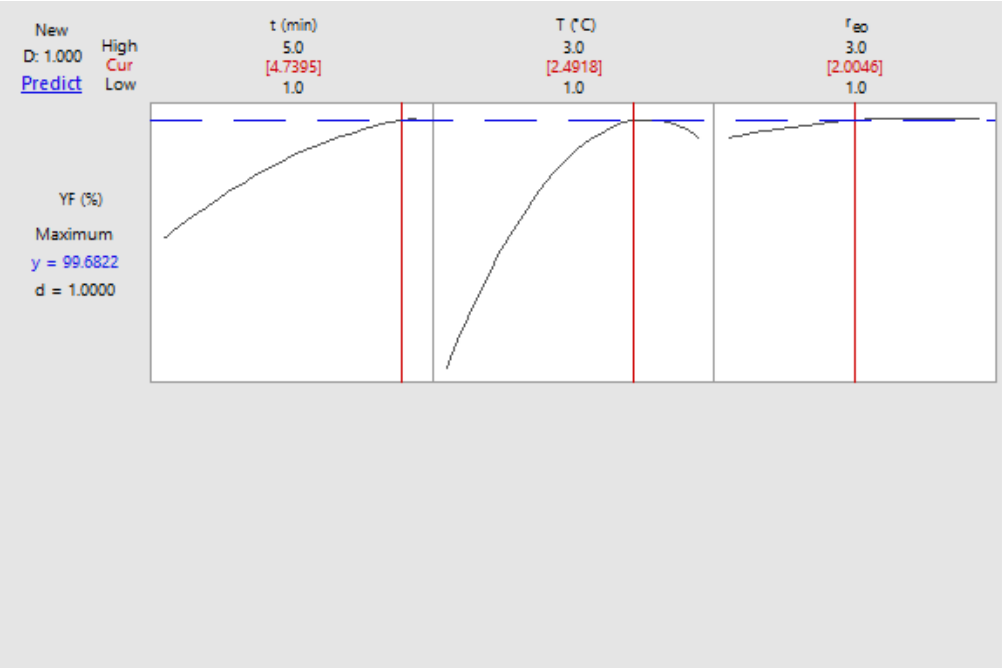

Figure 4. The response optimization plot of the three independent reaction variables (D = composite desirability, y = predicted response, d = desirability), generated by Minitab (version 18.1).

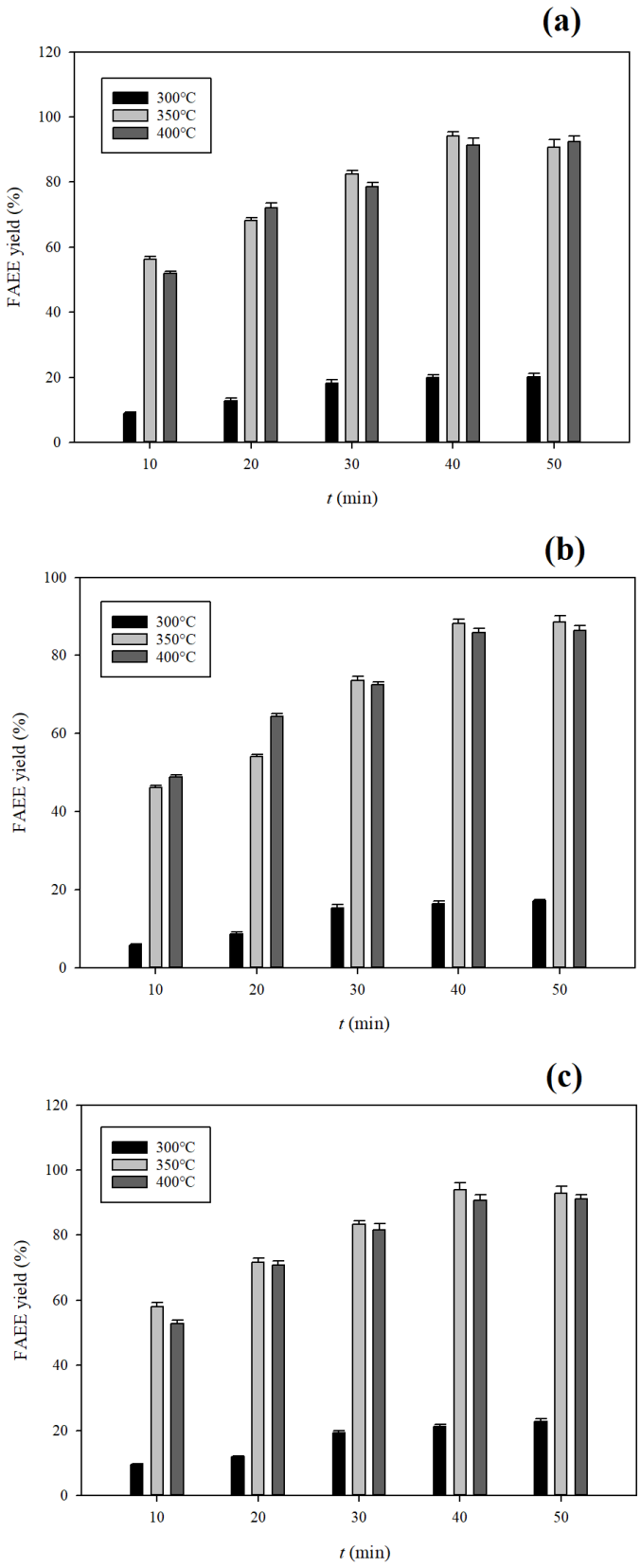

Figure 5. The variation of the experimental FAEE yield with time *t* (min) at different temperatures (*T* = 300, 350, 400°C) and a constant molar ratio of ethanol to LTW (a) r_{eo} = 35, (b) r_{eo} = 40, (c) r_{eo} = 45 (plotted by SigmaPlot version 14)

Your Submission

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Ms. Ref. No.: JBAB-D-19-01462R1
Title: A one-pot synthesis of biodiesel from leather tanning waste using supercritical ethanol: Process Optimization
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