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# Temperature-swing transesterification for the coproduction of biodiesel and ethyl levulinate from spent coffee grounds

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**Abstract**−This study introduces a temperature swing method for simultaneously producing biodiesel and ethyl levulinate through in-situ transesterification of spent coffee grounds. Effects of temperature and the amounts of catalyst and ethanol were investigated and it was found that the temperature predominantly affects the yield. Response surface methodology was employed to find the optimal conditions for maximizing biodiesel and ethyl levulinate yield. The highest biodiesel yield of 14.91±0.83 wt% was found at 140 °C, while the highest ethyl levulinate yield of 3.29±0.15 wt% was found at 160 °C. The maximum ethyl levulinate yield occurs at higher temperature than biodiesel due to decomposition of cellulose to produce ethyl levulinate, while the biodiesel yield decreases at elevated temperature due to unwanted humin formation. The proposed swing operation of the optimal temperature from 160 to 140 °C gives the highest yield of 15.02 wt% biodiesel and 2.76 wt% ethyl levulinate in the single-pot process.

Keywords: Temperature-swing, Spent Coffee Grounds, Biodiesel, Ethyl Levulinate, Single-pot In-situ Transesterification

## INTRODUCTION

Environmental issues caused by greenhouse gas emissions and rapid depletion of fossil fuels have driven the development of renewable and cleaner fuels [1,2]. Biodiesel has been considered a sustainable alternative due to its renewable and environmentally benign nature [3,4]. Its combustion leads to lower CO and NOx emissions than the conventional petro-diesel fuel [5,6]. The feedstock to produce biodiesel is mainly vegetable oil, such as palm oil, soybean oil, and other lipid-rich plants [7]. However, using these edible oils to produce biodiesel gives rise to ethical concerns and also has resulted in an increase in oil prices [8]. Another alternative that has showed remarkable potential is microalgae, as it is not used for human consumption and can grow up to tenfold greater annual aerial biomass than terrestrial plants, with some strains containing up to 60% lipids by dry weight [9]. However, an energy intensive drying process is required to produce biodiesel from microalgae, and the whole production is consequently not economical [9,10]. Using food wastes with less moisture as biodiesel feedstock can eliminate such problems while providing sustainable options without competing with the food supply chain.

Spent coffee grounds (SCGs) have emerged as a promising feedstock for biodiesel production considering the high consumption of coffee around the world and the problems that arise from untreated waste. Global coffee consumption from 2019 to 2020 reveals consumption is as much as 10.1 million tons annually [11]. Large amounts of SCG waste are not only toxic to aquatic organisms [12] but also raise environmental issues, such as land contamination due to their tannin, caffeine, and polyphenol contents [13]. It is also known that SCGs still contain 10-15 wt% of lipid content and more than 40 wt% of cellulose [14,15], which usually ends up as waste. Therefore, valorization of SCGs is deemed an opportunity to produce renewable energy while reducing the amount of waste at the same time.

Biodiesel, which is a fatty acid ester, is mainly produced by transesterification of triglyceride with alcohol under an acid or base catalyst. Depending on the feedstock, the conventional process usually requires drying and lipid extraction from the biomass to have a high product yield [9,16,17]. However, drying is an energy-demanding process that usually takes up to 30% of biodiesel production cost using microalgae as the feedstock [18,19]. Alternatively, wet in-situ transesterification (ISTE) appears to be a viable option as it combines multiple steps in one pot while maintaining a high yield of biodiesel even without a drying process [20-22]. Not only can this method proceed without a drying process, by utilizing the subcritical water properties, the moisture content inside the feedstock can be used to obtain a higher product yield. At high temperature and high pressure, self-ionization of water would increase the concentration of hydrogen ions and decrease the overall acidity of the system and catalyze the reaction [15,23,24]. Several studies report a high yield of biodiesel using agricultural biomass and residues, microbial biomass, and microalgae as the feedstock with this method [9,16]. It was also reported that the production of the valuable secondary chemical levulinic acid, which is a precursor for ethyl levulinate (EL), is possible using SCG [25]. Another study reported that EL is obtained from microalgae and fruit peels through cellulose hydrolysis to levulinic acid at high temperature and levulinic acid can be esterified to EL with ethanol [20,26]. Utilization of subcritical water for cellulosic hydrolysis was also studied at high temperature. It is found that acidic subcritical water can hydrolyze the cell wall with no catalyst used [3,27]. However, the energy requirement could be higher than catalyzed reaction for the same amount of

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yield produced. As ethanol is also employed as a reactant for wet ISTE, simultaneous production of biodiesel and EL is possible. Ethyl levulinate is known to have a wide range of uses, such as improving the cold flow property of biodiesel [28] and for artificial flavoring and fragrances [29], which can increase the value chain of the product and contribute to making the whole process more economical. However, the simultaneous production of biodiesel and EL through wet ISTE has rarely been studied using SCGs. Sulfuric acid can be employed as the catalyst in this system, disrupting the SCG cellulosic cell wall and exposing lipids inside the SCG matrix to react more readily with ethanol. To increase the solubility of lipids with the system, we also introduce chloroform as a co-solvent [22,30]. The relatively low polarity of chloroform could bind with lipids and thus it can help to extract the lipids from the SCG. It is conjectured that the reaction for EL production should be carried out at relatively higher temperature than that of biodiesel production because the cellulosic wall must be hydrolyzed. To achieve high yields of both biodiesel and EL through a single-time in-situ transesterification, a temperature swing reaction route is proposed as one of the possible solutions. To the best of our knowledge, there has been no study on optimum catalytic coproduction of biodiesel and EL from SCGs by introducing a temperature swing operation of in-situ transesterification.

This study investigated the concurrent production of biodiesel and the secondary chemical EL using SCGs as the feedstock through a temperature swing in wet ISTE. The effects of reaction temperature, SCG moisture content, ethanol, and acid catalyst volume on the biodiesel and EL yields were observed. Response surface methodology (RSM) was employed to identify the most dominant variable affecting the product yields and to obtain the optimal conditions for obtaining the maximum yield of biodiesel and EL. To achieve a compromise between the different temperature effects on the biodiesel and EL yields, a new temperature-swing operation was introduced for high coproduction yields of biodiesel and EL. Furthermore, the mechanism of product formation under temperature-swing operation was investigated.

## MATERIALS AND METHODS

### 1. Materials

Spent coffee ground (SCG) beans originating from Costa Rica were stored inside a freezer, and batches of approximately 15 g of SCG were oven-dried at 110 °C for 24 hours. For the reagent, extra pure 99.5% ethanol was purchased from Samchun Pure Chemicals Co., Ltd. Chloroform solvent with a purity of 99% was purchased from Junsei Chemical. 95% $H_2SO_4$ as an acid catalyst was purchased from Junsei Chemical. For the ethyl levulinate (EL) calibration curve in the gas chromatography (GC) analysis, 98% ethyl levulinate from TCI was used, and as an internal standard reagent for the GC analysis, 97% ethyl heptadecanoate from TCI was used.

### 2. Wet In-situ Transesterification (ISTE)

For the wet ISTE reaction, the modified procedure from a previous study [20] was conducted. For every experiment 0.3 g of dry SCG was used. For the wet SCG experiment, the moisture content of the SCG was varied by soaking the dried SCG with deionized water for 30 minutes as a pretreatment. The wet SCG was then mixed with 2 ml of chloroform, ethanol as a reactant with volume ranging between 1 ml to 3 ml, and sulfuric acid as a catalyst with the amount varied between 0.1-0.2 ml inside an SUS-316 bomb reactor equipped with a Teflon liner. The reaction was carried out at temperature ranging between 120-180 °C for two hours. After the reaction, the reactor was cooled to room temperature. The reacted mixture was then transferred to a 50 ml conical tube, and mixed with 2 ml of deionized water and 1 ml of chloroform to promote the phase separation. Subsequently, 1 ml of chloroform containing 0.5 mg ethyl heptadecanoate (C17) was added to the conical tube as an internal standard for calculating the biodiesel yield from gas chromatography results. A small amount of sodium hydroxide was also added to neutralize the mixture. The mixture was then centrifuged at 3,700 rpm for 15 minutes. Next, 1 ml of the sample was taken from the organic phase at the bottom of the mixture, which contains biodiesel and EL, and then transferred to a 1 ml autosampler vial. The yield of each target component was then analyzed with gas chromatography. All experiments were carried out in triplicates to ensure reproducibility of the data. The product yields are expressed by the following equation.

$$\text{Product yield} = \frac{\text{Weight of obtained products}}{\text{Weight of dry SCG used}} \times 100(\%) \quad (1)$$

### 3. Analytical Methods

To obtain the amounts of biodiesel and EL produced from the ISTE method, 1 μl of the sample was injected to an Agilent 7890B GC equipped with a DB-5ht column (30.0 m×0.32 mm×0.1 μm). A flame ionization detector was used as a GC detector and operated at 280 °C with helium continuously supplied at 2.1 ml/min as a carrier gas. The oven heating rate was set at 25 °C per minute until 175 °C, and then increased by 4 °C per minute until reaching 240 °C. From the GC analysis, the amount of all compounds in the samples can be obtained through the area profile. To calculate the amount of biodiesel that was produced, the area of biodiesel was compared to the area of the standard reagent ethyl heptadecanoate. The amount of EL produced was obtained by comparing the area obtained from the GC analysis with the EL calibration curve that was prepared beforehand by following the same procedure as in our prior work [20]. The biodiesel and EL yields were then calculated based on the mass of dried SCG. For the humin analysis, the solids that remained on the reactor after the reaction were analyzed using scanning electron microscopy (SEM Hitachi SU5000).

### 4. Optimization Using Response Surface Methodology (RSM)

The maximum yields of biodiesel and EL were determined using response surface methodology. The Box-Behnken design was selected to predict the maximum yield with fewer experimental runs. Temperature (A), sulfuric acid volume (B), and ethanol volume (C) were selected as variables and the ranges of each variable were determined from the experimental data. Design-Expert 13™ (Stat-Ease, Inc.) was used to build the model from the experimental data, generating 3D surface plots of the effect of variables on each target yield and predicting the optimum point of biodiesel and EL yield.

### 5. Temperature-swing Operation of Wet ISTE

High yields of biodiesel and EL were realized at different temperatures. The possibility of coproduction of biodiesel and EL with high yields was studied by conducting temperature-swing opera-

tion of wet in-situ transesterification. A similar procedure to that outlined in section 2.3 was carried out, with the total reaction time divided into two halves in which the temperature was changed after one hour of reaction. One-hour reaction of each temperature was also conducted to better understand the formation mechanism of the product under the temperature-swing operation.

## RESULTS AND DISCUSSION

### 1. Variation of Reaction Temperature and SCG Moisture Content

The effect of reaction temperature and moisture content on the product yield was investigated by varying the temperature of 120 to 180 °C and the SCG moisture content from 0 to 80% while maintaining constant volumes of chloroform (2 ml), ethanol (2 ml), and sulfuric acid (0.15 ml). Fig. 1(a) suggests that both temperature and moisture content affect the biodiesel and EL yields, but increasing the temperature is more effective for obtaining high yields at a high moisture content of 80%. Similar to a previous study [22], the biodiesel yield decreases as the temperature rises in a low moisture condition, indicating that 120 °C is sufficient to produce biodiesel, but further increasing temperature lowers the biodiesel yield. Another study reported that biodiesel can be decomposed with increasing temperature, and decomposition is intensified linearly from 20 to 352 °C [31]. A high temperature condition was also known to promote side reactions, such as humin production that can block acid catalyst active sites [6,32], and lead to the decreased biodiesel yield. Ethanol also evaporates at high temperature, which eventually can lower the yield because the reaction occurs in the liquid phase [33].

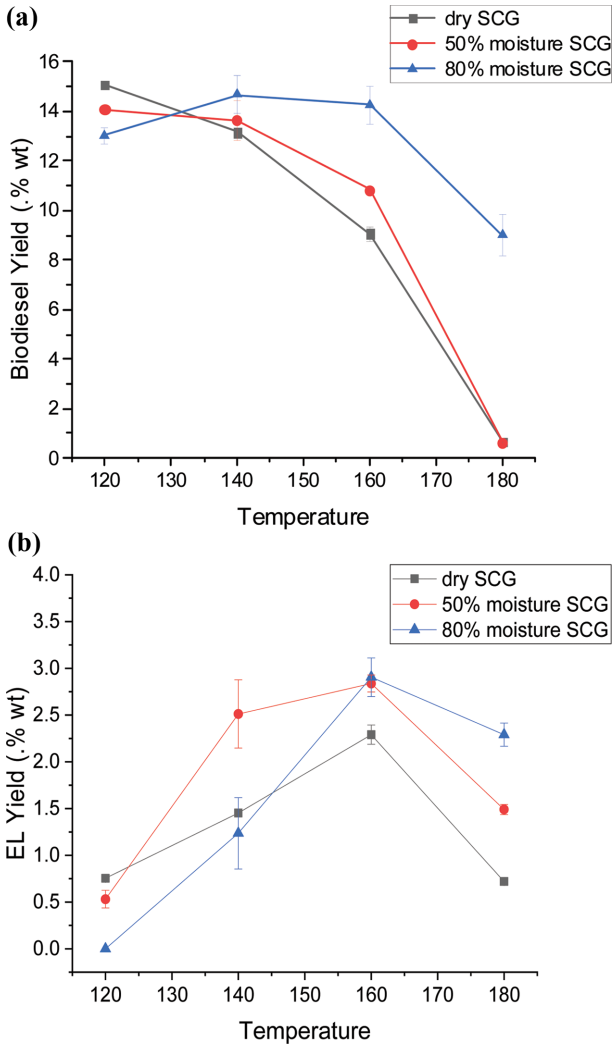


**Fig. 1. Effect of temperature and SCG's moisture content on (a) biodiesel and (b) EL yield (chloroform volume 2 ml, ethanol volume 2 ml, $H_2SO_4$ volume 0.15 ml).**

At 120 °C, high moisture levels of 50% and 80% have a negative effect on the biodiesel yield. The presence of water will limit the contact between non-polar solvent chloroform and lipids inside SCGs, which can lead to a reduced yield [20,21]. Transesterification of fatty acid to biodiesel is also a reversible reaction, and thus the presence of water could promote a reverse reaction and hydrolyze the biodiesel into fatty acid and ethanol [22]. However, water at higher temperatures could enter subcritical states, where water can exist as hydrogen and hydroxide ions [34]. Water in that state then can act as a catalyst for the reaction and can promote the hydrolysis of the SCG's cell walls, allowing the lipids to be freed and come into contact with the reactant easier [24]. Because of the water subcritical properties, the biodiesel yield becomes higher at increased temperature of 140-160 °C when the moisture content rises. For 80% moisture content, the yield peak is observed at 140 °C, with as much as 14.67 wt% biodiesel produced.

It is observed in Fig. 1(b) that high temperature is also needed to attain a high yield of EL. The highest EL yield, as high as 2.9 wt%, was obtained at 160 °C and 80% moisture. The EL is formed from a chain of reactions. The cellulosic wall is first depolymerized to glucose, which is then dehydrated to hydroxymethylfurfural (HMF) under an acidic condition. The HMF ring is then opened with the help of an acid catalyst, which yields levulinic acid (LA). The LA is then esterified with ethanol, to finally form EL [32,35]. As shown in Fig. 1(b), for all moisture contents, the EL yield increases sharply until it reaches its peak, and then decreases at 180 °C. As higher temperatures can weaken glycosidic bonds between celluloses, degradation of cellulose to form EL depends highly on temperature. Therefore, more heat is required for breaking the cellulose into glucose, which is the precursor of LA. Only a small amount of EL was formed at 120 °C, suggesting that this temperature is too low for cellulose decomposition. For higher moisture conditions, the EL generally has higher yields than at the dry condition at higher temperature. Water present in the SCG also facilitates the diffusion of $H^+$ ions into the cellulosic microstructure, while moisturization is needed for dry SCG before the acid catalyzed decomposition [36]. The presence of water at high temperature is also reported to disrupt the SCG cell walls, which facilitates mass transfer of the lipids [37].

The EL yield then decreases when the temperature is further increased. This is caused by the unwanted side reaction of glucose to form humin at high temperatures [3,38,39], resulting in a drop in the yield of EL. Humin is a carbon material that can be formed from HMF at very high temperatures, which can lower the EL yield because both humin and EL use HMF as the reactant. Moreover, humin is also reported to absorb the intermediate of levulinic acid,

5-HMF, and sulfuric acid, decreasing the EL conversion even further [32]. A study reported a significant increase in humin production when the temperature was increased from 140 °C to 180 °C [40]. Consistent with this, in the present study, at 180 °C, a black solid substance, presumed to be humins, was also observed at the bottom of the reactor when the sample was collected. Images of humin collected and SEM images of humin can be found in Fig. 2 (refer to Fig. S1 for its photographical image). The humin from the SEM images has a spherical shape and is formed in agglomerates with a diameter of around 5 μm, consistent with the description of humin in a previous study [41]. As high yields of biodiesel and EL are observed at 140 °C and 160 °C, and also are realized when 80% SCG moisture content was applied, the effect of the other variables on products yield for the next section is conducted on 140 and 160 °C, and 80% of moisture content. Furthermore, to compare the effect of SCG's moisture content on the product yield, the dry condition is also evaluated for the volume variation of acid and ethanol.

**2. Effect of Sulfuric Acid Volume on the Product Yield**

An experiment to observe the effect of sulfuric acid volume on

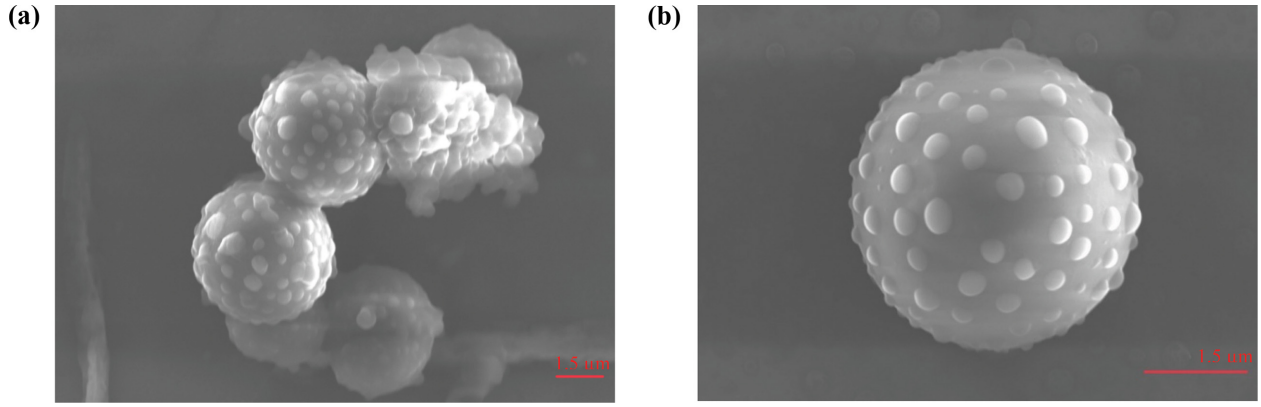


**Fig. 2. Microscopic humin images obtained under condition of 180 °C, 0.15 ml sulfuric acid, 2 ml of ethanol, 80% moisture content (a) SEM of cluster of humins (b) SEM of single humin particle.**

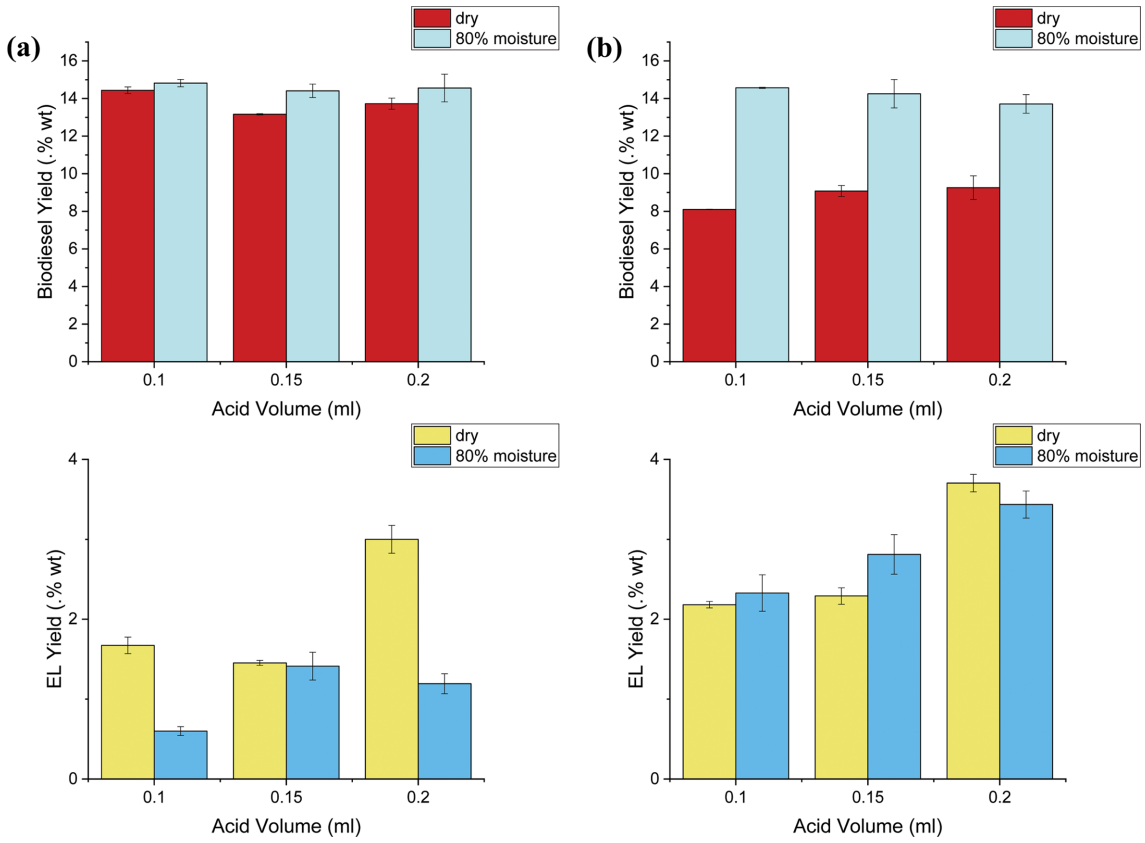


**Fig. 3. Biodiesel and EL yields of wet ISTE under different acid volume, moisture content, and temperature of (a) 140 °C (b) 160 °C.**

the product yield was carried out at the temperature that resulted in the highest yield from the previous section and by varying the moisture content of the SCG (dry & 80%). Due to moisture and free fatty acid inside the SCG, an acid catalyst is preferred because a base catalyst can react with free fatty acid and trigger a saponification reaction; this will lower the catalytic activity because the base catalyst is consumed and increases the viscosity of the reactant mixture due to soap formation [42,43]. Sulfuric acid was chosen because it showed good catalytic activity for biodiesel production [44], specifically from SCG [22], and was also reported to specifically degrade cellulose and dehydrate HMF to several compounds including LA [23,25,45], which is the precursor for EL. The sulfuric acid volume was varied from 0.1 to 0.2 ml, and other variables of chloroform volume and ethanol volume were held constant at 2 ml. A high yield of biodiesel was generally obtained at 140 °C, with up to 14.82 wt% observed for 0.1 ml of sulfuric acid, as shown in Fig. 3. Also, using a small amount of acid results in a high yield and 0.1 ml of acid was sufficient to convert almost all of the available lipids to biodiesel. The biodiesel yield for the dry condition at high temperature was significantly lower than the wet condition, possibly caused by the reaction conditions being too harsh rather than producing the target biodiesel, and a side reaction of humin formation is more dominant, thus decreasing the produced biodiesel as mentioned in the previous section.

The acid amount greatly affects the EL yield compared to the biodiesel yield. As presented in Fig. 3, for both temperature and moisture conditions, the yield increases as the acid volume rises. This is likely related to the role of acid in EL formation, as an acid not only works as a catalyst to form EL but also helps to hydrolyze the cellulosic wall to its glucose monomer, which can be further converted to EL [46]. An increase in the acid volume thus will make the reaction faster, eventually producing more EL. At higher temperature, the rate of hydrolysis becomes faster based on the enhanced forward reaction, and hence more EL can be formed even with the presence of catalyst in a small quantity.

### 3. Effect of Ethanol Volume on the Product Yield

Even though methanol is more commonly used as a reactant for biodiesel production, ethanol has some advantages over methanol: it is a considerably more sustainable option as it can be produced from agricultural sources, it is less toxic and easier to handle than methanol, and its biodiesel products have a better combustion characteristic compared to that of methanol [47]. Accordingly, ethanol was selected for this reaction. Ethanol has several known roles for this one-pot reaction: a reactant for biodiesel and EL, an agent to help break down the SCG's cell walls [20], and a reactant for ethanolysis, which is a preliminary step before conversion to EL [35]. Alcohol is also known to protect the active functional groups of the main intermediates for levulinate production by generating methyl glucosides and methoxymethyl-2-furaldehyde, which results in selectivity towards levulinate over humin [32]. To check the effect of ethanol in our method, an ISTE reaction with ethanol volume ranging from 1 to 3 ml was carried out. For other variables, the temperature was set the same as in the experiment from the previous section; the acid volume was set at 0.15 ml, and the volume of

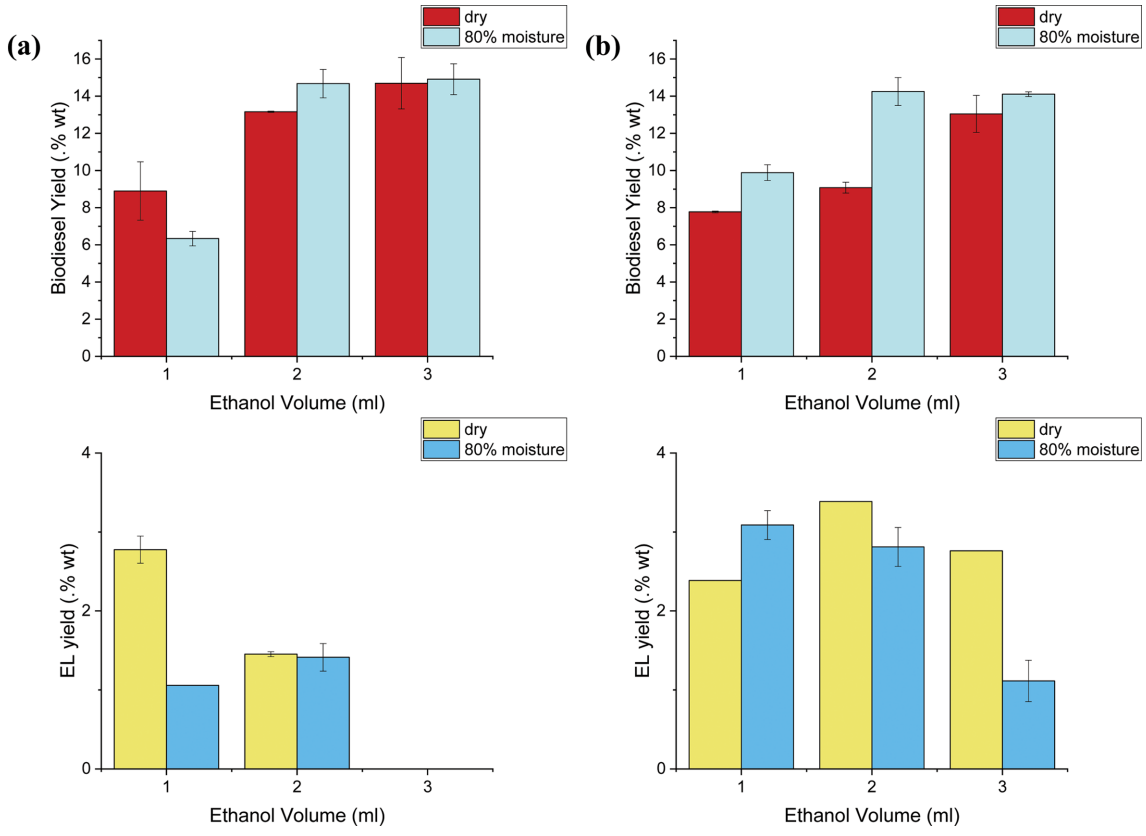


**Fig. 4. Biodiesel and EL yields of wet ISTE under different ethanol volume, moisture content, and temperature of (a) 140 °C (b) 160 °C.**

chloroform was set at 2 ml. The positive effect of ethanol on the biodiesel yield can be seen in Fig. 4. Regardless of the moisture condition and the reaction temperature, the biodiesel yield increases as the amount of ethanol increases. However, there is no significant increase in the yield when the ethanol volume rises from 2 to 3 ml. One possible explanation is all the lipids that are available on the SCG might be exhausted at 2 ml, and thus further addition of ethanol has no effect because there were no available free lipids to react with.

Fig. 4 shows the effect of the amount of ethanol on the EL yield. As ethanol helps to hydrolyze cellulose and is a reactant for EL, a low ethanol volume results in a low EL yield in some cases. A previous study also reported that the presence of alcohol could suppress the humin formation, thus increasing the selectivity towards the EL and showing an increased yield when the amount of ethanol was increased from 1 to 2 ml [48]. However, when 3 ml of ethanol was applied, the yield decreased significantly and even reached 0% at 140 °C. In this condition, the ethanol volume was too high and diluted the acid [20]. The decrease in acidity will decrease the rate of cellulose deterioration. The small number of building block monomers can thus react with the ethanol reactant, which leads to an overall decrease in the EL yield. The EL production at 160 °C is better than that at 140 °C, regardless of the ethanol volume, indicating that high temperature is more important for high EL production than a large amount of ethanol.

**4. Optimization of Biodiesel and EL Yield through Response Surface Methodology**

To obtain the optimum conditions that maximize the biodiesel and EL yield, respectively, RSM analyses using the Box-Behnken model were conducted. From the previous section, the high yield was still attainable at a high moisture content, and thus 80% moisture was set for this set of RSM experiments to assess how the wet

**Table 1. ANOVA result for quadratic model of biodiesel yield**

| Source | Sum of squares | Mean square | F-value | p-Value | Remarks |
|---|---|---|---|---|---|
| Model | 179.58 | 19.95 | 36.05 | 0.0005 | Significant |
| A-Temperature | 2.29 | 2.29 | 4.15 | 0.0974 | |
| B-Sulfuric acid volume | 6.51 | 6.51 | 11.76 | 0.0186 | |
| C-Ethanol volume | 101.47 | 101.47 | 183.34 | <0.0001 | |
| AB | 8.68 | 8.68 | 15.68 | 0.0107 | |
| AC | 10.44 | 10.44 | 18.86 | 0.0074 | |
| BC | 4.31 | 4.31 | 7.79 | 0.0384 | |
| $A^2$ | 32.10 | 32.10 | 57.99 | 0.0006 | |
| $B^2$ | 6.62 | 6.62 | 11.96 | 0.0181 | |
| $C^2$ | 12.98 | 12.98 | 23.45 | 0.0047 | |
| Residual | 2.77 | 0.5535 | | | |
| Lack of fit | 2.33 | 0.7783 | 3.60 | 0.2250 | Not significant |
| Pure error | 0.4324 | 0.2162 | | | |
| $R^2$ | | | | | 0.9848 |
| Adjusted $R^2$ | | | | | 0.9575 |

**Table 2. ANOVA result for quadratic model of EL yield**

| Source | Sum of squares | Mean square | F-value | p-Value | Remarks |
|---|---|---|---|---|---|
| Model | 13.60 | 1.51 | 48.15 | 0.0003 | Significant |
| A-Temperature | 5.11 | 5.11 | 162.83 | <0.0001 | |
| B-Sulfuric acid volume | 0.5053 | 0.5053 | 16.11 | 0.0102 | |
| C-Ethanol volume | 0.5780 | 0.5780 | 18.42 | 0.0078 | |
| AB | 0.0416 | 0.0416 | 1.33 | 0.3015 | |
| AC | 0.3015 | 0.3015 | 9.61 | 0.0269 | |
| BC | 0.7420 | 0.7420 | 23.65 | 0.0046 | |
| $A^2$ | 4.49 | 4.49 | 143.00 | <0.0001 | |
| $B^2$ | 0.1054 | 0.1054 | 3.36 | 0.1262 | |
| $C^2$ | 2.28 | 2.28 | 72.77 | 0.0004 | |
| Residual | 0.1569 | 0.0314 | | | |
| Lack of fit | 0.1369 | 0.0456 | 4.58 | 0.1846 | Not significant |
| Pure error | 0.0200 | 0.0100 | | | |
| $R^2$ | | | | | 0.9886 |
| Adjusted $R^2$ | | | | | 0.9681 |

ISTE method fares in high moisture. The temperature for the transesterification reaction was varied between 120 to 180 °C for biodiesel production. However, due to the sharp increase of the EL yield between 140 and 160 °C and the negligible production at 120 °C, the temperature variation was applied in a smaller range from 140 to 180 °C in order to obtain more accurate results for the EL RSM design. The other variables, such as sulfuric acid and ethanol amount, were varied from 0.1-0.15 ml and 1-2 ml, respectively. Based on the ANOVA quadratic model, the model equations for the biodiesel and the EL yield are as follows:

$$Y_1 = -136.73 + 1.256A + 367.53B + 22.25C - 0.982AB - 0.054AC - 20.76BC - 0.0032A^2 - 535.5B^2 - 1.87C^2 \quad (2)$$

$$Y_2 = -74.22 + 0.91A + 24.39B - 0.61C - 0.10AB + 0.014AC + 8.61BC - 0.003A^2 - 67.59B^2 - 0.78C^2 \quad (3)$$

where $Y_1$ and $Y_2$, respectively, denote the biodiesel yield and the EL yield, A is temperature, B is the sulfuric acid volume, and C is the ethanol volume. The experimental design alongside the yields is available in the Supplementary Information.

The ANOVA results and the $R^2$ values of the biodiesel and EL model are shown in Table 1 and Table 2. As for both models, when the P-value is less than 0.05, the variables are more influential on the model. Also, an $R^2$ value close to 1 indicates that both model results fit well with the experimental data. For both biodiesel and EL yields, the model is well fitted to the quadratic model. 3D surface graphs of the product yield were obtained from the RSM calculation and are shown in Fig. 5 and Fig. 6, respectively. Based on Fig. 5, the 3D plot for biodiesel agrees with the results from the previous section, where moderate temperature is required for a high yield of biodiesel. It is also observed that biodiesel needs sufficient ethanol to produce a high amount of biodiesel, with a high biodiesel yield being observed starting from 2 ml of ethanol. The amount of sulfuric acid does not result in a relatively dramatic change compared to the other two variables, as a small amount of sulfuric acid (0.15 ml) is already sufficient to produce a large amount of biodiesel, while a drop of biodiesel yield is observed when a large amount of sulfuric acid is used, owing to humin production.

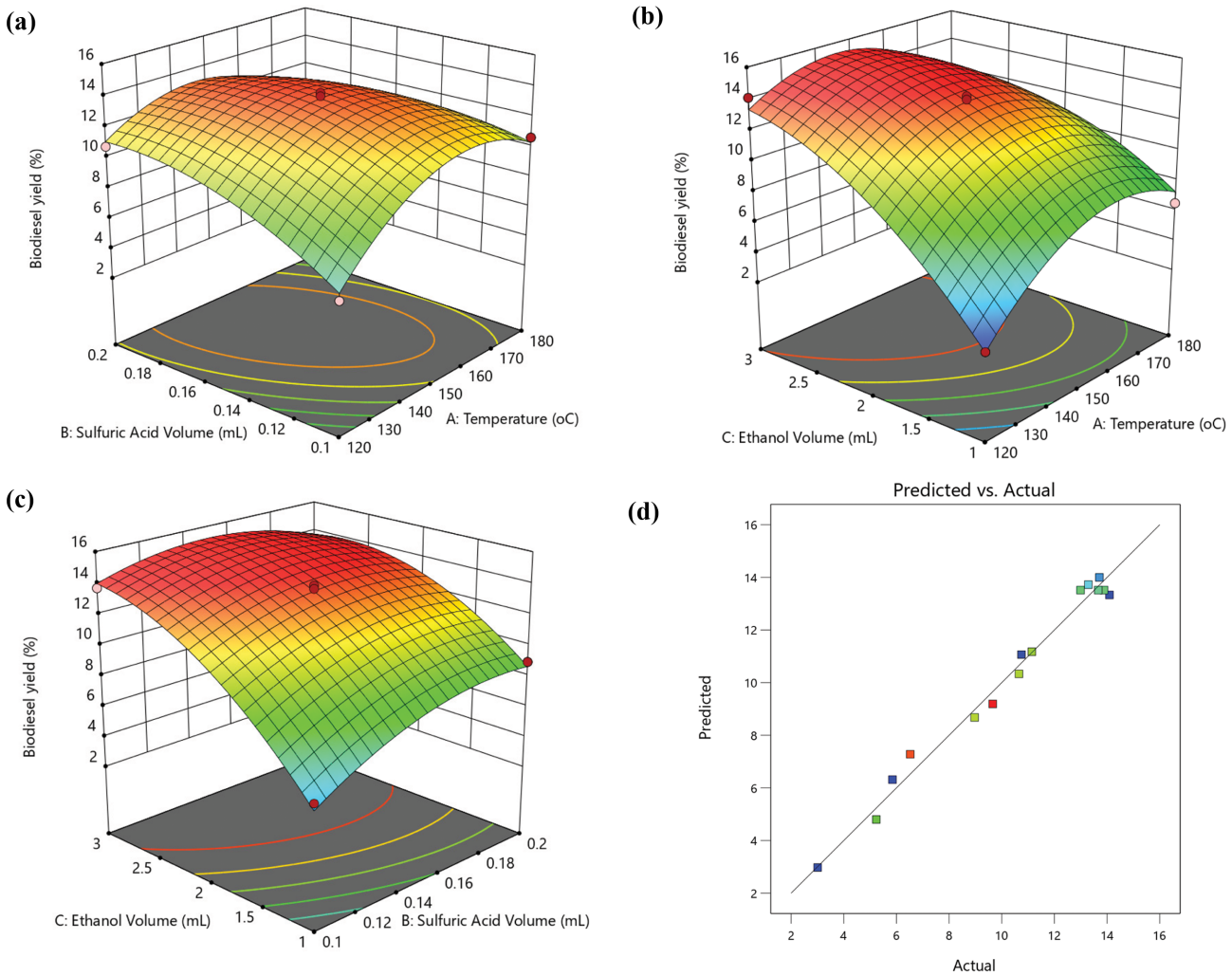


**Fig. 5. RSM results of biodiesel yield with reaction variables (a) sulfuric acid volume vs temperature (ethanol volume fixed at 2 ml) (b) ethanol volume vs temperature (sulfuric acid volume fixed at 0.15 ml) (c) ethanol volume vs sulfuric acid volume (temperature fixed at 150 °C) (d) comparison of predicted and experimental data plot where square represent the experimental data point.**

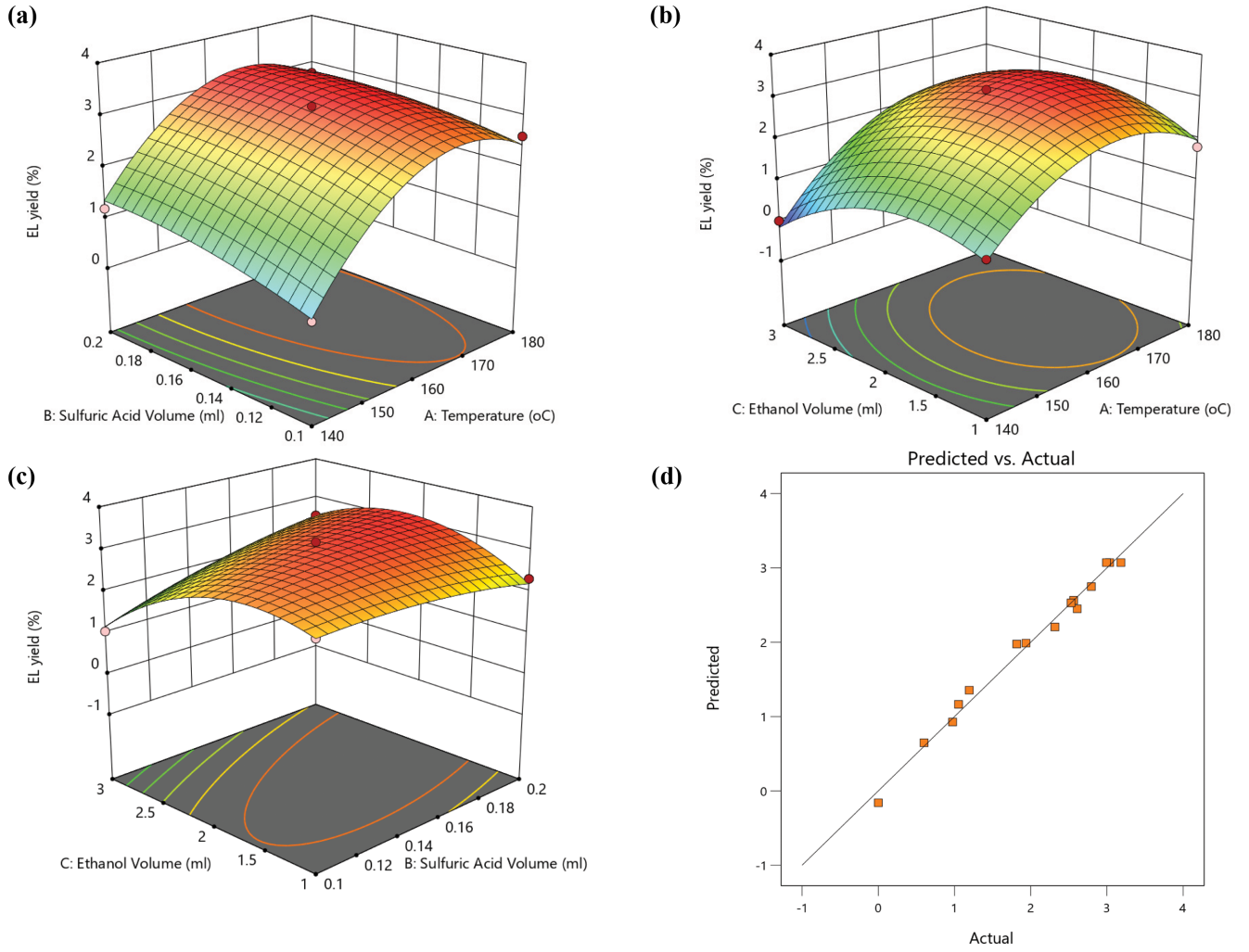


**Fig. 6. RSM results of EL yield with reaction variables (a) sulfuric acid volume vs temperature (ethanol volume fixed at 2 ml) (b) ethanol volume vs temperature (sulfuric acid volume fixed at 0.15 ml) (c) ethanol volume vs sulfuric acid volume (temperature fixed at 160 °C) (d) comparison of predicted and experimental data plot where square represent the experimental data point.**

**Table 3. Maximum yield of biodiesel and EL from this experiment**

| Yield | Temperature (°C) | Sulfuric acid volume (ml) | Ethanol volume (ml) | Calculated yield (wt%) | | Experimental yield (wt%) | |
|---|---|---|---|---|---|---|---|
| | | | | BD | EL | BD | EL |
| BD | 144 | 0.15 | 3.00 | 15.3 | - | 14.9±0.83* | - |
| EL | 162 | 0.19 | 2.23 | - | 3.22 | - | 3.29±0.15** |

* Experimental data at 140 °C. ** Experimental data at 160 °C.

The 3D plot for the EL yield is also aligned with the results from the previous section, where low temperature results in a low EL yield, but a side reaction occurs at higher temperature, lowering the EL yield. Also, the interaction between sulfuric acid and ethanol is important because these two factors are directly related to the ethanolic dilution of sulfuric acid.

The predicted maximum biodiesel and EL yields and their experimental results are shown in Table 3. Similar results between the calculated and the experimental yields show that the model from the RSM analysis is accurate. The maximum biodiesel yield was found at lower temperature and higher ethanol volume than EL, indicating that the lipids inside the SCG require ethanol to react with to produce biodiesel. On the contrary, the highest EL yield was found at higher temperature and higher sulfuric acid volume as the cellulose deterioration is needed to produce EL. The high EL yield was also found at lower ethanol volume, so that the sulfuric acid was not diluted. This result verifies that a high yield of biodiesel and EL from highly wet SCGs can be produced through the ISTE method.

## 5. Temperature-swing Operation of Wet ISTE for Maximizing the Coproduction

The maximum yield of each product was found at different tem-

**Table 4. Yield of biodiesel and EL from temperature-swing operation (with 0.2 ml of sulfuric acid and 2 ml of ethanol)**

| Temperature for the first 1 hour (°C) | Temperature for the second 1 hour (°C) | Biodiesel yield (wt%) | EL yield (wt%) |
|---|---|---|---|
| 140 | 160 | 14.5±0.018 | 1.88±0.016 |
| 160 | 140 | 15.0±0.030 | 2.76±0.15 |
| 140 | 140 | 14.5±0.74 | 1.19±0.12 |
| 160 | 160 | 13.7±0.50 | 3.43±0.16 |
| 140 | - | 13.7±0.018 | 0.468±0.012 |
| 160 | - | 14.1±0.030 | 1.77±0.042 |

peratures: 140 °C and 160 °C for biodiesel and EL. To determine whether high yields of biodiesel and EL can be obtained through single-pot ISTE in a one reaction experiment, temperature-swing operation of wet ISTE was introduced. The two-hour operation was divided into two 1 h reaction operations at each temperature of 140 and 160 °C. To ensure high yield for both products, 0.2 ml of sulfuric acid was used, as this amount led to high biodiesel and EL yields, and 2 ml of ethanol was used to provide enough reactant for the reaction to occur while preventing the dilution of acid. The results with each condition are shown in Table 4.

As explained in section 3.1, to produce a high yield of EL, a high temperature at 160 °C is required to break the SCG cellulosic cell wall, while the biodiesel yield peaked at lower temperature of 140 °C, indicating that the side reaction of unwanted humin formation occurred at the temperature that gives the maximum yield for EL. The higher temperature operation at the first half of the swing operation allows the cell wall to be broken down and release the lipids present inside the SCG matrix for biodiesel production, while the second half with the lower temperature is sufficient to convert the smaller sugar molecules that are deteriorated during the higher temperature step into EL without triggering the side reaction.

However, a lower EL yield is found when the reaction temperature swings in the opposite direction from 140 to 160 °C. Reaction at 140 °C for one hour is not enough to deteriorate the cell wall, and thus effective EL production only occurred in the second half of the operation when the temperature was increased to 160 °C. Also, the biodiesel yield (14.52 wt% in Table 4) slightly becomes lower than that at the temperature swing from 160 to 140 °C (15.02 wt% in Table 4), possibly because the conversion of the lipid that is trapped inside the cell wall can only occur on the second half of the reaction for the temperature swing from 140 to 160 °C. This hypothesis is further confirmed in Table 4 with two single experiments at 140 and 160 °C for 1 hour, where one hour of ISTE at 140 °C shows almost a zero yield of EL and the EL yield with the temperature swing from 140 to 160 °C is almost the same as that in the 160 °C experiment for one hour. The temperature-swing experiment from 160 to 140 °C was also compared with each experiment of 2 h reaction at the respective temperature. The temperature-swing reaction has a higher biodiesel yield than the 2 h reaction at 140 °C because it was operated at higher temperature in the first half. It also shows higher EL yield than the 2 h reaction at 140 °C due to lower temperature in the first half but slightly lower yield than the 2 h reaction at 160 °C. These experiments demonstrate that the destruction of the cellulose wall is the reaction-determining step leading to both higher biodiesel and EL production. Therefore, the temperature-swing operation at higher temperature of 160 °C for cellulosic decomposition and lipid extraction followed by lower temperature of 140 °C for EL and biodiesel formation leads to high yields of both products.

## CONCLUSION

This work demonstrates maximized biodiesel and EL yields by introducing a new temperature-swing method in wet ISTE of SCGs. EL production requires a higher temperature for hydrolyzing cellulose compared to biodiesel production. A large amount of ethanol is preferred for biodiesel production, but can lower the EL yield due to decreased acidity. The biodiesel and EL yields were maximized at different temperatures, and the temperature-swing operation was able to produce a high biodiesel yield of 15.02% and an EL yield of 2.76%.

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## SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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# Supporting Information

# Temperature-swing transesterification for the coproduction of biodiesel and ethyl levulinate from spent coffee grounds

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**Table S1. Box-Behnken design for RSM experiments and the corresponding biodiesel yield results**

| Run | Factor 1 | Factor 2 | Factor 3 | Yield |
|---|---|---|---|---|
| | A: Temperature | B: Sulfuric acid volume | C: Ethanol volume | Biodiesel |
| | °C | mL | mL | % |
| 1 | 120 | 0.15 | 3 | 14.09±0.04 |
| 2 | 120 | 0.15 | 1 | 3.01±0.06 |
| 3 | 150 | 0.20 | 1 | 8.97±0.04 |
| 4 | 180 | 0.15 | 1 | 6.52±0.04 |
| 5 | 180 | 0.15 | 3 | 11.14±0.62 |
| 6 | 150 | 0.10 | 3 | 13.71±0.02 |
| 7 | 150 | 0.15 | 2 | 13.89±0.23 |
| 8 | 150 | 0.20 | 3 | 13.29±0.04 |
| 9 | 180 | 0.20 | 2 | 9.66±0.01 |
| 10 | 150 | 0.10 | 1 | 5.24±0.02 |
| 11 | 150 | 0.15 | 2 | 13.66±0.01 |
| 12 | 120 | 0.10 | 2 | 5.85±0.01 |
| 13 | 120 | 0.20 | 2 | 10.75±0.02 |
| 14 | 180 | 0.10 | 2 | 10.65±0.01 |
| 15 | 150 | 0.15 | 2 | 12.99±0.17 |

**Table S2. Box-Behnken design for RSM experiments and the corresponding EL yield results**

| Run | Factor 1 | Factor 2 | Factor 3 | Yield |
|---|---|---|---|---|
| | A: Temperature | B: Sulfuric acid volume | C: Ethanol volume | EL |
| | °C | mL | mL | % |
| 1 | 160 | 0.20 | 1 | 2.32±0.02 |
| 2 | 160 | 0.15 | 2 | 3.04±0.06 |
| 3 | 140 | 0.15 | 1 | 0.98±0.10 |
| 4 | 180 | 0.15 | 1 | 1.82±0.08 |
| 5 | 160 | 0.15 | 2 | 2.99±0.03 |
| 6 | 140 | 0.20 | 2 | 1.19±0.12 |
| 7 | 140 | 0.10 | 2 | 0.60±0.05 |
| 8 | 180 | 0.10 | 2 | 2.61±0.15 |
| 9 | 160 | 0.10 | 1 | 2.56±0.13 |
| 10 | 180 | 0.20 | 2 | 2.80±0.09 |
| 11 | 160 | 0.15 | 2 | 3.18±0.06 |
| 12 | 140 | 0.15 | 3 | 0.00±0.00 |
| 13 | 160 | 0.20 | 3 | 2.53±0.08 |
| 14 | 180 | 0.15 | 3 | 1.94±0.01 |
| 15 | 160 | 0.10 | 3 | 1.05±0.01 |

**Table S3. Quantification of the selected humin sample by weight**

| No | Temperature (°C) | Biodiesel yield (wt%) | EL yield (wt%) | Total products yield (wt%) | Yield difference (%) |
|---|---|---|---|---|---|
| 1 | 140 | 14.56 | 1.19 | 15.75 | - |
| 2 | 160 | 9.25 | 3.70 | 12.95 | 2.8 |
| 3 | 180 | 9.08 | 2.30 | 11.38 | 1.57 |

*All experiments are under 80% moisture content, 0.2 ml of sulfuric acid and 2 ml of ethanol.

**Fig. S1. Solid humins collected from the bottom of the reactor after 2 hours of reaction obtained under condition of 180 °C, 0.15 ml sulfuric acid, 2 ml of ethanol, 80% moisture content.**