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Research Article

Biodiesel Production through Electrolysis Using an Ionic Liquid, 1-Ethyl-3-Methylimidazolium Chloride as a Supporting Electrolyte

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Electrolysis is a promising approach for biodiesel production. However, low electrical conductivity of a reaction mixture results in a low reaction rate. Thus, this study developed a novel catalyst-free electrolysis process using an ionic liquid as a supporting electrolyte for biodiesel production. Various ionic liquids were assessed, and 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) exhibited the highest electrical conductivity (4.59 mS/cm) and the best electrolytic performance for transesterification. Electrolysis in the presence of [Emim]Cl was subsequently optimized using response surface methodology to maximize biodiesel yield. A maximum biodiesel yield of 97.76% was obtained under the following optimal reaction conditions: electrolysis voltage, 19.42 V; [Emim]Cl amount, 4.43% (*w*/*w*); water content, 1.62% (*w*/*w*); methanol to oil molar ratio, 26.38 : 1; and reaction time, 1 h. Notably, [Emim]Cl could be efficiently reused for at least three cycles with a corresponding biodiesel yield of 94.81%. Moreover, the properties of the synthesized biodiesel complied with EN and ASTM standards. The findings of this study indicate that catalyst-free electrolysis using [Emim]Cl as a supporting electrolyte is an eco-friendly and efficient method for biodiesel production.

1. Introduction

The extensive use of fossil energy sources has caused a rapid depletion in their limited supplies and raised environmental concerns, such as global warming and the emission of carbon monoxide, particulate matters, and hydrocarbons. Hence, eco-friendly and renewable energy sources are urgently needed. Biodiesel, a biomass-originated fuel, is produced globally as an alternative to petroleum diesel [1, 2]. Compared with the use of fossil fuels, biodiesel substantially reduces greenhouse gas emissions [3, 4]. Therefore, studies have focused on the development of efficient and green methods for biodiesel production [5, 6].

Several methods have been explored for biodiesel production. A commonly used method is homogenous alkali-catalyzed transesterification [7]. For waste/nonedible oils containing high amounts of free fatty acids (FFA), homogenous acid-catalyzed esterification is usually performed to reduce FFA amounts before transesterifying the oils into biodiesel [8]. Although these methods are efficient for biodiesel production, the use of homogenous chemical catalysts (e.g., NaOH, KOH, and H_2SO_4) complicates

product purification and wastewater treatment [9]. Hence, various solid acid and alkali catalysts have been proposed to simplify biodiesel production because these solid catalysts can be easily recovered and reused [10–12]. However, heterogeneous catalytic reactions have a relatively low reaction rate because of mass transfer limitations [10]. Lipase-catalyzed transesterification is a green method used for biodiesel production [13]. This method is effective for the simultaneous conversion of FFA and oil (triglyceride) into biodiesel; however, its industrial application is limited because of the high cost of enzymes required in this process [14]. Transesterification using supercritical fluids [15], microwave-assisted techniques [16], and ultrasound-assisted techniques [17] have also been developed for biodiesel production. Although these methods help ensure a high biodiesel yield at a short reaction time, they retain several problems such as extremely high pressure (>20 MPa) and temperature (>300°C) of supercritical fluids, difficulty to scale up of microwave and ultrasound techniques, thus limiting their industrial applications [18, 19]. Therefore, new efficient and eco-friendly techniques are urgently needed for biodiesel production.

Recently, electrolysis has attracted considerable attention as a promising approach for biodiesel production because of its eco-friendly nature and insensitivity to FFA and water contents in oils [20–22]. In electrolysis, electrochemical reactions lead to the formation of OH^- ions on cathode, thus facilitating the transesterification of oil into biodiesel (Figure 1) [23]. To enhance reaction efficiency, various strategies have been devised for electrolysis, including the addition of a catalyst (e.g., H_2SO_4 [20], KOH [23], and NaOH [24]) into the reaction mixture or the use of different electrode materials [24, 25]. Another promising strategy for enhancing reaction efficiency is the use of additional electrolytes to increase the electrical conductivity of the reaction mixture [26–28]. NaCl has been commonly used as a supporting electrolyte, and its use increases the reaction rate [23, 27]. Although the use of supporting electrolytes is a promising approach for enhancing reaction rate in electrolysis, relevant studies are limited. Therefore, new supporting electrolytes must be developed for electrolysis.

Recently, ionic liquids (ILs) have garnered substantial attention owing to their unique physical and chemical characteristics, such as nonvolatility, eco-friendly nature, low vapor pressure, nonexplosive nature, recyclability, and excellent thermal and chemical stabilities [29–31]. ILs are liquid organic salts that comprise organic/inorganic anions and organic cations [32]. They have recently been used as a green substitute for traditional organic solvents in various fields, such as material sciences, biological sciences, environmental sciences, and medicine [32]. Notably, ILs exhibit high electrical conductivity and electrochemical stability, which makes them a promising medium/electrolyte for various applications, such as the electrochemical reduction of CO_2 [32, 33]. In particular, the use of ILs as electrolytes in water electrolysis has been demonstrated to promote hydrogen production successfully [34, 35]. This is because they can enhance electron transfers and intermolecular interactions and also change surface accessibility and local concentration of reactants on electrode surface [33, 34, 36]. Considering these benefits of ILs, this study proposes a novel electrolysis process for biodiesel production that utilizes ILs as supporting electrolytes without any additional catalyst. ILs offer several benefits such as enhancing reaction rates, shortening reaction times, and minimizing the use of harmful chemicals, resulting in a green and efficient process for biodiesel production. Although several electrolytes have been used in electrolysis, this study is the first to report the use of ILs as a green supporting electrolyte for biodiesel synthesis.

This study is aimed at producing biodiesel through electrolysis using ILs as supporting electrolytes. Various ILs, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-ethyl-3-methylimidazolium hydroxide ([Emim]OH), 1-ethyl-3-methylimidazolium chloride ([Emim]Cl), and 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH), were assessed for the reaction because they possess high electrical conductivity and are relatively low cost [32]. Response surface methodology (RSM) is a statistical and mathematical technique that has been proven to be highly effective in optimizing the conditions for biodiesel synthesis [37–39]. Therefore, it was used to optimize reaction conditions (electrolysis voltage, IL amount, water content, and methanol to oil molar ratio) to maximize biodiesel yield. The reusability of [Emim]Cl was subsequently evaluated. Finally, the fuel properties of the produced biodiesel were characterized using BiodieselAnalyzer software.

2. Materials and Methods

2.1. Materials. Soybean oil was provided by TTET Union Corporation (Tainan, Taiwan). Supelco 37 Component Fatty Acid Methyl Ester (FAME) Mix standard was obtained from Sigma-Aldrich Chemie (Taufkirchen, Germany). [Emim]Cl (≥97%) and [Bmim]Cl (≥98%) were purchased from Acros Organics, Geel, Belgium. [Emim]OH (>95%) and [Bmim]OH (>90%) were obtained from Combi-Blocks, San Diego, CA, USA. Methanol (99.5%), n-heptane (high-performance liquid chromatography grade), and tetrahydrofuran (THF; 99.9%) were purchased from ECHO Chemical (Taipei, Taiwan).

2.2. Biodiesel Production through Electrolysis. Biodiesel was produced in a closed electrolysis cell (a 100 mL glass reactor; Figure 1). The electrolysis cell contained two platinum-coated titanium plate electrodes (6 cm × 3 cm) at spaced 1 cm apart. The reactor contained 60 mL of a reaction mixture comprising water, THF, oil, methanol, and various ILs ([Bmim]Cl, [Bmim]OH, [Emim]Cl, and [Emim]OH) as supporting electrolytes. The electrical conductivity of the reaction mixture was measured using a pH/ISE–EC meter (Hanna Instruments, Woonsocket, RI, USA). The reaction conditions were as follows: electrolysis voltage, 18 V; supporting electrolyte amount, 4% (*w*/*w*; based on oil weight); water content, 1.5% (*w*/*w*; based on entire reaction mixture weight); methanol to oil molar ratio, 24 : 1; cosolvent THF to methanol molar ratio, 1 : 4; reaction time, 60 min; room temperature; and stirring. Comparative analyses where NaCl was used as a supporting electrolyte and without using any additional electrolytes were also performed under the similar reaction conditions to evaluate the effects of ILs on the

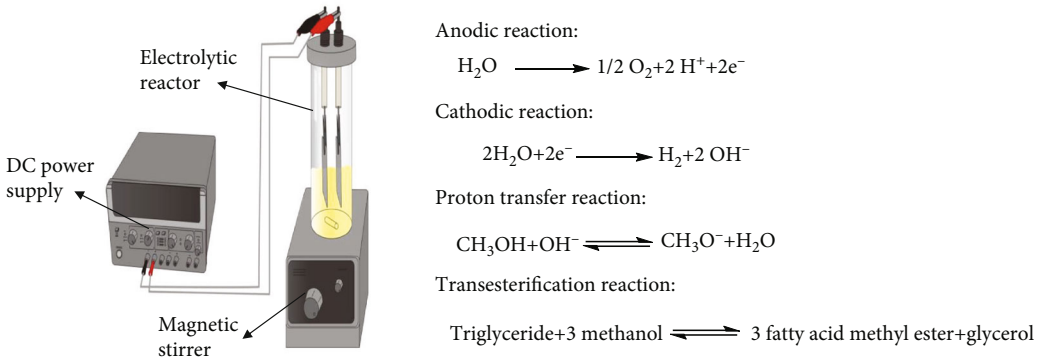

Figure 1: Schematic of the experimental setup and mechanism of biodiesel production through electrolysis.

reaction. The produced biodiesel sample was obtained using centrifugation after reaction completion and was assessed to determine biodiesel yield.

2.3. Reaction Optimization Using RSM. A Box–Behnken design (BBD) with three levels and four factors (input variables) was used to optimize the reaction conditions for maximizing biodiesel yield. As presented in Table 1, the four input variables were electrolysis voltage (X_1), IL amount (X_2), water content (X_3), and methanol to oil molar ratio (X_4). Table 2 details the experimental design matrix for the optimization. Electrolysis was performed in a glass reactor (Figure 1) containing 60 mL of reaction mixture, and different electrolysis voltages (15–21 V), IL amounts (3%–5% (w/w)), water contents (1%–2% (w/w) based on entire reaction mixture weight), and methanol to oil molar ratios (20 : 1–28 : 1) were adopted with other factors maintained at constant values (cosolvent THF to methanol molar ratio, 1 : 4; room temperature; and reaction time, 1 h) to investigate the effects of these factors on biodiesel production. The correlation between biodiesel yield (measured response, Y) and the reaction factors was then analyzed using a second quadratic model, written as follows:

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=2}^{4} \beta_{ij} X_i X_j, \quad (1)$$

where β_0, β_i, β_{ii}, and β_{ij} are the model parameters. These parameters were evaluated using analysis of variance (ANOVA) and regression analysis in Minitab 16. Finally, the optimal reaction conditions were determined using data from the model developed in this study.

2.4. IL Reusability. Biodiesel was produced through electrolysis under optimal conditions to assess the reusability of the best-performing IL. After reaction completion, the reaction mixture was collected and centrifuged to ensure phase separation. The biodiesel-containing upper phase was collected, and the remaining solution containing the IL was subjected to a rotary evaporator to recover IL. The recovered IL was subsequently mixed with fresh reactants for a new reaction. After the completion of each reaction cycle, biodiesel was collected to determine the yield.

Table 1: Effects of various supporting electrolytes on biodiesel production through electrolysis.

Supporting electrolyte	Biodiesel yield (%)	Electrical conductivity (mS/cm)
[Emim]Cl	97.67 ± 1.04	4.59 ± 0.79
[Bmim]Cl	96.76 ± 1.24	3.50 ± 1.08
[Emim]OH	91.92 ± 1.34	0.99 ± 0.56
[Bmim]OH	88.12 ± 0.90	0.73 ± 0.32
Control (NaCl)	93.40 ± 0.88	2.15 ± 0.93
Control (no supporting electrolyte)	1.49 ± 1.13	0.0023 ± 0.0014

Table 2: Predicted and experimental values of input variables for the Box–Behnken design matrix.

Variables	Symbols	Variable levels		
		-1	0	1
Electrolysis voltage (V)	X_1	15	18	21
[Emim]Cl amount (%)	X_2	3	4	5
Water amount (%)	X_3	1	1.5	2
Methanol to oil molar ratio	X_4	20	24	28

2.5. Determination of Biodiesel Yield, Fatty Acid Compositions, and Fuel Properties. The yield and composition of biodiesel were determined using a gas chromatograph system (Shimadzu, Kyoto, Japan) fitted with a flame ionization detector and a Stabilwax capillary column (Restek, USA), per a previously described method [40]. Supelco 37 Component FAME Mix was used to determine fatty acid compositions and establish a standard curve ($y = 159490x - 15678$; $R^2 = 0.9998$) for calculating the amount of biodiesel produced. Biodiesel yield was then calculated using the following equation [6, 24]:

$$\text{Biodiesel yield}\,(\%) = \frac{\text{Weight of biodiesel produced}}{\text{Weight of oil used}} \times 100. \quad (2)$$

Fuel properties of the produced biodiesel, such as cloud point, oxidation stability, viscosity, density, cold filter plugging point, pour point, and cetane number, were estimated on the basis of its fatty acid composition using BiodieselAnalyzer software (online version: http://www.brteam.ir/analysis/).

3. Results and Discussion

3.1. Supporting Electrolyte Screening. ILs exhibit high electrical conductivity, which makes them a promising electrolyte for electrolysis. To evaluate the effects of supporting electrolytes on biodiesel production, electrolysis was performed using different ILs and compared with electrolysis performed without using any additional electrolytes. As shown in Table 1, electrolyte-free electrolysis resulted in a considerably low biodiesel yield (1.49%). This might have resulted from the low electrical conductivity of the reaction mixture (the lowest electrical conductivity was 0.0023 mS/cm for the reaction mixture without any supporting electrolytes), which limited electron transfer in the reaction mixture, thus reducing biodiesel yield. To increase the rate of reaction, NaCl and different ILs were used as supporting electrolytes reaching a yield >88% (Table 1). As can be seen from Figure 1, when applying a voltage into an electrolysis cell containing NaCl (or ILs) and H_2O, the water electrolysis reaction occurred at anode to produce oxygen and electron. The presence of NaCl or ILs enhanced the electron transfer in the reaction mixture, which promoted the formation of hydrogen and hydroxyl ions (OH^-) at cathode. The OH^- produced at cathode then reacted with the methanol to form methoxide ion (CH_3O^-), which is an active species required for the transesterification of oil (triglyceride) and methanol. Subsequently, the produced nucleophilic methoxide ion attacked the carbonyl moiety in triglyceride molecules to produce methyl esters [25].

Data are shown as mean ± standard deviation ($n = 3$). The electrolysis reactions were conducted at an electrolysis voltage of 18 V, supporting electrolyte amount of 4% (w/w; based on oil weight), water content of 1.5% (w/w; based on entire reaction mixture weight), methanol to oil molar ratio of 24 : 1, cosolvent THF to methanol molar ratio of 1 : 4, reaction time of 60 min, and room temperature.

In addition, electrical conductivities of reaction mixtures containing supporting electrolytes were considerably higher than that of an electrolyte-free reaction mixture. Notably, biodiesel yield varied with electrical conductivity: a higher electrical conductivity of the reaction mixture was associated with a higher yield (Table 1). This finding is consistent with that of Guan and Kusakabe [25] who used NaCl as a supporting electrolyte. The use of supporting electrolytes increased the electrical conductivity of the reaction mixture, which increased electron transfer and intermolecular interaction, thus enhancing reaction efficiency. [Emim]-based ILs exhibited higher electrical conductivity values than [Bmim]-based ILs; this was probably because [Emim]-based ILs are less viscous. The finding is consistent with a study conducted by Yuan et al. [41] who reported that lower viscosity implies higher electrical conductivity and efficiency in mass transfer during electrolysis. Among the supporting electrolytes assessed in the present study (including NaCl), [Emim]Cl exhibited the highest activity and electrical conductivity. Therefore, it was selected for further experiments.

3.2. RSM Model. In the present study, a BBD-RSM model with four factors, namely, electrolysis voltage, [Emim]Cl amount, water content, and methanol to oil molar ratio, at three levels normalized from −1 to 1 (Table 2) was used to identify the correlation between these reaction factors and biodiesel yield. Biodiesel was produced under different reaction conditions (Table 3). The central runs (experiments 25–27) exhibited a low value of the coefficient of variance (CV = 0.15%), suggesting reproducibility and good precision of these experiments. Therefore, a model (quadratic polynomial equation) was developed to express the correlation between biodiesel yield and the reaction factors, which was as follows:

$$\begin{aligned} Y = {} & 98.20 + 0.59X_1 + 1.09X_2 + 1.89X_3 + 1.17X_4 - 1.31X_1^2 \\ & - 1.74X_2^2 - 3.65X_3^2 - 1.18X_4^2 + 0.91X_1X_2 - 0.22X_1X_3 \\ & + 0.49X_1X_4 - 0.13X_2X_3 + 0.05X_2X_4 - 0.04X_3X_4, \end{aligned} \tag{3}$$

where X_1, X_2, X_3, X_4, X_1X_2, X_1X_4, and X_2X_4 were positively related to the measured response, whereas the other parameters were negatively related.

Table 4 summarizes the ANOVA results obtained using the aforementioned model (equation (3)). A higher F value and a smaller p value show a significant impact of those parameters and a good representation of the actual results [42]. The model exhibited a low p value ($p < 0.0001$), indicating that it was statistically significant at a confidence level of 95%. In addition, the model exhibited a high value of the coefficient of determination ($R^2 = 0.97$ and adjusted $R^2 = 0.95$), demonstrating greater than 95% of the variations in the biodiesel yield occurred owing to the impact of four factors (electrolysis voltage, [Emim]Cl amount, water amount, and methanol to oil molar ratio). A well-fitted model was also validated by the linear correlation between actual and predicted values (Figure 2). Consequently, the model precisely predicted biodiesel yield. Moreover, the significance of each model parameter was examined using a t test; the results are summarized in Table 5. Significance ($p < 0.05$) was noted for the intercept, all linear coefficients, one interaction coefficient (X_1X_2), and all quadratic coefficients. Therefore, the model developed in this study yielded accurate predictions of the optimal conditions for maximizing biodiesel production.

3.3. Mutual Effects of the Reaction Factors. Figure 3 shows the mutual effects of electrolysis voltage and [Emim]Cl amount on biodiesel yield when other factors were constant. Correlations were noted between electrolysis voltage and [Emim]Cl amount. Although electrolysis voltage exerted no prominent effects on biodiesel production at a low [Emim]Cl amount, the yield increased considerably with increasing electrolysis voltage at a high amount of

Table 3: BBD matrix for electrolysis.

Run	Variable				Response (Y, %)
	X_1	X_2	X_3	X_4	
1	-1	0	0	-1	94.58
2	0	0	1	-1	93.54
3	1	1	0	0	97.41
4	-1	1	0	0	95.28
5	0	0	-1	-1	90.42
6	1	0	1	0	95.58
7	0	1	-1	0	91.56
8	0	0	1	1	95.99
9	0	-1	0	1	95.63
10	1	0	0	-1	95.17
11	0	0	-1	1	93.02
12	-1	-1	0	0	94.48
13	0	1	1	0	96.20
14	0	-1	1	0	94.49
15	-1	0	-1	0	90.57
16	1	0	0	1	97.97
17	1	0	-1	0	92.65
18	0	1	0	1	97.69
19	-1	0	0	1	95.44
20	1	-1	0	0	92.98
21	0	-1	-1	0	89.32
22	-1	0	1	0	94.37
23	0	-1	0	-1	93.07
24	0	1	0	-1	94.93
25	0	0	0	0	98.22
26	0	0	0	0	98.05
27	0	0	0	0	98.34

Table 4: Results for analysis of variance with the response surface methodology model.

Source	DF[b]	SS[b]	MS[b]	F value	Probability $(p) > F$
Model[a]	14	154.94	11.07	33.25	<0.0001
Residual (error)	12	3.99	0.33		
Total	26	158.93			

[a]$R^2 = 0.97$; adjusted $R^2 = 0.95$. [b]SS: sum of squares; DF: degree of freedom; MS: mean square.

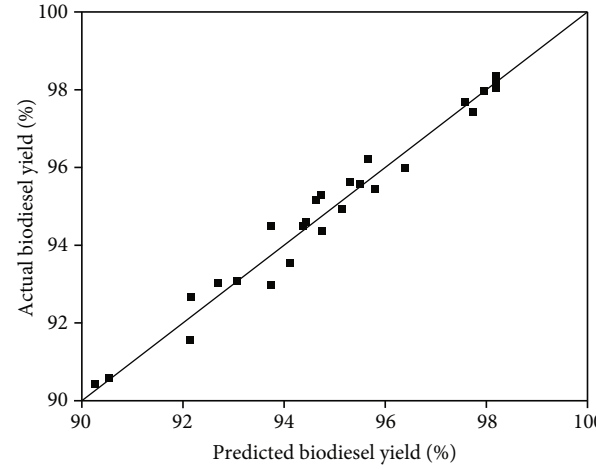

Figure 2: Correlation between the experimental and predicted biodiesel yields.

Table 5: Significance of the coefficients used in the response surface methodology model.

Model term	Parameter estimate	Standard error	t value[a]	p value
β_0	98.20	0.33	294.83	0.001[b]
β_1	0.59	0.17	3.52	0.004[b]
β_2	1.09	0.17	6.56	0.001[b]
β_3	1.89	0.17	11.32	0.001[b]
β_4	1.17	0.17	7.02	0.001[b]
β_{11}	-1.31	0.25	-5.23	0.001[b]
β_{22}	-1.74	0.25	-6.95	0.001[b]
β_{33}	-3.65	0.25	-14.62	0.001[b]
β_{44}	-1.18	0.25	-4.74	0.001[b]
β_{12}	0.91	0.29	3.15	0.008[b]
β_{13}	-0.22	0.29	-0.75	0.465
β_{14}	0.49	0.29	1.68	0.119
β_{23}	-0.13	0.29	-0.46	0.654
β_{24}	0.05	0.29	0.17	0.865
β_{34}	-0.04	0.29	-0.13	0.899

[a]$t_{\alpha/2,n-p} = t_{0.025,12} = 2.18$. [b]$p < 0.05$ indicates that the model terms are significant.

[Emim]Cl. Similarly, at a low electrolysis voltage, the effects of [Emim]Cl amount on biodiesel yield were nonsignificant. However, at a high electrolysis voltage, biodiesel yield was substantially better at higher [Emim]Cl amounts. These findings indicated the positive effects of both electrolysis voltage and [Emim]Cl on electrolysis. The conductivity and electric current of a reaction mixture are proportional to the electrolysis voltage and [Emim]Cl amount used in the reaction [23, 25]. Increasing the electrolysis voltage and [Emim]Cl amount results in increased electric current and electrical conductivity, respectively, which enhances the formation of H^+ and OH^- ions; it also increases electric charge transfer in the reaction mixture, thus enhancing the reaction rate [23, 25, 43]. Consequently, the combination of electrolysis voltage and [Emim]Cl amount (at a high level) resulted in the highest biodiesel yield in the present study (Figure 3). The finding is similar to those of Guan and Kusakabe [25] and Moradi et al. [23] who reported that biodiesel yield was the highest at high electrolysis voltages and NaCl (supporting electrolyte) amounts.

Figure 4 presents the mutual effects of [Emim]Cl amount and water content on biodiesel yield when the remaining factors were constant. At a given [Emim]Cl

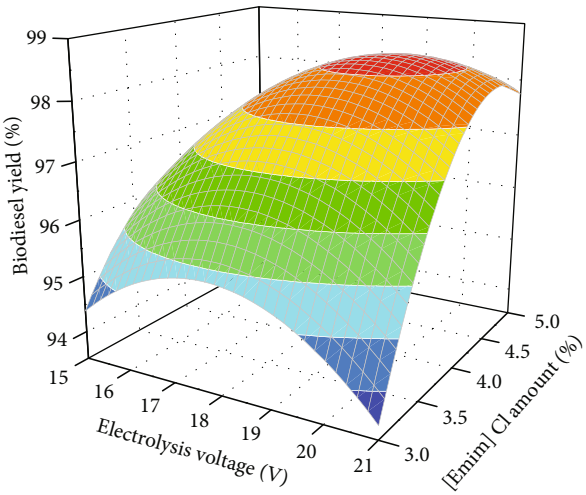

Figure 3: Mutual effects of electrolysis voltage and [Emim]Cl amount on biodiesel yield at constant water content (1.5%) and methanol to oil molar ratio (24 : 1).

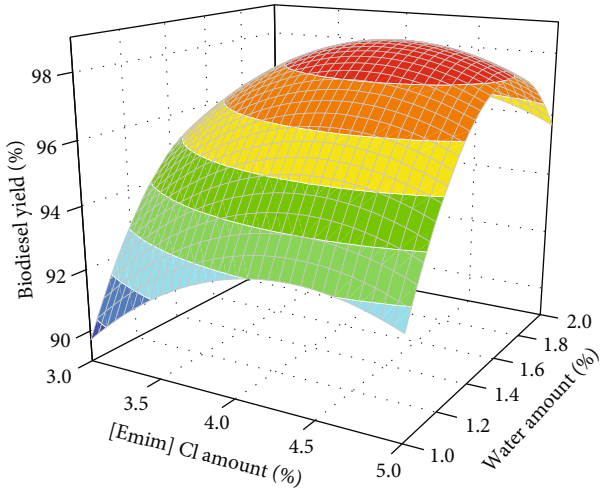

Figure 4: Mutual effects of [Emim]Cl amount and water content on biodiesel yield at constant electrolysis voltage (18 V) and methanol to oil molar ratio (24 : 1).

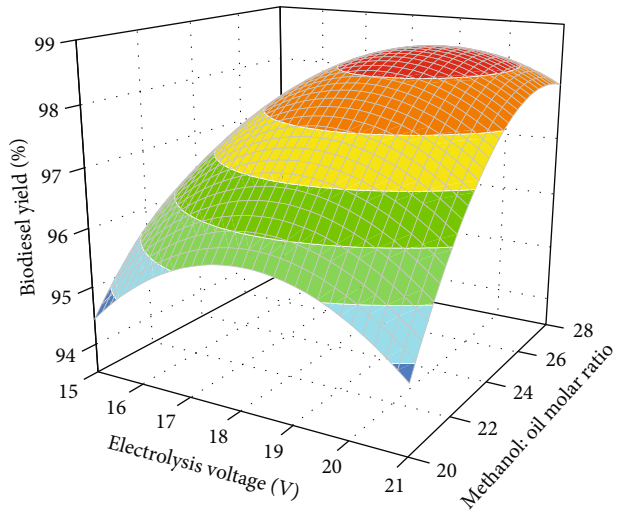

Figure 5: Mutual effects of methanol to oil molar ratio and electrolysis voltage on biodiesel yield at constant [Emim]Cl amount (4%) and water content (1.5%).

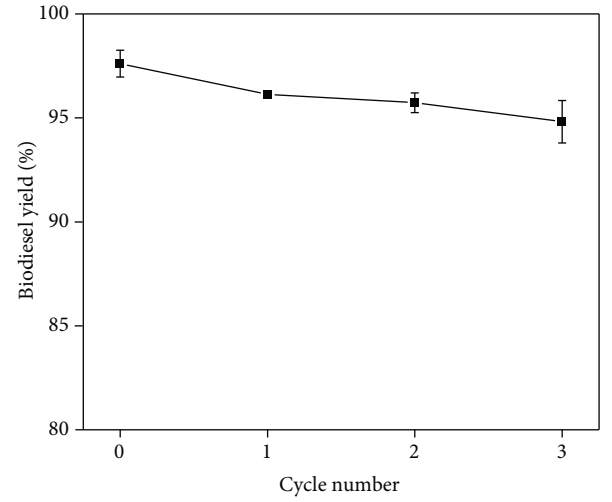

Figure 6: Reusability of [Emim]Cl in electrolysis for biodiesel production.

amount, biodiesel yield increased with increasing water content. This is because water is required for reactions on anode and cathode [24]. In electrolysis, water molecules are continuously electrolyzed to produce OH^- ions, which subsequently react with methanol to produce an active species (CH_3O^-) that facilitates the transesterification reaction for biodiesel production (Figure 1) [24, 25]. However, a further increase in water content resulted in a decrease in biodiesel yield in agreement with that of a previous study [25]. Adequate water was gradually applied during the reaction, whereas excess water negatively affected the transesterification reaction, thus reducing reaction efficiency [24, 25].

Figure 5 presents the combined effects of electrolysis voltage and methanol to oil molar ratio on biodiesel yield when other reaction factors were constant. At any electrolysis voltage, biodiesel yield increased to a peak before remaining constant with respect to the methanol to oil molar ratio. This might be because transesterification is an equilibrium reaction; thus, a high level of methanol is necessary to drive the reaction toward biodiesel production [43]. This finding is consistent with those of previous studies [25, 43],

Table 6: Fatty ester compositions of the biodiesel produced in the present study.

Fatty ester	Content (%)
Palmitic (C16:0)	10.62
Stearic (C18:0)	4.20
Oleic (C18:1)	23.02
Linoleic (C18:2)	55.24
Linolenic (C18:3)	6.92

Table 7: Comparison of the fuel properties of the biodiesel produced in the present study with those of the international standards.

Properties	ASTM D6751	EN14214	This study
Oxidation stability (h)	>3	>6	4.49
Viscosity (mm^2/s)	1.9-6.0	3.5-5.0	3.57
Density (kg/m^3)	na[a]	860-900	882
Cloud point (°C)	3-15	-4	0.59
Cold filter plugging point (°C)	Summer max 0, winter max <-15	na[a]	-6.54
Pour point (°C)	-15-10	na[a]	-6.18
Cetane number	>47	>51	41.98

[a]na: none reported.

indicating that methanol to oil molar ratio is a crucial factor in electrolysis for biodiesel production.

3.4. Optimal Conditions. The RSM model (equation (3)) was solved using the canonical method to predict the optimal conditions for biodiesel production. The optimal conditions were as follows: electrolysis voltage, 19.42 V; [Emim]Cl amount, 4.43% (*w*/*w*); water content, 1.62% (*w*/*w*); and methanol to oil molar ratio, 26.38 : 1; the corresponding biodiesel yield was 99.15%. Subsequent experiments were performed under the same conditions to validate biodiesel prediction. The experimental yield was 97.76% ± 1.16%, which was consistent with the predicted biodiesel yield, suggesting that the model developed in this study was satisfactory and feasible. Moreover, the CV value was 1.4%, indicating that the model was highly reproducible [44]. Thus, the model adequately expressed the correlation between the measured response and input variables in biodiesel production through electrolysis.

3.5. Reusability of [Emim]Cl. To enhance the commercial feasibility of the process, the reusability of [Emim]Cl in biodiesel production was assessed. Electrolysis was performed under the optimal conditions to investigate [Emim]Cl reusability. Biodiesel yield slightly reduced from 97.61% to 94.81% after three reuses (Figure 6), which indicated that [Emim]Cl can be efficiently reused in electrolysis for biodiesel production. The slight reduction in biodiesel yield could be due to the loss of [Emim]Cl during the recovery process. To retain the reaction efficiency, after several reuses, additional [Emim]Cl can be supplemented to the reaction mixture to compensate for the loss of [Emim]Cl. In addition, [Emim]Cl could be easily recovered from the reaction mixture. This finding suggests that [Emim]Cl is a promising supporting electrolyte, and its use increases the efficiency and economic feasibility of electrolysis for biodiesel production.

3.6. Compositions and Properties of Biodiesel. Table 6 summarizes the fatty ester compositions of the biodiesel produced in this study. The biodiesel samples mainly comprised methyl ester of linoleic (55.24%), oleic (23.02%), palmitic (10.62%), linolenic (6.92%), and stearic (4.2%) acids. Fatty ester profile was similar to those reported in previous studies [45, 46], indicating that the developed electrolysis method did not affect the fatty ester compositions and properties of the synthesized biodiesel. High levels (85.18%) of unsaturated fatty acids were noted, which might have reduced the melting point of biodiesel [47, 48]. Table 7 compares the fuel properties of the biodiesel produced in this study and those of the European standard EN 14214 and US standard ASTM D6751. Most fuel properties, such as oxidation stability (4.49 h), viscosity (3.57 mm^2/s), density (882 kg/m^3), cold filter plugging point (−6.54°C), and pour point (−6.18°C), were similar to those in the standards, indicating that the biodiesel produced in the present study is a promising alternative to petrodiesel.

3.7. Comparison of the Present and Other Electrolysis Methods for Biodiesel Production. Electrolysis methods have recently been developed as a substitute for other methods of biodiesel production. The major limitation of this method is its low reaction rate. Therefore, several studies have attempted to enhance the reaction efficiency of this method. Table 8 presents a comparison of various electrolysis methods developed for biodiesel production. It was first demonstrated by Guan and Kusakabe [25], where biodiesel was produced through a catalyst-free electrolysis method using NaCl as a supporting electrolyte. Although the use of NaCl enhanced reaction efficiency, the rate of reaction remained relatively low. In another study, additional catalysts were used to improve the efficiency of electrolysis. Consequently, electrolysis methods using various catalysts, such as NaOH [24], zeolite/chitosan/KOH [49], MgO-NaOH [50], KF/KOH-Fe_3O_4 [51], and phosphomolybdic acid/graphene oxide [43], have been developed for biodiesel production. Recently, electrolysis methods using the combination of an additional catalyst and NaCl (as a supporting electrolyte) have also been described for biodiesel production [23, 27]. These methods were effective in producing biodiesel, and the use of additional catalysts in electrolysis substantially increased biodiesel yield compared with the results of electrolyte-free electrolysis [22]. However, the use of these chemical catalysts requires an additional step involving catalyst removal and may negatively affect the environment. To overcome the aforementioned problems, catalyst-free electrolysis was performed in the present study with [Emim]Cl used as a supporting electrolyte for biodiesel production. The results suggested that the aforementioned method effectively produced biodiesel with a high yield (97.76%) within a shorter reaction time (1 h) compared with the previous electrolysis methods (Table 8), thus reducing time and energy

Table 8: Comparison of various electrolysis methods used for biodiesel production.

Supporting electrolyte	Catalyst	Electrodes	Cosolvent	Electrolysis voltage (V)	Reaction time (h)	Feedstock	Biodiesel yield (%)	Ref.
NaCl	—	Platinum	THF	18.6	2	Corn oil	97.9	[25]
—	NaOH	Graphite	THF	40	2	Waste cooking oil	98	[24]
—	Zeolite/chitosan/KOH	Graphite	Acetone	40	3	Waste cooking oil	93	[49]
—	MgO-NaOH	Graphite	THF	50	6	Waste cooking oil	98	[50]
—	KF/KOH-Fe_3O_4	Graphite	THF	54	2	Microalgae oil	96.8	[51]
—	Phosphomolybdic acid/graphene oxide	Graphite	THF	60	15	Waste cooking oil	90.39	[43]
NaCl	—	Graphite	Acetone	20	2	Oleic acid	42	[23]
NaCl	KOH	Graphite	Acetone	20	2	Oleic acid	52	[23]
NaCl	H_2SO_4	Graphite	Acetone	20	2	Oleic acid	95	[23]
NaCl	KF/KOH-Fe_3O_4	Platinum	THF	60	2	Microalgae oil	98.1	[27]
[Emim]Cl	—	Platinum-coated titanium	THF	19.42	1	Soybean oil	97.76	This study

consumption. Notably, [Emim]Cl could be effectively reused at least thrice without any prominent reduction in biodiesel yield. Therefore, the method described in the present study constitutes a green, efficient, and cost-effective approach to biodiesel production.

4. Conclusions

This study developed an eco-friendly and efficient electrolysis method using ionic liquids (ILs) as supporting electrolytes for biodiesel production. Electrolysis with a supporting electrolyte was found to be superior to that without any supporting electrolyte. Among the ILs tested, [Emim]Cl demonstrated the highest efficiency in enhancing the electrical conductivity of the reaction solution and the yield of biodiesel. Furthermore, RSM was utilized to investigate the combined impact of the reaction factors and establish a model to describe the relationship between the biodiesel yield and the reaction conditions. The reaction conditions were optimized using RSM, resulting in a maximum biodiesel yield of 97.76% under the optimal conditions. Moreover, [Emim]Cl was efficiently reusable in the electrolysis process for biodiesel production. These findings suggest that [Emim]Cl-assisted electrolysis is an economically viable, eco-friendly, and efficient approach to biodiesel production. However, further studies are necessary to evaluate the economic feasibility of this developed process for industrial-scale applications.

Data Availability

The data used to support the findings of this study are available from the corresponding authors upon request.

Conflicts of Interest

The authors have no conflict of interest regarding the publication of this paper.

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