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# Synthesis of biodiesel fuel using an electrolysis method

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ABSTRACT

The paper details the first use of a simple electrolysis method to produce biodiesel fuel (BDF) from corn oil and waste cooking oil at room temperature. This novel process exhibited a high fatty acid methyl ester (FAME) yield (>97%) even in the presence of a relatively high water content (as high as 2 wt.% of the total reaction mixture) when using a low concentration of sodium chloride (<1.2 wt.% based on oil weight). FAME yield was influenced by methanol/oil molar ratio, the amount of cosolvent addition, water content, NaCl concentration and electrolysis voltage. With the proceeding of electrolysis, the pH value of the electrolyte rapidly increased from 7 to 12, but the conductivity of the reaction mixture decreased. When the electrolysis was stopped on the way, the transesterification reaction was still continued, but the reaction rate became lower than that when continuing the electrolysis in the case of high water content. During the electrolysis process, no chlorine molecule in the evolved gas was detected (<0.5 ppm).

## 1. Introduction

BDF is a renewable energy source that can be made from vegetable oils, animal fats and waste cooking oils, and therefore is nontoxic, biodegradable and essentially free of sulfur and other harmful emissions [1–3]. Various production methods of BDF have been developed. Conventional transesterification methods require a homogeneous base or acid catalysts. An alkali metal hydroxide, such as potassium or sodium hydroxide is considered to be the most effective catalyst in promoting the transesterification of oil [4–8]. Transesterification of oil with methanol is a two-phase reaction system and the reaction occurs in the methanol phase. In order to improve the mass transfer between two phases, THF was added as a cosolvent in the reaction mixtures, which made the system homogeneous [4]. For low-quality waste oils containing a high proportion of free fatty acids (FFAs) and water, acid catalysts are sometimes selected in order to avoid the undesirable side reactions, such as saponification, which could lead to serious problem of product separation and low FAME yield [9–12]. Various heterogeneous base and acid catalysts have also been developed to simplify the BDF production process by reuse of the catalysts after filtration. However, transesterification rates for heterogeneous catalysts are relatively low. The active components in many solid catalysts, such as CaO, alkaline or alkaline-earth metal loaded $Al_2O_3$, $SO_4^{2-}/ZrO_2$, can be partly dissolved into the reaction mixtures so that an additional washing process would be required during the purification of the produced BDF [8,13]. The use of lipase as a catalyst for BDF production has shown promising results in recent years, but the research on this topic is still in progress due to the high cost of lipase and relatively low yield [14]. Transesterification of oil in supercritical methanol is a non-catalytic process that requires high temperatures (350 °C), pressures (20–40 MPa), and methanol/oil molar ratio (usually installation at 42–52:1) [15–18]. Therefore, the costs of energy consumption, equipment instillation and methanol separation must be reduced for practical use.

Many low-cost feedstocks contained large amount of water, and a pretreatment process to reduce the water content to less than 0.1 wt.% was necessary. In this study, an electrolysis method for the production of BDF from corn oil and waste cooking oil containing high water content at room temperature in the presence of NaCl is introduced. The effects of electrolysis voltage, methanol/oil molar ratios, addition of cosolvents, water content and NaCl concentration on the FAME yield were investigated.

## 2. Experimental

### 2.1. Chemicals

Corn oil with reagent-grade, dehydrated methanol, dehydrated tetrahydrofuran (THF) and sodium chloride were obtained from Wako Pure Chemistry Industry, Japan. Waste cooking oil was provided from a biodiesel production factory. The acid and saponification values of the oil were determined using standard titration methods [19]. The molecular weight of the oil was determined from the saponification and acid values. Water content in the oil was determined with Karl-Fisher automatic titrator (MKC-610, Kyoto Electronic Manufacturing Co. Ltd.). The physical properties of the oils were shown in Table 1.

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**Table 1**
Physical properties of used oils.

| Oil | Water content (wt.%) | Acid value (mg KOH $g^{-1}$) | Saponification value (mg KOH $g^{-1}$) | Molecular weight (g $mol^{-1}$) |
|---|---|---|---|---|
| Corn oil | <0.05 | 0.45 | 194.3 | 869.5 |
| Waste cooking oil | 0.65 | 7.7 | 223.6 | 779.5 |

### 2.2. Electrolysis method

As illustrated in Fig. 1, an electrolytic cell contains two Pt plate electrodes (20 mm × 20 mm) that are separated by a distance of 12 mm. The electrolysis cell was filled with 30 ml of reaction mixture containing methanol, oil, THF, water and NaCl as a supporting electrolyte. The methanol/oil molar ratio and THF/methanol molar ratio were adjusted to the range of 6–24 and 0–0.5, respectively. NaCl concentrations based on the oil weight were in the range of 0.14–1.12 wt.%. Based on the weight of the entire reaction mixture, 0.1–4.0 wt.% of deionized water was added. Electrolysis was carried out at room temperature using a constant voltage method. The electrolysis voltages were adjusted in the range of 5–20 V. The electrical conductivity and pH value were monitored with the electrolysis time. Electrical conductivity and pH value of the reaction mixtures were detected using a conductivity electrode cell and a pH/ORP electrode (TOA-DKK Co. Ltd.), respectively. The reaction mixture was agitated using a magnetic stirrer.

### 2.3. Analysis

For component analysis, the product of the fatty acid methyl ester (FAME) phase was washed with deionized water to remove the residual inorganic components. Concentrations of produced FAME and unreacted oils remaining in the product were analyzed using a high performance liquid chromatography (HPLC, TOSOH, Japan) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu, Japan) and a refractive index detector using a mobile phase of *n*-hexane/2-propanol = 99.5/0.5 (v/v). Column temperature was kept at 40 °C. The sum of FAMEs and the unreacted glycerides (sum of mono-, di- and tri-glycerides) were represented by two peaks separated in the chromatograph. The FAME yield in the product was calculated as follows:

$$\text{FAME yield} = \frac{C_{\text{FAME}}}{3C_{\text{oil}}} \times 100\% \qquad (6)$$

where $C_{\text{oil}}$ and $C_{\text{FAME}}$ are the concentrations of triglycerides in the feedstock and FAME in the product, respectively.

The gas evolved during the electrolysis for 2 h was collected in a sampling bag. The amount of $Cl_2$ in the sampling bag was detected by using a gas detection tube for chlorine molecules (detection limit = 0.5 ppm).

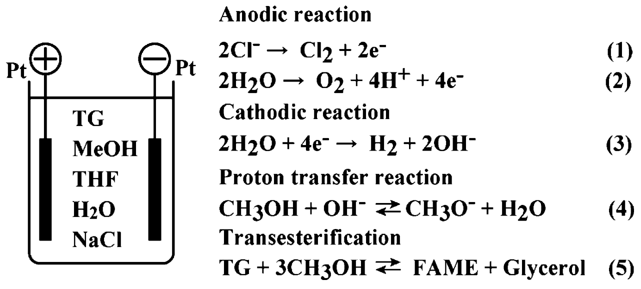

**Fig. 1.** Scheme of the electrolysis cell and the possible reactions.

## 3. Results and discussion

### 3.1. Electrolysis

As shown in Fig. 1, when the reaction mixture containing NaCl and $H_2O$ was introduced into the electrolysis cell, the evolutions of chlorine or oxygen might occur on the anode (Eqs. (1) and (2)). On the other hand, hydroxyl ions and hydrogen (Eq. (2)) were formed on the cathode. The transesterification of triglycerides (TG) with methanol (Eq. (4)) requires an active species, i.e., methoxide ion ($CH_3O^-$), in order to obtain reasonable FAME yield. Methoxide ion can form when methanol reacts with a hydroxyl ion ($OH^-$) (Eq. (3)), and once formed, the methoxide ion is strongly nucleophilic and attacks the carbonyl moiety in glyceride molecules to produce methyl esters [1,2]. As a result, BDF could be produced using this electrolysis method.

### 3.2. Effect of methanol/oil molar ratio

The effects of the solution composition and electrolysis voltage on the FAME yield were first investigated for the transesterification of corn oil. Fig. 2(a) shows the effects of the methanol/oil molar ratio and the NaCl concentration on the FAME yield. When NaCl concentration was as low as 0.14 wt.% in the presence of 2 wt.% $H_2O$, the FAME yield increased a little with the increase in the methanol/oil molar ratio. The FAME yield was only 18.7% with a methanol/oil molar ratio of 24. However, when the NaCl concentration was increased to 0.28 wt.%, the FAME yield increased sharply with the increase in the methanol/oil molar ratio. Transesterification of triglycerides with methanol is an equilibrium reaction [1]. Therefore, a large amount of methanol is necessary to force the reaction to proceed in the direction of FAME formation. In addition, as shown in Fig. 2(b), when the methanol/oil molar ratio was 6, the initial electrical conductivity of the reaction mixture before electrolysis was very low even at a relatively high NaCl concentration (only 0.156 mS $m^{-1}$ at NaCl concentration of 0.56 wt.%), and the active species formation rate, as well as the electric current at the cathode, could be very low, resulting in the formation rate of FAME becoming low. The electrical conductivity decreased to some extent when the methanol/oil molar ratio was varied from 12 to 24, because NaCl concentration was determined based on the oil weight and thus total NaCl content in the reaction mixture was decreased with the decrease in the oil content. However, the FAME yields at the methanol/oil molar ratio of 24 were still higher than those at 12, suggesting that the methanol/oil molar ratio plays a significantly more important role in transesterification.

### 3.3. Effect of electrolysis time

Fig. 3 shows the FAME yield increased with an increase in electrolysis time. The FAME yield at an NaCl concentration of 0.56 wt.% reached 93.7% in an hour and further increased to 97.9% in 2 h at the average electric current of 0.05 A in the presence of 2 wt.% $H_2O$. Although the reaction rate became lower at the NaCl concentration of 0.28 wt.%, a high FAME yield (94%) can also be obtained in 2 h with electrolysis at an average electric current of 0.03 A.

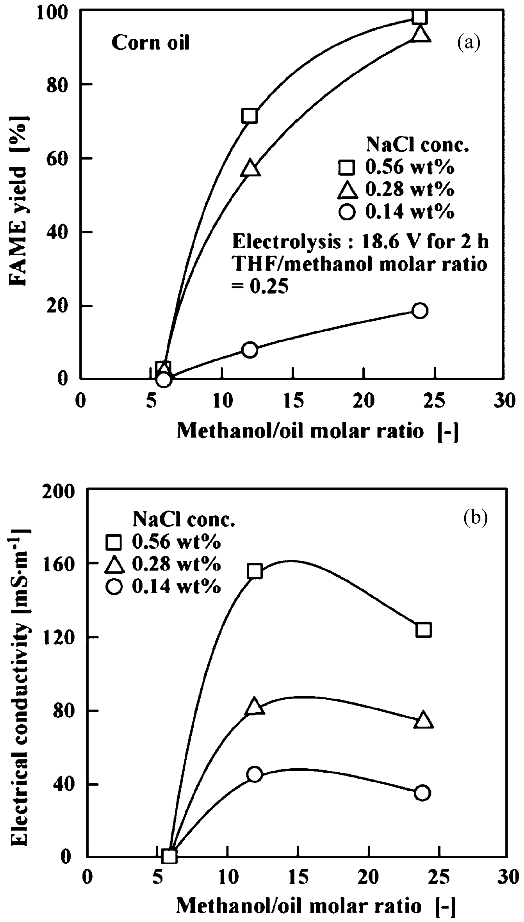

**Fig. 2.** (a) Effect of methanol/oil molar ratio on the FAME yield; (b) initial electrical conductivity of the reaction mixture changed with methanol/oil molar ratio. 2 wt.% $H_2O$ was added.

### 3.4. *Effect of electrolysis voltage*

The electric current as well as the conductivity of the reaction mixture were roughly proportional to the NaCl concentration in the solution. The electric current also increased with an increase in the electrolysis voltage, which resulted in more hydroxyl ions formed on the cathode. In the electrolysis method, hydroxide ions are continuously produced at the cathode and might react immediately with nearby methanol and the oil transesterification reaction happened in methanol phase. As a result, transesterification progressed mainly with the concentrated hydroxide ion that existed near the cathode. Therefore, the FAME yield increased with the increase in the electrolysis voltage, as shown in Fig. 4. It should be noted that FAME yield reached 88.7% even when the electrolysis voltage decreased to 9.5 V from 18.6 V in the case of 0.56 wt.% NaCl.

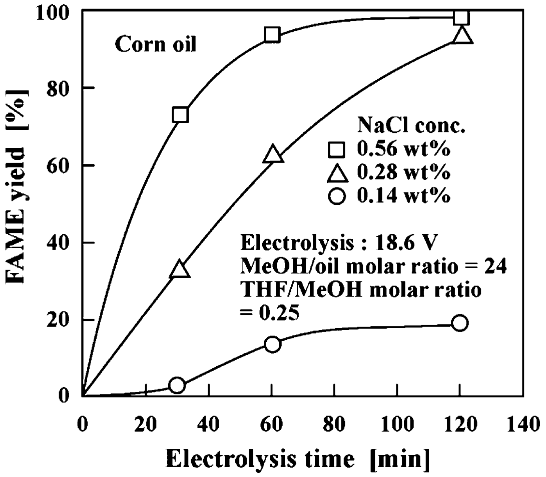

**Fig. 3.** Effect of electrolysis time on the FAME yield in the presence of 2 wt.% $H_2O$.

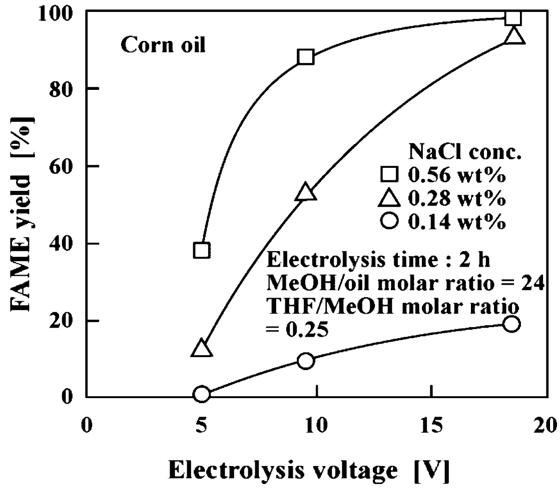

**Fig. 4.** Effect of electrolysis voltage on the FAME yield in the presence of 2 wt.% $H_2O$.

### 3.5. *Effect of cosolvent amount*

Fig. 5(a) shows the effect of THF concentration on the FAME yield in the presence of 2 wt.% $H_2O$. When no THF was added, a two-phase solution dispersed with methanol droplets was formed. However, the production of FAME by electrolysis occurred, and the FAME yield was as high as 65% at an NaCl concentration of 0.58 wt.%. When the THF/methanol molar ratio was 0.25, the reaction solution was initially heterogeneous. It turned homogeneous after 30-min of electrolysis. The FAME yield at an NaCl concentration of 0.56 wt.% reached 93.7% in an hour. Further addition of THF to the molar ratio of 0.5 realized the homogeneous state but reduced the FAME yield. The miscibility in the solution was improved by adding THF, which could reduce the mass transfer resistance for esterification. Meanwhile, initial electrical conductivity decreased with an increase in the THF/methanol molar ratio, as shown in Fig. 5(b). As a result, an optimum THF/methanol molar ratio should be chosen for electrolysis production of BDF.

### 3.6. *Effect of water content*

When a conventional method is applied in the production of BDF, water concentration in oil is generally limited to 0.1 wt.%, or less, because extra water in the reaction system promotes soap formation and a resultant drastic reduction in catalytic activity [20,21]. Although 2 wt.% of water was added in the electrolysis method, FAME yield reached 93.7% in an hour as shown in Fig. 6(a). In the electrolysis method, the most active region for transesterification might be the region near the cathode, where water molecules were continuously electrolyzed. However, FAME yield only reached 54.4% when water content increased to 4 wt.%, suggesting that extra water had negative effect on the transesterification reaction. Usually water plays an important role for the electric charge transfer between the electrodes. In addition, a small amount of water was electrolyzed and gradually consumed with the electrol-

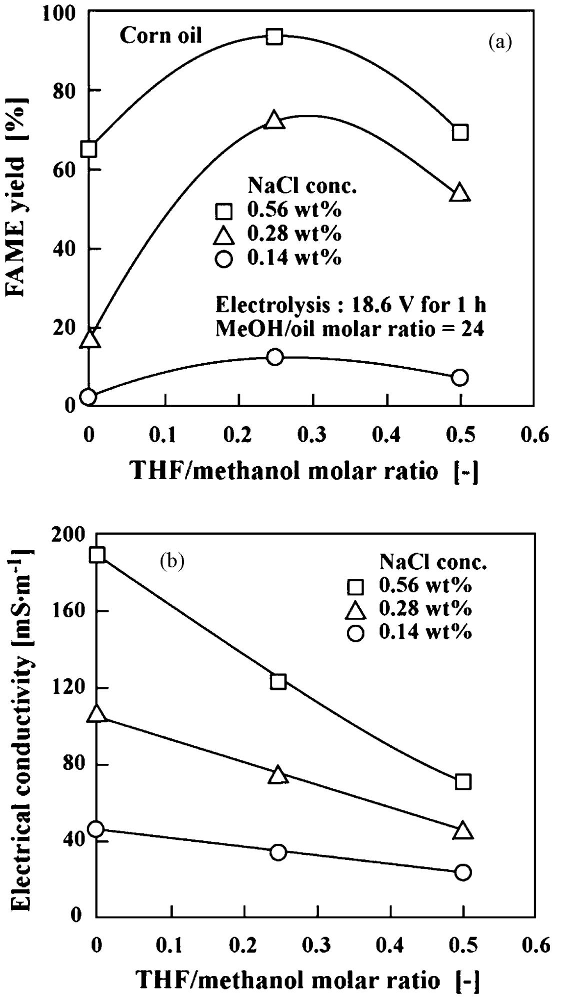

**Fig. 5.** Effect of THF/methanol molar ratio on the FAME yield (a) and initial electrical conductivity (b) in the presence of 2 wt.% $H_2O$.

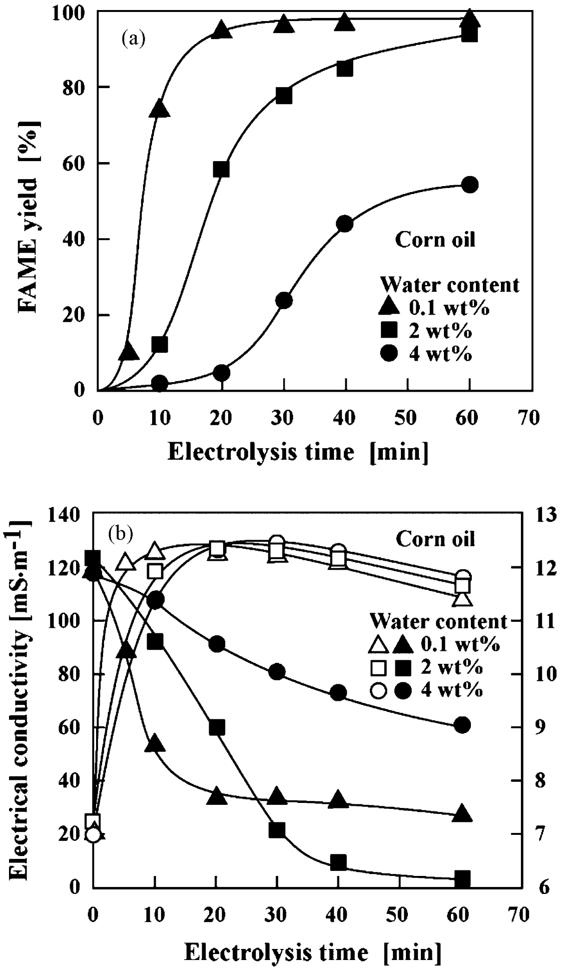

**Fig. 6.** Effect of water content on the FAME yield (a), and electrical conductivity and pH (b). Electrolysis voltage: 18.6 V; methanol/oil molar ratio = 24; THF/methanol molar ratio = 0.25

ysis time. When the water content was as low as 0.1 wt.%, FAME yield increased sharply between 5 and 10 min and reached 95.2% at 20 min, as shown in Fig. 6(a), On the other hand, electrical conductivity of the reaction mixture decreased between 0 and 20 min, and then kept a constant value, as shown in Fig. 6(b). However, the relation between the final electric conductivity and the water content was unclear.

Fig. 6(b) also shows the change of pH value with the electrolysis time. pH value increased from 7 to 12 within 20 min, and then almost kept at a constant value for subsequent 20-min intervals, which was benefit for the transesterification reaction. To clear the role of the basicity in the solution and the electrolysis, FAME yields were determined after the interruption of the electrolysis. As shown in Fig. 7, when the electrolysis was stopped at 10 min in the case of 0.1 wt.% $H_2O$, FAME yield reached 96.8% for 1 h, which was identical to that in the case of continuous electrolysis. However, when the electrolysis was stopped at 5 min, the FAME yield at the reaction time of 1 h was almost the same, but the reaction rate became low compared to that in the case of continuous electrolysis, because of low basicity in the solution. These results indicate that the transesterification rate was significantly affected by basicity in the solution produced by the electrolysis when the amount of water in the reaction mixture was small.

Meanwhile, when the electrolysis was stopped at 10 min in the case of 2 wt.% $H_2O$, the FAME yield only increased from 12.2% to 37.5% for subsequent 50-min intervals despite the high pH value (pH 11.9). Similar tendencies were observed when the electrolysis was stopped at 20 or 30 min. Because water content was still high in the reaction mixture after the interruption of the electrolysis, and the transesterification reaction was usually hindered by

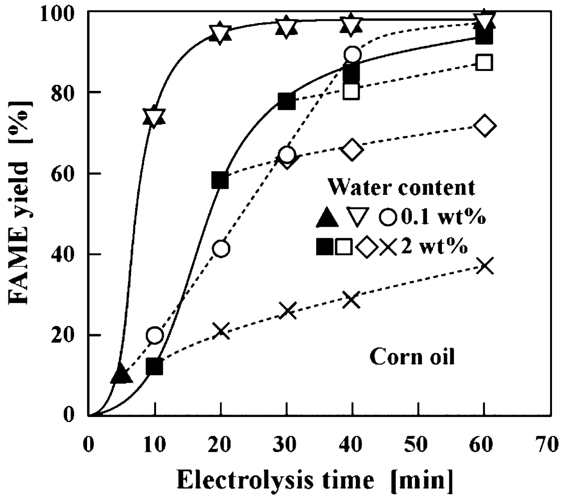

**Fig. 7.** FAME yield after the interruption of electrolysis. Solid lines: continuous electrolysis; dotted lines: without electrolysis; electrolysis voltage: 18.6 V; methanol/oil molar ratio = 24; THF/methanol molar ratio = 0.25.

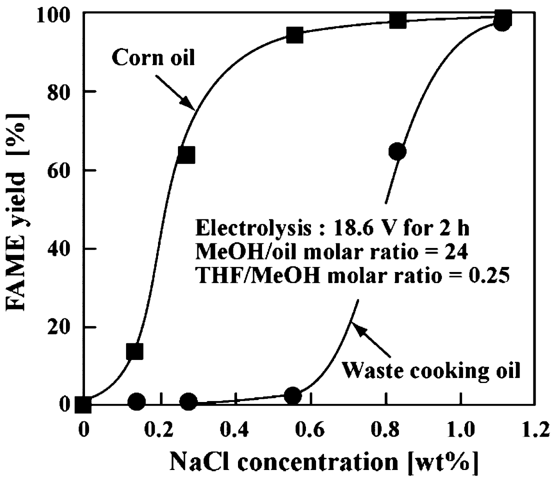

**Fig. 8.** Comparison of the results when using corn oil and waste cooking oil as feedstock.

reducing the catalytic activity with the existence of water in the reaction mixture [21]. Therefore, the electrolysis method was found to be useful for transesterification of oil containing high water content.

Although the evolution of harmful $Cl_2$ predicted by Eq. (1) was confirmed, no $Cl_2$ gas was detected for all the cases. Identification of the chlorinated compounds and the subsequent analysis of the reaction mechanism are remained in the future study.

### *3.7. Waste cooking oil as feedstock*

The FAME yield from the transesterification of waste cooking oil was compared to that from corn oil. For the waste cooking oil, high NaCl concentration was required in order to get a high FAME yield compared with the results for corn oil, as shown in Fig. 8. High water content (0.65 wt.%) in the waste cooking oil did not significantly affect the reaction properties, because 2 wt.% of water was added. However, sodium ion could be consumed by the reaction with the FFAs that existed in the waste cooking oil, which required high NaCl concentration to produce a high FAME yield. Future works will need to explore cheap electrode materials and reduction methods of electrolytic voltage for commercialization of the electrolytic BDF production.

## 4. Conclusions

Electrolysis method can be used for the production of BDF from oils containing relatively high content of water. The FAME yield using this method can be adjusted by changing electrolysis voltage, methanol/oil molar ratio, THF/methanol molar ratio, and NaCl concentration in the reaction mixtures. It was found that the pH value of the electrolyte rapidly increased to a high value and became constant with the proceeding of electrolysis, but the conductivity of the reaction mixture decreased with the reaction time and reached a constant value when the transesterification reaction was completed. Transesterification reaction continuously proceeded after the interruption of the electrolysis on the way, but the reaction rate was slowed down in the case of high water content in the reaction system. During the electrolysis process, no $Cl_2$ was detected.

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