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Optimization of a one-step direct process for biodiesel production from blended sewage sludge

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Abstract−Biodiesel production from blended sewage sludge (BSS) by a one-step direct process was investigated, and optimal conditions for this process were determined. The one-step direct process comprises extraction of lipids from BSS and simultaneous transesterification of these lipids with methanol. Among the organic solvents evaluated, pure methanol showed higher biodiesel yields compared with other solvents or solvent mixtures. The optimum conditions determined included 10 mL of methanol/g-BSS, 0.7% (g/g-BSS) of H_2SO_4, 60 °C, 4 h of reaction time and 300 rpm of agitation speed. Under these conditions, biodiesel yield was 3.1% (g-biodiesel/g-BSS), which was 63.2% higher than that obtained under initial conditions, and 24.0%-63.2% higher than those obtained in previous studies.

Keywords: Biodiesel, Blended Sewage Sludge, One-step Direct Process, Transesterification, Optimization

INTRODUCTION

Biodiesel is a renewable, sustainable, biodegradable, and nontoxic fuel that is produced conventionally by transesterification of vegetable oils, animal fats, or waste cooking oil [1,2]. As the production of biodiesel has increased remarkably, the price of feedstock for biodiesel has also risen substantially [3]. Therefore, the search is for sustainable and non-edible feed stock such as microalgae, spent coffee grounds, sewage sludge, jatropha, karanja, and waste cooking oil for biodiesel production [4-6].

Sewage sludge is considered a suitable substitute for conventional biodiesel feedstocks because of its two unique advantages: It is widely and consistently available, and contains considerable amounts of organic compounds; i.e., the total lipids extracted from sludge can reach about 12% of the dry weight of the material [7,8]. Municipal wastewater treatment plants in the USA produce over 6.2 million tons of dried sewage sludge every year [9], while annual production of sewage sludge in Korea was 4 million tons in 2013 and is expected to increase to 5.4 million tons by 2025 [10]. Disposal of sewage sludge in Korea was previously heavily dependent on ocean dumping (61.6% of the total sewage sludge generated in 2011); however, this was prohibited after 2012 by the London Convention '96 protocol [11]. Thus, currently, more than half of the sewage sludge produced is reused as fuel after drying. Applications include use as an additive in cement production or as a soil conditioner in agriculture. Any sewage sludge not reused is disposed either via incineration or in landfill sites [12,13].

Biodiesel is produced by either a two-step or one-step direct process. In the two-step process, lipid is extracted from feedstock with organic solvents and is converted to biodiesel by a catalyst, such as an acid or alkali with a short-chain alcohol (e.g., methanol). In the one-step direct process, lipid extraction and transesterification occurs simultaneously in a single reactor. Unlike the conventional two-step biodiesel production, the one-step direct process, also known as *in-situ* transesterification, uses intact biomass instead of purified lipids. Thus, it eliminates unnecessary and complex steps such as oil extraction, cleanup and refining [14-16]. Im et al. [17] also reported that *in-situ* transesterification using wet microalgae achieved high conversion yield (91%) without an energy-intensive drying process. In addition, since the one-step direct process can produce biodiesel in a single reactor using raw feedstock, this process can significantly reduce energy consumption [18]. However, the one-step direct process has certain disadvantages such as excessive amounts of solvent and catalyst are required [18].

Wang et al. [19] reported a maximum biodiesel yield of 1.9% (g-biodiesel/g-dry sludge) from the *in-situ* transesterification of dry secondary sludge using 1 g-sludge, 2.3% (w/w) of H_2SO_4, 5 mL of hexane/g-sludge, and 25 mL of methanol/g-sludge at 55 °C for 24 h. In another study, a maximum biodiesel yield of 2.5% was obtained using secondary sludge with 0.75% (w/w) of H_2SO_4 and 15 mL of methanol/g-sludge at 75 °C for 24 h in a one-step process [20].

As preliminary research for the development of an advanced biodiesel production process using blended sewage sludge (BSS) discharged from wastewater treatment facilities in Gangneung, a co-host city of the 2018 Winter Olympic Games, we evaluated a two-step process for biodiesel production [21]. We found that 20 mL of a solvent mixture with 2 : 1 ratio of chloroform to methanol was able to extract 92.9% of lipid from 1 g of dried BSS in the first step, and the use of an acid catalyst produced a much higher yield of biodiesel compared to an alkali catalyst in the second (transesterification) step. Under the optimized conditions for the second step, biodiesel yield was 5.25% (g-biodiesel/g-BSS) [21].

As another preliminary research, we evaluated the one-step direct process for biodiesel production using BSS in this study. The effects of catalyst concentration, ratio of methanol to sludge (RMS), reaction temperature, reaction time and agitation speed on biodiesel

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production were investigated and the optimal conditions were determined.

MATERIALS AND METHODS

1. Materials

Blended sewage sludge (BSS) was selected for use in this study, as the Gangneung wastewater treatment facility discharges sludge after mixing of the thickened primary and secondary sewage sludge. The mass ratio of primary to secondary sewage sludge in BSS was approximately 1/5. The BSS was dried in a fume hood for 4 d [20], and the dried BSS were mashed into small pieces then dried in an oven at 105 °C for 24 h prior to use in the following experiments. Methanol (99% purity, Showa, Japan) was used as an acyl donor for transesterification. In the one-step direct process, an organic extraction solvent is required. Six organic solvents were evaluated: chloroform (99% purity, Wako, Japan), methanol (99% purity, Showa, Japan), *n*-hexane (96% purity, Showa, Japan), acetone (99% purity, Junsei, Japan) and toluene (99% purity, Daejung, Korea). Sulfuric acid (99% purity, Showa, Japan) was used as an acid catalyst. Methyl heptadecanoate (Fluka, Japan) was used as an internal standard in gas chromatography (GC) analysis.

2. Biodiesel Production by a One-step Direct Process

Biodiesel was produced in a 30-mL glass bottle with a Teflon-coated cap by a one-step direct process. When lipid extraction and transesterification are conducted simultaneously, as shown in Fig. 1, the process is known as one-step direct process. In this study, the initial reaction conditions used were 1 g of BSS, 2.3% (w/w) of acid catalyst and 25 mL-solvent/g-BSS at 70 °C for 4 h [19,21]. Methanol and various solvent mixtures were evaluated as solvents for the one-step direct process. After the reaction was completed, the bottled reaction mixture was cooled to room temperature and 2 mL of distilled water was added. The biodiesel was then extracted twice with 10 mL of *n*-hexane by vigorously shaking the mixture for 1 min. Following centrifugation of the resulting mixture for 10 min, the organic layer was separated and dried in a fume hood at room temperature for 24 h. Finally, biodiesel yield (%, g-biodiesel/g-lipid) was determined by GC analysis of the organic layer.

3. Analysis

The biodiesel components were identified by using a GC-mass spectrometer (6890 GC/5973i MSD; Agilent, USA). Biodiesel conversion was determined with a GC (HP 5890 II, USA) equipped with an FID detector and an HP-5 column (30 m×0.32 mm×0.25 μm film thickness). The temperatures of the injector and the detector were set at 250 °C, and the column temperature was elevated from 150 to 250 °C at 5 °C/min after maintaining the oven temperature at 150 °C for 2 min. Helium was used as a carrier gas and the biodiesel conversion was quantified according to Eq. (1):

$$\text{Biodiesel conversion (\%)} = \frac{A_T - A_{C_{17}}}{A_{C_{17}}} \times \frac{V \times C}{M} \times 100 \qquad (1)$$

where, A_T and $A_{C_{17}}$ represent the total peak areas of the methyl esters and the internal standard (C_{17}), respectively. V, C, and M are the volume of the internal standard (mL), the concentration of the internal standard (mg/mL), and the sample mass (mg), respectively. The biodiesel yield was then quantified according to Eq. (2):

$$\text{Biodiesel yield (g)} = \frac{\text{Mass of product (g)} \times \text{Biodiesel conversion (\%)}}{\text{Mass of sewage sludge (g)}} \qquad (2)$$

4. Statistical Analysis

All experiments were conducted in triplicate and statistical analysis was carried out using statistical software Minitab® 14, PA, USA.

RESULTS AND DISCUSSION

We have previously shown that dried BSS consisted of 42.8% crude protein, 14.5% lipid, 17.8% ash, 8.9% carbohydrate and 16.0% other materials [21]. Our study also showed that an acid catalyst (H_2SO_4) performed better than an alkali catalyst, which may be due to the high content of free fatty acids (FFAs) (40.8%) in lipids [21]. These FFAs cause saponification upon reaction with an alkali catalyst such as NaOH, resulting in low biodiesel yield. Therefore, we used only an acid catalyst in the present study.

In the one-step direct process, major factors affecting biodiesel yield include types of catalyst and organic solvent, ratio of methanol to biomass, agitation speed, temperature and reaction time [14,22]. In the following sections, we initially evaluated various organic solvents affecting biodiesel yield, and optimized reaction conditions through one factor at a time method. That is, we investigated the effect of a factor on biodiesel production to find its optimal condition, and then we fixed the value of the factor previously determined and optimized the next factor and so on.

1. Effect of Organic Solvent on Biodiesel Yield

Organic solvents such as methanol are required for lipid extraction and dissolving FFAs, phospholipids, sterols, and phenols in feedstock. Methanol is a highly polar solvent, and since most triglycerides dissolve in non-polar solvents, poor triglyceride solubility

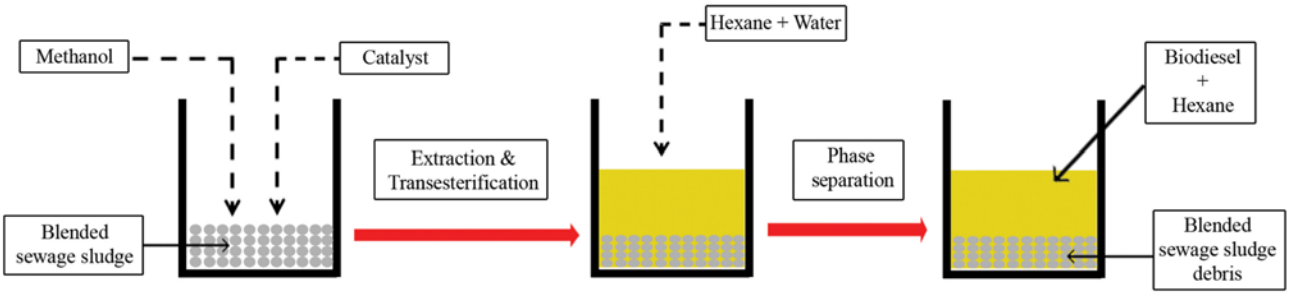

Fig. 1. Schematic diagram of the one-step direct process for biodiesel production.

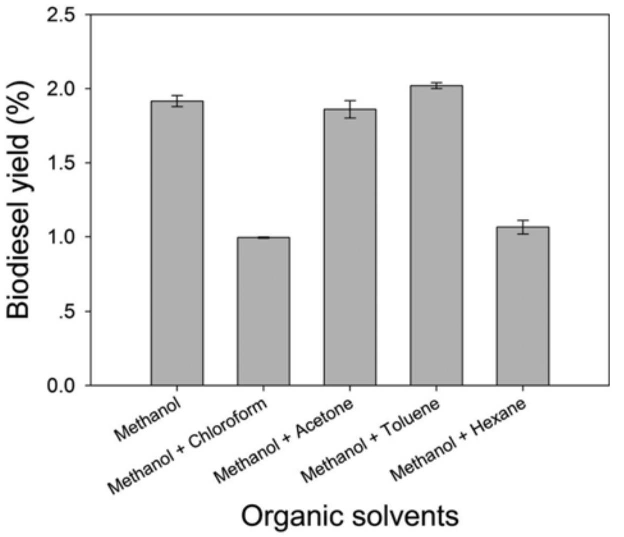

Fig. 2. Evaluation of organic solvents in the one-step direct process (Reaction conditions; 1 g-BSS, 25 mL-solvent/g-BSS, 2.3% H_2SO_4, 70 °C, 150 rpm, 4 h).

in methanol is expected [22]. In our previous study of lipid extraction from BSS, methanol was found to be the best single extraction solvent in terms of lipid yield (5.7%) corresponding to 39.2% of lipid extraction efficiency [21]. Among the solvent mixtures evaluated, a mixture of chloroform and methanol showed the highest lipid yield (7.5%), followed by mixtures of methanol and toluene, methanol and acetone and methanol and *n*-hexane. Based on our previous results, 25 mL of solvent was used to evaluate biodiesel production in the one-step direct process. As shown in Fig. 2, the mixture of methanol and toluene gave the highest biodiesel yield of 2.02% (g-biodiesel/g-BSS), followed by pure methanol (1.92%), methanol and acetone (1.86%), methanol and *n*-hexane (1.06%) and methanol and chloroform (1.00%). Although the yield of methanol and toluene was the greatest, it was only marginally higher than that of methanol only. Toluene is known to cause health and environmental problems, and its higher boiling point (100.6 °C) makes its recovery after lipid extraction less economical [5]. Therefore, methanol was chosen as the extraction solvent in the one-step direct process.

Sitthithanaboon et al. [23] also chose methanol as the only solvent in the one-step process in which methanol acts as both a solvent and a reactant for the extractive-conversion process. An excess of methanol increased contact between methanol and oil, which improved the methanolysis reaction. Kim et al. [18] studied the effect of pure alcohol and a mixture of alcohol and chloroform as solvents on the biodiesel yield from microalgae. They showed that pure alcohol performed much better than the mixture of alcohol and chloroform, and that biodiesel yield decreased as the fraction of methanol was reduced to a 1 : 2 ratio of methanol to chloroform.

Based on the results in the present study and literature survey, sole methanol was determined as the optimum organic solvent for the one-step direct process for biodiesel production using BSS.

2. Effect of the Ratio of Methanol to Sludge (RMS) on Biodiesel Yield

The presence of excess methanol is necessary to shift the equilibrium of the reaction to maximize biodiesel yield [24]. We estimated the theoretical methanol volume required to convert the entire lipids contents to biodiesel, with the assumptions of 100% of lipid extraction efficiency and biodiesel conversion, and the average molecular weights of FFAs and triglycerides being 282.4 g/mole and 872.4 g/mole, respectively. Since the transesterification of a fatty acid and a triglyceride requires one and three moles of methanol, respectively, approximately 0.02 mL of methanol is required to convert the entire lipids in 1 g of BSS to biodiesel. Excess methanol is required to increase contact between methanol and lipids, thus improving the methanolysis reaction [23]. As stated previously, the methanol volume used under initial reaction condition was 25 mL/g-BSS; however, we evaluated volumes of 5-25 mL/g-BSS in this study.

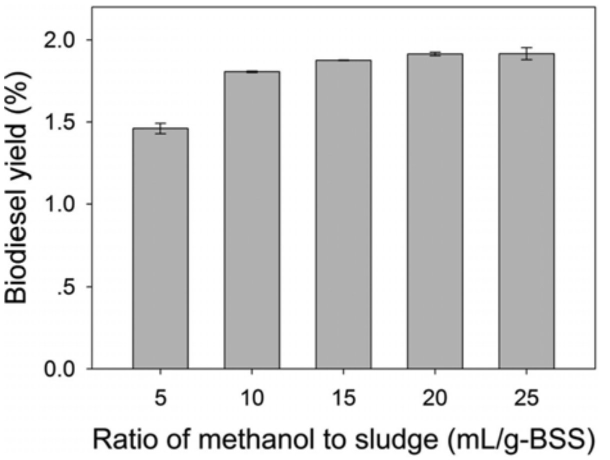

Fig. 3. Effect of the ratio of methanol to sludge on biodiesel yield in the one-step direct process (Reaction conditions; 1 g-BSS, 2.3% H_2SO_4, 70 °C, 150 rpm, 4 h).

The effect of RMS in the range of 5-25 mL/g-BSS was investigated in the presence of 2.3% (w/w) of H_2SO_4, at 70 °C and 150 rpm for 4 h. Biodiesel yield was 1.46% (g-biodiesel/g-BSS) at an RMS of 5 mL/g-BSS (Fig. 3). Biodiesel yield increased to 1.80% with the increase in RMS to 10 mL/g-BSS. Increase in RMS to 15 and 25 mL/g-BSS caused a slight increase in biodiesel yield. However, statistical analysis showed that there was no significant difference in biodiesel yield at RMS exceeding 10 mL/g-BSS. Therefore, an RMS of 10 mL/g-BSS was determined as the optimal value and was used to study the influence of the next parameters.

We have previously reported that biodiesel yield increased with methanol dosage at 15-25 mL/g-lipid in a two-step process. An increase in the methanol dosage to 35-55 mL/g-lipid resulted in a decrease in biodiesel yields due to dilution of the catalyst by excess methanol [21]. A similar observation, dilution effect of catalyst by excess alcohols, was previously reported by others where sulfuric acid, microalgae and ethanol were used as catalyst, biomass and organic solvent, respectively [25]. The researchers indicated that sulfuric acid was dissolved in excess ethanol and acidity gradually decreased, resulting in reduced cell hydrolysis and less esterification of microalgae in the *in-situ* transesterification [25]. Apart from solvent requirement in the lipid extraction step of the conventional two-step process, since lipid content of BSS is 14.5%, the methanol requirement of 25 mL/g-lipid corresponds to at least 172 mL/g-BSS. Therefore, a one-step direct process saves a large volume of methanol compared with conventional two-step process.

3. Effect of Catalyst (H_2SO_4) Concentration on Biodiesel Yield

Use of a catalyst during transesterification is necessary to convert triglycerides into biodiesel [26]. Therefore, the effect of catalyst at different concentrations (0.1-1.1% (w/w) of H_2SO_4) was investigated. The reaction was carried out at 70 °C and 150 rpm for 4 h using 10 mL-methanol/g-BSS. As shown in Fig. 4, biodiesel yield increased from 1.4% to 2.1% with the increase in catalyst concentration from 0.1 to 0.7% (w/w), which may be due to the increased interaction between the catalyst and the reactants [27]. Further increase in H_2SO_4 concentration had a negligible effect on biodiesel yield. Thus, 0.7% (w/w) of H_2SO_4 was determined to be the optimal value for all following experiments.

4. Effect of Reaction Temperature on Biodiesel Yield

The effect of reaction temperature on the one-step direct process was studied in the range of 30-80 °C, with 10 mL-methanol/g-BSS, 0.7% (w/w) of H_2SO_4, 150 rpm and 4 h reaction time (Fig. 5). Biodiesel yield increased from 1.47 to 2.25% with increasing reaction temperature from 30 to 60 °C. This could be due to a faster transesterification rate caused by high temperature. Moreover, high temperature may also improve cell disruption; therefore, oil in the biomass can contact the reactants more easily, resulting in a higher biodiesel yield [28]. In addition, high temperature can reduce viscosity and increase solubility of oil, both of which can increase the final extraction yield [22]. However, further increase in temperature to 70 °C and 80 °C led to a decrease in biodiesel yield to 2.13% and 2.10%, respectively. This might be due to the possible degradation of product under higher temperature as well as the vaporization of methanol, which inhibits the reaction on the three-phase interface [29,30]. Based on these results, we determined that the optimal reaction temperature was 60 °C.

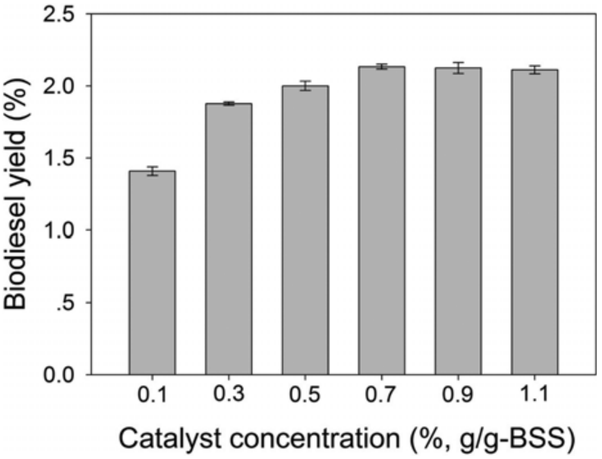

Fig. 4. Effect of acid catalyst (H_2SO_4) concentration on biodiesel yield in the one-step direct process (Reaction conditions; 1 g-BSS, 10 mL-methanol/g-BSS, 70 °C, 150 rpm, 4 h).

5. Effect of Reaction Time on Biodiesel Yield

To complete the transesterification, a sufficient reaction time is necessary to break down cell walls, release lipids and react lipids with methanol [15,31]. Fig. 6 shows the effect of reaction time on biodiesel yield. Biodiesel yield increased from 1.89% to 2.26% with increasing reaction time from 2 to 4 h. With the increase in the reaction time to 6 h, the biodiesel yield was slightly decreased to 2.17%. The decrease in biodiesel yield may be due to the backward reaction of transesterification resulting loss of esters [32]. Based on these results, 4 h was determined to be optimum reaction time.

6. Effect of Agitation Speed on Biodiesel Yield

The effect of agitation speed between 150-900 rpm was investigated with 10 mL-methanol/g-BSS, 0.7% (w/w) of H_2SO_4 at 60 °C and 4 h of reaction time. As shown in Fig. 7, biodiesel yield increased from 2.25% to 3.1% with increasing agitation speed from 150 to 300 rpm. However, further increase in speed higher than 300 rpm did not show any significant difference in the biodiesel yield. It is thought that high agitation speed plays two roles: 1) to aid in mixing of hydrophobic lipids with the catalyst-methanol mixture, and 2) to maintain uniform temperature throughout the reaction system [33]. In addition, higher agitation speeds prevent clumping and ensure that the biomass is adequately exposed to

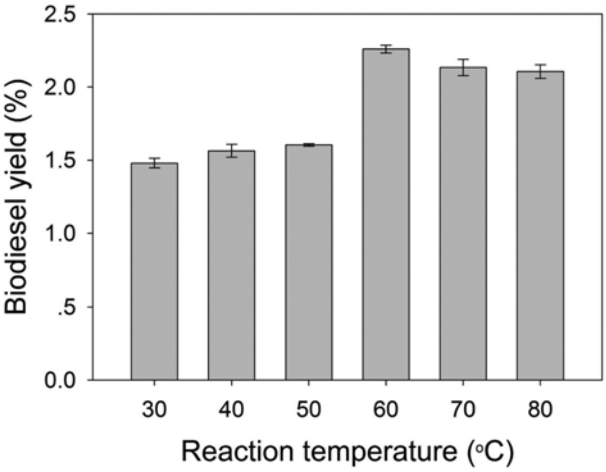

Fig. 5. Effect of reaction temperature on biodiesel yield in the one-step direct process (Reaction conditions; 1 g-BSS, 10 mL-methanol/g-BSS, 0.7% H_2SO_4, 150 rpm, 4 h).

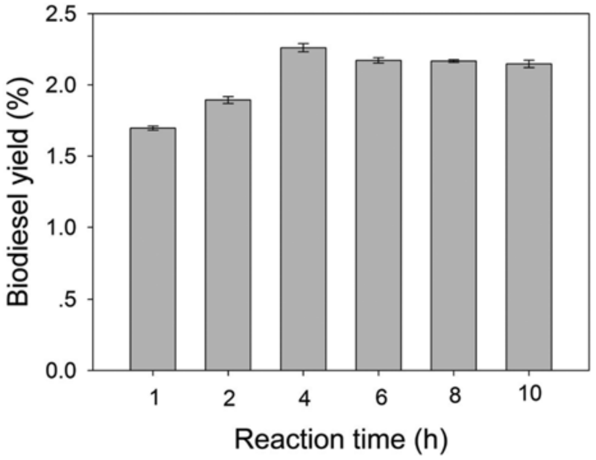

Fig. 6. Effect of reaction time on biodiesel yield in the one-step direct process (Reaction conditions; 1 g-BSS, 10 mL-methanol/g-BSS, 0.7% H_2SO_4, 60 °C, 150 rpm).

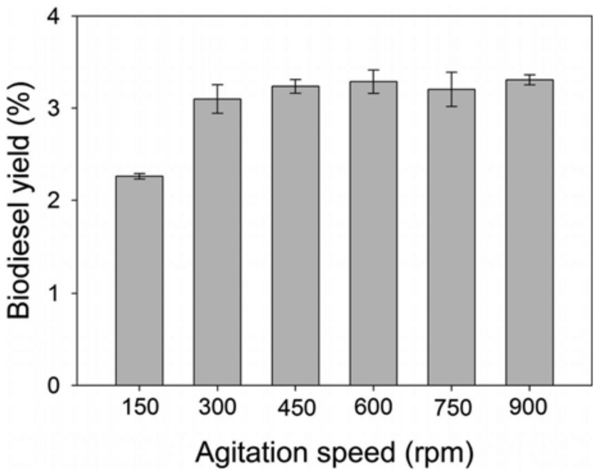

Fig. 7. Effect of agitation speed on biodiesel yield in the one-step direct process (Reaction conditions; 1 g-BSS, 10 mL-methanol/g-BSS, 0.7% H_2SO_4, 60 °C, 4 h).

methanol [15]. However, although biodiesel yield can be improved by increasing agitation speed, its effect is limited above some agitation speed. Based on these results, we suggested that the optimal stirring speed was 300 rpm. By this, all the factors considered in this study were optimized.

In this study, we initially investigated the performance of different organic solvents in biodiesel production. Biodiesel yield was 1.9% using 25 mL of methanol/g-BSS and 2.3% H_2SO_4 at 70 °C, and 150 rpm for 4 h. By optimizing the reaction conditions, we obtained biodiesel yield of 3.1%. As shown in Table 1, although the agitation speed was increased from 150 to 300 rpm, the reaction temperature was lowered from 70 to 60 °C. In addition, we could save H_2SO_4 and methanol by 69.5% and 60.0%, respectively. In the present study, we obtained 24.0 to 63.2% higher biodiesel yields than those in previous studies (Table 2).

CONCLUSION

The optimal conditions of a one-step direct process for biodiesel production using BSS were determined. Among the organic extraction solvents evaluated, pure methanol showed a higher biodiesel yield compared to various solvent mixtures. The optimal conditions were determined to be 10 mL of methanol/g-BSS, 0.7% (w/w) of H_2SO_4, 60 °C of reaction temperature, 4 h of reaction time, and 300 rpm of agitation speed. Under these optimized conditions, we obtained a biodiesel yield of 3.1% (g-biodiesel/g-BSS), which was 63.2% higher than that obtained under initial conditions, and 24.0%-63.2% higher than those obtained by previous studies.

Although we substantially improved the biodiesel yield by optimizing the reaction conditions, this yield is not still satisfactory, when considering the 5.2% (g-biodiesel/g-BSS) biodiesel yield using a two-step process in our previous study. Nevertheless, as stated above, the one-step direct process has several advantages against the conventional two-step process in the aspect of operation time, facilities required and production cost. Note that these efforts to optimize the process of utilizing sewage sludge will contribute to the reduction in biodiesel production cost and protection of the environment.

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Table 1. Comparison of biodiesel yield under initial conditions and optimized conditions

Conditions	Biodiesel yield (%)
Initial condition: 2.3% (w/w) H_2SO_4, 25 mL of methanol, 70 °C,150 rpm, 4 h	1.9±0.03
Optimum condition: 0.7% (w/w) H_2SO_4, 10 mL of methanol, 60 °C, 300 rpm, 4 h	3.1±0.15

Table 2. Comparison of biodiesel yield obtained in this study with previous studies

Type of sludge	Lipid content (%)	H_2SO_4 concentration (% w/w)	Methanol amount (mL/g-sludge)	Temp. (°C)	Time (h)	Biodiesel yield (%) (g-biodiesel/g-dried sludge)	Ref.
Secondary sludge	16.9	2.3	25	55	24	1.9	[19]
Secondary sludge	-	0.75	15	75	24	2.5	[20]
Blended sludge	14.5	0.7	10	60	4	3.1±0.15	This study

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