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In Situ Transesterification of Wet Activated Sludge under Subcritical Conditions

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Abstract

Commercial production of biodiesel uses refined vegetable as the feedstock with base as the catalyst. However, pure vegetable oil contributes up to 80% of the overall biodiesel production cost. Activated sludge is a rich source of lipid and a potential feedstock for biodiesel production. It was estimated that drying and oil extraction constitutes more than 50% of the cost of biodiesel production from wet activated sludge. In this study, wet activated sludge was directly used as the feedstock to react with methanol under subcritical water condition. At 250°C and a methanol to wet sludge ratio of 3.0 mL/g, a Fatty Acid Methyl Ester (FAME) yield of 33% can be achieved in 4 h. Acetic acid was employed as the catalyst to decrease the amount of methanol to 2.25 mL/g and reaction time to 1 h that were required to reach the same FAME yield (33%). This process can be applied to maximize biodiesel conversion of feedstock with high FFA and moisture contents.

Keywords: Activated sludge; Biodiesel; Subcritical condition; Transesterification

Nomenclature

BD: Biodiesel; AS: Activated Sludge; AA: Acetic Acid; FFA: Free Fatty Acid; FAME: Fatty Acid Methyl Ester

SCW: Subcritical Water

Introduction

Biodiesel (BD) can be synthesized by reaction between oil and an alcohol such as methanol or ethanol. The feedstock for BD production can be vegetable oil, animal fat, recycled restaurant grease or lipid contained in microorganism [1]. Commercial production of BD mostly uses refined edible oil as the feedstock such as soybean, canola, rapeseed, sunflower, palm and coconut oils. However, one major problem with BD is its economic viability that is likewise faced by all biofuels. Pure vegetable oil constitutes about 70% to 85% of the overall BD production cost [2]. For this reason, researches have been undertaken to investigate the possibility of using agriculture/industry wastes as feedstock for BD production, which in principle should significantly reduce the overall price of BD and avoid the competition between food and fuel often faced in producing biofuel.

The development of environmentally friendly processes has become highly desirable for reasons such as pollution prevention, public acceptance and hazard elimination. Many studies employed water as the solvent in sub or supercritical state to prevent problems associated with volatile organic solvents. Water at subcritical state is a rich source of H^+ and OH^- and can act as a neutral acid-base catalyst for extraction and chemical reactions such as hydrolysis and degradation [3]. Therefore, the idea of using Subcritical Water (SCW) can be applied to the treatment of biomass from agriculture and industrial wastes such as Activated Sludge (AS) and micro-algae which have high water content.

AS is the product of a biological process and is a rich source of lipid. Using a sulfuric acid catalyzed reaction with primary sludge as the feedstock, a maximum BD yield of 14.5% was obtained by Mondala et al. [4]. Revellame et al. [5] achieved a BD yield of 4.79% by using a sulfuric acid catalyzed reaction. The same authors also carried out the production of BD using wet AS [6]. Huynh et al. [7] reported the production of BD from wet AS under subcritical condition without using conventional acid/base catalyst. Recently Acetic Acid (AA) was introduced to produce triacetin as well as free fatty acid (FFA) and avoid by-product glycerol in BD production [8]. AA and carbon dioxide were found to play important role in transesterification process [9].

In situ production of Fatty Acid Methyl Ester (FAME) without using conventional acid/base catalyst was investigated in this work. The effect of adding AA in methanol on FAME yield was studied with the objective of shortening the reaction time and reducing the amount of methanol required.

Experimental

Materials

FAME standard (47885-U, a mixture of 37 FAMEs) was purchased from Supelco (Bellfonte, PA). Standards of FFA were obtained from Sigma Aldrich Corp. (St. Louis, MO). All chemicals used are analytical reagent grade and were purchased from commercial sources.

The AS sample was collected from a food processing plant (Hsin-Tung-Yang LTD Da-Yuan Factory) and was stored at - 84°C before use.

In situ transesterification reaction

A schematic description of the equipment for the SCW treatment of AS and the in situ reaction of AS to produce BD under subcritical condition is given in Figure 1. Details of the high pressure reactor can be found elsewhere [7]. In situ reaction was carried out following

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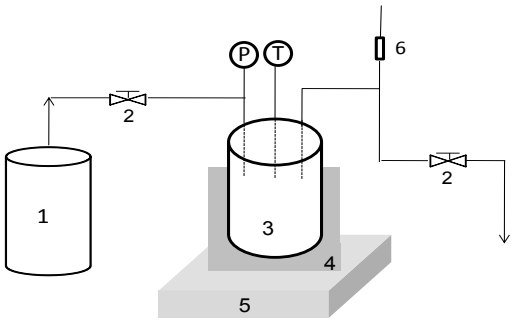

Figure 1: Layout of equipments for SCW treatment and in situ reaction of wet AS. [1] N_2 cylinder, [2] needle valve, [3] reactor, [4] heater, [5] magnetic stirrer, [6] safety valve, [P] pressure gauge, [T] thermocouple.

	Weight percentage (wt.%) in dry AS	
	Before SCW treatment	**After SCW treatment[a]**
Unsaponifiable	0.50	5.75
Wax and gum	1.21	1.71
Neutral lipid	16.28	37.96

[a]SCW treatment of AS at 175°C for 15 min

Table 1: Crude lipid content in AS obtained by hexane extraction [10].

Fatty Acid (%)	Without SCW treatment	With SCW treatment [a]
C12:0	0.23	0.24
C13:0	0.07	0.07
C14:0	1.87	2.03
C15:0	0.37	0.36
C16:0	46.2	50.4
C17:0	0.56	0.58
C18:0	30.5	31.6
C18:1	2.88	4.29
C18:2n6c	2.99	1.49
C20:0	0.94	0.96
C22:n	1.22	0.55
Others	12.1	7.5

[a] SCW treatment of AS at 175°C for 15 min

Table 2: Fatty acid profiles of AS before and after SCW treatment [10].

the procedure presented elsewhere [7-10]. In short, wet AS (5 g) and methanol (30 mL) were mixed and added into a glass chamber and placed in a reactor. The reactor is equipped with an external electric heater and a magnetic stirrer. Temperature in the reactor was controlled to within ± 2°C. The reactor was sealed and nitrogen was applied to the reactor to keep the reaction system in subcritical condition. The desired reaction temperature (250°C) was reached in about 45 min. After a predetermined reaction time, the pressure was released and the reactor was cooled to room temperature. Liquid and solid in the reaction product were separated by vacuum filtration. The solid residue was washed twice, each with 50 mL methanol. The collected filtrate, combined with the subsequent methanol washings were concentrated using a rotary evaporator and at the same time to recover the methanol. Hexane (50 mL) was then added to the concentrated organic product together with 20 mL of 5% NaCl solution. The mixture was then transferred into a separation funnel and allowed the mixture to separate into 2 distinct phases. The upper phase, rich in FAME was then collected for further analysis. Hexane was removed with the aid of a rotary evaporator and the left over product was weighed and recorded as the crude FAME produced. All experiments were carried out in triplicate.

In situ transesterification with AA addition:

Wet AS (5g) and mixture of methanol and AA (10% by volume) were loaded into the reactor. The reaction was carried out at 250°C with various methanol to solid ratios (0.5 to 3 mL g^{-1}). After reacted for 1 h the reactor was cooled to room temperature. FAME produced was collected as described in the previous section.

Results and Discussion

Water content of the wet sludge sample was 89.01%. Table 1 shows the crude lipid content of AS and the fatty acid profiles of AS before and after SCW treatment are shown in Table 2. After SCW treatment, the amount of neutral lipid extracted increased 2.33 times (Table 1). This is the main reason that much higher FAME yield can be obtained in the producing of BD from wet AS under subcritical condition than that using conventional acid/base catalyzed reaction.

Fatty acid profiles of neutral lipids before and after SCW treatment are very similar (Table 2). Palmitic acid and oleic acid occupy about 80% of the total fatty acids. The most abundant fatty acid in the AS is palmitic acid which reflects the fact that palm oil is widely used by food industry in Taiwan. The overall fatty acid profile of lipid from AS is similar to that of most vegetable oils.

Effect of reaction time on FAME yield

It has been reported that temperature was the most important parameter in affecting BD yield [9,11]. Although the critical temperature of methanol (239.6°C) is lower than the reaction temperature used in this study (250°C), taking into consideration the presence of lipids which have much higher critical temperatures, it is safe to say that the reaction was carried outunder subcritical condition. The second most important factor is reaction time. As can be seen from Figure 2, FAME yield increased with reaction time. It took 40 to 45 min to reach 250°C, at that instant (0 h) the FAME yield was about 14%. The FAME almost doubled after 1 h and kept increasing slowly to about 33% after 4 h.

Effect of AA on FAME yield

To improve FAME yield and reduce the amount of methanol used, AA (10% in mixture of methanol and AA) was used as the catalyst in the in situ transesterification of wet AS. As shown in Figure 2, without using AA, FAME yield only reached about 28% after 1 h. When AA was employed in the reaction, after 1 h FAME reached 33% at a ratio of solvent (methanol + AA) to wet AS of 2.5 mL/g (Figure 3). The

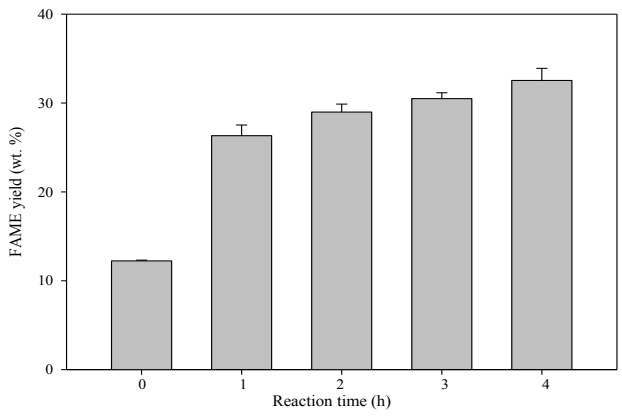

Figure 2: Effect of reaction time on FAME yield. Ratio of methanol to wet AS = 3 mL/g.

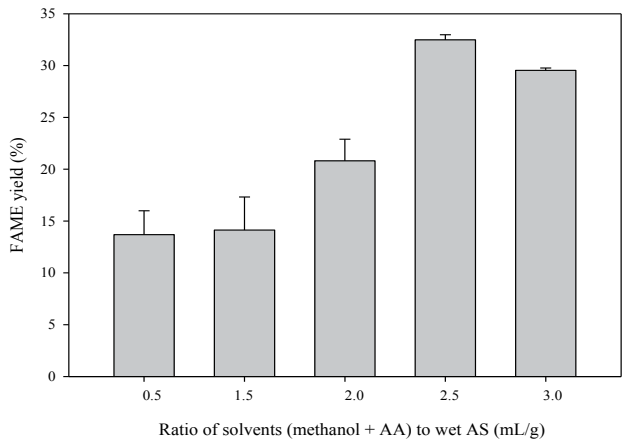

Figure 3: Effect of ratio of solvent (methanol + AA) to wet AS on FAME yield. Reaction time 1 h.

advantages of using 10% AA can be seen by considering the reaction conditions to reach the same FAME yield of 33%, which is 86.8% of the theoretical maximum FAME yield of 38.0%. Without AA, it took 4 h and needed 3 mL methanol per gram wet AS. With AA, the methanol amount needed was 2.25 mL per gram of wet AS (a reduction of 25%) and the reaction time needed was only 1 h (a reduction of 75%). Adding AA not only promoted the hydrolysis of triglyceride into FFA but also catalyzed the esterification of FFA to improve FAME yield. The presence of AA may act as an acid catalyst and help tolerating high water content in wet sludge (about 90% water).

Moreover, methanol can react with AA to form methyl acetate which is a good extracting solvent thus may help improving solubility between oil and methanol [8]. In this study, in situ production of FAME was carried out at 250°C and 10.0 MPa using wet AS in a mixture of water, methanol and AA under subcritical condition. A FAME yield of 33.0% was obtained which is 86.8% of the theoretical maximum FAME yield of 38.0%.

Summary and Conclusion

This research investigated the effect of adding AA on FAME yield in the in situ production of BD from wet AS. By adding AA in methanol (10% AA in mixture) with a ratio of solvent mixture to wet sludge of 2.5 mL/g, an FAME yield of 33% based on dry sludge can be achieved in 1 h at 250°C.

Acknowledgement

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