DIRECT LIQUID-LIQUID LIPID EXTRACTION METHOD FOR BIODIESEL PRODUCTION FROM SEWAGE AND PETROCHEMICAL INDUSTRY SLUDGES

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Abstract

Sewage sludge has gained importance in biodiesel production due to its high lipid content. Morevover, the oily sludges from petrochemical industry wastewater treatment plants (WWTPs) have high lipid content, phospholipids, free fatty acids, neutral lipids and can also be used as a feedstock for biodiesel production. Lipid extraction is the first step of biodiesel production from sludges. Standard reference drying lipid extraction method necessitates expensive sludge dewatering/drying steps, holding almost 50% of overall conventional biodiesel production cost, to remove high water content in sludge. The aim of this study was to explore lipid extraction from sewage and petrochemical industry sludges by using the novel direct liquid-liquid extraction method, which does not require expensive sludge dewatering/drying steps, and to compare it to standard reference drying method. The study also investigated the effect of acid pre-treatment on lipid yields of the sludge samples. The results of the study showed that, in both of the lipid extraction methods. Acid pre-treatment increased the lipid yields noticably. The highest lipid yield was obtained from pre-acidified petrochemical industry sludge by using liquid-liquid lipid extraction method. Compared to conventional reference drying method, direct liquid-liquid lipid extraction is found to be more efficient for petrochemical industry sludge samples. However, standard dry lipid extraction method was more effective for sewage sludge samples.

Keywords

biodiesel, lipid, sewage sludge, petrochemical sludge, liquid-liquid extraction

Introduction

With the increase of industrialization and urbanization, the over-consumption of the energy causes energy crisis. Nowadays, most of the energy demand is satisfied from fossil fuel sources which are non-renewable, and will be run out in the future [17]. 'Sustainable development' is an important idea for our country and even the world which we can reach by using renewable and environmentally friendly energy [6]. Among the alternative fuel sources such as biogas, biomass, synthetic fuels; biodiesel represents a better alterrnative to conventional diesel [19]. Biodiesel can be used directly without any modification requirements. It is also biodegradable, renewable, less harmful, safer for utilization and storage and has low emmission profiles [12].

The basic raw materials used in biodiesel production like sunflower, canola, soybean, palm, rapeseed, and coconut oils are not applicable due to the high price of these oils and lack of agricultural land for growing them. Therefore, alternative sources of oils and fats such as waste frying oil, jatropha oil, microalgae, and sewage sludge draw attention in recent years [2, 10, 14, 15, 18]. Among these sources sewage sludge has begun to attract attention around the world as a lipid feedstock for biodiesel production due to its high lipid content originated from the adsorption of lipids, in the form of triglycerides, diglycerides, monoglycerides, phospholipids, and free fatty acids onto the sludge solids [7, 21]. Second attractive point is that sewage sludge is plenty and free of cost as raw material making the biodiesel production profitable [10, 21]. Moreover, using sludge as feedstock for biodiesel production is an alternative sludge disposal method. The treatment and disposal of sludge is a complex challenge for any wastewater treatment plant, holding 20-60% of total WWTP operating cost [5]. Recycling sewage sludge to take advantage of the sludge as a source of lipid feedstock for biodiesel production helps to solve some environmental problems associated with sludge tretment and disposal [1, 10].

The main obstruction in biodiesel production from wastewater sludges is an efficient lipid extraction from sludges having very high water content of about 95-98 wt.%. Hence, the cost of necessary dewatering and drying processes costitute almost 50% and makes the production very expensive and difficult to scale up [4, 13].

A significant amount of oily sludge is generated from the petroleum industry wastewater treatment plants [20]. The oily sludge obtained from thickening unit of petrochemical industry wastewater treatment plant (WWTP) contains sludges from oil separators, primary clarifier, and the waste activated sludge from secondary clarifier and can be used as a feedstock for biodiesel production. The petrochemical industry WWTP sludge comprises of various organic and inorganic compounds consisting water-soluble metals, salts, phospholipids, suspended solids, petroleum hydrocarbons (PHCs), neutral lipids and free fatty acids (FFA) sourced from the oils that cannot be removed in WWTP and sourced from biological (waste activated) sludge in the plant [8 ,11]. It can also cause serious environmental and human health problems when it disposes without applying any treatment due to release of toxic and carcinogenic contaminants [9]. Because of its hazardous composition and population growth around the world, the effective treatment of oily sludge has gained importance in recent years. Consequently, biodiesel production from this sludge as an effective option to common sludge treatment methods will be a solution to the energy and emvironmental problems.

Olkiewicz et al. (2012) [12] evaluated the suitability of different types of wastewater sludges (primary, secondary, stabilized and blended) for biodiesel production. They extracted lipids in a Soxhlet extractor, using hexane as a solvent and converted lipids into biodiesel by acid catalyzed transesterication. The highest lipids and biodiesel yields were obtained from primary sludge. Pastore et al. (2013) [14] obtained the maximum yield of fatty acid methyl esters (18 w%) by a new two-step approach based on hexane extraction carried out directly on dewatered acidified sldge followed by methanolysis of extracted lipids.

Olkiewicz et al. (2014) [13] explored an alternative method, the direct liquid-liquid extraction because of the high cost of sludge drying and dewatering steps. In this method, hexane was used as an organic solvent after pre-acidification in batch mixer settler reactor at room temperature. The results of this study demonstrated that higher lipid yield (27%, dry sludge) was obtained from primary sewage sludge via direct liquid-liquid extraction technique, whereas 25% (dry sludge) of lipid was produced by using the standard method.

Until now, studies in biodiesel production from sludge have commonly focused on sludge drying methods requiring high costs and energy input, decrease the yield of lipids as well as the biodiesel production. The use of freeze-drying or conventional thermal drying to remove sludge water causes the loss of valuble organic compounds. These processes can also result in the loss of lipids in the sludge thus reducing biodiesel production yield. The alternative, direct liquid-liquid extraction method has rather limited information on the biodiesel production from sludge. Surprisingly, the direct liquid-liquid extraction of lipid from petroleum refinery oily sludge has neither been reported, so the sludge drying and dewatering can thus become unnecessary and the yield of biodiesel can increase due to the high concentration of fatty acids and lipids in petroleum sludge through this extraction method. This study focuses on the production of biodiesel from sewage sludge and oily petrochemical industry WWTP sludge by using direct liquid-liquid extraction method which does not require expensive sludge dewatering and drying processes. Compared to conventional reference drying method 5520E, liquid-liquid lipid extraction method makes the biodiesel production effective in terms of time, energy and cost. This research also includes application of pre-acidification to the sludges to show the effect of acid pre-treatment on biodiesel production.

Materials and Methods

Sludge Characterization

In the study, the sewage sludge samples were collected at the bottom of the primary clarifier and from the secondary clarifier of a municipal wastewater treatment plant located in İstanbul; whereas the oily sludge samples will be obtained from sludge thickening unit of the wastewater treatment plant of a petrochemical industry in Turkey. The plant has activated sludge unit for biological treatment. Sludge samples were characterized by measuring their total solid (TS), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), chemical oxygen demand (COD) and soluble chemical oxygen demand (sCOD) concentrations, viscosity and pH before and after the sludge pretreatments. All of the analyses were duplicated and conducted according to the Standard Methods of the Examination of Water and Wastewaters [16].

Sludge Acid Pre-treatment (Pre-acidification)

Sludge samples were used with and without pre-acidification in experiments to estimate the effect of the acid pre-treatment on the lipid extraction yields. The samples were acidified with 0.6 mL of concentrated hydrochloric acid (HCl) to reduce the pH to about 2, before the lipid extraction process.

Lipid Extraction

Reference sludge drying method

For a comparison study, sludge samples were dried according to standard method 5520E [16] to be the reference method. In the drying stage, sludge samples were acidified with hydrochloric acid before adding magnesium sulfate monohydrate for drying.

This drying method was studied because recent studies proved that when comparing with $MgSO_4.H_2O$ drying, the other drying methods show a decreasing result on both extracted lipids and potential biodiesel yield [13].

Direct liquid-liquid lipid extraction method

Direct liquid-liquid lipid extraction was performed sequentially by processing the 40 mL of sludge samples with hexane, in a 6-paddle mixer-settler batch reactor set at ambient temperature as described by Olkiewicz et al. (2014) [13]. The sludge samples were mixed with hexane at 200 rpm for 20 minutes and settled at 60 rpm for 15 minutes. First, the extraction was repeated up to 9 stages. Then, the extraction experiments continued with 4 and 3 stages for sewage sludge and petrochemical industry WWTP sludge samples throughout the study. After each consecutive extraction stage, samples were re-extracted with additional solvent and then the solvent phase was filtered using a 4μm filter paper to remove residual solids and dried by using anhydrous sodium sulfate. Later, the solvent was recovered using Soxhlet apparatus and reused in each sequential stage. Selection of suitable variables provided the optimisation of liquid-liquid extraction. After the extraction process, solvent was removed and lipids will be weighed to determine the extraction yield.

Transesterification / Lipid and biodiesel analysis

The lipids obtained from sludge samples will be converted into fatty acid methyl esters (FAMEs – biodiesel) via acid catalysed esterification/transesterification by modifying Christie's method [3]. The FAMEs will be analyzed by gas chromotograph-flame ionization dedector (GC-FID) and for the calibration of the method, a 37 component FAME standard mixture will be used. The results of the GC-FID will be used to determine the amount of saponifiable matters in extracted lipids and hence the mass of biodiesel produced from the sludge.

RESULTS AND DISCUSSION

Sludge characterisation

The sewage sludge samples were collected were collected from a municipal wastewater treatment plant located in Istanbul; whereas the petrochemical industry WWTP sludge samples were collected from a petrochemical industry located in Turkey. Sludge samples were analysed for TS, VS, COD, sCOD, viscosity and pH. The initial characteristics of the sludge samples are given in the Table 1.

Table 1. Characteristics of sludge samples used for different experiments in this work.

Parameter	Unit	Sewage Sludge		Petrochemical industry WWTP thickener sludge
		Primary sludge	Secondary sludge	
TS	%	4.2	1.3	3.4
VS	%	2.4	0.78	2.07
COD	mg/l	40280	8780	63220
sCOD	mg/l	3090	2240	10800
Viscosity	mPa.s	8	6.4	29.2
pH	-	6.2	6.1	6.8

Effect of extraction methods on the lipid yield

As previously mentioned, the water content of sludge was found to be a limiting factor in the biodiesel production process. For this reason, the liquid-liquid extraction method and standard drying method were investigated by using wet (raw) sludge in this study. The lipid yields extracted from the two types of sewage sludge and three types of petrochemical industry sludge using standard $MgSO_4.H_2O$ drying and direct liquid-liquid extraction methods are presented in Table 2. The values represent the average of at least three different samples collected in WWTP during several months.

Table 2. Lipid yields obtained from standard drying and liquid-liquid lipid extraction methods.

<table>
<tr><th colspan="2" rowspan="2">Sludge type</th><th rowspan="2">Extraction method</th><th colspan="2">Lipid yield (%)[a]</th></tr>
<tr><th>Acidified</th><th>Non-acidified</th></tr>
<tr><td rowspan="4">Sewage Sludge</td><td rowspan="2">Primary sludge</td><td>Standard drying method[b]</td><td>24</td><td>22.8</td></tr>
<tr><td>Direct liquid-liquid extraction method</td><td>19.7</td><td>10.5</td></tr>
<tr><td rowspan="2">Secondary sludge</td><td>Standard drying method[b]</td><td>7.2</td><td>6.5</td></tr>
<tr><td>Direct liquid-liquid extraction method</td><td>2.9</td><td>1.6</td></tr>
<tr><td colspan="2" rowspan="2">Thickener petrochemical sludge</td><td>Standard drying method[b]</td><td>20.3</td><td>18.2</td></tr>
<tr><td>Direct liquid-liquid extraction method</td><td>31.2</td><td>27.3</td></tr>
<tr><td colspan="5">[a] Each value is the average of at least 3 samples collected on different days.
[b] Extraction according to standard $MgSO_4.H_2O$ method, lipid yield on the basis of dry sludge.</td></tr>
</table>

The results of the study showed that, in both of the lipid extraction methods. Pre-treatment (pre-acidification) increased the lipid yields obtained from the sludge samples noticably. The highest lipid yield was obtained from pre-acidified petrochemical industry sludge by using liquid-liquid lipid extraction method. Compared to conventional reference drying method, direct liquid-liquid lipid extraction method is found to be more efficient for petrochemical industry (oily) sludge samples. However, standard dry lipid extraction method was more effective for sewage sludge samples. As seen in the table, both extraction methods from the secondary sewage sludge is not so efficient for extraction of lipids present in the sludge. Therefore, experiments for this study were conducted over the primary sewage sludge and thickener petrochemical sludge.

Effect of Solvent Type on the Lipid Yield of Sewage Sludge

In the lipid extraction step, different solvents were used to determine the most appropriate solvent type resulting with the highest lipid yield. For this purpose, hexane, petroleum ether, chloroform, and toluene were used to extract the lipids from primary and secondary sludges.

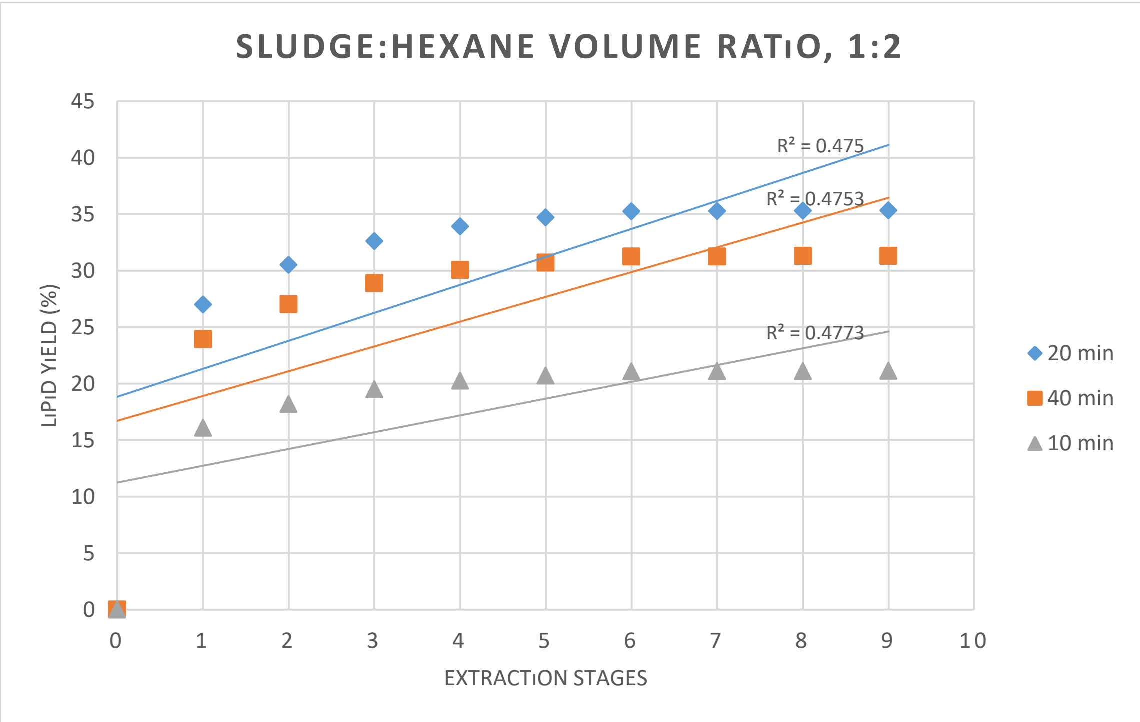
Table 3. Effect of different solvents on the lipid yield obtained from primary and secondary sewage sludges.

	LIPID YIELD (%)			
	Liquid-Liquid Method		**Drying Method**	
Solvent Type	Primary sewage sludge	Secondary sewage sludge	Primary sewage sludge	Secondary sewage sludge
Hexane	19.35	2.7	24	7.2
Petroleum ether	13.4	2.27	23.8	11.9
Chloroform	12.3	1.27	23.1	10
Toluene	11.3	1.3	22.9	10.33

The results showed that lipid extraction using hexane as a solvent gave the highest yield, then followed with petroleum ether in the liquid-liquid lipid extraction method for both of the sewage sludges. In dry lipid extraction method, the lipid extraction performance of all of the solvents were almost same for primary sludge samples. In this study, hexane was used as solvent in both liquid-liquid and dry lipid extraction methods.

Optimisation of the Liquid-Liquid Lipid Extraction Method

The optimisation of lipid extraction from acidified primary sewage sludge and petrochemical WWTP sludge samples was performed for 9 stages at different contact times of 10, 20 and 40 minutes and different sludge to hexane volume ratios of 2:1, 1:2 and 1:1. The experiments were performed at ambient temperature by using 40 ml of sludge samples. Figure 1 and 2 show the results of the optimisation of the lipid extraction process.



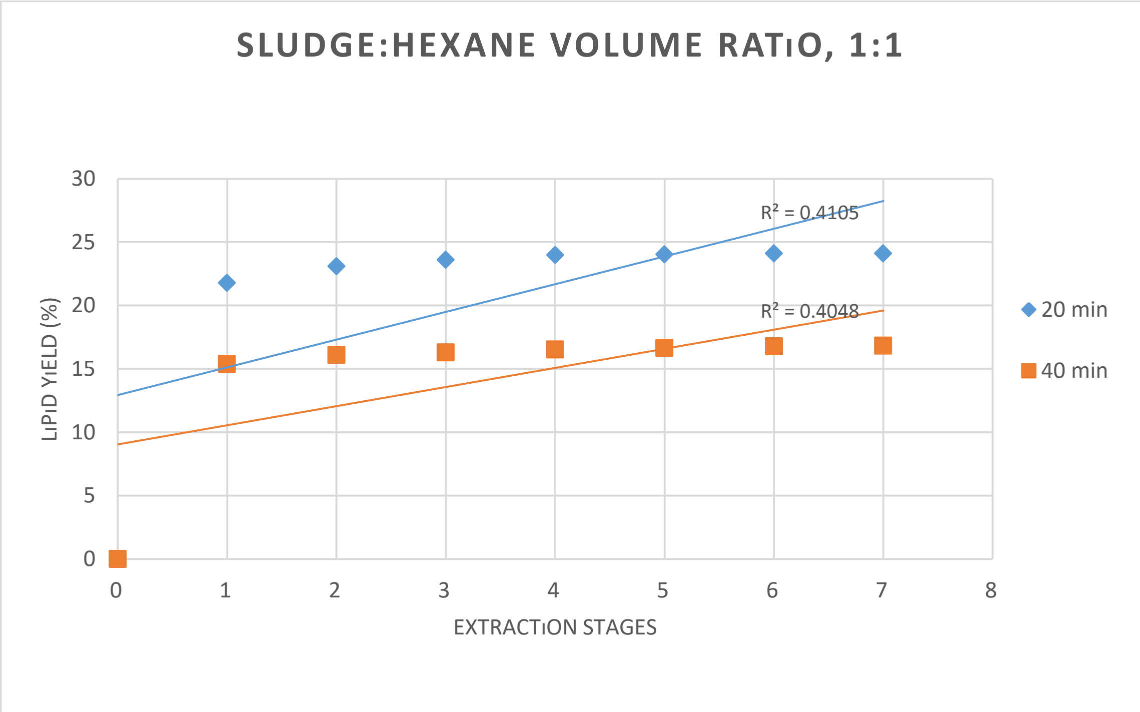


Figure 1 Effect of extraction time on the lipid yields of petrochemical thickener sludge with different sludges to hexane volume ratio

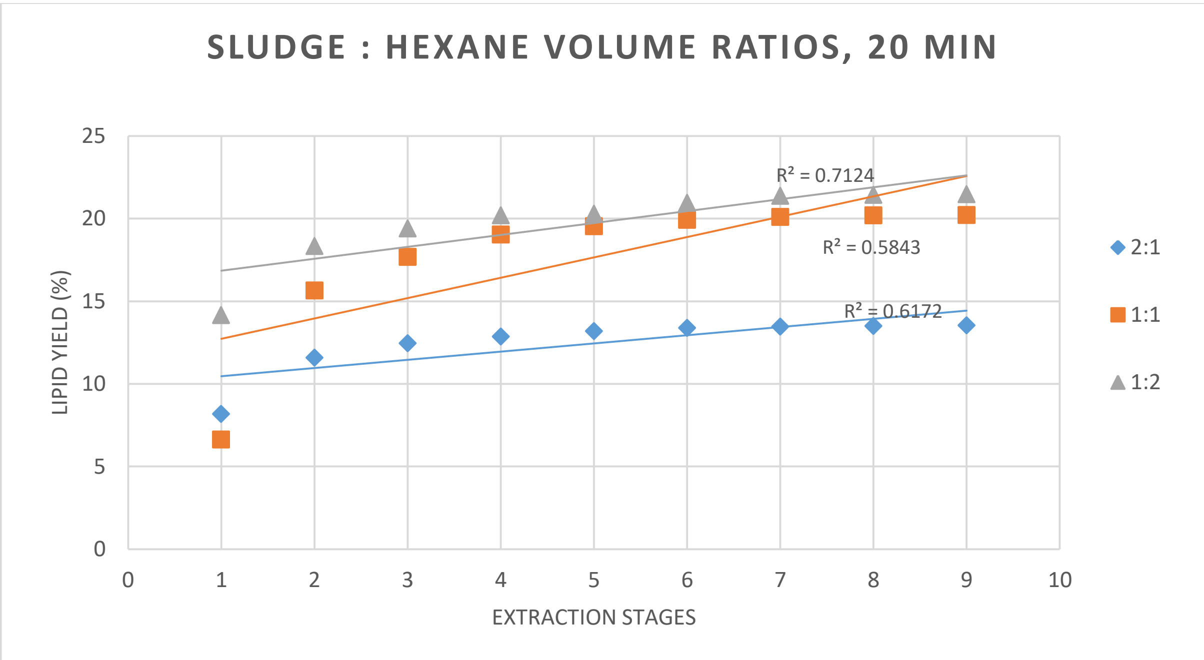


Figure 2 Effect of different sludges to solvent volume ratios on lipid yields obtained from primary sludge

The results of lipid extraction optimization studies showed that the amount of the increase in lipid yield decreased gradually in each extraction stage and lipid extraction was then terminated at the end of the 9th step. The optimum extraction step numbers were selected to be three and four for petrochemical industry sludge and primary sewage sludge, respectively. The optimisation study also demonstrated that, after three extraction stages, 92% of lipid from thickener sludge and after four extraction stages, 94% of lipid from primary sewage sludge were recovered. According to Olkiewicz et al. (2014) [13], three sequential extraction steps are enough to achieve 91% of lipids existing in wastewater sludge samples. The highest lipid yields were obtained at 1:2 sludge to hexane volume ratio for the 20 min mixing time for both of the sludge samples. The mixing time plays an important role in terms of lipid extraction yield. Based on the results of the optimization studies, the lower the amount of solvent, the lower the lipid extraction yield was attained. The lowest lipid yields were obtained at sludge to hexane volume ratio of 1:1 for thickener sludge and 2:1 for primary sewage sludge, suggesting that the amount of hexane was not enough to extract high quantities of lipid in the sludge.

Biodiesel Production

The results of lipid transesterification from primary and thickener sludges were presented in Table 4. The biodiesel (FAME) yields of the lipids extracted from standard drying extraction method and direct liquid-liquid extraction method were %14.5 and %14.7 (on the basis of lipid) for the acidified primary sludge, and 14.1% and 22.15% (on the basis of lipid) for the acidified thickener sludge. The highest lipid and biodiesel yields were obtained from pre-acidified petrochemical industry sludge by using liquid-liquid lipid extraction method. Compared to conventional reference drying method, direct liquid-liquid lipid extraction method is found to be more efficient for petrochemical industry sludge samples. Although, standard drying lipid extraction method was more effective for sewage sludge samples, biodiesel yield was higher than that of the standard drying method in liquid-liquid extraction method.

Table 4. extraction and transesterification yields of sludge samples.

Sludge type	Extraction method	Yield (%)$^{(a)}$	Non-acid.	Acid.
Primary sewage sludge	Standard drying method$^{(b)}$	Lipid	22.8	24
		Biodiesel	12.5	14.5
	Direct liquid-liquid extraction method	Lipid	10.5	19.7
		Biodiesel	5.25	14.7
Petroleum thickener sludge	Standard drying method$^{(b)}$	Lipid	18.1	20.3
		Biodiesel	12.55	14.1
	Direct liquid-liquid extraction method	Lipid	27.3	31.2
		Biodiesel	18.8	22.15

(a) All transesterification experiments were performed at least twice.
(b) Extraction according to standard $MgSO_4.H_2O$ method, lipid yield on the basis of dry sludge.

Conclusions

The results have indicated that municipal sewage sludges and petrochemical industry WWTP sludges have high lipid content and can be used as lipid feedstocks for biodiesel production. However, secondary sewage sludge samples were found to be an inefficient to be used as lipid feedstock for biodiesel production. Direct liquid-liquid lipid extraction method resulted with higher lipid and biodiesel yields for petrochemical industry WWTP sludge samples than that of obtained by standard drying method. Furthermore, almost the same biodiesel yields were achieved for primary sewage sludge by both of the extraction methods. Pre-acidification has also showed an increasing effect on the lipid and biodiesel yields. Using direct liquid-liquid extraction method, eliminating sludge drying or dewatering steps, reduces the total cost of biodiesel production process. Furthermore, biodiesel production from sludge decreases the amount of waste sludges produced in WWTPs, requiring expensive handling and disposal methods. The optimization studies of lipid extraction improves both lipid/biodiesel yield and economy of the whole process.

Acknowledgments

This study has been supported by the Research Fund of Boğaziçi University (Project No: 10580).

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