Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.801788

52 (2014) 2996–3003
April

Taylor & Francis
Taylor & Francis Group

Treatment of oily wastewater from waste glycerol by acidification and the coalescer process

Hor Kosal[a], Wachirapan Pattanachot[b], Chaisri Suksaroj[a,*]

[a]*Faculty of Engineering, Department of Civil Engineering, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand*
Tel. +66 74287116; Fax: +66 74459396; email: schaisri@eng.psu.ac.th
[b]*Department of Material Science and Technology, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand*

Received 24 December 2012; Accepted 17 April 2013

ABSTRACT

In this study, treatment of grease and oil (G&O) and other impurities in waste glycerol from biodiesel production was performed by a two-step process, by acidification and the coaleser process. 1 M hydrochloric acid (HCl) was used to acidify waste glycerol to destabilize the emulsion and remove the suspended solids (SS), soap and methyl ester. For acidification, a pH of 6 was selected, before testing with coalescer. The study was investigated with a wide range of factors and parameters including two media materials (polypropylene (PP) and polyethyleneterephthalate (PET)), two configure shapes (granular and fiber), pH (3–6), bed height (50–150 mm), and flow rate (5–18 dm^3/h). The results of the study in the same experiment conditions showed, PP media material gave better results than PET media materials where the fiber sharp material performed better than the granular sharp material. G&O concentration of treated waste glycerol reduced to 0.081 g/L under operating conditions with 120 mm bed height, 5 dm^3/h flow rate and PP fiber media.

Keywords: Acidification; Biodiesel; Coalescer; Emulsion; Waste glycerol

1. Introduction

In general, the transesterification process of biodiesel production produces about 10% glycerol as a by-product in every unit of biodiesel produced [1]. The total world production of biodiesel reaches up to 10.8 million tons per year [2], which means about 1.08 million tons of glycerol per year is produced, too. While the glycerol refinery demand market is limited, we are faced with the problem of managing this waste. It was reported that waste glycerol contains very high impurities include a pH of 9.7–10.4, chemical oxygen demand (COD) of 1,700–1,900 g/L, biological oxygen demand (BOD) of 900–1,200 g/L, total suspended solid of 213–387 g/L, and grease and oil (G&O) of 3.77–5.35 g/L [3]. Accordingly, treating waste glycerol by biological treatment is very difficult.

Waste glycerol has less economic value and due to its impurities, it is harmful to discharge into the environment [4]. To minimize the negative effects and to also make use of glycerol, research has been proposed to utilize this waste in several ways. For example, waste glycerol was used to convert to various of valuable chemical products such as 2-propanediol [5],

---

*Corresponding author.

dihydroxyacetone, succinic acid, propionic acid, citric acid, pigments, polyhydroxyalcanoate, biosurfactants [6,7] and polymers (poly ester) [8]. It has also been used to produce Hydrogen by a steam reforming process [9,10]. Other researchers reported using glycerol to produce ethanol [11,12] and methanol [13]. It has also been reported that glycerol can be used directly for animal feed to replace grain when corn production is down [14,15]. There are also the applications of waste glycerol as a co-digester to improve methane gas production [16] and as a co-substrate to enhance hydrogen and methane production [17].

However, Xie et al. [3] proposed a treatment method as a proper way to dispose waste to the environment to reduce water pollution as well as being able to reuse some organic matters by acidification and coagulation processes.

Acidification was used to destabilize the emulsion as well as used as part of the pretreated process. Xie et al. [3] used HCl to naturalize and destabilize the waste glycerol in order to separate the impurities and recover them. Rattanapan et al. [18] used this process to destroy the oil emulsion in waste water from biodiesel processing before using the coagulation process. Krit et al. [19] also used acidification to break emulsion and recover oil and fatty acids before using the coagulation process.

To enhance the phase separation of oil from water, the coalescer process was widely applied. It has been reported that the coalescer process has a high efficiency in treating oily waste water and emulsion [20,21]. Coalescer, an improved filtration system, is a commonly used system to separate liquid-liquid dispersion and emulsion. The principle of the coalescer process is to accelerate the merging of small droplets to enlarge the diameters of droplets, which increases the buoyant force enabling them to float to the surface. The mechanism of coalescence can be described in three simple steps; collecting individual droplets on the surface of the medium, coalescing droplets and detaching them from the medium surfaces. The media is considered to be a vital part of coalescence, as it enhances the overall performance of the coalescing process and their selection can be based on its wetting conditions, being hydrophilic or hydrophobic [22–24]. Moreover, their size and shape, which is normally fiberous or granular also effects the coalescing efficiency due to their surface area [25]. Besides, the mechanism of the coalescer process is the key in developing it to reach the optimum removal result. Regarding that, many studies have investigated the performance of different geometries including the horizontal bed, vertical bed, step bed, pip in pipe, etc. The operation conditions (flow rate, wastewater types, pressure drop, pH) and media configuration (type of material, shape, size, bed length, density and porosity) have also been studied [22,24,26]. Sokolovic [21] pointed out that the advantages of coalescers are that they are easy to install, maintain and automatize, while its disadvantage is that the bed needs to be replaced from time to time depending on the concentration of particles in the effluent.

In this work, the coalescer process is used to enhance the removal of G&O of waste glycerol after acidification. The efficiency of both the acidification and coalescer process were investigated and will be presented separately.

2. Materials and methods

2.1. Material

2.1.1. Waste glycerol

Waste glycerol was taken from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Faculty of Engineering, Prince of Songkla University, Thailand. The plant uses alkali-catalyzed transesterification to produce bio-diesel from waste cooking oil and palm oil as feed stock. The concentration of COD, BOD_5, total suspended solids (TSS) and G&O, were analyzed by following the Standard Method (APHA, AWWA and WEF. 2005). The other concentrations of parameters were analyzed with different methods; total glycerol (ASTM D7637, 2010), soaps (AOCS 1996), and the pH value was measured by the pH meter, Hanna (HI 98140).

2.1.2. Coalescing material

The characteristic of the coalescing medium are shown in Table 1 below.

2.2. Experiment set up and operation process

2.2.1. Acidification

(a) To study the role of acidification affect, the pH value was adjusted by hydrochloric acid (HCl) 1 N. The pH values of raw waste glycerol were adjusted to a range of 3–9 to study the appropriate value for pre-treating grease, oil and soap;
(b) Parameters analysis—an appropriate pH range for acidification was selected which provided a concentration of G&O, COD, TSS, and soaps.
(c) The appropriated treated waste glycerol with pH was taken to the next process.

Table 1
Characteristic size of the coalescing media

Coalescing medium	Granular		Fiber	
	PET	PP	PET	PP
Characterize medium size (mm)	1.5–2	1.5–2	0.3−0.8	0.3−0.8
Surface energy (mN/m)	44.4	30	44.4	30
Bulk density (kg/m^3)	950	467.54	206.95	189.15
Porosity	0.21	0.21	0.8	0.8

2.2.2. Continuous coalescer operation

The apparatus for the coalescence treatment process consisted of a feed tank, a peristaltic pump and a vertical-column coalescer. The column had a 60 mm inner diagram and was 400 mm in height. It was divided into three parts: an inlet section (100 mm in height), a coalescence section (150 mm in height) and a settling section (150 mm in height). Fig. 1 shows the schematic diagram of the experimental set up.

In the coalescer process, samples from the acidification process with the chosen pH were used for the study. The sample was mixed by a stainless steel impeller then forced by a peristaltic pump into the coalescer. The experiments were done in a steady state condition at room temperate. The samples were taken at 45 min during a 1 h run of the experiment. The samples were acidified to pH 2 before analyzed for oil content. The efficiency of the oil removal in this process was calculated based on the following expression:

$$\text{Efficiency}\ (\%) = [(C_i - C_e)]/C_i \times 100 \qquad (1)$$

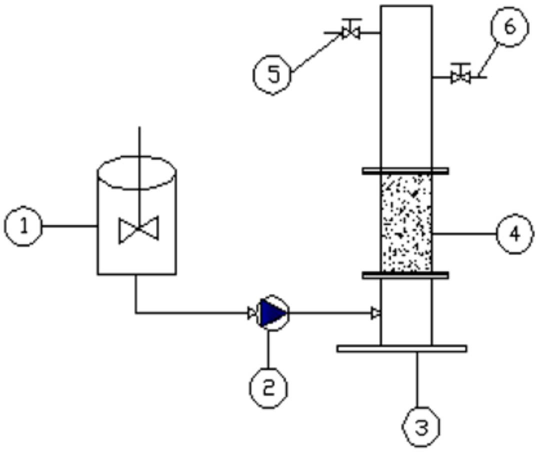

Fig. 1. Schematic diagram of coalesce apparatus in the experiment (1) feed tank; (2) peristaltic pump; (3) coalescer body; (4) medium section; (5) oil discharge; and (6) effluent outlet.

where C_i is the inlet G&O concentration (after acidification) and C_e, the effluent concentration of G&O.

3. Results and discussion

3.1. Characteristics of waste glycerol

The glycerol contains high impurities such as G&O, glycerol, suspended solids (SS), soap and methanol. For example, waste glycerol has a high pH > 9, COD has about 1,630–1,850 g/L, G&O is around 230–337 g/L, total glycerol is around 385–450 g/L and TSS is around 10.5–20.4 g/L (as shown in detail in Table 2). Since these numbers of impurities are very high, it makes waste glycerol harmful to dispose in any environment; moreover, it cannot be used for fuel as it contains water. The BOD/COD ratio is too small, being inadequate for biological treatment; therefore, a pretreatment is recommended prior to the following treatment. Furthermore, the high content of TSS (oily sludge) makes it unsuitable for the coalescence process as the SS (oily sludge would be absorbed on the interface of emulsion by the repulsion force of different charges of solid particles and oil–water emulsion, which prevents the droplets from colliding or intercepting with the media [27]. Therefore, acidification is needed to demulsify the droplets.

3.2. The role of acidification on COD, G&O removal

Waste glycerol was acidified with 1 M HCl to a pH from 3 to 9 in order to study the effect of acidification on G&O removal from waste glycerol. As the next step of the study (coalescer process) is mainly to improve only G&O removal, G&O, and COD are the important characteristics to be analyzed in this step. Thus this step analyzed G&O and COD after the acidification samples were taken.

Raw waste glycerol has high pH, soap, and free fatty acids keeping it in a very stable emulsion form. When the acid was added, it first reacted with the alkali remaining from the esterification, then it reacted with the soap and formed into salt and free fatty acid.

Table 2
Some basic characteristics of waste glycerol before and after treatment at the optimum condition

Parameter		Raw glycerol	After treatment	Oil terminal effluent standards of Thailand
	Unit	Value	Value	Value
pH		9.12– 9.86	6.0	5.5–9.0
COD	g/L	1,630–1,850	550	0.2
BOD_5	g/L	700–1,100	379	0.06
G&O	g/L	230–337	0.081	0.015
TSS	g/L	10.5–20.4	0.15	0.06
Total glycerol	g/L	385–450	350	–
Soap	ppm	200,000–230,000	2,300	–

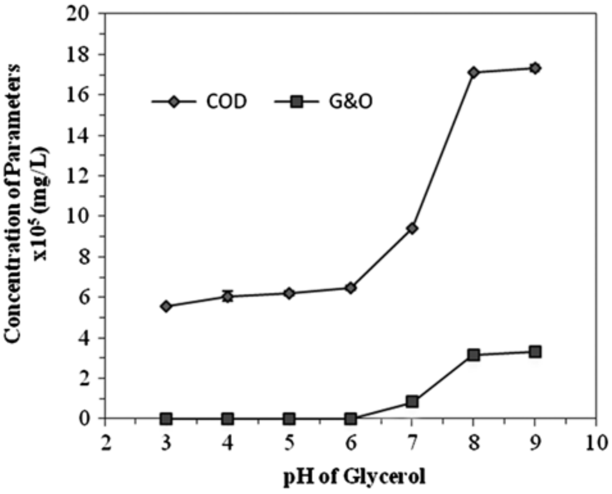

Fig. 2. Effect of acidification on COD and G&O.

At pH = 9, the appearance did not change much, but when the pH dropped from 9 to 8 the appearance started to change, however, the value of COD and G&O did not change much as shown in Fig. 2. When the pH reduced from 8 to 6, the emulsion broke down and the solution separated into layers; the lower layer was predominantly aqueous with glycerol since glycerol is soluble in water, and the upper layer consisted of soap, methyl ester and free fatty acid. The concentration of G&O and COD slightly decreased when the pH reduced from 6 to 3.

3.3. *The role of acidification on soap and TSS (oily sludge) removal*

To see how acidification affected soap and TSS characteristic change in the waste glycerol, samples from both lower and upper layers were taken to analyze the soap and samples were taken from just the lower layer to analyze TSS. The change of soap concentration is shown in Fig. 3 and the change of concentration of TSS is shown in Fig. 4. Two distinct layers could be seen when the pH was between 7 and 3, whereas there was no layer separation when the pH was above 7. The soap concentration response with the pH decreased as the pH was reduced. This demonstrated that the soluble soaps were converted to salts and unassociated free fatty acids. Fig. 3 shows that most of the soaps were in the upper layer, this was a result of soaps with negative charges being absorbed to the interface of the water-in-oil emulsion in the upper layer.

TSS (oily sludge) could also explain the presence of soap, G&O that remained in the aqueous layer. Fig. 4 shows that when the pH decreased from 9 to 8 the concentration of TSS increased dramatically. This was mainly because when pH reached 8, the waste glycerol began to produce an emulsion that absorbed solid particles at the oil/water interface forming oily sludge, and as the pH continued to reduce from 7 to 3 the emulsion destabilized causing TSS (oily sludge) to

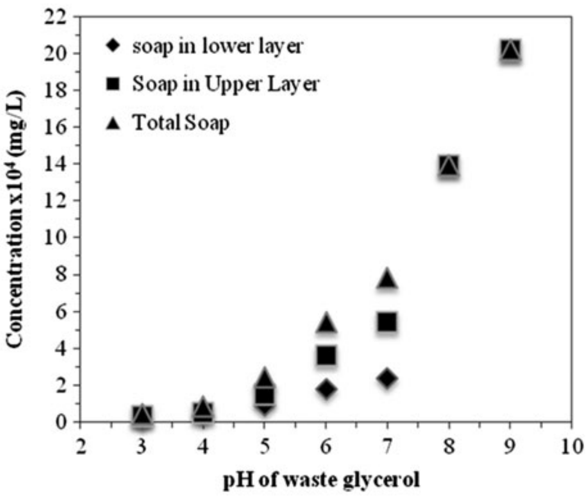

Fig. 3. Effect of acidification on soap.

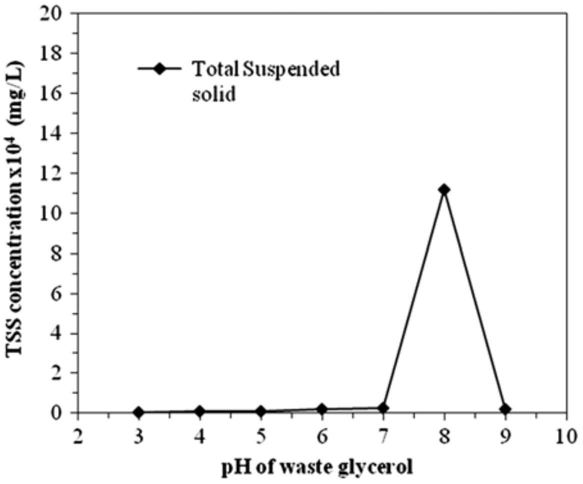

Fig. 4. Effect of acidification on suspended solid (oily sludge).

mainly separate to the top layer, whereas in the lower layer it slightly decreased.

3.4. The coalescer process

3.4.1. Effect of oil concentration

The effect of G&O on the coalescence efficiency was investigated by a variety of pH during the acidification process. The amount of oil present in the aqueous phase solution was different, it increased when the pH was raised. The investigation was conducted with the range of pH being 3–6. The condition for the process was set with a fix flow rate of 5 dm^3/h, a PET fiber bed height of 90 mm, and run in room temperature. As presented in Fig. 5 with different concentrations of inlet G&O concentrations which shown by pH value, the removal efficiency of G&O increased while the inlet concentration also increased. It can be understood that when there was an increase of inlet oil concentration, higher oil droplets would be present in the solution flowing through the column.

This would increase the chance of the oil droplets colliding and the chance of interception between the oil and surface of media getting saturated faster, which would result in better coalescence. However, since the concentrations of G&O investigated were lower than 1,500 mg/L, the coalescence caused by interception with the surface of the media, is most likely to be dominant [25].

As shown in Fig. 6, the concentration of COD at each pH slightly decreased. This result reflects to the fact that the coalescer process is a physical process which mainly improves the removal of G&O from the influent. For this reason, it will not effect the concentration of soluble matters in the influent after passing this process. Thus, the concentration of COD is likely to persist. As the process is a pre-treatment process, the concentration of COD after the process is still considerably high so the effluent required the secondary treatment.

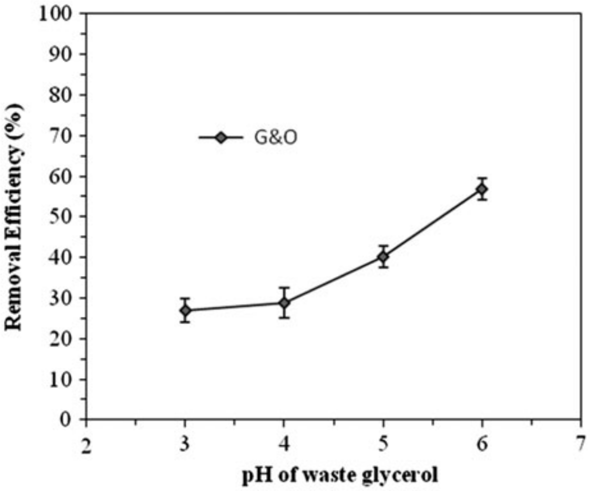

Fig. 5. Effect of different pH in acidification process on G&O removal efficiency in coalescer process at fixed bed high 90 mm, PET granular media and flow rate 5 dm^3/h.

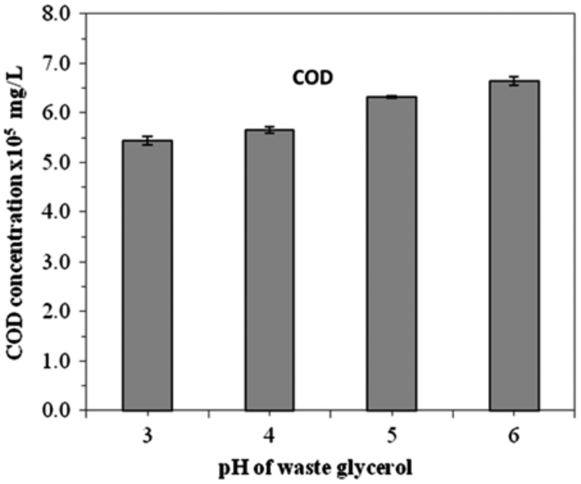

Fig. 6. Effect of different pH in acidification process on COD concentration in coalescer process at fixed bed high 90 mm, PET granular media and flow rate 5 dm^3/h.

3.4.2. Effect of bed height

To study the effect of media bed height to the G&O removal, the experiment was investigated with a fixed flow rate of 5 dm^3/h and various bed high ranges of 50, 70, 90, 120 and 150 mm. Two material types were investigated, polypropylene (PP) and polyethyleneterephthalate (PET), which are in two forms, granular and fibrous. All materials were conducted in the same experiment conditions. As shown in Fig. 7, the optimum G&O removal obtained at the 120 mm bed high in the four media of PP fiber, PET fiber, PP granular and PET granular had a removal efficiency of 81.80, 77.68, 65.03, and 59.18% respectively.

The results showed that when the bed high increased from 50 to 120 mm, the Oil removals increased from 56.33 to 81.80% in PP fiber media and then decreased to 79.29% when the bed high reached 150 mm. It was observed that after passing the bed height of 120 mm (the critical height), the efficiency decrease. This finding was also suggested by other similar research [28]. At beyond the critical bed high, coalesced oil drops that have occurred in a previous bed, may redisperse.

The nature of the coalescing material does affect the coalescing process [22]. Fig. 7 describes this nature. From this Fig. 7, it can be seen that the material made from PP performed better than the material made from PET in the same investigated experiment conditions. This effect could be varied by the difference of material surface energy because PP has a lower surface energy resulting in higher wetting conditions with oil, and thus it can absorb the droplets and coalesce later.

Within the same material, the results showed that in the same experiment conditions different shapes give different results. From above, the results of the two types of materials investigated, all proved that fibrous material gives a better result than granular ones. Fibrous material is smaller in size and has a larger surface area that can improve the contact surface for the oil drops.

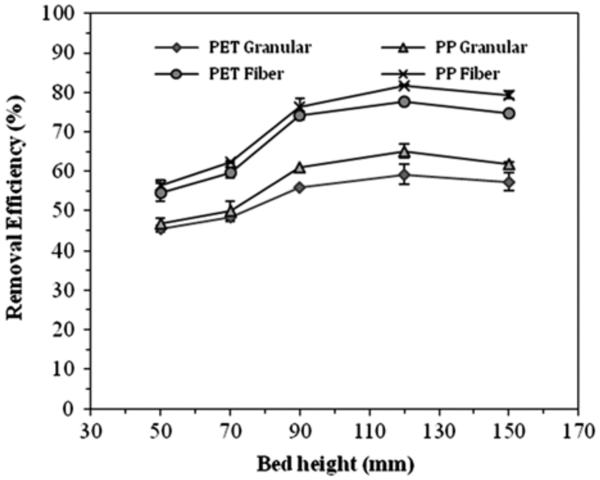

Fig. 7. Dependence of G&O removal efficiency of different material for different bed high in fixed flow rate 5 dm^3/h and pH = 6 in acidification.

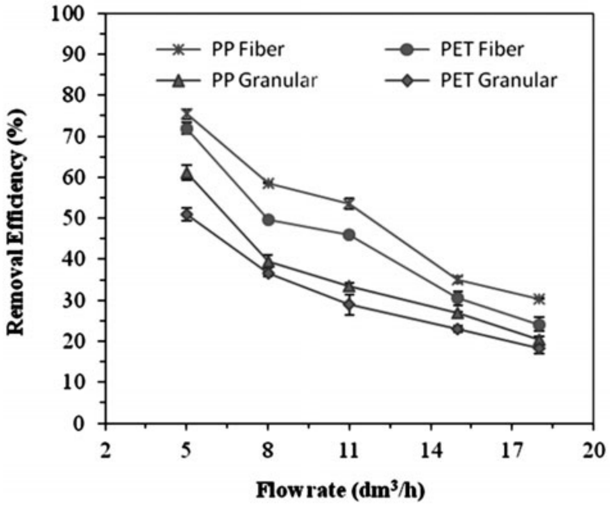

Fig. 8. Depend of removal efficiency in various flow rates at fixed bed high 90 mm.

3.4.3. Effect of flow rate

Flow rate has a very significant effect on oil coalescence [29]. The influence of flow rate on different media was investigated with four media, PET fiber, PET granular, PP fiber, and PP granular at a fixed bed high of 90 mm and a flow rate range of 5, 8, 11, 15, and 18 dm^3/h. The results shown in Fig. 8 demonstrate that at lower flow rates the result is better for all the media investigated. The results obtained for all four media, PP fiber, PET fiber, PP granular, and PET granular at flow rate 5 dm^3/h were 75.38 ± 1.63, 71.97 ± 1.93, 61.12 ± 2.55 and 51.03 ± 2.14%, respectively, which then all decreased as the flow rate grew higher. This state might be best explained by understanding that oil drops can be held in media and coalesce when the retention time is longer. When the flow rate increased, the retention time decreased and as the fluid flow force is dominant, it can drag the oil globule with the flow. Fig. 9 demonstrates the change

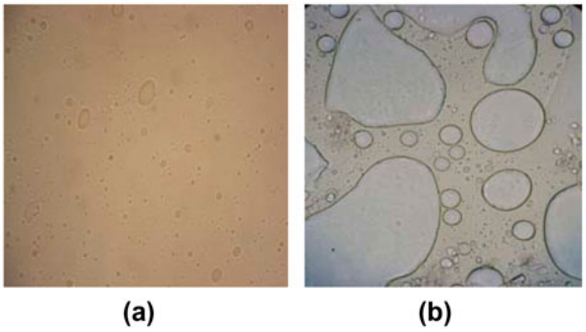

Fig. 9. Microscopic image of oil drops (methyl esther) 20× magnitude: (a) before passing the coalescer and (b) after passing the coalescer that collapsed on the surface.

of oil drops before and after the coalescer process. The image (a) shows small size oil drops present in waste after acidification, and image (b) shows oil drops collapsing on the top layer after passing the coalescer. This shows that the coalescer can be applied to improve the separation of dispersed oil.

4. Conclusion

The waste glycerol was treated in two steps. First, acidification was applied to break the emulsion and remove part of the impurities and at value $\mathrm{pH} = 6$ was found to be appropriated for next step process. Second, the coalescer was applied to promote the coalescing of the remaining oil.

Acidification can reduce the viscosity, SS and G&O prior to the coalescer process. The value of pH of waste glycerol should be adjusted to below six where parts of methyl ester can be recovered and reuse as raw material. The coalescer process can be applied to remove fractions of G&O remaining in the waste glycerol in dispersed forms. To reach the optimal performance of the coalescer process, the working conditions like flowrate, bed height and coalescence material should be taken into account.

This process can be very applicable in the growing of biodiesel industries for managing and disposal of waste glycerol. Moreover, this process can be applied for treatment of oily wastewater beyond the biodiesel industries.

After treatment, the ratio of BOD:COD of the effluent was about 0.68 which was an improvement and at this ratio it can be treated by biological process.

Acknowledgments

The authors would like to acknowledge the financial support from the Graduate School, Faculty of Engineering, Prince of Songkla University, and the Austria government for support through the ASEA-UNINET Thailand on the place scholarship program, and the Specialized R&D Center for Alternative Energy from Palm Oil and Oil crop, and the Faculty of Engineering, Prince of Songkla University, for providing wastewater samples.

References

[1] J. McNeil, Glycerine from biodiesel: The perfect diesel fuel, Process Saf. Environ. 90 (2012) 180–188.

[2] W. Thurmond, Biodiesel 2020: A Global Market Survey, 2008.

[3] Q.G. Xie, W. Taweeprada, C. Musikavong, C. Suksaroj, Removal of organic impurities in waste glycerol from biodiesel production process through the acidification and coagulation processes, Water Sci. Technol. 65 (2012) 1158–1163.

[4] J.V. Gerpen, Biodiesel processing and production, Fuel Process. Technol. 86 (2005) 1097–1107.

[5] Z. Yuan, J. Wang, L. Wang, W. Xie, P. Chen, Z. Hou, X. Zheng, Biodiesel derived glycerol hydrogenolysis to 1,2-propanediol on Cu/MgO catalysts, Bioresour. Technol. 101 (2010) 7088–7092.

[6] G.P. Silva, M. Mack, J. Contiero, Glycerol: A promising and abundant carbonsource for industrial microbiology, Biotechnol. Adv. 27 (2009) 30–39.

[7] P.F.F. Amaral, T.F. Ferreira, G.C. Fontes, M.A.Z. Coelho, Glycerol valorization: New biotechnological routes, Food Bioprod. Process. 87 (2009) 179–186.

[8] R.D. Ashby, D.K.Y. Solaiman, T.A. Foglia, Bacterial poly (hydroxyalkanoate) poly-mer production from the biodiesel co-product stream, J. Polym. Environ. 12 (2004) 105–112.

[9] H.P. Sabourin, G. Provost, High yield conversion of a crude glycerol fraction from biodiesel production to hydrogen by photofermentation, Bioresour. Technol. 100 (2009) 3513–3517.

[10] T. Ito, Y. Nakashimada, K. Senba, T. Matsui, N. Nishio, Hydrogen and ethanol production from glycerol-containing wastes discharged after biodiesel manufacturing process, J. Biosci. Bioeng. 100 (2005) 260–265.

[11] J.A. Posada, C.A. Cardona, Design and analysis of fuel ethanol production from raw glycerol, Energy 35 (2010) 5286–5293.

[12] B.R. Oh, J.W. Seo, S.Y. Heo, W.K. Hong, L.H. Luo, M.H. Joe, D.H. Park, C.H. Kim, Efficient production of ethanol from crude glycerol by a Klebsiella pneumoniae mutant strain, Bioresour. Technol. 102 (2011) 3918–3922.

[13] D. Goetsch, I.S. Machay, L.R. White, Production of methanol from the crude glycerol by-product of producing biodiesel, United States Patent, US7388034B1, 2008.

[14] S.S. Donkin, S.L. Koser, H.M. White, P.H. Doane, M.J. Cecava, Feeding value of glycerol as a replacement for corn grain in rations fed to lactating dairy cows, J. Dairy Sci. 92 (2009) 5111–5119.

[15] E.R. Carvalho, R.N.S. Schelz, H.M. White, P.H. Doane, S.S. Donkin, Replacing corn with glycerol in diets for transition dairy cows, J. Dairy Sci. 94 (2011) 908–916.

[16] S. Robra, R.S. Cruz, A.M. Oliveira, J.A. Almeida Neto, J.V. Santos, Generation of biogas using crude glycerin from biodiesel production as a supplement to cattle slurry, Biomass Bioeng. 34 (2010) 1330–1335.

[17] M.S. Fountoulakis, T. Manios, Enhanced methane and hydrogen production from municipal solid waste and agro-industrial by-products co-digested with crude glycerol, Bioresour. Technol. 100 (2009) 3043–3047.

[18] C. Rattanapan, A. Sawain, T. Suksaroj, C. Suksaroj, Enhanced efficiency of dissolved air flotation for biodiesel wastewater treatment by acidification and coagulation processes, Desalination 280 (2011) 370–377.

[19] N. Krit, K. Sasipan, C. Preeya, T. Ungsika, C. Sulalit, J. Pattaraluk, L. Prarinya, H. Mali, Remediation of biodiesel wastewater by chemical- and electro-coagulation: A comparative study, J. Environ. Manage. 92 (2011) 2454–2460.

[20] S. Maiti, I.M. Mishra, S.D. Bhattacharya, J.K. Joshi, Removal of oil from oil-in-water emulsion using a packed bed of commercial resin, Colloid Surf. A. 389 (2011) 291–298.

[21] R.M.Š. Sokolovic, D.D. Goverdarica, D.S. Sokolovic, Separation of oil-in-water emulsion using two coalescers of different geometry, J. Hazard. Mater. 175 (2010) 1001–1006.

[22] R.M.Š. Sokolovic, S.M. Sokolovic, Effect of the nature of different polymeric fibers on steady-state coaleser bed coalescence of an oil-in-water emulsion, Ind. Eng. Chem. Res. 43 (2004) 6490–6495.

[23] P. Painmanakul, K. Kongkangwarn, N. Chawaloesphonsiya, Treatment of oily wastewater by fibrous coalescer process: Stage coalescer and model prediction, World Acad. Sci. Eng. Technol. 58 (2009) 317–322.

[24] T. Ban, M. Shibata, F. Kawaizumi, S. Nii, K. Takahashi, Enhancement of phase separation using a drop coalescer in an aqueous two-phase system, J. Chromatogr. B 760 (2001) 65–72.

[25] J. Li, Y. Gu, Coalescence of oil-in-water emulsions in fibrous and granular beds, Sep. Purif. Technol. 42 (2005) 1–13.

[26] H. Speth, A. Pfenning, M. Chatterjee, H. Franken, Coalescence of secondary dispersions in fiber beds, Sep. Purif. Technol. 29 (2003) 113–119.

[27] K. Arnold, Emulsions and Oil Treating Equipment, Elsevier Inc., 2008.

[28] R.M.Š. Sokolovic, T.J. Vulic, S.M. Sokolovic, Effect of bed length on steady-state coalescence of oil-in-water emulsion, Sep. Purif. Technol. 56 (2007) 79–84.

[29] R.M.Š. Sokolovic, S.M. Sokolovic, B.D. Dokovic, Effect of working conditions on bed coalescence of an oil-in-water emulsion using a polyurethane foam bed, Ind. Eng. Chem. Res. 36 (1997) 4949–4953.