The 10th International PSU Engineering Conference
May 14-15, 2012

Enhancement of Oil Removal from Biodiesel Washing Wastewater by Coalescer Process

Hor Kosal[1], Chaisri Suksaroj[2]
[1, 2]Department of Civil Engineering, Faculty of Engineering, Prince of Songkla University,
Hat Yai, Songkhla 90112
E-mail: schaisri@eng.psu.ac.th[2]

Abstract

Oily waste water from Biodiesel washing process treated by acidification and coalescer process was studied in the Lab scale. Two types of wastewater samples from different washing methods, with and without adding acid, were compared in terms of their characteristic. The result showed that wastewater from washing with tap water by adding acid has comparably low concentration of impurities. In the study of treatment process, sulfuric acid (1N H_2SO_4) was used in acidification to convert soaps into free fatty acid and salt which could be recovered after treatment. After 15 min of retention time; the lower layer was taken to treat with coalescer unit. The coalescer unit aimed to improve the coalecscence of dispersed oil droplets which could reduce the retention time after acidification. The result showed that at pH=2, the enhancement of G&O, COD and TSS were improved from 85-95.6%, 65%-66.9% and 96-98% for wastewater from washing process with addition of acid and 96.21%-98.98%, 64.14%-64.50% and 94.51%- 98.98% for wastewater from washing process without addition of acid respectively. This result showed that coalescer unit can enhance the oil separation process which also can reduce to shorter retention time.

Key Words: Biodiesel wastewater, oil-in-water emulsion, acidification, coalescer

1. Introduction

The global energy consumption rises up very year. This trend leads to non-renewable energy resources allocation depletion while it threatens the global environment. To secure the future energy consumption for the sustainability development, the renewable energy is the hope. Biodiesel is currently one of the promising renewable energy sources. From 2006- 2008, the global production of biodiesel increasing from 250 million gallons per year to 650 million gallons per year[1]. In Biodiesel production process, the washing off the impurity of methyl ester (biodiesel) is unavoidable. In very 100L of biodiesel produced, 20- 120 L of water is being used which resulting in high concentrated of oil wastewater[2]. With the conventional washing process with water, the reported of characteristic of waste water were pH =8.5-10.75, suspended solid(SS) range 1,500-28790mg/L, chemical oxygen demand (COD) range 60,000 – 588,800mg/L, biological oxygen demand (BOD) range 105,000 – 300,000 mg/L and Grease & Oil range 7,000 – 22,000 mg/L [3, 4]. With the present of high concentrated of Grease & Oil, the waste his inhabit of microorganism which made it most likely impossible or maybe very difficult to biologically treated [2].

Currently, various treatment processes have been proposed. Suehara et al. (2005)[2] studied the biological treatment process by using oil degradable yeast Rhodotorula mucilaginous. The result showed that 97% oil was degraded. In their study Siles et al.(2011)[5], used physical-chemical and biomethanization treatment process. The wastewater was first acidified by sulfuric acid to acidic phase to remove free fatty acid then neutralize by NaOH before treated by coagulation- flocculation and electro coagulation to demulsified the remaining organic matters. The result showed that 45% and 63% of COD was reduced after the first pretreatment of acidification- coagulation and flocculation while 98% COD reduced with acidification-electro coagulation and anaerobic biodigestion and yielded 297 mL/CH_4 COD_{remove} (at 1 atm, 0 ^oC) of methane. By their result, It could be suggested that the combination of acidification- electro coagulation with anaerobic digestion is to appropriate for treat wastewater from biodiesel production process. Rattanapan et al. (2011)[6] enhanced efficiency of Dissolved air flotation (DAF) for biodiesel wastewater treatment process by acidification and coagulation process. They pointed out that DAF alone could not separate Grease and Oil from wastewater. The efficiency of DAF after acidification and alum coagulation was found to be 85-95% of grease and oil removal and 20% and 40% of COD with 20%-30% and 40%-50% DAF recycle rate used. Furthermore, suspended solid were all remove by the process with $\geq$ 150 mg/L of alum dose. Chavalparit and Ongwandee (2009)[7] by using electro-coagulation process, showed that in the optimum conditions of pH 6.06, voltage 18.2 V and 23.5 min reaction time, the efficiency was found to be 55.43%, 98.42% and 96.59% of COD, G&O, and SS were removed. Besides Jaruwat et al. (2010)[8] by using the combination of chemical recovery and electrochemical treat approach, showed that in the first stage of treatment by sulfuric acid to pH range 2.5-6, the portion of recovery was found to be 6-7 % (w/w) while BOD, COD and G&O were reduced by 13-24% , 40-74% and 87-98% respectively which depend on pH value. In the second step of treatment, the aqueous rich phase was then treated by electro-oxidation with or without the addition of NaCl at the optimal 0.061 M, the result showed greater than 95% of BOD and 100% of COD and grease and oil were effectively removed within 6, 7 and 2 h by applying current density of 4.28 mA/cm^2. Due to the variety of characteristics of waste water used in these studies, to point out best method in all term of benefits might be inaccurate.

Coalescer have been reported that have a high efficiency of treating oily waste water and emulsion [9, 10]. Coalescer, an improved filtration system, is a commonly used system to separation liquid-liquid dispersion and emulsion. Its principle is to accelerate the merging of many small droplets to the larger in diameters droplets which increase the buoyant force and be able to float to the surface. The simple steps of coalescence in the system are collecting individual droplets on the surface of medium, coalescing droplets and detaching from the medium surfaces. Media is a vital part of coalescer which enhances the overall performance of coalescing process. Media selection can be based on its wetting conditions hydrophilic or hydrophobic.[11-13] . Its size and shape which normally fiber or granular is also effecting the coalescing efficiency due to their surface area [14]. Beside, the mechanism of coalescer is the key in developing it to reach the optimum removal result. Regarding to that, many studies investigate the performance of different geometries include horizontal bed, vertical bed, step bed, pip in pipe etc. The operation conditions (flow rate, waste water types, pressure drop, pH) and media configuration (type of material, shape, size, bed length, density and porosity) were also being studied [11, 12, 15]. Solokovic (2010)[9] pointed out that the advantages of coalescers are easy to install, maintain and automatize while its disadvantage is that the bed need to replace time to time which depend on the concentration of particle in effluent.

In this work, coalescer is used to enhance the separation of oil droplets after demulsifying by acidification. The aim of this work is to apply the coalescer to improve the oil droplets coalescence chances which could shorten the separation time.

2. Material and Method

2.1 Wastewater

Biodiesel wastewater was taken from 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 produced bio-diesel from waste cooking oil and palm oil as feed stock. Two different samples were taken from two different washing methods, with and without addition of citric acid.

2.2 Measurement

The wastewater characteristics were analyzed by following Standard Method (APHA, AWWA and WEF. 2005)[16]. The grease and oil was analyzed by Soxhlet Extraction Method, total Suspended Solid was analyzed by Dried at 103- 105 ^{0}C, the COD was analyzed by Open Reflux Method and the pH value was measured by pH meter HACH (Sention1).

2.3 Experiment set up

The apparatus for coalescence treatment process consist of a feed tank, a peristaltic pump and a vertical column coalescer. The column has 60 mm inner diagram and 400 mm in height which divided into three parts, inlet section (100 mm in height), coalescence section (150 mm in height) and settling section (150 mm in height). The figure 1 shows the schematic diagram of the experimental set up.

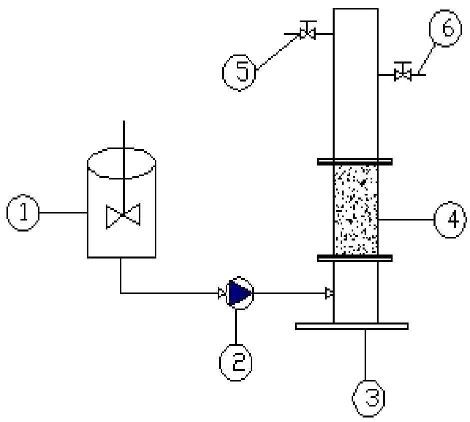


Figure 1. Schematic diagram of coalesce apparatus in the experiment (1) Feed Tank; (2) Peristaltic pump; (3) Coalescer body; (4) Medium section; (5) Oil discharge; (6) Effluent outlet

Table 1 Characteristic of the PET granular bed

Characteristic	Value
Density (kg/m^3)	1410
Bulk density (kg/m^3)	950
Porosity (%)	21.5
Granular average diameter (mm)	2

The wastewater was first adjusted pH by 1N Sulfuric acid (H_2SO_4) before passing coalescer. After acidified, the mixture was mixed by rapid mixing at the rate of 300 rpm for 10 min to allow complete reaction then left for 15 min to allow separated layers and being removed. The lower layer was mixed in low speed by stainless steel impeller then forced by peristaltic pump into coalescer. Micro droplets of oil were captured by the granular media in the coalescer forming the oil film on surface of media.

Table 2 Characteristic of wastewater before and after treatment

Parameter	Raw Wastewater		After Acidification		After Acidification & Coalescer	
	Value[1]	Value[2]	Value[1]	Value[2]	Value[1]	Value[2]
pH	8.5-10.5	5.34-5.82	2.0	2.0	2.0	2.0
COD (mg/L)	60,000-150,000	38,800-42,000	53,066	13,792	52,533	13,332
BOD_5 (mg/L)	30,000-60,000	19,500-22,000	NA	NA	NA	NA
G&O (mg/L)	15,000- 20,200	5,100-8,500	626.50	1,010	168.5	226
TSS (mg/L)	1,500-5,700	5,000-5,200	310	163	57.5	127
Soap (ppm)	12,637	1,950	NA	NA	NA	NA

*Value[1] Characteristic of wastewater from washing process without adding acid
*Value[2] Characteristics of wastewater from washing process of biodiesel with adding acid
* NA: Not Analyzed

The large droplets sheared off upward by buoyancy force and rise to surface of the column where it collapse and form oil layer.

3. Result and Discussion

3.1 Comparison of wastewater characteristic from two difference washing methods

Water washing of biodiesel generally is carried out to wash out the undesired product like soap, catalyst, methanol and other impurities by using deionized water or tap water. In some case, acid was added to improve the removal of catalyzed and decompose soap form[17]. As shown in **Table 2** below, the characteristic of waste water from the two washing methods are dramatically different. The value of pH was greater than 8.5 consist of high concentrate of grease and oil and other organic matters. For instance, the grease and oil was around 15,000-20,200 mg/L, TSS was around 1,500-5,700 mg/L and COD was around 60,000-150,000 mg/L wastewater from washing process without addition of acid. On the other hand, the characteristic of wastewater from washing process with acid addition decrease. For example, pH value was about 5.34-5.82, Grease and Oil was 5,100-8,500 mg/L and COD was around 38,000-42,000 mg/L. The main cause of the different of these two characteristic was due to its original pH value. In the washing process with tap water without adding acid, the produced water form a strong and stable emulsion where the dispersed oil droplets were stabilized by soap surfactant.

3.2 Effect of pH on grease and oil removal

When acid was added into wastewater, the soaps were converted to free fatty acid and salt. As the result shown that when the pH drop from original pH to 5 and below, dispersed oil drop start to coalescence to form larger drop size. This phenomenal was the hydrogen proton from hydrochloride acid was first neutralized the catalyst and then replaced the sodium ion of the free fatty acid soap which then converted to free fatty acid. Once the soaps were removed from interfacial surface of oil droplets, small oil droplets tend to merge together to reduce its surface energy. The larger drops size were separated to top layer which significantly be remove for reusing as raw material.

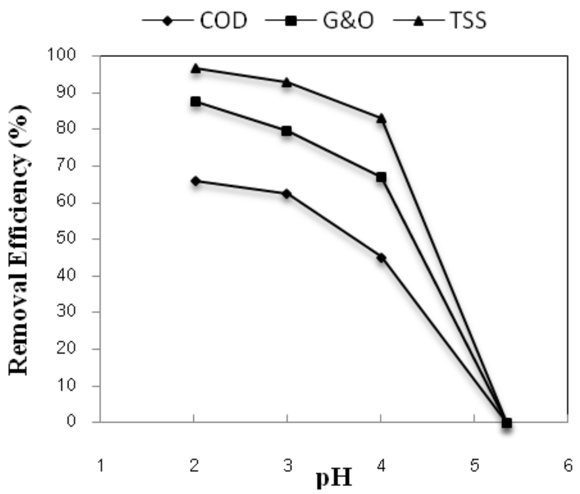


Figure 2. Effect of pH on the removal efficiency of COD, G&O and TSS after acidification on waste water from washing process with acid adding

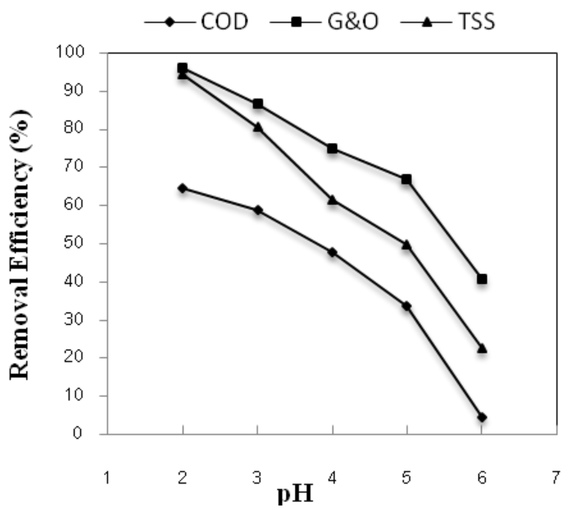


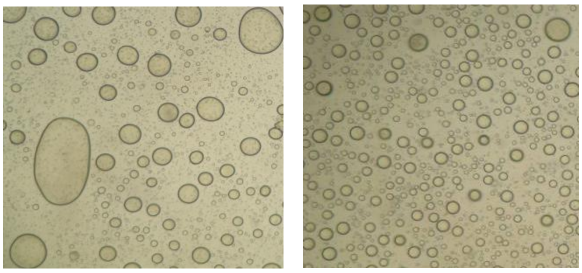
Figure 3. Effect of pH on the removal efficiency of COD, G&O and TSS after acidification on waste water from washing process without acid adding

The ratio of oil removal was functioning to the pH value. In **Figure 2** shown that the lower the pH, the higher grease and oil removal efficiency can be obtained. In the case of, waste water from washing process with addition of acid, the grease and oil removal efficiency jump up from 66% to 80% when pH drop from 4.0 to 2.0, while the removal of COD were also increase from 50% to 65%. Similarly, the removal efficiency of grease and oil and COD also increase due to pH value decrease for wastewater from washing process without addition of acid. As shown in **Figure 3**, at the higher pH=6.0 the grease and oil removal efficiency was only 44.87% while at the lower pH=2.0 the removal efficiency can reach as high as 96.21%.

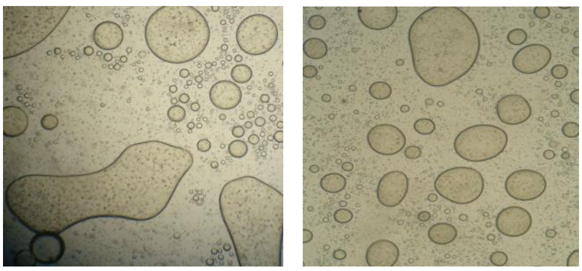
The settling retention is also play a significant role in this separation process. After acidification the micron oil droplets still suspend in the lower layer (water-rich phase) for several days to complete separation (data not shown) which also found by other authors in similar study [3, 6].

3.3 Effect of pH on grease and oil removal by Coalescer

The study of the enhancement of the coalescence was conducted in the same operation condition with vertical coalescer. The flow rate was 5 dm^3/L operated under the steady state regime. The coalescing bed property was the PET granular bed and has 50 mm height. The wastewater after acidification with 15 min settling time was then passed through coalescer column. As demonstrate in **Figure 4**, the oil drops sizes were merged together to form larger drop size after it passed the coalescer.



(a) (b)



(c) (d)

Figure 4. Microscopic Image (8x) of droplets coalescence after acidification and coalescer at pH 2 (a, c) and 4 (b, d); (a, b: after acidification; c, d: after coalescer)

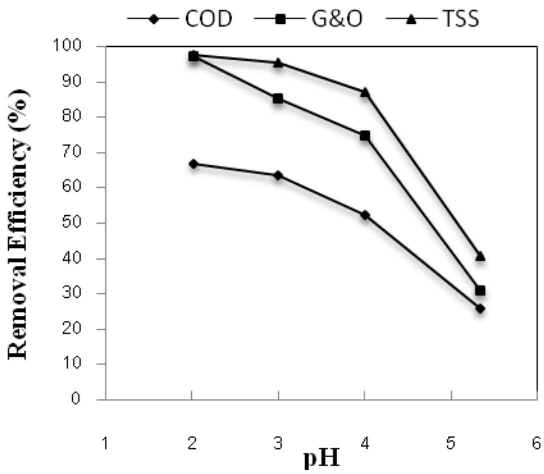


Figure 5. Effect of pH on removal efficiency by acidification and coalescer process on COD, G&O and TSS on waste water from washing process with acid adding

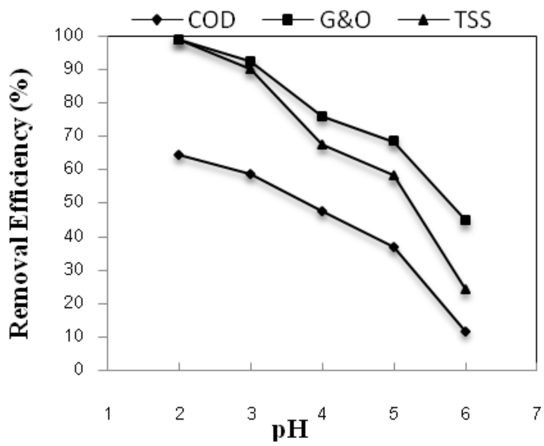


Figure 6. Effect of pH on removal efficiency by acidification and coalescer process on COD, G&O and TSS on waste water from washing process without acid adding

These larger droplets then separated from the aqueous phase. The result demonstrated that as efficiency was fluctuated with the efficiency of acidification process. In all tested of pH value, the result were in the same manner which the efficiency increased as the pH value decrease. As shown in **Figure 5** and **Figure 6**, the efficiency can reach 97.5% at the lowest pH value 2.0 which was 17.5% improved after the acidification in case of wastewater from washing process with acid addition. The improvement also found in case wastewater from washing process without acid adding. The efficiency reach 98.98% of grease and oil removal at the same pH=2.0.

The mechanics of coalescer can be explained that the dispersed oil droplets were capture by the granular media by the direct or indirect interception due to the wettibility surface (hydrophobic) nature of media while it form oil film on the surface. The aggregated oil droplets tend to minimize its surface energy[18].

4. Conclusion

The method of washing biodiesel has a significant effect of the wastewater it produced. The wastewater from washing process which added acid to it has less impurity than the one washing with just only water. This can be vital for the consideration of treatment process choices.

In the study of enhancement of oil removal after acidification with coalescer, the oil removal efficiency can be increased by 10% for wastewater from washing process with acid addition and about 3% for wastewater from washing process without acid addition respectively within the same 15 min retention time after acidification at pH=2. It can be suggested that coalescer can improve grease and oil removal and reduce to very short retention time in both wastewater. This could be the great benefit for reducing the operation cost of wastewater from biodiesel production treatment process. However, further tested need to be done for coalescer with this type of wastewater in term of its operation conditions and media material in order to achieved the optimum efficiency.

Acknowledgements

This research was financially supported by the Graduate School, Faculty of Engineering, Prince of Songkla University, Thailand. We would like to thank Austria government for support through the ASEA-UNINET Thailand on place scholarship program and we also want to thank the Specialized R&D Center for Alternative Energy from Palm Oil and Oil crop, Faculty of Engineering, Prince of Songkla University, Thailand for providing us wastewater sample.

Reference

[1] http://www.emerging-markets.com/biodiesel/.

[2] Suehara K. I., Kawamoto Y., Fujii E., Kohda J., Nakano Y. and Yano T. 2005. Biological treatment of wastewater discharged from biodiesel fuel production plant with alkali-catalyzed transesterification. Bioscience and Bioengineering, 100: 437-442.

[3] Aneak S., Wirach T., Udomphon P. and Chaisri S. 2009. The Effect of pH on the Stability of Grease and Oil in Wastewater. Proceeding in The 10th Annual Conference of Thai Society of Agricultural Engineering, Surasammanakhan, Suranaree University of Technology, Nakhon Ratchasima, Thailand, 2009.

[4] Ngamlerdpokin K.K., Sasipan C., Preeya T., Ungsika C., Sulalit J., Pattaraluk L., Prarinya H. and Mali. 2011. Remediation of biodiesel wastewater by chemical- and electro-coagulation:A comparative study. Environmental Management , 92: 2454-2460.

[5] Siles J.A., Gutiérrez M.C., Martín M.A. and Martín A. 2011. Physical–chemical and biomethanization treatments of wastewater from biodiesel manufacturing. Bioresource Technology, 102: 6348-6351.

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

[7] Chavalparit O. and Ongwandee M. 2009. Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology. Environmental Sciences, 21: 1491-1496.

[8] Jaruwat P., Kongjao S. and Hunsom M. 2010. Management of biodiesel wastewater by the combined processes of chemical recovery and electrochemical treatment. Energy Conversion and Management, 51: 531-537.

[9] Soković R.M., Govedarica D.D. and Soković D.S. 2010. Separation of oil-in-water emulsion using two coalescers of different geometry. Hazardous Materials , 175: 1001-1006.

[10] Maiti S., Mishra I.M., Bhattacharya S.D., Joshi J.K. 2011. Removal of oil from oil-in-water emulsion using a packed bed of commercial resin. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 389: 291-298.

[11] Radmila M.. S.S. and Slobodan M. S. 2004. Effect of the Nature of Different Polymeric Fibers on Steady-State Bed Coalescence of an Oil-in-Water Emulsion, Ind. Chem. Eng. and Res. 43: 6490-6495.

[12] Takahiko B., Masamichi S., Fumio K., Susumu N. and Katsuroku T. 2001. Enhancement of phase separation using a drop coalescer in an aqueous two-phase system. Chromatography, 760: 65-72.

[13] Pisut P., Kotchankorn. K., and Nattawin Chawaloesphonsiya. 2009. Treatment of Oily Wastewater by Fibrous Coalescer Process: Stage Coalescer and Model Prediction. World Acedemy of Science, Engineering and Technology, 58: 317-322.

[14] Li J. and Gu Y. 2005. Coalescence of oil-in-water emulsions in fibrous and granular beds. Separation and Purification Tec., 42(1): 1-13.

[15] Hauke S., Andreas P., Michael C. and Heinz F. 2002. Coalescence of secondary dispersions in fiber beds. Separation and Purification Technology , 29: 113-119.

[16] APHA A., WEF. 2005. Standard methods for the examination of water and wastewater. American Public Health Association, Maryland.

[17] Atadashi I.M., Aroua M.K. and Aziz A.A. 2011. Biodiesel separation and purification: A review. Renewable Energy, 36(2): 437-443.

[18] Bansal S., von Arnim V., Stegmaier T. and Planck H. 2011. Effect of fibrous filter properties on the oil-in-water-emulsion separation and filtration performance. Hazardous Materials, 190(1-3):45-50.