Treatment of Oil Emulsion from Biodiesel Processing Waste by Coalescer Process

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Thesis Title	Treatment of Oil Emulsion from Biodiesel Processing Waste by Coalescer Process
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ABSTRACT

In biodiesel production process, it produces two types of oily emulsion waste, waste glycerol and wastewater. These wastes are harmful to the environment and the discharge of these wastes can cause serious water pollution. Treatment of grease and oil and other impurities in waste glycerol from biodiesel production was performed by a two-step process, acidification and coalescer process. For acidification, a pH of 6 was performed, 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). PP media material gave better results than PET media materials whereas the fiber sharp material performed better than the granular sharp material. Grease and oil concentration of treated waste glycerol obtained was 0.081g/L under operating conditions with 120 mm bed height, 5 dm^3/h flow rate and PP fiber media. Similarly, wastewater was also treated by acidification and coalesce process. The acidification process is very efficient to transform the soap surfactants present in wastewater, by adjusting pH, soap can be converted to be salt and free fatty acid. pH was adjusted to 4.0 prior to the coalescer process. In coalescer process, it is very effective in removing the separated oil from the wastewater and small dispersed oil droplets which are stable in wastewater. However, the best result could be found in the optimum condition. At pH 4.0, the best performance of coalesecer was found at the flowrate of 5 dm^3/h, with the media bed height of 120 mm, and the PP fiber material. The study found that materials with different surface energy provide different state of coalesce. Moreover, the geometries of their shapes also have significant influence on coalescence performance.

Keywords—Acidification, Biodiesel, Coalescer, Emulsion, Waste glycerol, Wastewater

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

Introduction

1.1 Motivation

The global energy consumption rises up every 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. Currently, new form of renewable energy like wind energy, solar energy, thermal energy, wave energy etc. have been used widely around the globe; however, the limits of technology transferring and its high investment cost is a barrier of its success.

Biodiesel is currently one of the promising renewable energy sources. During 2000-2005, the world production and consumption of biodiesel grow in average of 32%. From 2006- 2008, the global production of biodiesel was increased from 250 million gallons per year to 650 million gallons per year[1]. In Thailand, because of the low cost of biodiesel production from palm oil, biodiesel become a promising energy for transportation sector [2]. The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil or animal fat and an alcohol to yield fatty acid alkyl esters (i.e., Biodiesel) and glycerol [3].

During the biodiesel production process, it produces wastewater and waste glycerol. Wastewater contains white muddy particle like milk cause by the oil emulsified in the water [4]. In the 100L of biodiesel fuel being produced generated 20L-120L wastewater [3]. Because of this wastewater is in the form of emulsion, so it was difficult to remove by the conventional grease and oil trap method [4]. Due to this kind of wastewater contain low biodegradable material which difficult to treat by conventional treatment plant and its low nutrient for microorganism so it is needed to remove grease and oil before treating by conventional treatment unit [4].

Waste glycerol, one of main streams separated after the transesterification, contains 50%-60% by weight of glycerol, 8%-12% of methanol, 12%-16% of soaps, 15%-18% of methyl ester, 9%-11% of water, 1%-3% of oil and grease and other components [5]. The disposal of waste glycerol can caused serious water pollution for its components. To minimize its causes, it has been suggested that the proper treatment to remove organic matters should be taken.

Acidification was used to destabilize the emulsion as well as used as part of the pretreated process. Xie at el. [6] used HCl to naturalize and destabilize the waste glycerol in order to separate the impurities and recover them. Sawain et al. [4] used this process to destroy the oil emulsion in wastewater from biodiesel processing before using the coagulation process. Krit et al. [7] also used acidification to break emulsion and recover oil and fatty acids before treating by 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 wastewater and emulsion [8, 9]. 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 [10]. Moreover, their size and shape, which is normally fiberous or granular also effects the coalescing efficiency due to their surface area [11, 12]. 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 [11, 13]. Solokovic [14] 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, 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.

1.2 Objectives of the work

- To study the pre-treatment of wastewater and waste glycerol from biodiesel production process by acidification and coalescer process.
- To compare the performance of coalescing media, polyethyleneterephthalate (PET) and polypropylene (PP), in enhancing the separation of grease and oil of the coalescer process.
- To evaluate the working condition of coalescer process.

1.3 Advantages

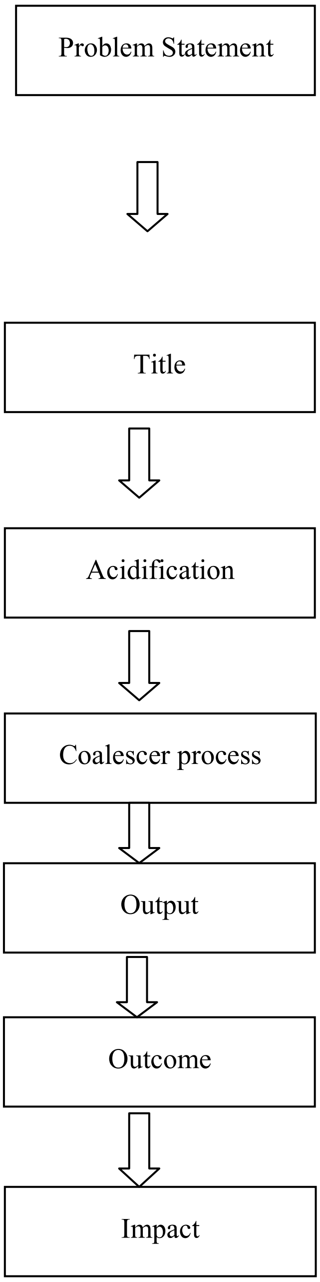
Since both Thailand and other countries biodiesel production increase year by year in order to secure energy consumption and environmental healthy, the amount of wastewater also increase. As this type of wastewater known as emulsion is not able to be treated by conventional method, the more economical and high efficiency should be developed.

Regarding to that matter, coalescer known as an inexpensive and high efficiency device is introduced to treat oil-in-water emulsion from biodiesel production process. Taking the benefit of material surface technology, it’s believed that suitable media use in the coalescer will greatly improve the performance.

Due to this process doesn’t involved coagulant, the removal oil property doesn’t contaminate and possibly can be reuse as raw material. Moreover, it’s believed that this coalescer also be able purify biodiesel by-product (Glycerol) at significant rate, though at the optimum successful condition will also test with glycerol in this study.

1.4 Scope of works

The structure of scope of study shown below:



Problem Statement	- Wastewater and waste glycerol from biodiesel contain high impurities and in form of emulsion. It can't be disposed directly to environment or treated by biological process.
Title	- Treatment of oil emulsion from biodiesel processing waste by coalescer process
Acidification	- Control variable: pH - Study: change of pH effecting on impurities
Coalescer process	- Control variable: pH, bed height, flowrate, - Fix variable: media type
Output	- Efficiency of grease and oil removal
Outcome	- Enhance separation of grease and oil in wastewater and waste glycerol
Impact	- Decrease the use of coagulants - Low operation cost - Reduce the size of the storage tank.

1.5 Summary

In this chapter 1, it presents the overall views of proposal of this thesis. It gives the specific reasons and significant of doing this particular research. The second part provides the objective of the research. The third section provides the benefits and advantages of the research. The fourth part shows the research scope.

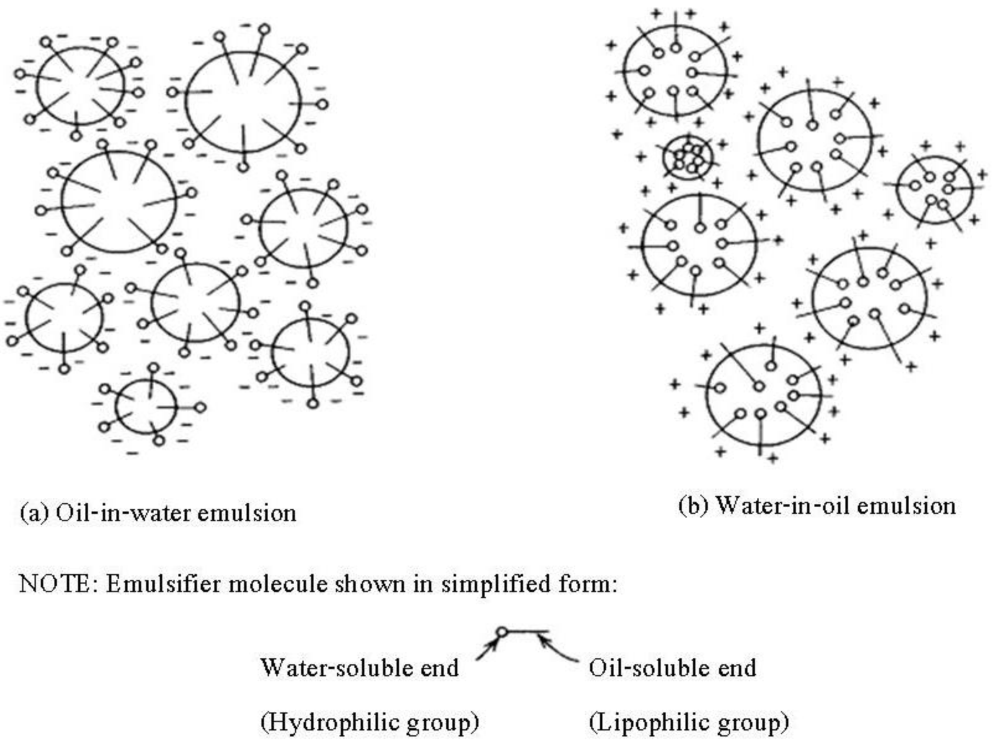
Chapter 2

Literature review

2.1 Research background

2.2 Overview of emulsion

In many industrial processes water and oil combine together and resulting in emulsion form. Oil-in water or water in oil emulsion and others contaminated substances can be found in various industries such as steel, machinery, automobile, petroleum, petrochemical, textile, paint, food processing, leather and etc., which form by different processes.



(a) Oil-in-water emulsion

(b) Water-in-oil emulsion

NOTE: Emulsifier molecule shown in simplified form:

Figure 2.1 Oil-in-water and water-in- oil emulsion [15]

Emulsion normally appear in two phases, oil and aqueous. When oil dispersed in water the term is Oil-in-water (O/W) emulsion, when water disperse into oil the term is water-in-oil (W/O) emulsion as demonstrates in **Figure 2.1**. These emulsions can be stabilized by three types of mechanisms: ionization, absorption and friction contact. Ionization happens when the surfactant which carried ionic charge interacts with the surface of emulsified droplets. Absorption occurs when the small particle attach to the interface of oil-water droplets. Frictional contact happens when the two phases oil and water mix together [16]

The application of oil-in-water emulsion is vary. It has been used in many industries like petroleum, pharmaceutical, food, polymer, agriculture, textile, paper, cosmetic and etc. The used emulsion is discharged in the form of wastewater. This wastewater due to its oil containing, is very harmful to the environment if it is not treated. Thus, it is very crucial to study the separation behavior of oil-in-water emulsion in order to keep our environment safe. In biodiesel production process particularly, waste emulsion can be found in the form of wastewater and waste glycerol. Water that use to wash the impurity in biodiesel, produce an emulsion which oil is the disperse phase and soap which occur during the reaction play as the surfactant to keep the disperse phase stable. In similarity, waste glycerol also appears in oil-in-water emulsion form [6].

2.3 Overview of biodiesel

2.3.1 Biodiesel production process and its washing process

There are two common methods to produce biodiesel in Thailand; transesterification technology and acid etherification technology. **Figure 2.2** shows the schematic diagram of the processes of biodiesel production.

Alcohol, oil feed and catalyst combine in the reactor for about 1 h at 60 ^{o}C. 80% of alcohol by weight was added in the first reaction. Glycerol is separate by gravity separation, in the separator where the rest 20% alcohol added, due to it insoluble with methyl ester. After separating from the glycerol, methyl ester enters a neutralization step then through methanol tripper and washing steps. Glycerol stream need to separate the excess ethanol by adding acid [17]

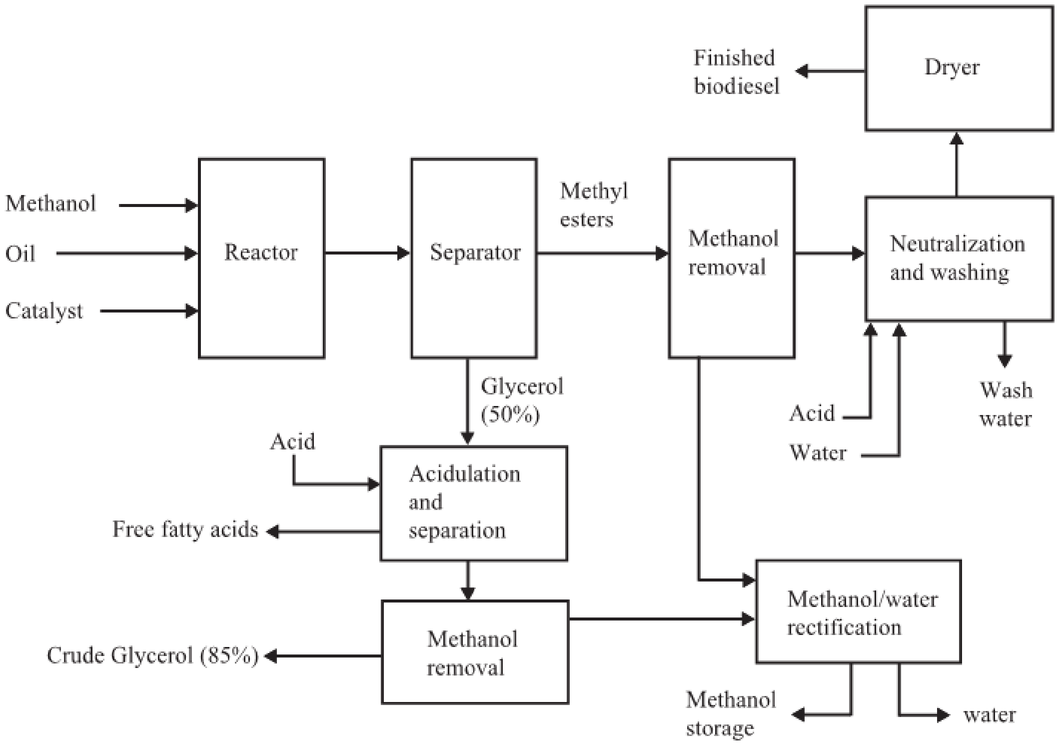


Figure 2.2 Process flow schematic for biodiesel production [17]

Alcohol used in the reaction can be methanol, ethanol, pro-panol, bu-tanol and amyl alcohol but since methanol and ethanol are low cost, these two are commonly used. In trans-esterificantion reaction, there are three type of catalyst can be used: enzymatic, acid and alkali catalyst. Alkali catalysts include NaOH and KOH are commonly used due to its short reaction time [18].

2.3.2 Advantages and disadvantages of biodiesel

Biodiesel has several main advantages and disadvantages as state below [19].

Advantages:

- Renewable fuel, obtained from vegetable oils or animal fats.
- Low toxicity, in comparison with diesel fuel.
- Degrades more rapidly than diesel fuel, minimizing the environmental conse-quences of biofuel spills.
- Lower emissions of contaminants: carbon monoxide, particulate matter, poly-cyclic aromatic hydrocarbons, aldehydes.
- Lower health risk, due to reduced emissions of carcinogenic substances.
- No sulfur dioxide (SO_2) emissions.
- Higher flash point (100 ^{o}C minimum).

Disadvantages:

- Slightly higher fuel consumption due to the lower calorific value of biodiesel.
- Slightly higher nitrous oxide (NO_x) emissions than diesel fuel.
- Higher freezing point than diesel fuel. This may be inconvenient in cold climates.
- It is less stable than diesel fuel, and therefore long-term storage (more than six months) of biodiesel is not recommended.
- May degrade plastic and natural rubber gaskets and hoses when used in pure form, in which case replacement with Teflon components is recommended.

2.4 Overview of wastewater from biodiesel washing process

The main source of wastewater comes from the final process of biodiesel production, since in this process water is being used to remove the impurities. The washing step is repeated for 2-5 times. For this reason, the large amount of wastewater is generated by 20-120 L per 100L of biodiesel fuel being produced [17]. The wastewater looked like a milky form, has a very high COD and contains mixed oils/fats disperses in water as oil-in-water emulsion which is difficult for the biological treatment [20]. According to several researches, the wastewater characteristic is shown in Table 2.1 below.

Table 2.1 Characteristics of the biodiesel wastewater [21]

Characteristics	**Value**
Chemical oxygen demand(COD) (g/L)	14.80-150.00
Grease and oil (g/L)	1.50-15.00
Biological Oxygen Demand (BOD_5)(g/L)	30.00-60.00
Glycerol (g/L)	1.36
Methanol (g/L)	10.66
SS (g/L)	0.34-5.00
Conductivity (µS/cm)	350
pH	8.9-10.5

2.5 Overview of waste glycerol

After separating for methyl ester, waste glycerol stream contain 50% of glycerol. It contain the excess methanol most of catalyst and soap. In this form, the glycerol has slightly value and difficult to disposal. Due to methanol content waste glycerol, glycerol considered to be hazardous waste. The characteristic of raw waste glycerol shows in **Table 2.2** below [22].

Table 2.2 Selected characterization of raw waste glycerol [22]

Characterization	Unit	Concentration
pH		9.7-10.4
COD	g/L	1,700-1,900
BOD_5	g/L	900-1,200
TSS	g/L	213-387
Oil and Grease	g/L	3.77-5.35
Total glycerol	g/L	413-477
Soaps	ppm	210,000-270,000
Methanol	g/L	112-203
Water	% by weight	9.3-11.9

2.6 Overview of acidification process

In biodiesel production process, the glycerol stream contains excess water, soap, catalyst and methanol. In which it makes the waste glycerol hazardous to be disposed into the environment, moreover, it can’t be utilized as burning material. Due to the occurrence of water, and the soap, it makes a good condition to form the strong emulsion which it can’t be separated by the conventional settling method. In the process, the acid was introduce to destabilize the emulsion by reacting with excess catalyzes and then transform soap surfactant into salt and fatty acid [23]. At this step, a large proportion of free fatty acid was able to separate due to the difference of density.

Acidification has been used to destabilize the emulsion in oily wastewater in order to improve the coalescence of oil drops. The pH has a significant effect on stability of the emulsion. By lowering pH, it provides hydrogen (H^+) ions for neutralization of negative charges surrounding oil in oil-in-water emulsions [15].

Acidification was used to destabilize the emulsion as well as used as part of the pretreated process. Xie at el. [6] used HCl to naturalize and destabilize the waste glycerol in order to separate the impurities and recover them. Sawain et al.[4] used this process to destroy the oil emulsion in wastewater from biodiesel processing before using the coagulation process. Krit et al. [7] also used acidification to break emulsion and recover oil and fatty acids before using the coagulation process.

2.7 Overview of the coalescer process

Coalescence filtration enhances the removal of smaller droplets of the dispersed phase from the continuous phase by facilitating their growth to form bigger drops. Coalescence filtration can be used where oil is to be separated from a compressed air stream. Similarly coalescence filtration is applied for secondary dispersions of immiscible organic liquids and water. Parameters used to evaluate the performance of coalescer filters are pressure drop across the filter media and separation efficiency of the fibrous bed.

Separation efficiency of the fibrous bed is found to be dependent on characteristics of the dispersion like density, viscosity, composition and droplet diameter. And also on properties of the fibrous bed like fiber diameter, material, and surface energy of the fibers. The factors that control the performance of coalescer filter media are wettability, surface properties of the fiber beds, direction of flow, pore size, electrokinetic properties of fiber, humidity, temperature, mixed fibers,arrangement of coalescer, bed permeability etc.

2.7.1 Introduction to coalescer

Coalescer, an improved filtration system, is a commonly used system to separate 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. Several researches have been done to investigate the performance of different materials in coalescing process [10]. Moreover, the medium size and shape which normally fiber or granular is also effecting the coalescing efficiency due to their surface area. Li and Gu [24] found that the higher surface area of the media, the better coalescing.

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, wastewater types, pressure drop, pH) and media configuration (type of material, shape, size, bed length, density and porosity) were also being studied [25]. Solokovic et al. [14] pointed out that the advantages of coalescers are easy to install, maintain and automatize while its disadvantage is that the bed needs to be replaced time to time which depend on the concentration of particle in effluent.

2.7.2 Current state of coalescer application

There are various parameters which important in the coalescers design. These parameters can be grouped into two main factors: fluid velocity (as it controls the capture, coalescence, and drainage) and bed length (determines the filter efficiency). In the fiber bed coalescer, the efficiency of coalesce is greatly dependent on the characteristic properties of the dispersion (e.g. composition, density, viscosity, droplet diameter) and on the fiber bed (e.g.

material, diameter, surface structure, porosity) [11]. The effects mentioned parameters have been investigated in the past and many generalizations are accepted in this field of research. The accepted generalizations summarize in the effects of the parameters from [26] are listed below:

1. The coalescer provide better performance efficiency while the pore size is degrease.

2. Reduction of fiber size from micron to submicron or nanofibers enhances the performance of coalescers as they have large surface area to volume ratio and smaller pores.

3. Increasing the flow velocity has a positive effect on overall performance of coalescers as it controls the capture mechanism and probability of droplet capture.

4. Emulsions with higher interfacial tensions coalesce better than lower interfacial tension.

5. Dispersed phases with larger mean particle size are found to coalesce more easily.

6. Lower viscosity of continuous phase helps in coalescence better than higher viscosity.

7. Influence of electrostatic potential barrier have a negative effect and can prevent coalescence.

8. Presence of surfactants and dirt tend to reduce the chance of coalescence of dispersed phase.

9. Higher temperature improves coalesce performance.

10. Intermediate values of surface energy of fibers perform better than high or low surface energy fibers in coalescing filters. This is generally accepted but very few data are reported in literature. However, many authors disagree on the effect of contact angle of the dispersed phase drops on the fibers.

2.8 Mechanism of coalescence

Coalescer is an inexpensive device for separating dispersed liquid or emulsion. It attracts more and more industries due to its low cost and high efficiency. It is used to accelerate the capturing and merging of the small droplets size to the larger drop size. Larger drops size help to increase the buoyancy force in the Stokes law equation. Larger drops size settling time in the downstream could be less than the smaller drop size. The mechanism of coalescer operation can be described in three steps [27]:

1) Droplets capture
2) Droplets coalescence and
3) Stokes settling

These steps can be illustrated in Figure 2.3 below.

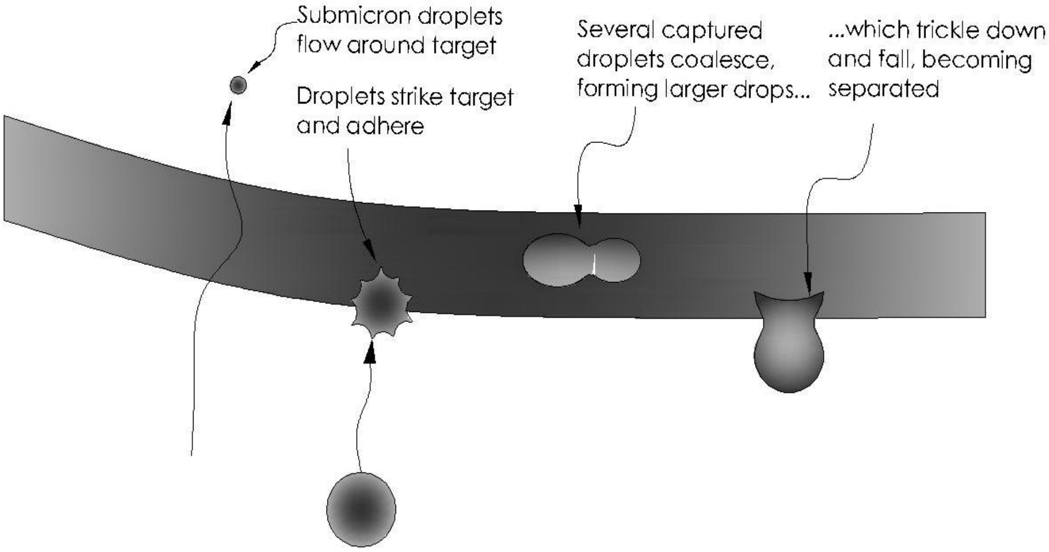


Figure 2.3 Illustration of 3 steps of droplets coalescence [27]

2.8.1 Droplets capture

The first stage of coalescence is collection of droplets either by intra Stokes media or direct interception. Direct interception happens when a droplet follows a stream around the target and when it reaches the distance of haft of its diameter, it colloid as illustrated in Figure 2.4 below.

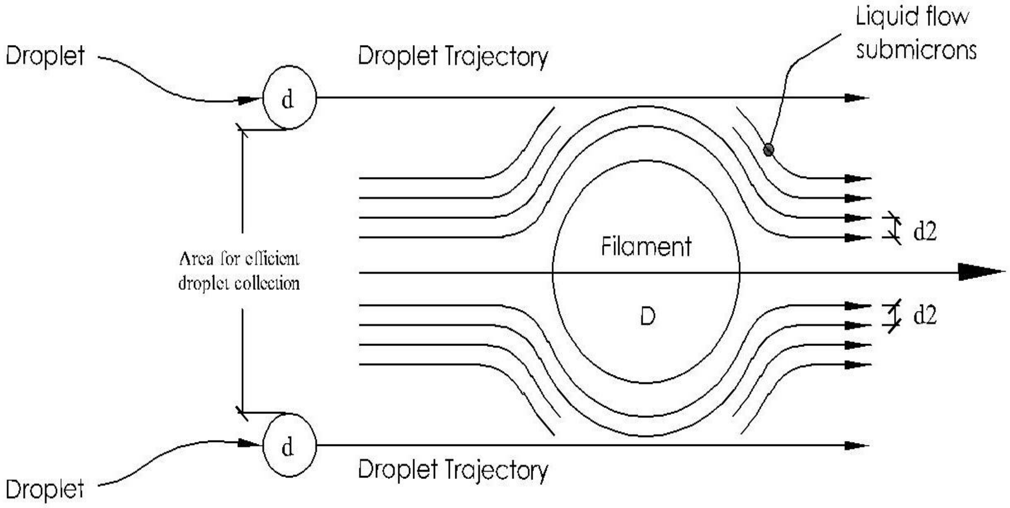


Figure 2.4 Schematic of interception mechanism [27]

The efficiency of direction interception in fiber coalescing media is mathematically shown as below.

$$\eta_D = \frac{E(1-\alpha)}{K}\frac{(d/D)^2}{1+(d/D)} \qquad \text{eq. (1)}$$

Where:

η_D is collection efficiency of single target

E is Effective Length Multiplier (m)

α is Volume Fraction of fibers (m^3)

d is Droplet Diameter (m)

K is Kuwabara's Hydrodynamic Factor

2.8.2 Droplets coalescence

The second stage of coalescer is the process of combining the aggregate captured droplets. Increasing the tendency for droplets to adhere to a medium, increases the probability that subsequent droplets will have the opportunity to strike and coalesce with those that already have been retained. Whether the coalescer media is hydrophilic or hydrophobic depends on the solid/liquid interfacial tension between it and the dispersed phase.

When several droplets are collected on a coalescing medium, they tend to combine together in order to minimize their interfacial energy.

Coalescers work better in laminar flow due to several reasons. First of all, the droplets will stay in the streamlines around the media. Second, high fluid velocities overcome surface tension forces and strip droplets out of the coalescer medium. And third, slower velocities give more residence time in the media so there are more time for droplets to target impact and droplet to droplet collisions [27].

2.8.3 Stokes settling

The third stage of process is the Stokes Settling of the coalesced droplets downstream of the medium. In the Stokes settling, the different densities between the phases cause the droplets to rise by the buoyancy forces. In figure 2.5 shows the Stokes settling. In this figure, the rise of droplets slows down by the friction force and the viscous effect of the liquid. The stokes settling law is given as follow:

$$V_t = \frac{gd^2(\rho_d - \rho_c)}{18\mu_c} \qquad \text{eq. (2)}$$

Where:

g is acceleration due to gravity (m/s)

d is droplets diameter (m)

ρ_d is dispersed phase density (kg/m3)

ρ_c is continues phase density (kg/m3)

μ_c is viscosity of continuous phase (Pa.s)

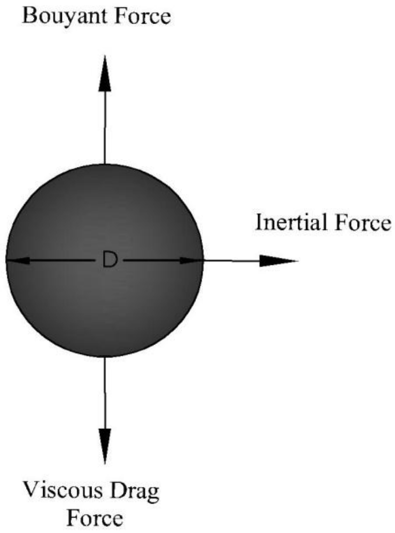


Figure 2.5 Force acting on droplets in Stokes settling [27]

2.9 Parameters effecting the coalesce process

2.9.1 pH

pH has a significant effect on the coalescence of the emulsion. In their study, Deshikan and Papadopoulos [24] described the main stages in coalescence process in the following stages first approach of one drop toward another in the liquid phase followed by formation of a thin liquid film between two interfaces that begin to drain and finally the rupture of the film as it reduces in thickness to a very small value of 100nm. They observed the influence of London-van der Waals and electrostatic forces by studying the effect of pH on coalescence.

This study was done using n-hexadecane oil drops which were produced – in situ and confined inside the aqueous phase. They observed rapid spontaneous coalescence at low pH less than 2.5. At high pH of 13 and greater coalescence was observed after some time when the drops were made to contact. They found no coalescence at intermediate pH of 5.2, 7.1 and 10.9. Similar results were found for with increase in velocities from 100 to 2100 µm/s.

This observation was explained by using DLVO theory which explained that reduction of pH caused a decrease in repulsion between interfaces which reduced surface charge on drops however the increase in pH on the basic side increased the surface charge and reduced the chance of coalescence of oil drops.

2.9.2 Coalescing material

Media selection is very important in improving efficiencies of coalescer. In oil-in-water emulsion separation, hydrophobic material proofed to be more effective in adhering the oil droplets and improve the coalescing efficiency. Ji et al. [29] improve the hydrophobic condition of polyacrylonitrile by alcoholys reaction to improve wetting surface for oil removal from oily wastewater.

From the novel, numbers of authors have suggested the use of some polymeric materials like Teflon, polyurethane, glass fibers and natural cotton fibers for coalescence filtration. The effects of the chemical nature of the solid surface of fibers on coalescence media is normally considered only on the basis of two material classifications: low-surface energy and high-surface energy materials. Thus, solid surface wettability with a dispersed liquid is designated as a crucial factor in coalescence phenomena. The ratio of the critical surface tension of a solid to the liquid surface tension determines the character of solid wettability. It is commonly believed that intermediate wettability gives the most effective separation, thus for the best performance the filter should be sufficiently water-wetted to coalescence the water, but not so saturated as to produce excessive pressure drop by the accumulated water. It has been found that in some cases the fiber contact surface area is more important than pore size. The water droplets in water-in-oil emulsions must displace the oil film from the wet fiber for the attachment to be effective. A water droplet easily displaces oil on a hydrophilic surface. The displacement of the continuous phase by the discontinuous phase on a low energy surface, such as polyethylene or PTFE (polytetrafluoroethylene, i.e.Teflon) should be considerably less than on a high energy surface, such as glass. The wetting behaviors of the water-in-oil or oil-in-water emulsions are considered to be important in determining the performance of the coalescence efficiency.

Sokolovic et al. [30] tried to investigate the effect of chemical nature of solid surfaces with similar surface energies on oil drop coalescence in high porosity media. They differentiated bed properties by using material with similar diameters and different porosity, permeability and pore size. The medium used in packed beds consisting of polyethylene, polyester and polyurethane fibers were tested. The bed permeability was varied to determine the critical permeability for optimal separation efficiency. They also inspected the effect of velocity by varying it from 16 to 70 m/h. The bed geometries were varied over a broad range with permeability ((5.39-0.18).10^{-3} mm^2), porosity 0.97-0.85) and solid surface (3.00-12.00 mm^2 /mm^3) and pore size to drop size (25-10 µm). They found that the efficiency of the bed could be explained based on the critical velocity that determined the extent of interaction of the dispersed phase with the fibrous material. They found that effluent oil concentration was independent of the nature of bed material. The values of critical velocity for the beds were found to be 45 m/h for polyurethane, 55 m/h for polyethylene and 65 m/h polyester. They correlated critical velocity to critical surface tension and found that polymeric fibers which had highest critical surface tension allowed maximum critical or working velocity. Their results were correlated to polyethylene fibers showing an increase in critical velocity corresponds with an increase in critical surface tension.

2.9.3 Arrangement and flow direction of emulsion

In separating oil-in-water emulsion, flow direction plays a vital role in coalescing process. When the flow direction is changed, the floating characteristic of oil is also changed which cause the overall removal efficiency. Several researchers have investigated the different dimension of coalescer in order to improve the efficiency. The special design of coalescer model is very important. Several coalescer models found in literature are shown in below.

Painmanakul et al [28] investigated the flow in the fibrous stage vertical coalescer. In their study, the medium were packed at two different level of the column by providing space between the two stages of media, lower stage and upper stage. The flow come at the bottom of the column and come out at the top. They found that two stages medium column provide better coalescence result than conventional one stage coalescer.

Sokolovic [25] studied three different directions of fluid flow in liquid-liquid bed coalescers. They used smooth polyurethane fiber as medium, and packed with different bed porosities and permeabilities. Their first model was horizontal coalescer which the fluid flow in one side and come out another side. The arrangement is inlet section follow by media packed section and separation section. The second model was the down vertical model; and the third model was upward vertical model. In all three models, the influent oily wastewater flow through the inlet section pass the media then separation at settling section.

Their results found that, the separation efficiency of steady-state bed coalescence is highly influenced by flow mode. At high fluid velocities, horizontal flow bed coalescers are more efficient than vertical configurations, whereas at low velocities, there is no significant difference. At high fluid velocities, upflow operation is the least efficient. If critical velocity is considered, horizontal steady-state coalescers have more advantages.

Sokolovic et al.[8] investigated another flow orientation in the pipe in pipe coalesce. The main principle of their set up was oily water emulsions flow radically through filter material and cylindrical screens with polyurethane foams and polystyrene granules used as filter media. The last cylindrical wall allowed water to leave at top of the vessels and oil was discharged continuously.

The bed depth was varied from 2 to 6 cm. The inlet droplet diameter was maintained at around 20 μm. The experimental design consisted of a 150 mm diameter filter and a flow rate of 0.45 m^3 /h and a 330 mm in diameter filter and 1.5 m^3 /h flowrate. They found their results were in agreement with their findings of the two stage coalescer and polyurethane beds had higher efficiency compared to polystyrene granules. The radial coalescers had similar properties as two stage coalescers.

Anderson [29] observed the use of glass fibers or porous metals by placing them in a gas stream for aerosol removal using them as coalescing medium. Vertical metal tubes that were used in the direction of flow enhanced the formation of drops and also their deposition.

They observed that liquid particles which were placed in the direction of flow coalesced into larger drops.

Zee et al. [30] investigated the axial dispersion of water flow in packed beds consisting of randomly aligned fibrous sorbent materials. They used a tracer pulse technique for determining the dispersion of tracer in water with dispersion as a function of flow velocity, bed porosity and fiber diameter. They developed an experimental technique to compare results for dispersion of 10 wt% potassium chloride solution in water to the Koch and Brady model [31]. The model predicted the contributing phenomena for dispersion of tracer including molecular dispersion, hydrodynamic dispersion and boundary layer dispersion. In the experiments, fibers tested included polypropylene (diameter 50 and 100µm) and polyethylene (15µm). Majumdar et.al. [32] proposed the use of a hydrogel hollow fiber membrane for removal of salts that are present in fuels. They employed Cuprophan regenerated cellulose hollow fibers which was hydrophilic and had an internal diameter of 200 µm and outer diameter of 222 µm. The set up used was a shell and tube type structure with counter current arrangement for the flow of wash water with salt and fuel. They found that there was an effective increase of salt removal from wash water with time and it reached a steady value which demonstrated a potential use of cellulose fibers for salt removal.

Chapter 3

Material and methodology

3.1 Experiment design

As shown in Fig. 3.1, the experiments are separated into two main parallel experiment processes. Each of experiment contain two main steps, the acidification process and the coalesce process. Each step of the process will be described in the following section.

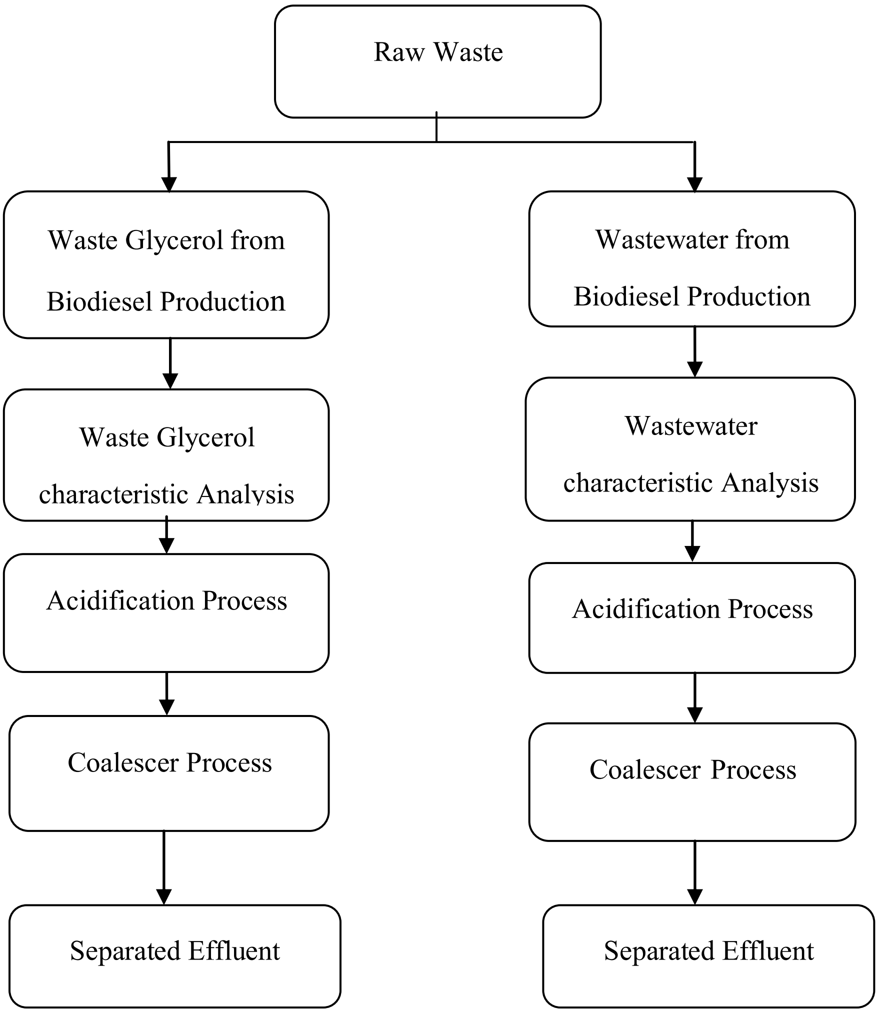


Figure 3.1 Diagram of experiment process

3.2 Waste glycerol

3.2.1 Materials and method

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, TSS and Grease and Oil, 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).

Table 3.1Characterizations and Standard methods

No.	Characterizations	Analytical Methods
1	COD	Standard Method 5220 C
2	BOD_5	Standard Method 5210 B
3	TSS	Standard Method 2540 D
4	pH	Standard Method 4500-H+ B
5	Glycerol	ASTM D7637
6	Grease and Oil	Standard Method 5520 D
7	Soaps	AOCS method Cc 17-19

3.2.2 Coalescing material

The coalescence material used in this study was selected based on its nature and its geometry. The nature of material was considered on its characteristics of associating with water. Thus two types of materials were use in the research, the one with higher surface energy polypropylene (PP) and PET. The materials were also categorized into two geometry shape granular (smaller in surface area) and fiber sharp (bigger surface area).

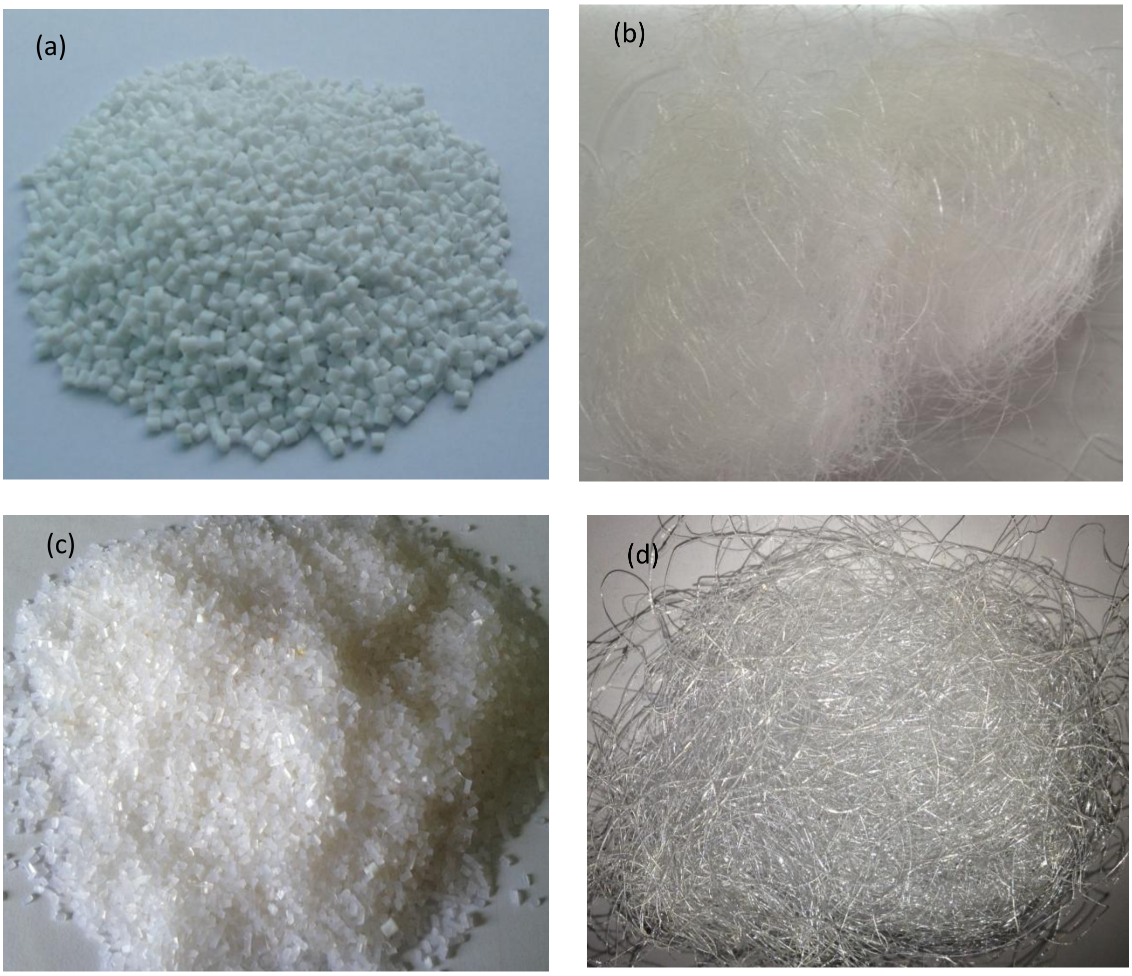


Figure 3.2 Figuration of media material; (a) PET granular, (b) PET fiber, (c) PP granular and (d) PP fiber.

Table 3.2 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)	44.40	30.00	44.40	30.00
Bulk Density (Kg/m^3)	950.00	467.54	206.95	189.15
Porosity	0.21	0.21	0.80	0.80

The selection of these two types of media is to demonstrate the effectiveness of the commonly used media structure. The granular media can be easily packed and fabricated, however this media provide lower surface area and lower porosity. With this characteristic, it should be investigated with the waste glycerol and wastewater emulsion. The fibrous media were suggested by researches that it provides better coalescence efficiency than other types of media structure. Fibrous media, one the most commonly used in colescer process, provide higher surface area and higher porosity. Even though that fibrous media type performs better in colesence, it will be limited to the type wastewater containing high suspended solids and high viscosity. So the investigation of this with the experiment is important. The configuration of the coalescence media used in this study are shown in **Figure 3.2.** **Table 3.2** above shows the details of their characteristics. The porosity of the granular media is 0.21 and the fibrous media is 0.80. To maintain the steady porosity for all the experiments, the packing condition needs to be controlled in same condition. Three factors used in packing process; first is controlling of media quantity, second is controlling of media high and third is controlling the compression level. The same quantity of media were used for each desired high after applying the compression force then the porosity was measured. With this process, the same porosity can be obtained.

3.2.3 Acidification

a) To study the role of acidification affect, the pH value was adjusted by hydrochloric acid (HCl) 1N. The pH values of raw waste glycerol were adjusted to a range of 3 to 6 to study the appropriate value for pre-treating soap;

b) Parameters Analysis- an appropriate pH range for acidification was selected which provided a concentration soaps.

c) The appropriated treated wastewater with pH was taken to the next process.

3.2.4 Continuous operation of coalescer process

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 diameter 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). The vertical column coalescer was selected for the experiment due to its simplicity of operation and more applicable. The vertical coalescer contains the settling zone (separation zone) at the upper part of the device; it requires less space to install than horizontal coalescer. This is also suitable for small factory with little space. **Figure 3.3** below 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.

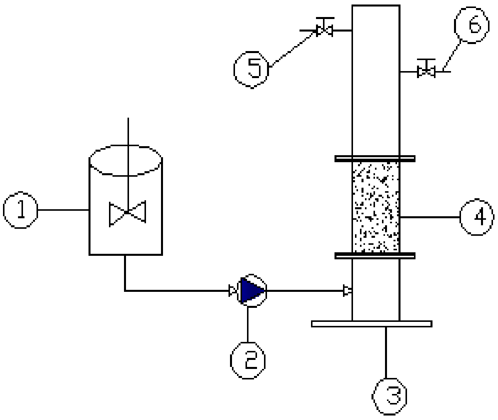


Figure 3.3 Schematic diagram of coalesce apparatus in the experiment (1) Feed Tank; (2) Peristaltic pump; (3) Coalescer body; (4) Medium section; (5) Oil discharge; (6) Effluent outlet

The experiments were done in a steady state condition. This condition will be maintained fix steady flow through each experiment. The samples were taken at 45 min during a 1 hr run of the experiment. The samples were acidified to pH 2 before analyzed for oil content.

In the experiments, coalescence material bed height ranges from 50 mm to 150 mm were selected as suggested in the literature review [9]. Similarly, the influent flowrate ranges were selected from 5 dm^3/h to 18 dm^3/h [8].

The efficiency of the oil removal in this process was calculated based on the following equation:

$$E(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \qquad \text{eq. (3)}$$

Where:

E(%) is the removal efficiency

C_i is the inlet grease and oil concentration (after acidification) mg/L

C_e is the effluent concentration of grease and oil (after coalesce) mg/L

3.3 Wastewater

3.3.1 Materials and methods

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.

The wastewater characteristics were analyzed by following Standard Method (APHA, AWWA and WEF. 2005). 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).

3.3.2 Coalescing material

The coalescence material used in this study was selected based on its nature and its geometry. The nature of material was considered on its characteristics of associating with water. Thus two types of materials were use in the research, the one with higher surface energy polypropylene (PP) and PET. The materials were also categorized into two geometry shape granular (smaller in surface area) and fiber sharp (bigger surface area). The detail of coalescence materials was shown in **section 3.2.2** above.

3.3.3 Acidification

a) To study the role of acidification affect, the pH value was adjusted by hydrochloric acid (HCl) 1N. The pH values of raw wastewater were adjusted to a range of 3 to 6 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 wastewater with certain pH will be taken to the next process.

3.3.4 **Continuous operation of coalescer process**

Figure 3.2 shows the schematic diagram of the experimental set up. The apparatus which was also used in previous glycerol waste experiments consisted of a feed tank, a peristaltic pump and a vertical-column coalescer. The column had a 60 mm inner diameter 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).

In the coalescer process, sample after adjusted pH was mixed by a stainless steel impeller then forced by a peristaltic pump into the coalesce at the inlet section. The experiments were done in a steady state condition at room temperate. The samples were taken at 45 min during a 1 hr 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 equation 3.

Chapter 4

Experimental results

4.1 Demulsification of waste glycerol by acidification process

The demulsification of waste glycerol were done by adjusting pH by using 1 M Hydrochloric acid (HCl). The values of pH were adjusted to range of 3-9. In this process, pH were adjusted to destabilize the emulsion, thus it allowed the oil drop to coalesce and separated. As acid introduce to the solution, the positive of hydrogen (H^+) that surrounds the oil droplets are transform to negative charge [15]. The parameters include grease and oil (G&O), chemical oxygen demand (COD), Total suspended solids (TSS), soap and glycerol were shown in the result.

4.1.1 Introduction

In general, the transesterification process of biodiesel production produces about 10% glycerol as a by-product in every unit of biodiesel produced [33]. The total world production of biodiesel reaches up to 10.8 million tons per year [1], 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, biochemical oxygen demand (BOD) of 900- 1,200 g/L, total suspended solids 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 [34]. 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 [35] , dihydroxyacetone, succinic acid, propionic acid, citric acid, pigments, polyhydroxyalcanoate, biosurfactants [36, 37] and polymers (Poly ester) [38]. It has also been used to produce Hydrogen by a steam reforming process [39, 40]. Other researchers reported using glycerol to produce ethanol [41, 42] and methanol [43]. It has also been reported that glycerol can be used directly for animal feed to replace grain when corn production is down [44, 45]. There are also the applications of waste glycerol as a codigester to improve methane gas production [46] and as a co-substrate to enhance hydrogen and methane production [47].

However, Xie at el. [48] 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. In the study, sulfuric acid was used to acidify waste glycerol to remove the impurities. After acidification process, the waste glycerol treated by coagulated with PACI and PAM-A or electotreat C-7123. At optimum condition after acidification, PACI coagulation and PAM-A flocculation, the treated waste glycerol still can't be discharge to environment. The COD, BOD_5, TSS and Oil and grease removal efficiency were 85%, 75%, 99% and 97%, respectively.

Acidification was used to destabilize the emulsion as well as used as part of the pretreated process. Xie at el. [48] used HCl to naturalize and destabilize the waste glycerol in order to separate the impurities and recover them. Sawain et al. [4] used this process to destroy the oil emulsion in waste water from biodiesel processing before using the coagulation process. Krit et al. [49] 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 [9, 50]. 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 [51-53].

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

4.1.2 Characteristics of raw waste glycerol

The glycerol contains high impurities such as grease and oil, glycerol, suspended solids, soap and methanol. For example, waste glycerol has a high pH>9, COD has about 1,630-1,850 g/L, grease and oil 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 4.1)**.

Table 4.1 Some basic characteristics of waste glycerol

Parameter		**Raw Glycerol**
	Unit	Value
pH		9.12- 9.86
COD	g/L	1,630- 1,850
BOD_5	g/L	700-1,100
Grease and Oil	g/L	230- 337
TSS	g/L	10.5-20.4
Total Glycerol	g/L	385- 450
Soap	ppm	200,000- 230,000

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 [20]. Furthermore, the high content of TSS (oily sludge) makes it unsuitable for the coalescence process as the suspended solids (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[54]. Therefore, acidification is needed to demulsify the droplets.

4.1.3 The role of acidification on COD, grease and oil removal

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

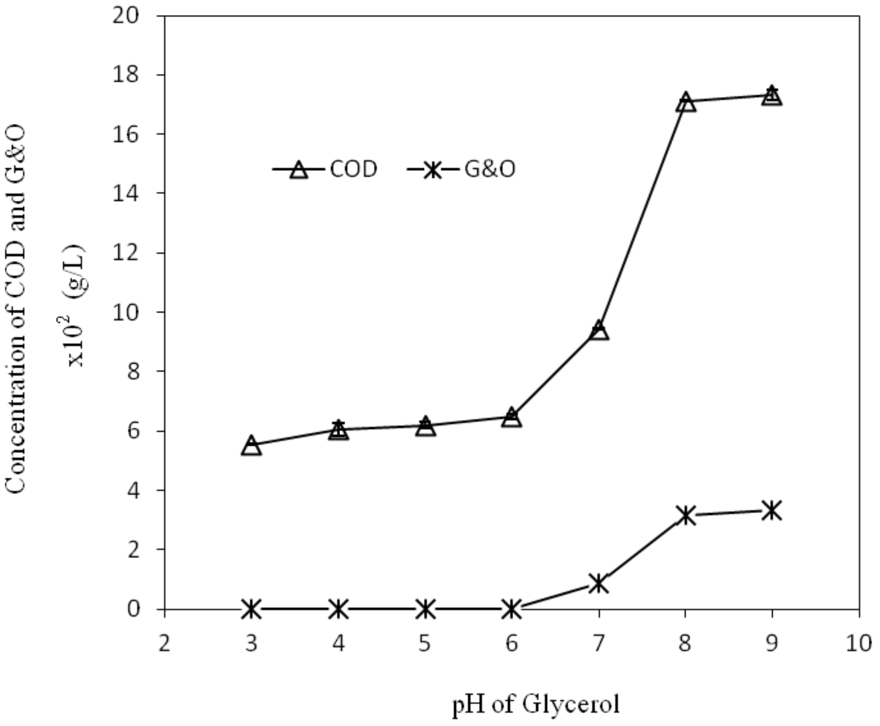


Figure 4.1 Variations of COD and grease and oil concentration of waste glycerol (lower layer) at difference pH

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 in to salt and free fatty acid. 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 grease and oil did not change much as shown in Fig.4.1. When the pH reduced from 8 to 6, the emulsion broke down and the solution separated in to 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 grease and oil and COD slightly decreased when the pH reduced from 6 to 3.

4.1.3 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.4.2** and the change of concentration of TSS is shown in **Fig.4**.3 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.

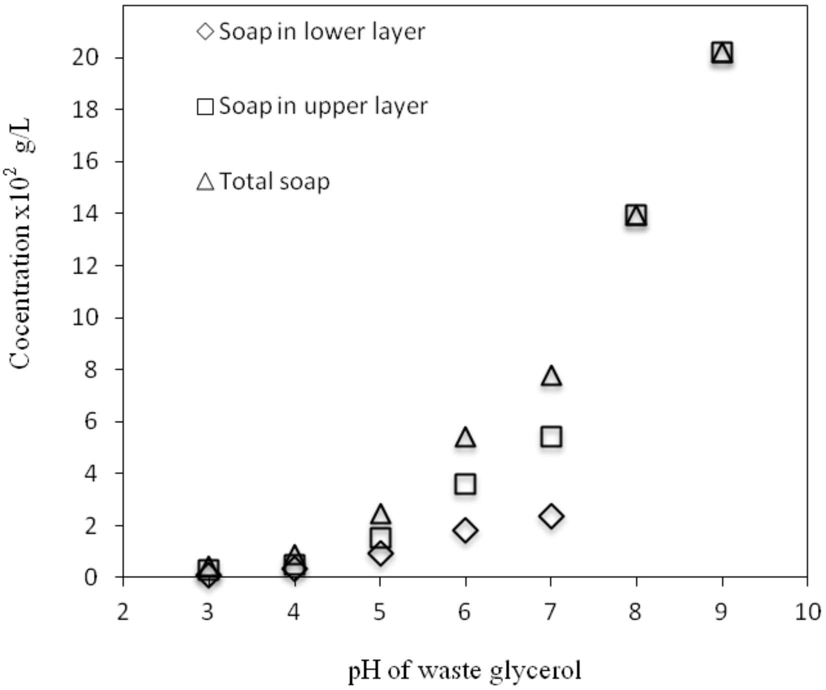


Figure 4.2 Variation of soap concentration in different layer of waste glycerol (lower layer) at difference pH

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, grease and oil that remained in the aqueous layer. Fig. 4.3 shows that when the pH decreased from 9 to 8 the concentration of TSS increased dramatically.

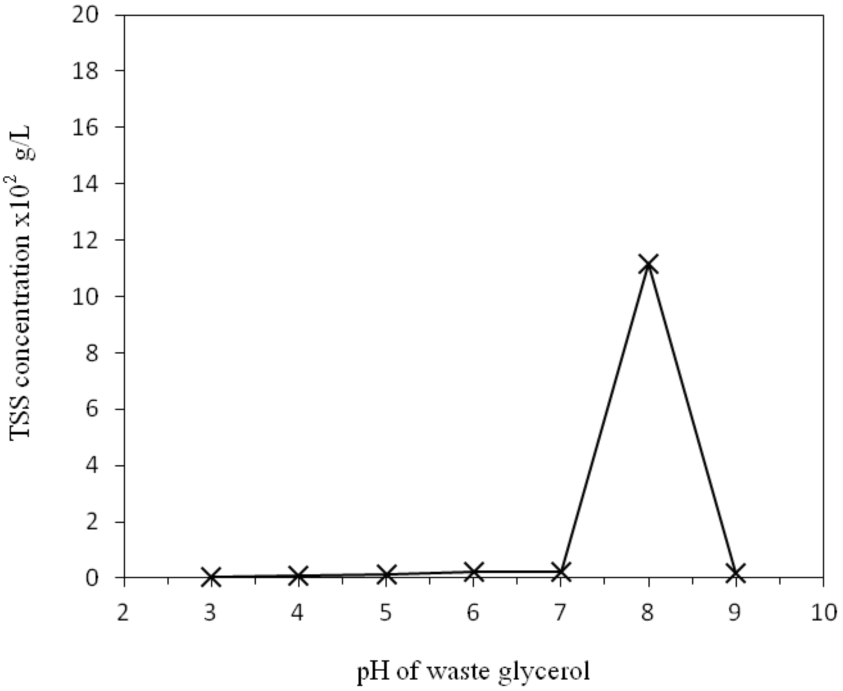


Figure 4.3 Variation so total suspended solids concentration at lower layer at different pH

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

4.2 Enhancement of grease and oil removal by coalescer process

4.2.1 Effect of pH control on the separation of oil emulsion by coalescer process

The effect of grease and oil 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, 4, 5, and 6. The condition for the process was set with a fix flow rate of 5dm^3/h, a PET fiber bed height of 90 mm, and run in room temperature. As presented in **Fig. 4.4** with different concentrations of inlet grease and oil concentrations which shown by pH value, the removal efficiency of grease and oil 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 presented in the solution flowing through the column.

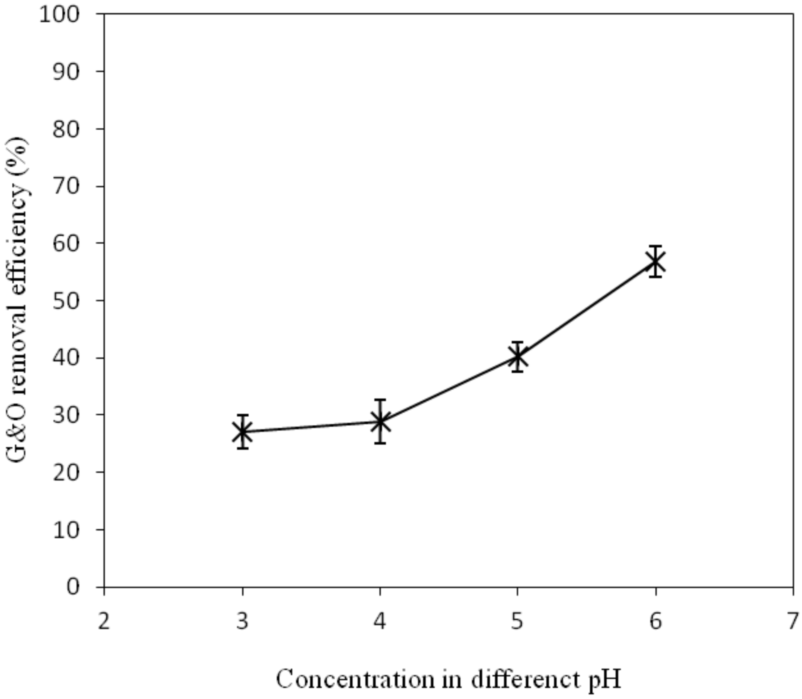


Figure 4.4 Effect of different pH in acidification process on grease and oil removal efficiency in coalescer process at fixed bed high 90 mm, PET granular media and flow rate 5dm^3/h

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 grease and oil 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 [55].

As shown in **Fig.4.5**, 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 grease and oil 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.

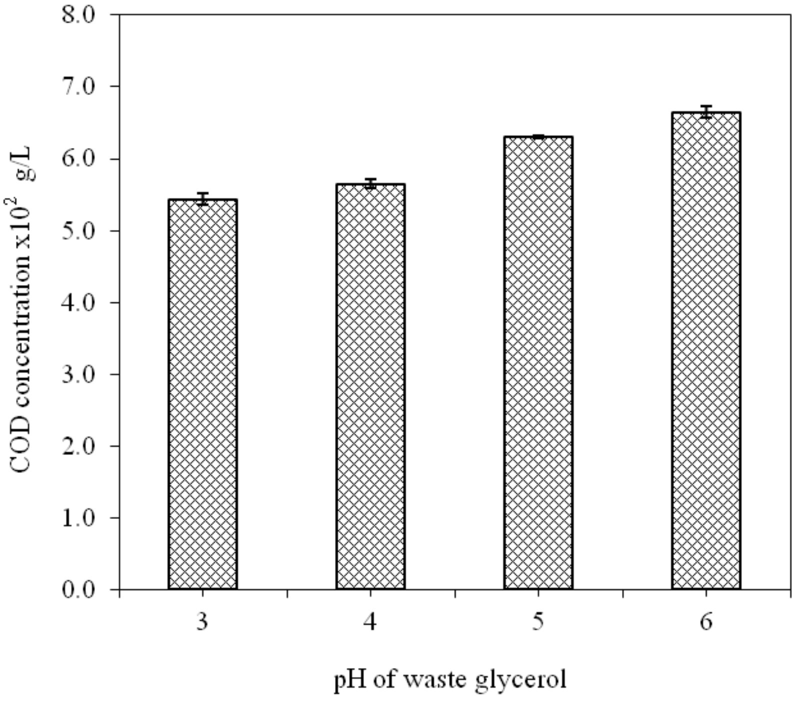


Figure 4.5 Effect of different pH in acidification process on COD concentration in coalescer process at fixed bed high 90 mm, PET granular media and flow rate 5dm^3/h

4.2.2 Effect of coalescence material bed height on grease and oil removal efficiency

To study the effect of media bed height to the grease and oil 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.4.6**, the optimum grease and oil 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.

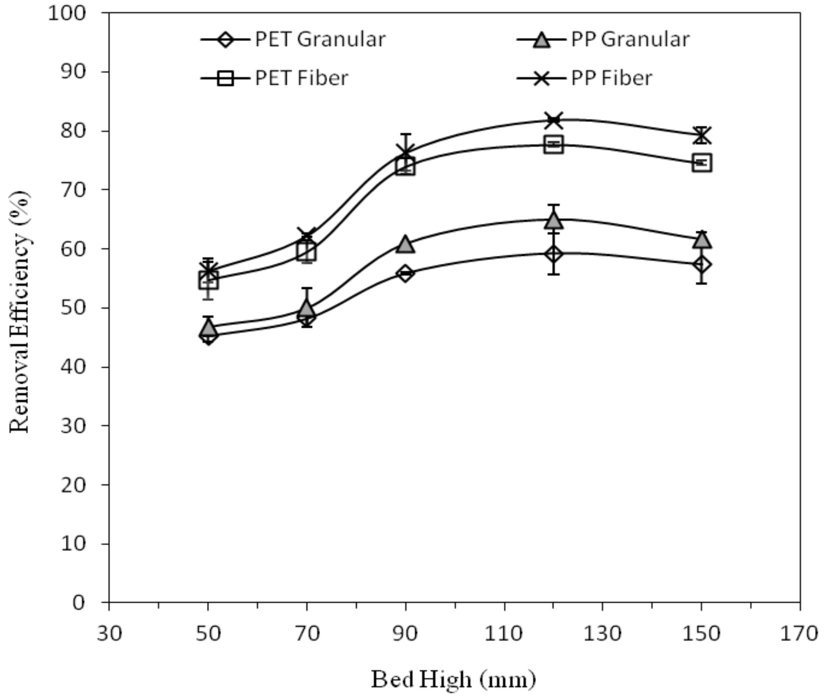


Figure 4.6 Dependence of grease and oil removal efficiency of different material for different bed high in fixed flow rate 5 dm^3/h and pH=6 in acidification

The results showed that when the bed high increased from 50 mm 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 [51]. **Figure 4.7** describes this nature. From this **Figure 4.7**, 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.

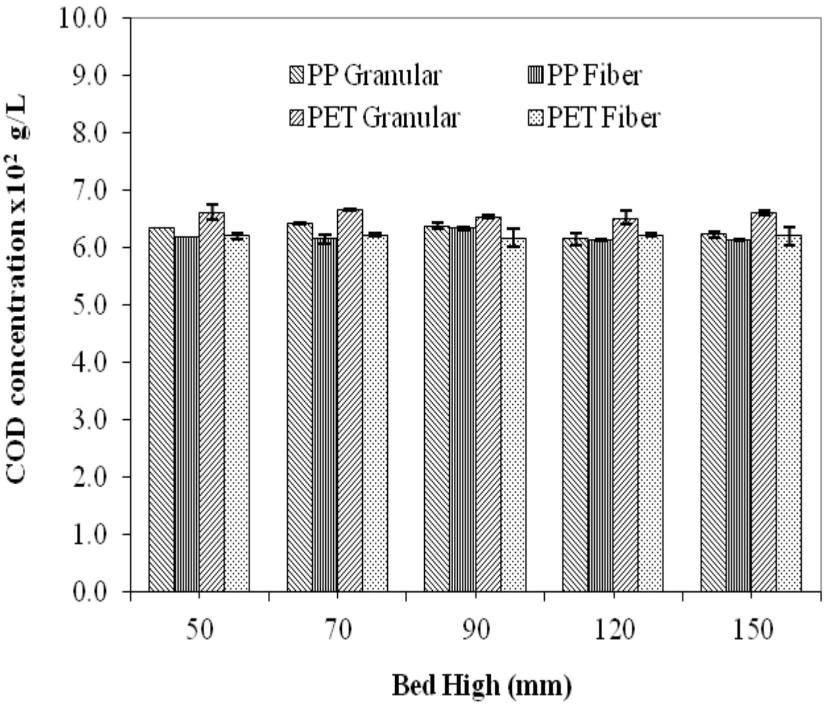


Figure 4.7 COD concentration for different material in different bed high in fixed flow rate 5 dm^3/h and pH=6 in acidification

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.

However, the COD value shown in **Figure 4.7** and **Figure 4.9** doesn't seem to change much while the grease and oil removal efficiency decrease or increase. This result demonstrated that the COD value of this waste glycerol after the acidification are mainly the soluble COD where it can't be remove by the coalesce process. Thus, using COD to predict the efficiency of coalescing process in this case is seemingly difficult.

4.2.3 Effect of flow rate on grease and oil removal efficiency by difference materials

Flow rate has a very significant effect on oil coalescence [56]. 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 **Figure 4.8** demonstrated that at low 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 5dm^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.

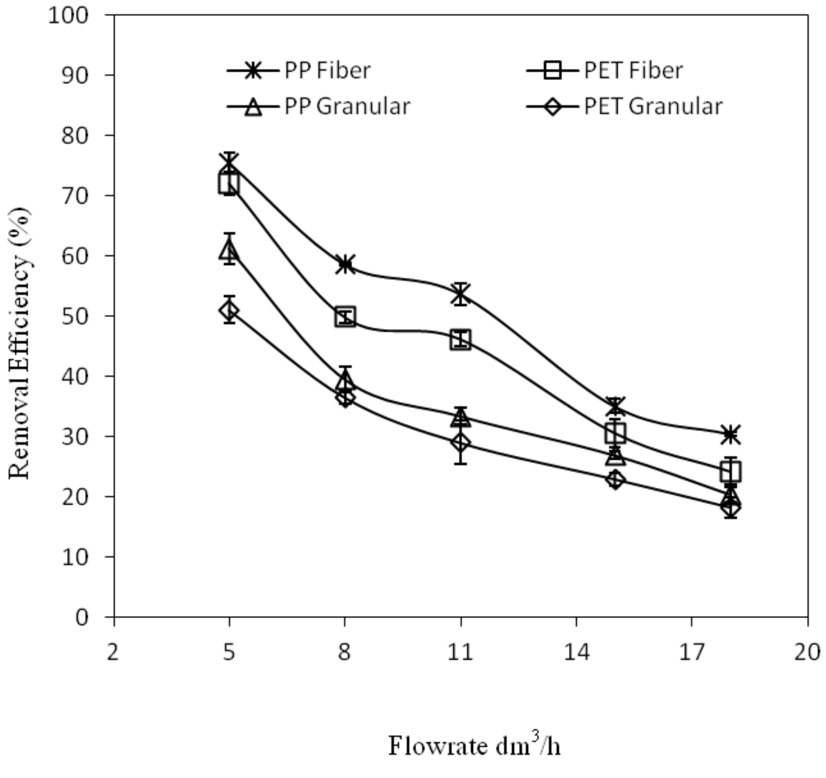


Figure 4.8 Dependence of removal efficiency in various flow rates at fixed bed high 90 mm

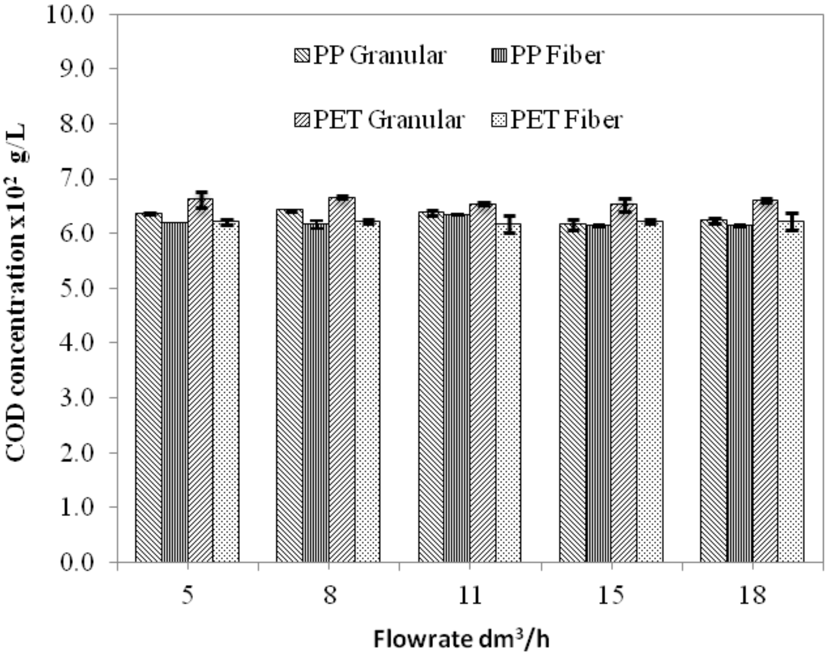


Figure 4.9 COD concentration in various flow rates at fixed bed high 90 mm

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. **In Figure 4.10**, it shows the change of oil drops in waste glycerol before and after adjusting pH. Image (a) shows the small droplets of oil in the waste glycerol where it stable as emulsion; image (b) in contrast present the coalescence of oil drops after destabilized by acid. Image (c) and (d) demonstrates the change of oil drops before and after the coalescer process. The image (c) shows small size oil drops present in waste after acidification, and image (d) shows oil drops collapsing on the top layer after passing the coalescer. This shows that the acidification and coalesce process can be applied to improve the separation of dispersed oil.

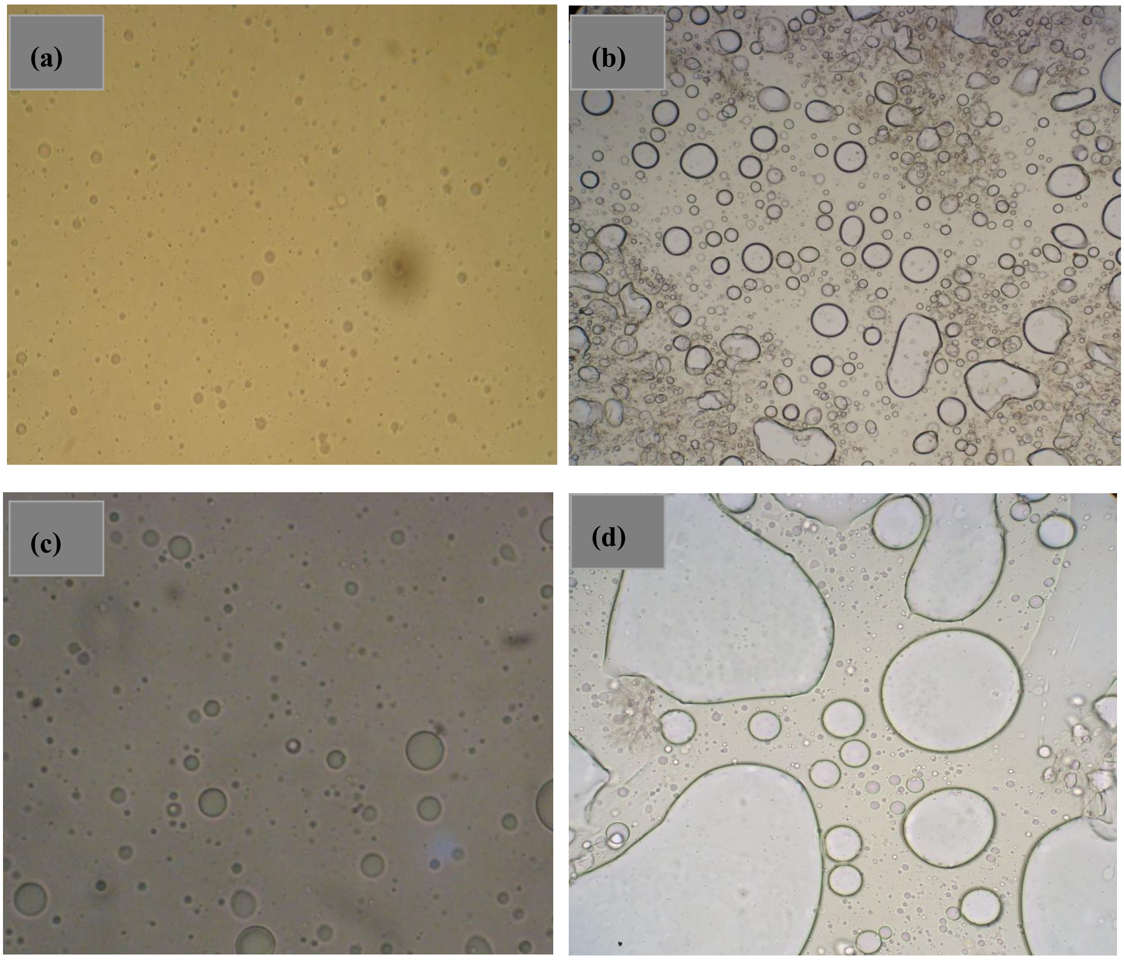


Figure 4. 10 Microscopic image of oil drops (methyl esther) 20x magnitude: (a) raw waste glycerol; (b) after adjusting pH before phase separation. ; (c) after acidification before passing the coalescer; (d) after passing the coalescer that collapsed on the surface.

4.2.4 Summary

The acidification process is very efficient to remove the impurities from raw waste glycerol, the study found that the pH below 6 most of grease and oil and suspended solids were removed. For the range of pH from 3-6, the study found that removal of the COD grease and oil, total suspended solids were slight change. However, at the extreme low pH could provide better efficiency. For the consideration of acidic of treated waste, pH=6 was selected for further process.

In investigating of coalescer process, the study found out that it is effective in helping separated oil from the wastewater. However, the best result could be found in the optimum condition. The oil concentration in the inlets liquid, the height of the coalescence bed, the inlet flowrates of liquid are the criteria influence the efficiency. In investigating of optimum coalescence bed height, the study found that for in range of 50 mm-150mm, at height of 120 mm provides best result of coalesce. At the same time, the operation flowrate was found at the smallest flow of 5 dm^3/h. For both investigation of optimum media bed height and flowrate were found out the same result of all type of media being used in this study. Furthermore, in comparison of coalescence media type the study found that at the same operation conditions the PP fiber performed better result than the rest. The characteristics of treated waste glycerol are presented in **Table 4.2** below. Since the treated waste of process still contained high concentration of impurities which don’t reach the effluent standard of industrial discharge in Thailand [57], further biological treatment is required.

Table 4.2 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 [57]
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
Grease and Oil	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	-

4.3 Demulsification of wastewater by acidification process

4.3.1 Introduction

The global energy consumption rises up every 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 [13]. 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 [58].

With the conventional washing process with water, the reported of characteristic of waste water were pH =8.5-10.75, suspended solid (SS) range 1.5-28.79g/L, chemical oxygen demand (COD) range 60 – 588.80 g/L, biological oxygen demand (BOD) range 105 – 300 g/L and Grease & Oil range 7 – 22 g/L [59, 60]. 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 [58].

Currently, various treatment processes have been proposed. Suehara et al. (2005) [58] 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) [61], 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 ^{0}C) 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. [4] 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 ⩾ 150 mg/L of alum dose.

Chavalparit and Ongwandee [21] 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. [62] 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.

4.3.2 Characteristics of raw wastewater

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 cases, acid was added to improve the removal of catalyzed and decompose soap form [63]. As shown in **Table 4.3** below, the characteristic of wastewater 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 15-20.2 g/L, TSS was around 1.5-5.7 g/L and COD was around 60-150 g/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 5.1-8.5 g/L and COD was around 38-42 g/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.

Table 4.3 Characteristic of raw wastewater

Parameter	Raw Wastewater		
	Unit	Type 1	Type 2
pH		8.5-10.5	5.34-5.82
COD	(g/L)	60 -150	38.8-42
BOD_5	(g/L)	30-60	19.5-22
G&O	(g/L)	15- 20.2	5.1-8.5
TSS	(g/L)	1.5-5.7	5 -5.2
Soap	(ppm)	12,637	1,950

Type 1: Characteristic of wastewater from washing process without adding acid

Type 2 : Characteristics of wastewater from washing process of biodiesel with adding acid

Due to the common biodiesel washing process today, the raw wastewater in Type 1 will be used in further experiments.

4.3.3 The role of acidification on soap removal (surfactants)

The present of high concentration of soap as surfactant in the wastewater will reduce the interfacial of the liquid phase. It will cause the inefficient of coalescence filtration process. It will also caused the filtration media to have short life performance which can lead to frequent change of coalescence material that will increase cost of operation [64].

Sample of raw wastewater were took to adjust pH to 3 to 5 by 1 M hydrochloric acid then measure the concentration soap changed in each pH.

In **Figure 4.9** shows that as pH reduced, the concentrations of soap remaining in wastewater were also decrease. It indicated the fact that the soap reacted with the added acid and converted to salt and free fatty acids.

The result shown that at pH 5, the concentration of soap remained in wastewater at pH 5, 4, 3, 2 were 67.4%, 48.8 %, 25.5%, and 0% respectively. It could be understood that as pH reduced, the emulsion were destabilized and unstable.

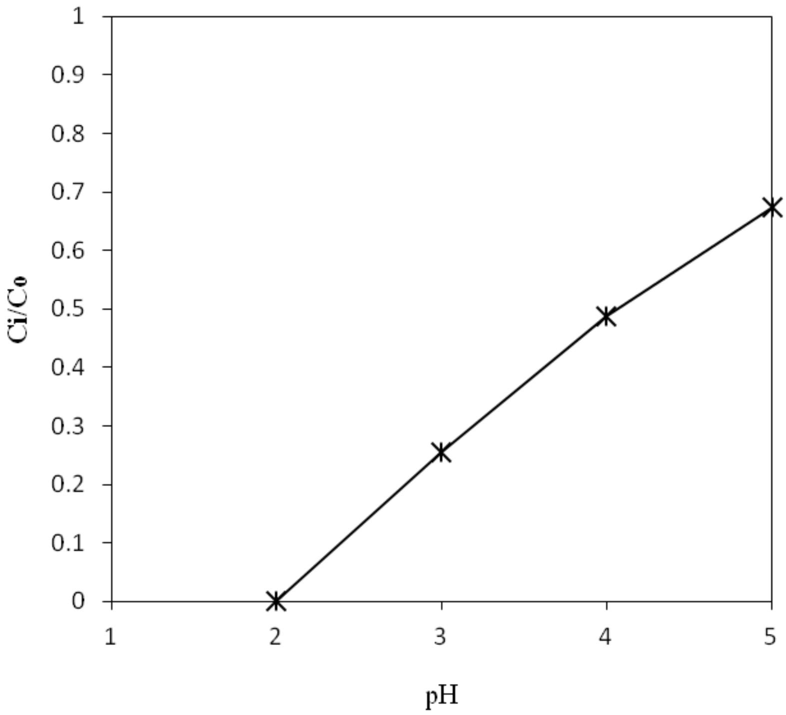


Figure 4.11 The removal of soap surfactants at different pH

However, the result also shown that the surfactant soap were completely converted only at the extreme low pH value. The consideration of corrosion factor and acid added value are needed to be considered.

4.4 Enhancement of grease and oil removal by coalescer process

4.1.1 Introduction

In the coalescence filtration process, there are three steps involve. First, the droplets are captured on the coalescence material surface, then the collected oil or water drops migrated through the coalescence material and coalesce with other droplets to enlarge its size. The final steps is that the larger drop size are release from the surface of the media material [27].

The continuous phase flow rate is important as it controls the mechanism of droplet capture on the fibers, inertia force available for drop-drop collision and coalescence, and the drag force on the coalesced drops to cause the drops to migrate through the filter. In liquid-liquid coalescence, wettability of filter media significantly affects the filter performance [65].

The performance of coalescing filters is measured in terms of separation efficiency and pressure drop. The separation efficiency is dependent on properties of the emulsion (e.g. composition, density, viscosity, drop size etc.). It also depends on the filter properties including the fiber surface wetting properties, fiber size, fiber orientation, porosity, binder content, and filter bed length [66, 67].

The effect of wettability of filter media is more significant when interfacial tensions between liquids are low. The wettability of fibrous filter media depends on surface properties of fibers and porosity of the medium. Wettability of fibers can influence the capture of droplets on fiber surface, migration of droplets on fiber surface, enlargement of droplets, time for which droplets stay on fiber surface and drainage and release of drops from filter medium.

4.4.2 Effect of coalescence material bed height on coalescer process efficiency

To understand the effect of media bed height to the grease and oil 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.4.12**, the optimum grease and oil 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 79.10%, 67.11%, 62.18%, and 55.97% respectively.

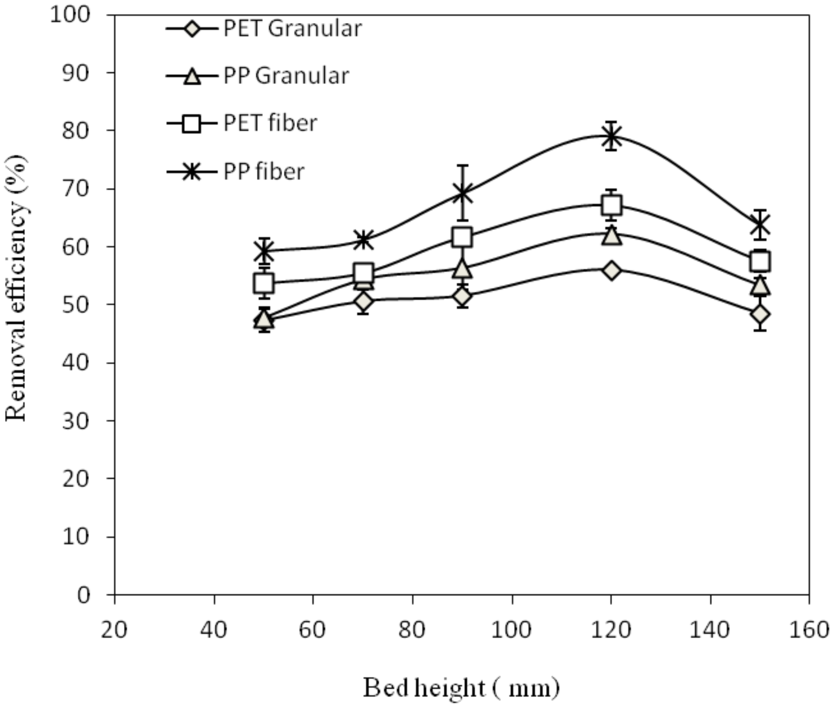


Figure 4.12 Dependence of Grease and Oil removal efficiency of different material for different bed high in fixed flow rate 5 dm^3/h and pH= 4 in acidification

The results showed that when the bed high increased from 50 mm to 120 mm, the Oil removals increased from 59.27% to 79.10% in PP fiber media and then decreased to 63.78% 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.

4.4.3 The role flowrate in coalescence efficiency

Flow rate has a very significant effect on oil coalescence[56]. 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 dm3/h.

The results shown in **Figure4.13** demonstrate that at lower flow rates the result is better for all the media investigated. The results obtained for all four media at 120 mm bed height, PP fiber, PET fiber, PP granular, and PET granular at flow rate 5dm^3/h were 79.10%, 67.89%, 62.18% and 56.06% 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.

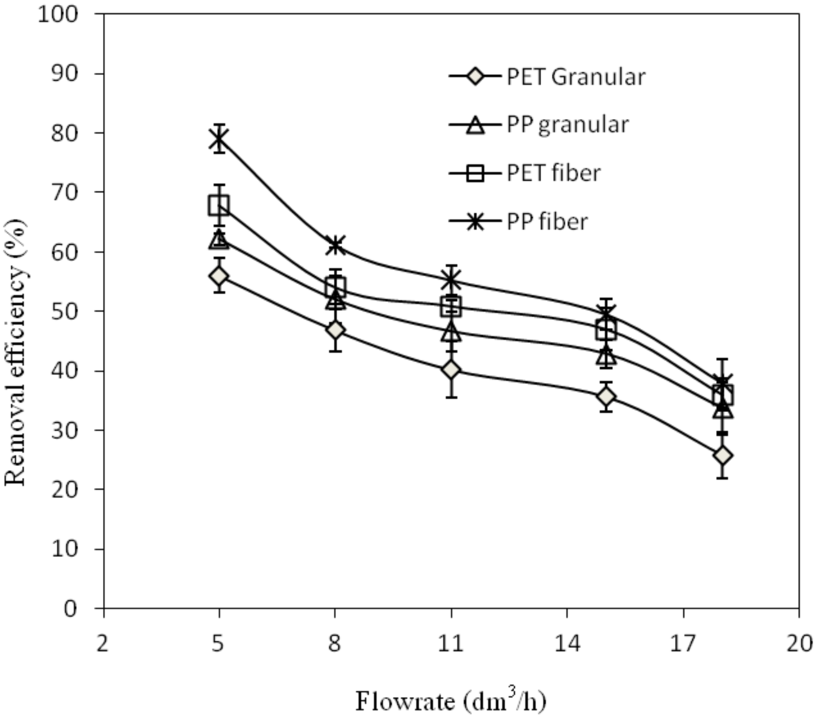


Figure 4.13 Dependence of removal efficiency in various flow rates at fixed bed high 90 mm

4.4.4 Comparison of nature of coalescing material

One of the important factors of coalescence filtration is the coalescence material. It is understood that the ratio of the critical surface tension of a solid to the liquid surface tension deter-mines the character of solid wettability. Coalescence materials are normally cauterized into two group based on its surface critical tension: low-surface energy material and high surface energy materials.

The two materials that were used in this study are also listed in above category. Their critical surface tensions are basically linked to their surface chemical components. In this study, polypropylene (PP) which has 30 mN/m surface energy and polyethyleneterephthalate (PET) which has 44.4 mN/m surface energy are presented. Both materials have same granular size ranged from 1.5 -2 mm, and porosity 21%.

The experiments were run at the same conditions of pH of wastewater at 4.0, flowrate at 5 L/h, and bed height of 50-150 mm. From **Figure 4.15**, the result shows that for the material PET granular the removal efficiencies are 47.22%, 50.55%, 51.52%, 55.97%, and 48.48% at difference bed height of 50 mm, 70 mm, 90 mm, 120 mm, and 150 mm respectively. At the same condition the PP coalescence media provides better grease and oil removal efficiency. The removal efficiency were 47.8%, 54.35%, 56.37%, 62.18% and 54.5 % at the same order of bed height respectively.

The result demonstrates that, for the material with higher surface energy in this case is PET provide lower coalesce result than the lower surface energy material which is PP that can provide higher coalescence result. For this phenomenon, Radmila et. al [10] also confirmed by their research on the effect of material nature on coalesce process.

Another phenomenon that we can draw from **Figure 4.10** is the influence of the bed height in the coalescence performance. For both of the materials provide the same characteristics of changing efficiency with the change of bed height. As the height increase from 50 mm to 120 mm, the efficiency were slightly increased, but when it passed the critical point of height which is 120 mm then efficiency slide down as the bed height go higher. It was suggested that too high of the bed, can cause the secondary diffusion of the droplets, thus the efficiency decrease.

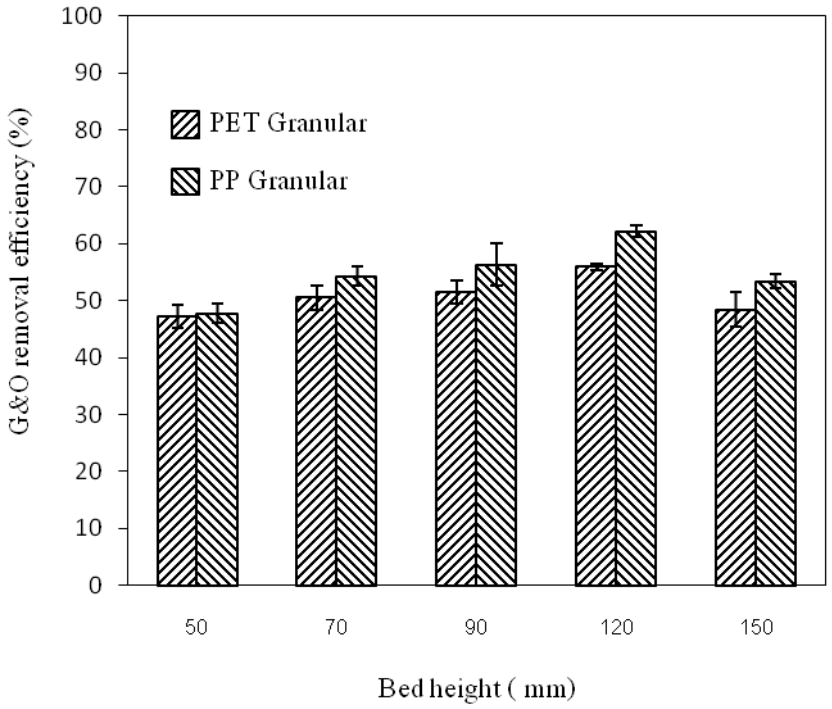


Figure 4.14 Grease and oil removal efficiency by two different materials at the condition

4.4.5 Comparison of shape of material

Another way to measure the efficiency of material performance on grease and oil performance is their geometry sharp. Difference shape and size of media materials provide difference surface area. As the novel pointed out the higher surface area of material could give better coalescing result. To investigate this phenomenon, we selected the same materials with difference sharp and size.

The two materials that we use in this study are also listed in above category. In this study, tow geometry sharp of polyethyleneterephthalate (PET) are used. First, the granular PET which has 44.4 mN/m surface energy, size ranged from 1.5 -2 mm, and porosity 21% and the other one is PET fiber which has the same surface energy of 44.4 mN/m, size 0. 3-0.8 mm, and porosity of 80%.

The experiments were run at the same conditions of pH of wastewater at 4.0, flowrate at 5 L/h, and bed height of 5-15 cm. From **Figure 4.16**, the result shows that for the material PET granular the removal efficiencies are 47.22%, 50.55%, 51.52%, 55.97%, and 48.48% at difference bed height of 50 mm, 70 mm, 90 mm, 120 mm, and 150 mm respectively.

Where, at the same condition the PET fiber media give better grease and oil removal result. The removal efficiency were 53.68%, 55.44%, 61.60%, 66.33% and 57.52 % at the same order of bed height respectively.

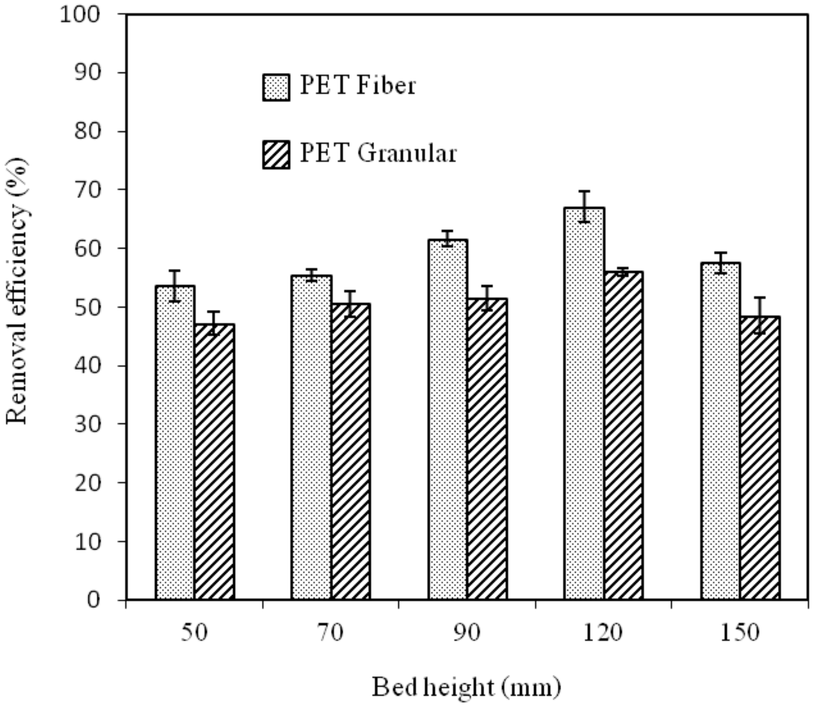


Figure 4.15 Grease and oil removal efficiency by two different sharp of material at the same operation condition

4.4.6 Summary

The acidification process is very efficient to transform the soap surfactants present in wastewater, by adjusting pH soap can be converted into salt and free fatty acid. In this case of study, pH was adjusted to 4.0 prior to the coalescer process.

In investigating of coalescer process, the study found out that is effective in helping removing the separated oil from the wastewater where it's not ease to separate by gravity. Small dispersed oil droplets which are stable in wastewater. However, the best result could be found in the optimum condition. At pH 4.0, the best performance of coalesecer was found at the flowrate of 5 dm^3/h, with the media bed height of 120 mm, and the PP fiber material.

Table 4.4 Characteristic of waste water before and after treatment by acidification and coalescer process

Parameter	Unit	Raw Wastewater		Oil terminal effluent standards of Thailand [57]
		Raw waste water	After	
pH		5.34-5.82	4.00	5.5-9.0
COD	(g/L)	38.8-42	25.5	0.2
BOD_5	(g/L)	19.5-22	15.5	0.06
G&O (mg/L)	(g/L)	5.1-8.5	1.3	0.015
TSS	(g/L)	5 -5.2	5	0.06
Soap	(ppm)	2,900-4,500	1,500-2,000	-
BOD_5 : COD	-	< 0.6	0.72	-

The study found that materials with different surface energy provide different state of coalesce. Moreover, the geometries of their shapes also have significant influence on coalescence performances. The characteristic of wastewater after treat with acidification and coalescer process were summarized in **Table 4.3** above.

4.5 Comparison between waste glycerol and wastewater

Biodiesel production generates wastewater up to 120% and 10% of waste glycerol in every unit of biodiesel being produced [17]. Quantitatively, wastewater from biodiesel production is up to 12 times more than waste glycerol. Due to both waste characteristics as stated in Table 4.2 and **Table 4.4**, however, both wastes cannot be discharged to the environment without proper treatment. Thus, it needs to be equally considered on treatment before discharge.

The cost of treatment process of wastewater and waste glycerol can be compared in terms of operational cost. The operational cost can be broken down into two step cost, cost in acidification process and cost coalescer process. However, the cost in coalescer process is most likely equal because for both wastewater and waste glycerol are operated in the same optimal condition. Thus, the energy consumption for coalescer unit to treat 1 m^3 of wastewater and waste glycerol is presumably equal.

In acidification process, the consumption of sulfuric acid H_2SO_4 98% to adjust pH of waste glycerol to pH=6 is 0.025 m^3 / 1 m^3 of waste glycerol. The price of H_2SO_4 98% is 7,750 Baht/ton [68]. The calculation for treated 1 m^3 of waste glycerol can be done as follow:

1) Price of sulfuric acid H_2SO_4 98%
   7,750 Baht/ton x 1.84 ton/m^3 = 13,950 Baht/m^3
2) The cost of acidification of 1 m^3 of waste glycerol
   13,950 Baht/m^3 x 0.025 m^3 = 348.75 Baht

For wastewater, sulfuric acid H_2SO_4 98% required to adjust pH to 4 is 0.41×10^{-3} m^3 per 1 m^3 of wastewater. The calculation for acidifying 1 m^3 of wastewater can be done as follow:

1) Price of sulfuric acid H_2SO_4 98%

   7,750 Baht/ton x 1.84 ton/m^3 = 13,950 Baht/m^3

2) The cost of acidification

   13,950 Bth/m^3 x 0.041×10^{-3} m^3 = 0.57 Baht

The waste glycerol treatment cost is comparatively very much higher than treatment cost of wastewater. The cost for treatment of 1 m^3 of waste glycerol and wastewater are 348.75 Baht and 0.57 Baht respectively. The cost of energy consumption was not included in above calculation.

Table 4.5 Comparison of treated waste glycerol and wastewater with effluent standards of Thailand

Parameter		**Treated waste glycerol**	**Treated wastewater**	**Terminal effluent standards of Thailand [57]**
pH	-	6.0	4.00	5.5-9.0
COD	g/L	550	25.5	0.2
BOD_5	g/L	379	15.5	0.06
Grease and Oil	g/L	0.081	1.3	0.015
TSS	g/L	0.15	5	0.06
Total Glycerol	g/L	350	-	-
Soap	ppm	2,300	1,500-2,000	-
BOD_5 / COD	-	0.68	0.72	-

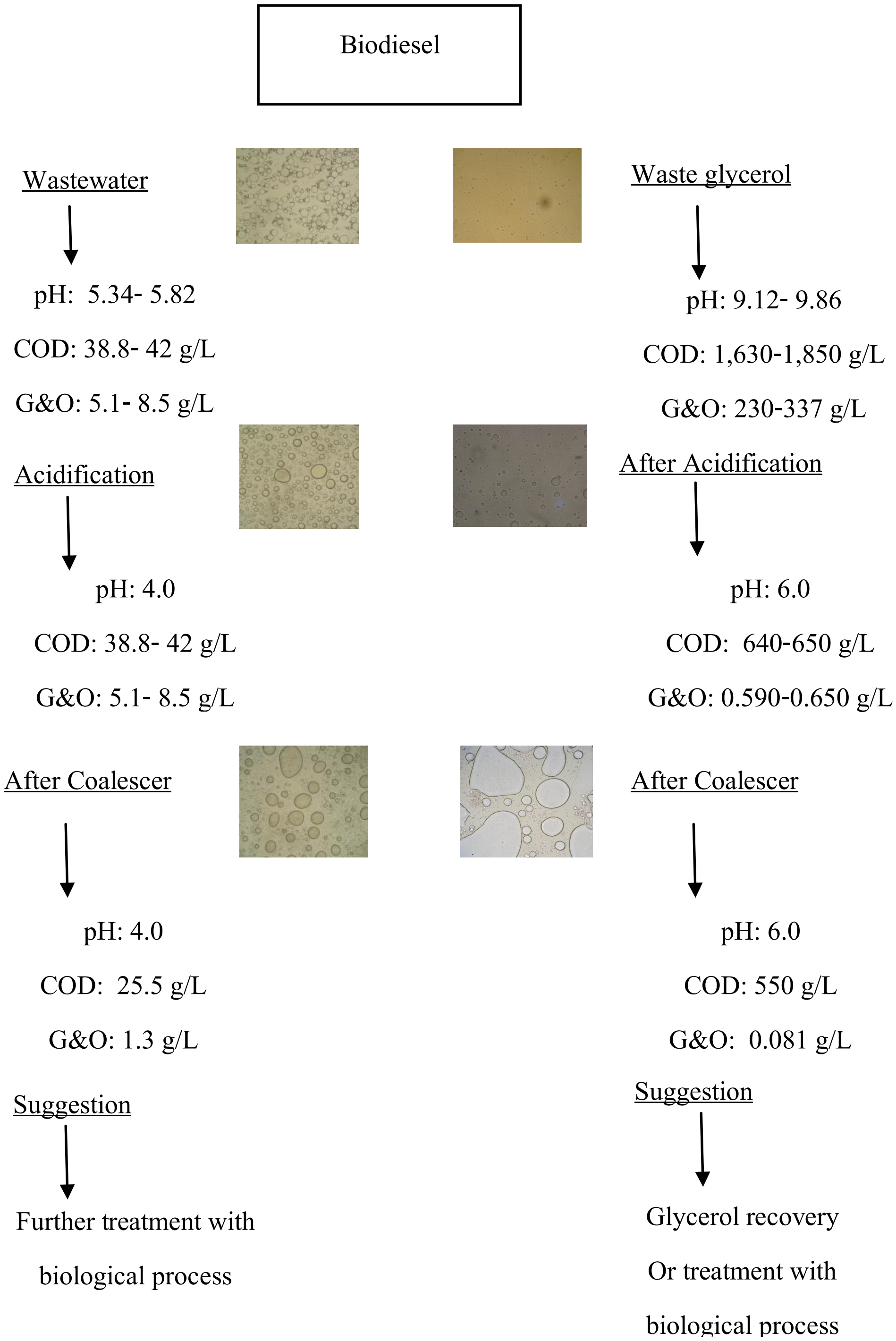


Figure 4.16 Schematic of step by step comparison of treatment system performance

The comparison of treated wastewater and waste glycerol shows in **Table 4.5** and in **Figure 4.16** shows the comparison of treatment system performance. The value of pH, COD and G&O of raw wastewater are lower than raw waste glycerol; this is the factor of the treatment cost difference between the two wastes. In step by step results summary in **Figure 4.16**, it's clearly seen that the treatment process were very successful in removing oil emulsion. In wastewater, 85% of emulsified oil was removed where in waste glycerol over 99% of emulsified oil was removed. Both treated wastewater and waste glycerol qualities however didn't reach the effluent standard [57]. Therefore, acidification and coalesce process can be suitable for primary treatment process which can be followed by biological treatment process. As shown in **Table 4.5**, the COD and BOD_5 of treated waste glycerol were 550 g/L and 379 g/L which it's rich in carbon source. This treated waste glycerol contains sufficient volatile acidity (VA), BOD_5/COD and VA/Alkalinity which is suitable for anaerobic treatment to produce biogas [22]. Also, the COD and BOD_5 of treated wastewater were 25.5 g/L and 15.5 g/L. The G&O and BOD_5/COD were 1.5 g/L and 0.72, respectively. This treated wastewater can be treated by biological treatment process to reach the effluent standard. However, this wastewater has insufficient amount of nutrients elements which is required for bacteria growth, the addition of these nutrients for treatment is needed and pH need to be neutralized [20].

The coalescer system is very effective in oil and grease removal, emulsified and dispersed oil from liquid water. From the study, it showed that the coalescer column has the capacity to remove grease and oil in wide rage loading. At the selected optimum operating condition, the grease and oil laoding was in between 1.5 – 78.0 g (G&O).hr/m^2. The grease and oil loading might affect the coalescing media age. Sokolovic [8] stated that the coalescing media need to be replaced from time to time; however, the coalescing media age can be improved by washing and cleaning process.

4.6 Application of the process

Oil emulsion waste from biodiesel production, waste glycerol and wastewater, can be treated by acidification coalesce process. There is slightly different scenario in treating two types of waste as shown in **Figure 4.17** below.

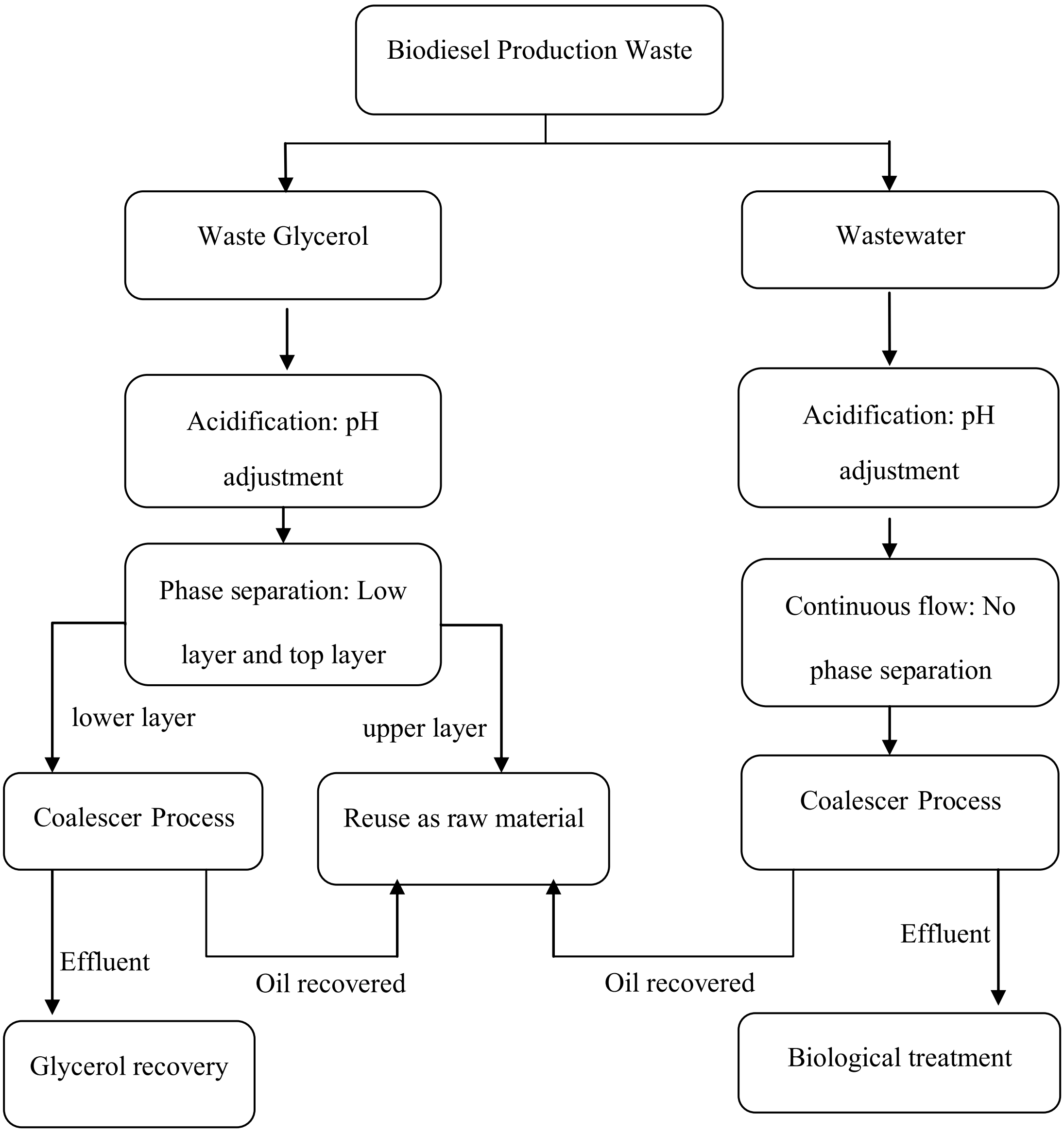


Figure 4.17 Schematic diagram of suggested application of the process

Waste glycerol can be first acidified. Oil-in-water emulsion was destroyed in this process; the excess catalyst was neutralized and soap was converted to salt and free fatty. After the flush mixing for complete reaction, the phase separation occurred which separated into two layers; upper layer consist of free fatty acid, soap and methyl ester and lower layer consist of mainly aqueous and glycerol. The upper layer is to be recovered and reuse as the raw material in biodiesel production; the lower layer however still contain the unseparated grease and oil to be further removed.

For waste glycerol which contain high suspended solids and grease and oil with high viscosity, the phase separation step is necessary prior to coalescer process due to these characteristic can troublesome the coalescence efficiency.

After the phase separation, the lower layer passed through the coalescer process to enhance the removal of dispersed oil suspended in treated wasted glycerol. In this system, dispersed oil can be removed from aqueous by passing through the coalescence media then the separated oil is to be recovered and reused. In the influent, the concentration of glycerol doesn’t change which is the advantage and this glycerol can be recovered.

For the wastewater, it’s also first need to be acidified to destabilized the oil-in-water emulsion. As shown in schematic diagram in **Figure 4.17**, after acidification wastewater doesn’t required for the phase separation prior to coalescer process like waste glycerol. It’s because wastewater has low viscosity and low concentration of suspended solids. For this reason, the wastewater can pass to the coalescer process after acidification.

In the coalescer system, dispersed oil can be removed from aqueous by passing through the coalescence media then the separated oil is to be recovered and reused. The influent from coalescer process can be further treated by biological process.

Chapter 5

Conclusion and future works

5.1 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 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, suspended solids (SS) and grease and oil prior to the coalescer process. The value of pH of waste glycerol should be adjusted to below 6 where parts of methyl ester can be recovered and reuse as raw material. The coalescer process can be applied to remove fractions of grease and oil 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.

For the waste glycerol, the condition of acidification found at the pH below 6.0 where large amount of organic compounds can be removed. However, at extreme pH around 3 it can provide slightly better result. For the consideration of adding cost of acid as well as the acidic of wastewater after acidification, pH=6.0 was selected.

Similarly to waste glycerol, wastewater was also treated by two step process, acidification and coalescer process.

Acid was introduced to convert soap surfactant to salt and free fatty acid to destabilize the emulsion. For wastewater contains less impurity than waste glycerol, the acid was added into flow stream directly without waiting to separate the impurities. The pH was selected at pH= 4.0 to be appropriate for the process.

In the coalescer process, it was found that the best performance of coalesecer was at the flowrate of 5 dm^3/h, with the media bed height of 120 mm, and the PP fiber material. The operation condition was found for both wastewater and waste glycerol.

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 increase which was an improvement and at this ratio it can be treated by biological process.

5.2 Limitation

- When the concentration of suspended solids is too high, it can cause clogging problem and coalescer can't work.
- The grease and oil concentration in effluent of wastewater is a bit high, however it can be reduced by improve the porosity of the coalescence media.

5.3 Future works

The recommendations for future work are explained below.

- The size of coalescence materials should be investigated in smaller size range in order to promote the coalesce efficiency.
- In order to increase the interception of the oil drop with coalescing media, the study of removal suspended materials prior to coalescer process.
- The study of effect of nature of coalescence material needs to be investigated with broader range of surface energy material.
- In order to improve the performance of coalescence materials, the higher porosity of materials should be studied and applied.

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List of Publication and Proceedings

[1] Hor Kosal, Chaisri Suksaroj, "Enhancement of oil removal from biodiesel washing wastewater by coalescer process", *Proceeding of the 10th International PSU Engineering Conferences,* Thailand, May 14-15 2012

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