Treatment of Waste Glycerol from Biodiesel Production Process

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ABSTRACT

Biodiesel as an alternative fuel has attracted increasing interest worldwide in recent year. During the biodiesel production process by transesterification, oils/fats (triglycerides) are mixed with methyl alcohol and alkaline catalysts to produce esters of free fatty acids, with waste glycerol as a primary by-product. In general, production of 100 kg of biodiesel yields approximately 10 kg of waste glycerol, which is impure and of low economic value. Waste glycerol contains about 50% by weight of glycerol and other organic matters, including 1%-3% oil and grease, 15%-18% methyl ester and 12%-16% soaps, which can cause water pollution and environment problems, since it cannot be disposed in the environment. The aim of this research was to study the treatment of waste glycerol. To reach this objective, acidification and coagulation processes were applied to treat waste glycerol. These processes can reduce water pollution and recover organic matters, such as free fatty acids, methyl ester and glycerol, from waste glycerol to bring significant economic benefits for the biodiesel facilities. Another method is transforming raw waste glycerol into gelatinous waste glycerol which can be used as a fuel. The manufacture process of gelatinous waste glycerol can save the cost of waste glycerol treatment.

In order to remove organic impurities from waste glycerol, acidification process was needed as a pretreatment to adjust pH value, convert soaps into free fatty acid and demulsification of oil-in-water emulsion (O/W) in waste glycerol. Then, the waste glycerol was treated by coagulation process with electotreat C-7123, polyaluminium chloride (PACl) and polyacrylamide (PAMs). The coagulation conditions (pH value of waste glycerol, dosage of coagulants) were adjusted. The optimum conditions were selected that provided the best results for coagulation processes. Finally, the appropriate coagulant was selected by comparison of the

results of different coagulants at their optimum conditions.

The results show that the coagulation process with electotreat C-7123 can reduce water pollution of waste glycerol effectively, but remain a small amount of glycerol (147 g/L) in treated waste glycerol. Moreover, the cost of electotreat C-7123 for treating waste glycerol is quite expensive (200 Baht/m^3). The cost of polyaluminium chloride (PACl) and anionic PAM (A-9934) is cheaper than electotreat C-7123, which is about 11 Baht/m^3; and there is a large amount of residual glycerol (230 g/L) in treated waste glycerol. During the comparison of four types of PAM, including cationic PAM (C-8385), cationic PAM (C-8800), anionic PAM (A-9770) and anionic PAM (A-9934), the effect of anionic PAM (A-9934) on removing large organic compounds from waste glycerol is the best in the four types of PAMs. However, the COD and BOD$_5$ of treated waste glycerol by coagulation with PACl and PAM-A (A-9934) are over the Oil Terminal and Industrial Effluent Standards of Thailand due to less significant removal of glycerol and methanol. Therefore, the coagulation process with PACl and PAM-A can be used as a primary treatment of glycerol recovery process. The residual glycerol can be recovered by CDs from treated waste glycerol, but the amount of included glycerol is small. The free fatty acid can be recovered during coagulation process with electotreat C-7123 and PACl and PAM-A; and the coagulation productions which contains a large amount of organic compounds can be reused as a fuel. In addition, the manufacture of gelatinous raw waste glycerol provides another method of reusing waste glycerol as a fuel. The heating value of gelatinous waste glycerol made by waste glycerol, stearic acid, methanol and NaOH is the highest (8519 kcal/kg), which is closed to heating value of natural gas (8600 kcal/kg).

Keywords: Biodiesel, Waste glycerol, Acidification, Coagulation, Glycerol, Gelatinous waste glycerol

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Chapter 1

Introduction

1.1 Motivation

Biodiesel is one of the most promising alternative fuels in Thailand, particularly when its price is comparable with standard diesel. Biodiesel, the mono alkyl esters of long-chain fatty acid, is an alternative fuel for diesel engines produced by chemical reaction of vegetable oil or animal fat with an alcohol. In Thailand, the government has promoted the production and the use of biodiesel as a substituted diesel fuel to reduce the importation of oil, enhance the energy security, and promote the use of alternative energy made from domestic crops. The government projects that the quantity of biodiesel sold in the market in 2012 will account for 10% of the total diesel sold (Gonsalves, 2006). At present, the existing capacity of biodiesel production is approximately 1.5 million liters per day with 43 biodiesel plants registered with the Department of Industrial Work (DEDE, 2007).

Over 90% of the biodiesel production in Thailand uses palm oil as the raw material by a transesterification reaction method using alkali catalysis. This method produces a high conversion of oil (triglycerides) to biodiesel (methyl esters) by a simple chemical reaction which occurs in a short time (Marchetti et al., 2007). During biodiesel production, two phases are produced after transesterification. The upper ester phase contains the main product-the biodiesel. The lower waste glycerol phase consists of 50%-60% by weight of glycerol, 12%-16% of soaps, 15%-18% of methyl ester, 1%-3% of oil and grease, 8%-12% of methanol, 9%-11% of water and other components (Hutnan et al., 2009). The waste glycerol can cause water pollution and environmental problems, since it cannot be disposed of in the environment (Yazdani and Gonzalz, 2007). In order to reduce the costs involved in disposing raw waste glycerol, it has been suggested to use some methods to reduce water pollution and recover organic matters, such as free fatty acid, methyl ester and glycerol, to create economic benefits for biodiesel factories.

Coagulation is one possible treatment method used to revalorize abundant and low-priced glycerol streams because this method is widely used in water and wastewater treatment and is well known for its capability of destabilizing and aggregating colloids. There are a number of different mechanisms involved in a coagulation process, including ionic layer compression, adsorption and charge neutralization, inter-particle bridging, and sweep coagulation (Menezes et al., 1996). These mechanisms are very important in forming flocs of oily sludge and suspended solids which can easily float and be removed. Numerous researchers have reported the treatment of oily mill effluents, which is similar to waste glycerol, containing high concentrations of organic impurities, using coagulation, filtration and a settling procedure (Ahmad et al., 2006). As soaps are surfactant in waste glycerol, they can form complexes with oil to be micelle which can be oil emulsified in water (O/W) (Sawain et al., 2009). Coagulants are wasted when raw waste glycerol is directly mixed with them, the O/W emulsion coagulates and floats from the liquid, and thus the coagulants are also removed with the O/W emulsion (Yang, 2007). The destabilization or demulsification of O/W can be achieved with reducing electric force or destroying electrical double layers in acidification process. Additionally, the high pH value of raw waste glycerol is not always suitable for coagulation processes (Kemmer, 1987). Moreover, the soaps can convert into free fatty acid and salts in solution with a low pH value. In order to adjust the pH value for coagulation, remove soaps from waste glycerol and destroy the stability of O/W emulsion, the acidification process is needed as pretreatment before coagulation process. In addition, the transformation raw waste glycerol into gelatinous waste glycerol may provide another method to reuse raw waste glycerol as a fuel, since raw waste glycerol contains a large amount of organic compounds.

In this work, the effect of acidification on treatment of waste glycerol was studied. Additionally, the optimum conditions of coagulation processes with electotreat C-7123, polyaluminium chloride (PACl), cationic polyacrylamide (PAM-C) and anionic polyacrylamide (PAM-A) were separately studied; and then, their remove efficiencies of organic impurities through coagulation process at optimum conditions were compared. Finally, the methods of recovery organic matters from treated waste glycerol were discussed in this study. In addition, the production of gelatinous waste glycerol for reusing waste glycerol as a fuel was studied in this work.

1.2   Objectives

➢ To study the treatment of waste glycerol from biodiesel production process by acidification and coagulation.

➢ To recover the organic matters, such as glycerol, free fatty acid and methyl ester, from treated waste glycerol.

➢ To transform liquid waste glycerol into gelatinous waste glycerol (similar to solid alcohol) that can be reused as a fuel.

1.3   Advantages

➢ It is expected to provide an effective, cheap, easy to handle and available method to treat waste glycerol.

➢ It is expected to apply the coagulation process in different types of biodiesel plants which produce biodiesel from waste oil and palm oil by transesterification.

➢ It is expected to recover free fatty acid from waste glycerol, which can be reused as a material in the biodiesel production process.

➢ It is expected to recover glycerol from the waste glycerol after treatment.

➢ It is expected to coagulate the organic matters, such as oil and grease and soaps, and flocculate them into larger agglomerate which can be used as a carbon source for burning.

➢ It is expected to transform liquid waste glycerol into gelatinous waste glycerol, which was easy to transport and can be used as a fuel.

1.4   Scope of work

➢   The treatments of waste glycerol were compared. The possibility of waste glycerol treatment by coagulation process was discussed in the work.

➢   The conditions of acidification and coagulation processes had been adjusted, such as pH and dosages of coagulants and flocculants. The optimum conditions of acidification and coagulation were selected that provided the best results in the treatment process.

➢   The results of coagulation processes with different chemical coagulants at their selected conditions were compared.

➢   The methods of recovery organic matters from waste glycerol were discussed.

➢   The methods of making liquid raw waste glycerol into gelatinous waste glycerol.

1.5   Summary

In this chapter, it introduces some information about the thesis proposal. It shows the reasons to do this research and the important of the thesis. The second section provides the objectives of the thesis. The third section shows the benefits or advantages that we expect to get from this study. The forth section is the research scope.

Chapter 2

Literature review

2.1 Research background

As one of ongoing developing countries of Asia, Thailand experienced one of the world's highest economic growth rates with the average annual growth rate (AAGR) of 8.3% during 1985 to the economic crisis in 1997, and recovered again since 1999. By the end of 2003, Thailand economic situation was known as the world's second highest in gross domestic product (GDP) growth rate of 6.7% and the GDP still continuously grows till now (Jaruyanon and Wongsapai, 2007).

Considering on the country's final energy consumption under the 70% energy imported, transport sector plays a dominant role as more than one-third in shares of total energy consumption every year. The main fuel uses in transport sector, at 72% of total energy uses in transport sector, is diesel which mainly used in trucks, vans, locomotive, marine transport, and agricultural equipment (DEDE, 2007). This means that if Thailand can domestically produce Thailand own biodiesel unit, which can automatically substitute to the convention biodiesel, the benefits would greatly impact to the country.

2.2 Overview of Biodiesel

Biodiesel as an alternative fuel has attracted increasing interest worldwide in recent years. During the biodiesel production process, oils/fats (triglycerides) are mixed with methyl alcohol and alkaline catalysts to produce esters of free fatty acids, with glycerol as a primary by-product (Gerpen, 2005).

As an alternative, biodiesel has many merits. It is derived from a renewable, domestic resource, biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favorable combustion emission profile, such as low emission of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect (Korbit, 1999). Biodiesel has a relative high flash point (150℃), which makes it less volatile and safer to transport or handle than petroleum diesel (Krawczyk, 1996). It provides lubricating properties that can reduce engine wear and extend engine life (Wedel, 1999). In brief, these merits of biodiesel make it a good alternative to petroleum-based fuel and have led to its use in many countries, especially in environmentally sensitive areas.

The most common way to produce biodiesel is by transesterification, which is shown in **Figure 2.1**. Triglycerides, as the main component of oils/fats, consist of three long chain fatty acids esterified to a glycerol backbone. When triglycerides react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME). Glycerol is produced as a by-product. Methanol is the most commonly used alcohol because of its low cost and methanol is the processes developed in this study. In general, a large excess of methanol is used to shift the equilibrium far to the right (**Figure 2.1**).

| Triglyceride | Methanol | Glycerol | Methyl Esters |
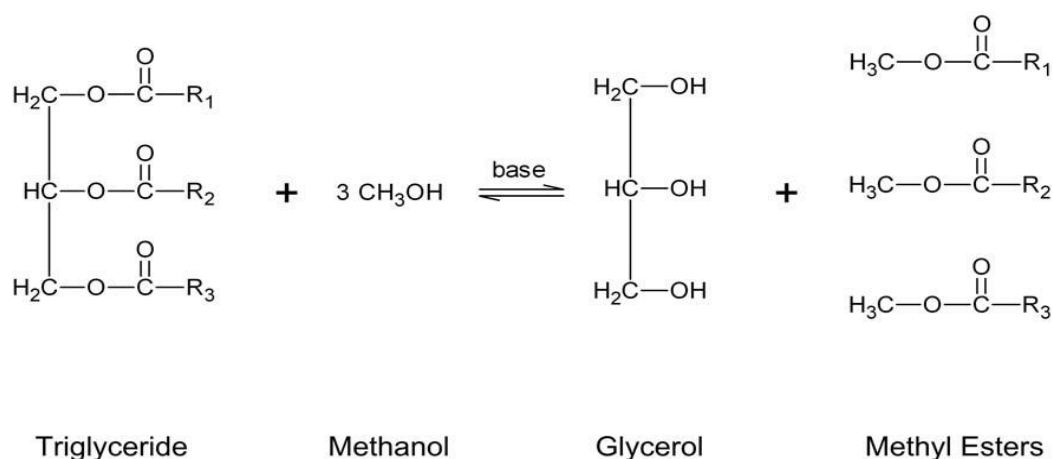
Figure 2.1 The transesterification of biodiesel product process (Gerpen, 2005)

2.2.1 Advantage of Biodiesel

1. It is renewable with energy efficient and also displaces pretroleum derived diesel fuel;

2. It can be used in most diesel equipment and no or only minor modifications;

3. It can reduce greenhouse gases emissions and tailpipe emissions, including air toxics and smogs;

4. It is domestically production from either agricultural (crude palm oil) or recycled resources (used cooking oil).

2.2.2 Disadvantages of Biodiesel

1. It increases NOx especially in some kinds of B100, such as those high in polyunsaturated fatty acid, it produces more NOx than petrol gas in saturated fatty acids (Jaruyanon and Wongsapai, 2007);

2. It contains 10% less calorific value than the conventional diesel.

2.2.3 Biodiesel Production Processes

Even there are various biodiesel production technologies, but there are two main technologies widely used in biodiesel production in Thailand; (1) transesterification technology, (2) acid etherification technology. In this study, the biodiesel is produced from the used cooking oil from various sources, such as oil gathering from fresh markets, school canteens, or restaurants. By using the transesterification processes, as shown in **Figure 2.2**, it converts triglycerides to biodiesel at the temperature of 60 to 70 ℃ and at the atmospheric pressure. The waste glycerol and crude biodiesel would then separate. The separated crude biodiesel is washed with mildly acidic water to remove the neutralized catalysts, water solution glycerol, soaps and methanol. For

the remaining crude glycerin, it would then refine to various grades according to various purposes.
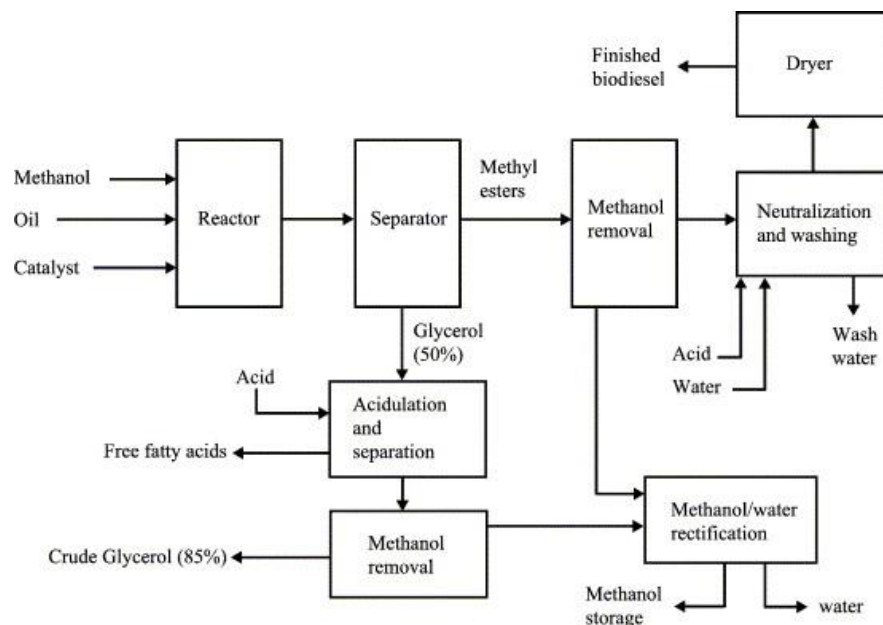
Figure 2.2 Transesterification process of biodiesel production (Gerpen, 2005)

2.3 Overview of Waste Glycerol

2.3.1   Introduction of Waste Glycerol

The waste glycerol stream leaving the separator of biodiesel production process by transesterification with waste oil and palm oil is about 50% glycerol. It contains some of the excess methanol and most of the catalyst and soap. In this form, the waste glycerol has a small value and disposal may be difficult (Gerpen, 2005). The methanol content requires the glycerol to be treated as hazardous waste.

The production of 100 kg of biodiesel yields approximately 10 kg of waste glycerol. Glycerol is generated as a by-product not only when biodiesel fuels are produced chemically, but also when they are produced enzymatically (Du et al., 2003) and during the production of biodiesel (Yazdani and Gonzalez, 2007). The dramatic growth of the biodiesel

industry has created a surplus of glycerol that has resulted in a dramatic 10-fold decrease in crude glycerol prices over the last few years and generated environmental concerns associated with contaminated glycerol disposal (Yazdani and Gonzalez, 2007).

2.3.2 Application of Waste Glycerol

At present, due to properties of pure glycerol, it has more than 2000 different application (Elvers et al., 1990). However, the cost of glycerol purification from waste glycerol is quite high (Chi et al., 2007). Although waste glycerol can be burnt, it has low fuel value because of 10 % water content (Peereboom et al., 2007). Several strategies based on chemical and biological transformations are being pursued to convert waste glycerol into more valuable products (Yazdani and Gonzalez, 2007). Examples of some of these include:

➢ The conversion of glycerol into propylene glycol and acetone, through thermo-chemical processes (Chiu et al., 2006; Dasari et al., 2005);

➢ The etherification of glycerol with either alcohols (e.g. methanol or ethanol) or alkenes (e.g. isobutene) and the production of oxygen-containing components, which could have suitable properties for use in fuel or solvents (Karinen and Krause, 2006);

➢ The microbial conversion (fermentation) of glycerol to 1,3-propanediol, which can be used as a basic ingredient of polyesters (Barbirato et al., 1998; Ito et al., 2005);

➢ Other products such as butanol (Bieble, 2001), propionic acid (Bories et al., 2004), ethanol and formate (Jarvis et al., 1997), succinic acid (Lee et al., 2001), dihydroxyacetone (Bories et al., 1991; Claret et al., 1994), polyhydroxyacetones (Koller et al., 2005), or hydrogen and ethanol (Ito et al., 2005) were also obtained using glycerol as a carbon source.

2.4 Acidification process

2.4.1   The effect of acidification on oil and grease remove

Return to **Figure 2.2**, the waste glycerol stream leaving the separator is only about 50% glycerol. It contains some of the excess methanol and most of the catalyst and soap. In this form, the waste glycerol has little value and disposal may be difficult. The methanol content requires the glycerol to be treated as hazardous waste. The first step in refining the glycerol is usually to add acid to split the soaps into free fatty acids and salts. The free fatty acids are not soluble in the glycerol and will rise to the top where they can be removed and recycled. The salts remain with the waste glycerol although depending on the chemical compounds present. Mittelbach and Koncar (1998) described a process for esterifiying these free fatty acids and then returning them to the transesterification reaction stream.

2.4.2   The effect of acidification on demulsification of O/W

The waste glycerol contains a lot of O/W emulsion which can affect coagulation process (Rios et al., 1998). Thus, the O/W emulsion should be destroyed by acidification process before coagulation process.

O/W emulsion may be broken by chemical, electrolytic, or physical methods. The breaking of an emulsion is also called resolution, since the result is to separate the original mixture into its parts. Traditionally, hydrochloric acid has been used in oily waste treatment plants as the first step in emulsion breaking. Acid converts the carboxyl ion in surfactants to carboxylic acid, allowing the oil droplets to agglomerate. Chemical coagulating agents, such as salts of iron or aluminum, can be used in place of acid, with the additional benefit that these aid in agglomeration of the oil droplets. However, generally break emulsions more effectively than coagulant salts, but the resultant acidic wastewater must be neutralized after oil/water separation.

2.4.3   Application of acidification on waste glycerol pretreatment

Chi et al., (2007) found that when waste glycerol was directly mixed with artificial seawater, soaps precipitated from the liquid, which later proved detrimental to cell growth. To avoid this phenomenon, the waste glycerol was pretreated with HCl prior to use in the algal culture.

Lopez et al., (2009) pretreat waste glycerol with phosphoric acid and centrifugation in order to reduce the catalyst used in the transesterification reaction (KOH). The waste glycerol after acidification was treated by anaerobic digestion to produce biogas.

2.5 Overview of Coagulation

Coagulation method is widely used in water and wastewater treatments and well known for its capability of destabilizing and aggregating colloids. There are a number of different mechanisms involved in a coagulation process, including ionic layer compression, adsorption and charge neutralization, inter-particle bridging and sweep coagulation (Menezes et al., 1996). These mechanisms are very important in forming flocs of residue oil and suspended solid which could be easily settled and finally removed.

Combined with a dynamic separator, the most suitable coagulation mechanism is sweep coagulation, since large settle-able flocs are formed in this mechanism. The coagulation process can be enhanced by the addition of flocculants which assist the collection of dispersed particles, strengthen the flocs and agglomerate the flocs to larger sizes for improved effluent clarity. Polymers, which can be negatively or positively charged, or have no charge, are normally used as the flocculants. They contain adsorbing groups which help to form bridges between the flocs to increase the floc size of the coagulated particle.

Coagulation-flocculation is a frequently applied process in the primary purification of industrial wastewater (Renault et al., 2009). Coagulation using chemical coagulants consists of combining insoluble particles and dissolved organic matter into large aggregates, thereby facilitating their removal in subsequent sedimentation, floatation and filtration

stages. It usually involves the dispersal of one or several chemical reagents which destabilizes the colloidal particles, leading to the formation of micro-floc. Bonding the micro-floc particles together by the addition of a flocculation additive forms larger, denser flakes that are easier to separate. A simple separation step then eliminates the floc. The coagulants and flocculants frequently used are mineral additive including metal salts such as polyaluminium chloride (PACl) and synthetic polymers such as polyacrylamide (PAM).

In conventional wastewater treatment systems, coagulants such as aluminum chloride ($AlCl_3$), ferrous sulphate ($FeSO_4$), aluminum sulphate [$Al_2(SO_4)_3$], ferric chloride and hydrated lime are the most widely used. This is because of their effectiveness, cheap, easy to handle and availability. Among the available coagulants, PACl is one of the most extensively used coagulants for sludge conditioning and dewatering coagulation process.

The electotreat C-7123 (20 g/L) was composed of cationic polyamine (PA) 6% and PACl 94% by weight. The mechanism of PA blend with PACl to flocculate raw waste glycerol is that cationic polymeric flocculants destabilize the particle and coloring matters through the compression of electrical double layers, charge neutralization, and the adsorption and subsequent formation of particle-polymer-particle bridges (Besraa et al. 2002, Avci et al. 2002), high removal efficiency can still be achieved even with a small amount of cationic polymeric flocculants, which generate a small volume of sludge output (Yue et al 2008).

2.6 Overview of PACl

Polyaluminium chloride (PACl) is one of the most extensively used coagulants for sludge conditioning and dewatering process (Ahmad et al., 2006). Concentrated solutions of partially prehydrolyzed aluminum salts such as PACl are commonly used as coagulants for water treatment and other coagulation application (Liu et al., 2003). Much attention has been paid to partially prehydrolyzed aluminum salt in recent years because of their higher efficiency and relatively lower cost compared with the traditional coagulants. A good understanding of the characteristics of PACl is of benefit in optimizing operational conditions of water treatment. It is generally thought that the higher efficiency of these coagulants depends on characteristics such as

the content of active species and the particle size distribution. It has been demonstrated that the active species responsible for coagulation or precipitation is the highly charged polymeric aluminum Al_{13} ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) species (Liu et al., 2003). Al_{13} is composed of one tetrahedral center surrounded by 12 octahedral Al units (Liu et al., 2003). Besides the characteristic of higher positive charge (+7) and resultant strong ability to bind to particles, Al_{13} polymer possess fairly stable structure against hydrolysis before adsorption to particle surfaces. There properties contribute to their superior behavior in coagulation.

2.6.1 PACl coagulation on removal of oil and grease

Chesters et al., (2009) found that PACl showed moderately good removal oil and grease. These positively charged aluminium salts interact with negatively charged particles to assist in charge aggregation. The PACl under appropriate pH, temperature and salinity conditions reacts with water to form insolution aluminum hydroxide which, on precipitation, link together to form long chains or meshes, physically trapping small particles into the larger floc.

In Malaysia, palm oil-processing mills are the most prominent vegetable oil industry which discharges large volumes of oily and colloidal wastewater. The palm oil mill effluent contains about 4,000-6,000 mg/L of oil and grease, which are similar with the waste glycerol from biodiesel facility that uses alkali-catalyzed transterification to produce biodiesel from cooking oil and palm oil. Ahmad et al., (2006) used PACl to coagulate residue oil and suspended solid; they found that when dosage of PACl was 6 g/L and pH of 4.5, more than 95% of suspended solid and residue oil were removed.

PACl was widely used in oily waste water treatment, since it is more effective at low temperatures, a broad pH range and forms positive charged aluminum species that adsorb to negatively charged natural particles resulting in charge neutralization. PACl has been shown to be effective as a pretreatment coagulant to separate oil and grease by destabilizing oil droplets and destroying emulsions (Eilbeck and Mattock, 1987).

2.6.2 Application of PACl on oily wastewater treatment

Zeng et al., (2007) used PACl and PAM-A to treat heavy oil wastewater (HOW) which contains oil droplets, suspended solids and dissolved salts. The results showed that under the optimum experimental conditions of coagulation (PACl dosage: 100 mg/L, PAM-A dosage: 1 mg/L, setting time: 40 mins and pH 6.5-9.5). More than 99% of oil was removed and suspended solid value less than 5 mg/L.

Zhao et al., (2008) used PACl and PAM-C as flocculants to treat simulated oily wastewater. The results indicated that the light transmission of wastewater got to the maximum in a range of flocculants concentration and then decreased with the increasing flocculants concentration. Flocculation performance improved with the increasing temperature while PACl was used. However, the performance decreased while PAM-C was used. The flocculation performance decreased markedly with the concentration of hydrolyzed polyacrylamide (HPAM) residue increasing as to these two kinds of agents. When HPAM residue in wastewater increased from 100 mg/L to 600 mg/L, the light transmission decreased from 96.4% to 70% after treating with PACl of 600 mg/L at 37 °C. It decreased from 87.3% to 50% with PAM-C of 150 mg/L. The flocculation effect of PACl was excellent.

2.6.3 PACl reaction

The term PACl refers to a class of soluble aluminum products in which aluminum chloride has been partly reacted with base. The relative amount of OH-, compared to the amount of aluminum, determines the basicity of a particular PACl product. The chemistry of PACl is often expressed in the form $Al_n(OH)_mCl(3n-m)$. Basicity can be defined by the term $m/(3n)$ in that equation. Because PACl is more expensive to produce than aluminum sulfate, it is important to note the most important differences between these two products. Solutions of PACl are not as acidic as alum; consequently they do not tend to decrease the pH of the furnish nearly as much as an equivalent amount of alum. Another difference is that PACl is formulated so that it already contains some of the highly cationic oligomers of aluminum - materials that are especially

effective for the modification of colloidal charges in an aluminum sulfate furnish. A particularly stable and important ionic species in PACl and related soluble aluminum chemicals has the formula $Al_{12}(OH)_{24}AlO_4(H_2O)_{12}^{7+}$.

In the solution with low pH value (< pH 4.5), there is no alkalinity in solution. Thus, the PACl cannot form $Al_n(OH)_mCl(3n-m)$. However, the Al^{3+} from PACl can neutralization small compounds with negative charge and absorb them at its surface (Polyaluminum chloride, 2001).

PACl coagulation not only can coagulate organic compounds, but also can break O/W emulsion. This is destruction of the emulsifying properties of the surface-active agent or neutralization of the charged oil droplet (Kemmer, 1987).

2.7 Overview of PAM

As **Figure 2.3** shown that polyacrylamide (PAM) is a kind of linear water-soluble polymer material. PAM can be divided into three types: PAM-A, PAM-C and nonionic PAM. In general, appearance of PAM is a white powder, and it can be dissolved in the water. But it cannot be dissolved in organic solution, except glycol, glycerol, glacial acetic acid, formammide, lactic acid and acrylic (Ping and Pei, 1995). So it is widely used in mining, coal preparation, petrochemical, papermaking, textile, refine sugar, medicine and environment industries.

Therefore, PAM has been used as the flocculant to treat waste glycerol and separate glycerol. Moreover, PAM is non-toxic and PAM is much cheaper than most other polymers (Wang et al., 1996).

As we know that there are many organics in waste glycerol, like glycerol, soaps, methanol and fatty acid, the major component of biodiesel is methyl ester, and it can react with PAM (Fuad and Ruan, 2009). Roberts (1994) uses PAM to remove fatty acid. Moreover, the PAM can flocculate large molecule organic compounds, but not easy to flocculate the small organic compounds, such as glycerol and ethanol (Wang et al., 1996). Thus, It is also hoped that

glycerol will be separated from other organics by PAM.

The benefits of PAM to separate glycerol are:

1.   PAM is non-toxic, thus will not cause secondary pollution;

2.   The operation of PAM flocculation is very easy and it does not need large and expensive instruments;

3.   PAM flocculation reaction is fast, if the condition is correct.

The shortcomings of using PAM to separate glycerol are:

1.   The effect of pH, reaction time, mix speed and concentration range is large;

2.   PAM may flocculate glycerol with others organics.
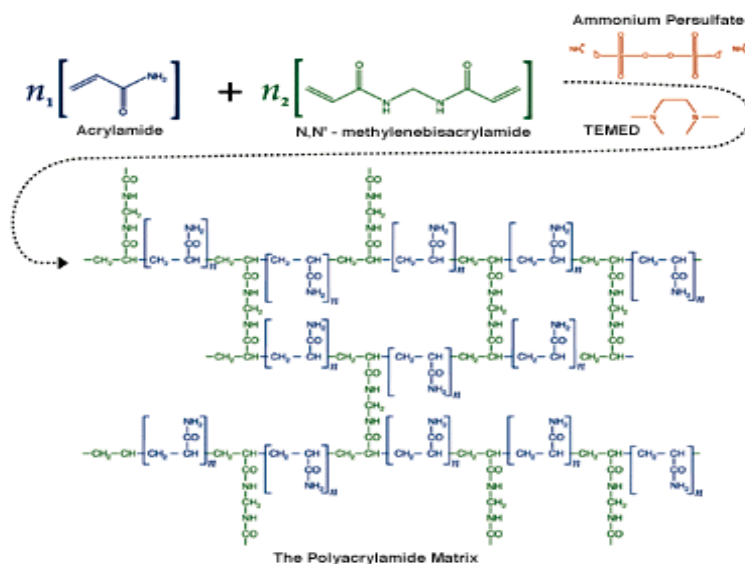
Figure 2.3 The polymerization of a polyacrylamide matrix with methylenebisacrylamide cross-linking (National Diagnostics, 2010)

2.7.1   Theory of PAM flocculation

As shown in **Figure 2.4**, flocculation is the action of PAM polymers to form bridge between the flocs, and then bind the particles into large agglomerates or clumps (Wang, 2006). Finely dispersed solids (colloids) suspended in wastewaters are stabilized by negative

electric charges on their surfaces, causing them to repel each other. So it is impossible to remove these colloids by natural precipitation. The PAM flocculants need to be put into wastewater to make these colloids become large agglomerates and deposit, and then remove them.

The process of colloids become flocculation sediments, when PAM flocculants are put into wastewater, is dividing into three stages:

1. Flocculation hydrolyzes and form molecular state polymer;

2. Bridging or charge neutralization occurs when segments of the polymer chain adsorb on particles and help particles aggregate.

3. Suspended particles are flocculated into larger particles and depositing.
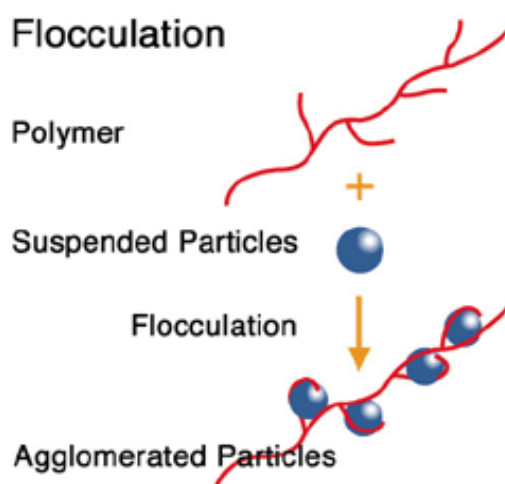
Figure 2.4 Process of polymer flocculation (Agronomy for Sustainable Development, 2000)

2.7.2 Different between flocculation and coagulation

In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water. Although the terms coagulation and flocculation are often used interchangeably, or the single term "flocculation" is used to describe both; they are, in fact, two distinct processes. Knowing their differences can lead to a better understanding of the clarification and dewatering operations of wastewater treatment.

Finely dispersed solids (colloids) suspended in wastewaters are stabilized by negative electric charges on their surfaces, causing them to repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocs, they do not settle. To assist in the removal of colloidal particles from suspension, chemical coagulation and flocculation are required. These processes, usually done in sequence, are a combination of physical and chemical procedures. Chemicals are mixed with wastewater to promote the aggregation of the suspended solids into particles large enough to settle or be removed.

As shown in **Figure 2.5**, the coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid. Care must be taken not to overdose the coagulants as this can cause a complete charge reversal and restabilize the colloid complex (Effluent treatment, chemical coagulation, water treatment, 2011).

Flocculation is the action of polymers to form bridges between the flocs, and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. An anionic flocculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization. In this process it is essential that the flocculating agent be added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles. The newly formed agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Care must also be taken not to overdose the polymer as doing so will cause settling/clarification problems. Anionic polymers themselves are lighter than water. As a result, increasing the dosage will increase the tendency of the floc to float and not settle.

Once suspended particles are flocculated into larger particles, they can usually be removed from the liquid by sedimentation, provided that a sufficient density difference exists between the suspended matter and the liquid. Such particles can also be removed or separated by media filtration, straining or floatation. When a filtering process is used, the addition of a

flocculant may not be required since the particles formed by the coagulation reaction may be of sufficient size to allow removal.   The flocculation reaction not only increases the size of the floc particles to settle them faster, but also affects the physical nature of the floc, making these particles less gelatinous and thereby easier to dewater.
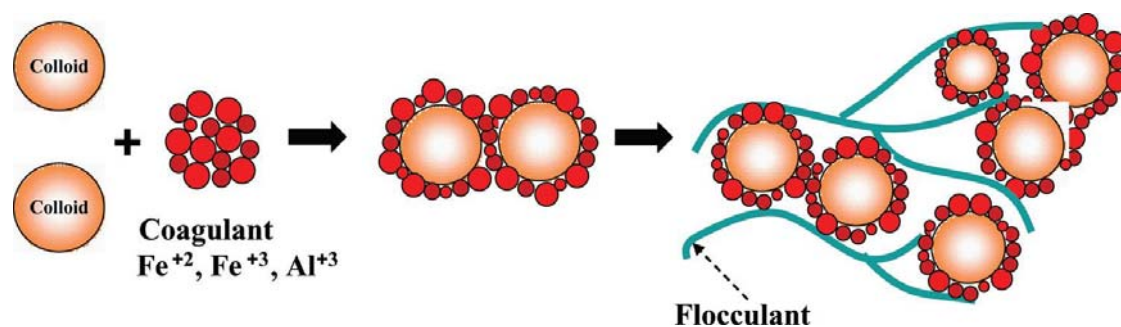
Figure 2. 5 The different of coagulation process and flocculation process (Informaworld, 2011)

2.7.3   Ionic form of PAM reaction

The ionic form of PAM has found an important role in the potable water treatment industry. Trivalent metal salts like ferric chloride and aluminium chloride are bridged by the long polymer chains of PAM. This results in significant enhancement of the flocculation rate. This allows water treatment plants to greatly improve the removal of total organic content (TOC) from raw water.

PAM flocculants can demulsification of O/W. This is agglomeration of the neutralized droplets into large, separable globules. The organic demulsifiers are extremely effective emulsion breaking agents, giving more consistent results and producing better effluent quality than an inorganic program. In many treatment plants, organic emulsion breakers have replaced traditional alum treatment for exactly those reasons. In addition to yielding a better quality effluent, organic emulsion breakers often require lower dosage than a corresponding inorganic treatment. In addition, Organic emulsion breakers reduce the amount of sludge generated in a treatment program by as much as 50 to 75% (Kemmer, 1987).

2.7.4   Application of PAM and PACl on oily wastewater treatment

Yu et al., (2002) used cationic PAM flocculants to treat emulsified oil wastewater. The result showed that it had no treatment effect when cationic organic flocculants were put into emulsified oil wastewater alone. However, if cationic organic flocculants and PACl were complexed together to use, the sedimentation would be big and density is high. At the same time, dose need of PACl was reduce 30%，   scum volume was small and water content of sedimentation was low.

Zhang et al., (2002) used polyacylamide (PAM) to treat the oil-contained wastewater of high thick oil in continuous industrializing operation. The results showed that the wastewater with 26,000 mg/L of oil was treated in the normal period of wastewater quality, the reduction of oil was 99.8% at concentration of PAM   was 14~18 mg/L, the oil content was about 16~34 mg/L. The wastewater with 56,000 mg/L of oil was treated in the fluctuating period of wastewater quality, the reduction of oil was 99.6% at   concentration of PAM was 22 mg/L, the oil content was about 220 mg/L. PAM had a good compatibility with demulsifiers, and it had some cooperative effect with demulsifying agent.

2.8 Overview of CDs

The majority of cyclodextrins (CDs) are α-CD, β-CD and a small quantity of γ-CD, consisting of six, seven or eight units of glucose, respectively (Tonkova, 1998), which was shown in **Figure 2.6**. CDs have the ability to encapsulate a wide range of organic and inorganic molecules altering the stability, reactivity and solubility of the inclusion complexes formed with them (Brewster and Loftsson, 2007; Szerman et al., 2007). These characteristics make CDs, and their derivatives, suitable for applications in biotechnology (Singh et al., 2002), agriculture (Valle, 2004), pharmaceutical (Brewster and Loftsson, 2007; Lottsson and Duchêne, 2007), food (Szente and Szejtli, 2004) and cosmetics (Valle, 2004) industries.

The β-CD is the most widely used in Natural CD, because it is much cheaper than α-CD and γ-CD. Liu (2006) putted 1 g β-CD in 150ml of water solution containing 200ppm

alkylphenol ethoxylate (APE); and 85% of the APE can be absorbed by the β-CD. Then he used lower aliphatic alcohol is used to elute and recover the CD. So CD can be used repeatedly.

Glycerol, a 1, 2, 3-propanetriol, is a simple alcohol used as industrial chemicals. Glycerol is a kind of viscous liquid-like has no color, no smelly and its hygroscopic is good. It can dissolve in water, alcohol and phenol. The molecular diameter is 612 nm, but the inside diameter of CDs is 800 nm. The CDs can include glycerol molecule (Song et al., 2008).

Furthermore, Song et al. (2008) listed one hundred and one representative inclusion complexes formed by organic or inorganic guest molecules or ions with α-, β-, γ-CD and modified CD, as well as their chemical stoichiometric ratio (CSR) values, inclusion number (IN) and the number of crystal water (CRW). They used X-ray diffraction to analysis and find that the chemical stoichiometric ratio (CSR) values between β-CD and glycerol is 1: 1, and the number of crystal water is 7.2 (Song et al., 2008).

That means β-CD can absorb glycerol, but there is no one uses β-CD to absorb residual glycerol from waste glycerol before. If it works, it will be very useful for recovering industrial glycerol. The benefits of adsorption of β-CD are:

1. β-CD is non-toxic, it's easy for biodegradable and will not cause secondary pollution;

2. The equipments are simple, may be it just need a mixer, and not expensive;

3. Chemical is cheap and operation is easy;

4. β-CD can be recovered and reused.

The shortcoming of adsorption of β-CD:

1. The affect of pH, react time, temperature and concentration is big;

2. β-CD may react with methanol and salts in the waste glycerol.
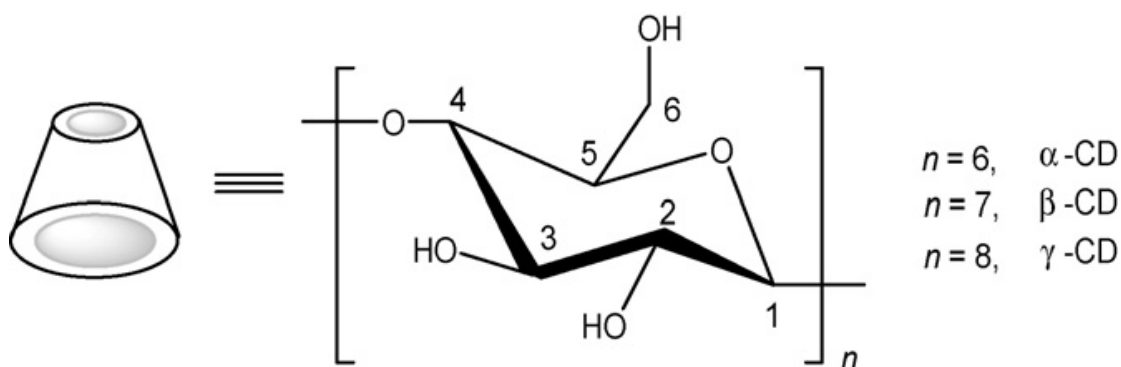
Figure 2.6 Molecular structures of CDs (Song et al., 2008)

2.9 Overview of HPMC and stearic acid

2.9.1 Introduction of HPMC and stearic acid

Hydroxypropyl methylcellulose (HPMC), a so-called polymeric emulsifier, is able to absorb at liquid interfaces and to lower the interfacial tension. The use of HPMC as an emulsifier for oil-in-water emulsions was first described by Daniels and Barta (Wollenweber et al., 2000).

Stearic acid is the saturated fatty acid with 18 carbon chain and has the IUPAC name octadecanoic acid. The stearic acid is useful as an ingredient in making candles, plastics, dietary supplements, oil pastels and cosmetics, and for softening rubber (Wootthikanokkhan and Tunjongnawin, 2002). It is used to harden soaps, particularly those made with vegetable oil. Stearic acid is used in aerosol shaving cream products. Batte et al. (2007) used stearic acid to form monostearin-oil-water gel. It means that the stearic acid may be able to form waste glycerol gel, since waste glycerol contains oil-water emulsion also.

2.9.2 Application of HPMC and stearic acid

Wollenweber et al., (2000) investigated the physicochemical properties of the aqueous solutions of three different types of Hydroxypropyl methylcellulose (HPMC 2208,

HPMC 2906 and HPMC 2910) and those of HPMC stabilized O/W emulsions. It was found that the O/W emulsion stability depends on HPMC substitution type. Emulsion stabilized by HPMC 2208 and HPMC 2906 as compared with HPMC 2910 show higher stability of the droplet size when stored in a temperature cycle test for 6 months

Batte et al., (2007) used stearic acid to form monostearin-oil-water into gels. It was found that the conditions of homogenization rate, cooling rate and homogenization temperature can affect the formation and stability of a gel comprised of oil, water, monostearin and stearic acid.

Chapter 3

Material and methodology

3.1 Experiment design

As shown in **Figure 3.1**, there are three main experiment processes and one preliminary study of CDs recover glycerol in this research. The steps of each experiment processes will be described in following sections.

```
                        ┌─────────────────────┐
                        │ Raw waste glycerol  │
                        │      samples        │
                        └─────────────────────┘
          ┌──────────────────────┼──────────────────────────────┐
          ▼                      ▼                               ▼
  Electotreat C-7123      PACl and PAMs             Production of gelatinous
  coagulation (3.2)       coagulation (3.3)         waste glycerol (3.5)
          │                      │              ┌────────┬──────────┬──────────┐
          ▼                      ▼              ▼        ▼          ▼
  ┌──────────────────┐  ┌──────────────┐  ┌──────────┐┌──────────┐┌──────────┐
  │ Characteristics  │  │Characteristics│  │Stearic   ││Stearic   ││HPMC and  │
  │ analyze (3.2.1)  │  │analyze (3.3.1)│  │acid      ││acid and  ││methanol  │
  └──────────────────┘  └──────────────┘  │(3.5.1)   ││methanol  ││(3.5.3)   │
          │                      │         └──────────┘│(3.5.2)   │└──────────┘
          ▼                      ▼              │      └──────────┘     │
  ┌──────────────────┐  ┌──────────────┐        │           │          │
  │ Acidification    │  │Acidification │        ▼           ▼          ▼
  │ pretreatment     │  │pretreatment  │  ┌──────────────────────────────┐
  │ (3.2.2)          │  │(3.3.2)       │  │ Comparison of three types of  │
  └──────────────────┘  └──────────────┘  │ gelatinous waste glycerol     │
          │                      │         └──────────────────────────────┘
          ▼                      ▼
  ┌──────────────────┐  ┌──────────────┐
  │Coagulation with  │  │PACl coagulation│
  │commercial        │  │process (3.3.3) │
  │coagulant (3.2.3) │  └──────────────┘
  └──────────────────┘          │
          │                      ▼
          ▼              ┌──────────────┐
  ┌──────────────────┐  │4 types of PAMs│
  │The optimum        │  │flocculation   │
  │conditions of      │  │(3.3.4)        │
  │coagulation        │  └──────────────┘
  └──────────────────┘          │
          │                      ▼
          │              ┌──────────────┐
          │              │The appropriate│
          │              │PAM as the     │
          │              │flocculant     │
          │              └──────────────┘
          │                      │
          │                      ▼
          │              ┌──────────────┐
          │              │The optimum    │
          │              │conditions of  │
          │              │coagulation    │
          │              └──────────────┘
          ▼                 │         │
  ┌──────────────────┐      ▼         ▼
  │ Comparison of two │◄──┌──────────┐┌──────────┐   ┌──────────────┐
  │ coagulation       │   │Glycerol  ││          │──►│Comparison with│
  │ processes         │   │recovery  │           │pure glycerol  │
  └──────────────────┘   │with CDs  │           │recovery with  │
                         │(3.4)     │           │CDs            │
                         └──────────┘           └──────────────┘
```

Figure 3.1 The flow chart of experiment design

3.2 Coagulation process with electotreat C-7123

The commercial coagulant named electotreat C-7123 was used to treat waste glycerol in this process. Acidification process was used as pretreatment before coagulation process.

3.2.1 Chemicals and material

The electotreat C-7123 was bought from Electronics Chemical Co. Ltd. The coagulant is 20 g/L, which was composed of cationic polyamine (PA) 6% and polyaluminium chloride (PACl) 94%.

Raw waste glycerol samples were collected on October 2009, from the waste glycerol tank in the Specialized R & D Center for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University, Thailand. This facility uses alkali-catalyzed transesterification to produce biodiesel from waste cooking oil and palm oil. The parameters to be characterized and the standard methods (APHA, AWWA and WEF, 1998) are shown in **Table 3.1**

Table 3. 1 Selected characterizations and standard methods

No.	Characterizations	Analytical methods
1	pH	Standard method 4500-H+ B
2	COD	Standard method 5220 B
3	BOD_5	Standard method 5210 B
4	TSS	Standard method 2540 D
5	Total glycerol	ASTM D7637
6	Soaps	AOCS method Cc 17-79
7	Methanol	ASTM D7059

3.2.2   Acidification pretreatment

The pH value is one of the main factors involved in coagulation. In addition, concentrations of soaps in raw waste glycerol can be reduced in the acidification process. The acidification pretreatment protocol was as follows:

1. The pH value was adjusted with 0.8 M HCl. Titrate the 400 mL of raw waste glycerol with HCl to adjust the pH value, and measure the relation of HCl volume and pH changing of waste glycerol;

2. The COD, BOD_5 and TSS were measured when pH values were 3, 4, 5, 6, 7, 8 and 9 to study the effect of acidification on treatment of raw waste glycerol;

3. The concentrations of grease and oil, free fatty acid, methyl ester and soaps were measured at different pH values to study the effect of pH on oil and grease and soaps removal. The free fatty acid and methyl ester were analyzed with gas chromatography (EN 14103, 2003);

4. The concentrations of glycerol and methanol were measured at different pH values between 3 - 9 to study the effect of pH on glycerol and methanol removal;

5. An appropriate pH range for acidification was selected, which provided the concentration of parameters, such as COD, BOD_5, TSS and soaps;

6. When pH values of waste glycerol were adjusted below 7, the waste glycerol separated into two layers. The upper and lower layers were respectively taken by dropper to measure the concentration of soaps (AOCS method Cc 17-79)

7. After acidification, the treated waste glycerol with appropriate pH was taken to coagulation-flocculation process.

3.2.3 Coagulation process

1. After acidification pretreatment, the pH value of the 400 mL waste glycerol was adjusted to pH 8 with 6 M NaOH and 0.8 M HCl, since the PA is normally used at pH values between 7 and 9 due to the pH optimize value (Tzoupanos et al., 2008).

2. Adjust the concentration of electotreat C-7123 to 2 g/L, 3 g/L, 4 g/L, 5 g/L and 6 g/L in waste glycerol. The waste glycerol was mixed by jar test at 100 rpm for 2 mins and then at 35 rpm for 15 mins (Meyssami and Kasaeian, 2005).

3. After settling waste glycerol for 60 mins, the samples were taken from waste glycerol to measure COD, BOD_5 and TSS.

4. The optimum concentration of electotreat C-7123 was measured by comparison of these parameters removal efficiencies. This optimum concentration was taken to the next step to measure the optimum pH value for coagulation.

5. After acidification process, the pH values of waste glycerol samples were adjusted to 3, 4, 5, 6, 7, 8 and 9 with NaOH and HCl.

6. The optimum concentration of electotreat C-7123 measured in the last step was put into the different pH values of waste glycerol.

7. The waste glycerol samples were mixed by jar test at 100 rpm for a period of 2 mins and then at 35 rpm for 15 min.

8. The COD, BOD_5, TSS, methanol and glycerol from waste glycerol were measured.

9. The optimum pH value was ascertained by comparing the removal efficiencies of these parameters.

3.3 Coagulation process with PACl and four types of PAMs

In this process, HCl was used as acidification to convert soaps into salts and fatty acids, the same as the coagulation process with electotreat C-7123. Four typical of PAMs, cationic PAM (C-8385), cationic PAM (C-8800), anionic PAM (A-9770) and anionic PAM (A-9934), were used as coagulant aids to enhance the PACl coagulation process. The effects of these four types of PAMs on waste glycerol treatment were compared. The effect on destroying oil-in-water emulsion in waste glycerol by acidification and coagulation was studied.

3.3.1 Chemicals and material

The required quantity of PACl was prepared just before the experiment in an aqueous solution with 20 g/L as a stock solution so there would not be any inaccuracies in results due to chemical changes. The cationic PAM (C-8385), cationic PAM (C-8800), anionic PAM (A-9770) and anionic PAM (A-9934) were all prepared in stock solutions with 0.1 g/L.

The waste glycerol samples were obtained on 26 January 2010 from the waste glycerol tank, the same place as last time. The characteristics of raw waste glycerol were analyzed according to the standard methods (APHA, AWWA, WEF, BS, AOCS and ASTM, 1998).

3.3.2 Acidification process

1. The pH values of waste glycerol were adjusted to pH values of 3, 4 and 5. The waste glycerol separated into two layers. The upper layer is mainly free fatty acid and methyl ester, the lower layer is mainly water, salts, glycerol, methanol and soaps.

2. The upper layer was taken by dropper to take the pictures of oil drop coalescence with a 40 time microscope enlargement.

3. The lower layer was taken to analyze the parameters and take to the next coagulation process

3.3.3   PACl coagulation process

1. After acidification process, the pH values of treated waste glycerol samples were adjusted to 3, 4, 5, 6, 7, 8 and 9 with HCl and NaOH.

2. 2 g/L PACl was added to waste glycerol with different pH values (from 9 to 3) (Abdul et al., 2010), and the total volume of waste glycerol and PACl solution was 400 mL.

3. The waste glycerol and PACl solution were mixed with a jar test apparatus at 100 rpm for 1 min, and then reduced to 20 rpm for 15 mins (Ustun, 2007).

4. After the coagulation process, the treated waste glycerol were taken to measure parameter concentrations, such as COD, BOD_5, TSS and glycerol. Since the treated waste glycerol was diluted with HCl, NaOH, and coagulant after treatment, these parameter values should decrease because of dilution. Thus, the parameters should be calculated and compared with the parameter values that were measured in experiment. Then, the removal efficiencies of different pH values were measured by compared with the parameter values.

5. The optimum pH value of waste glycerol samples were ascertained and carried out in the next step.

6. The pH values of the lower layer waste glycerol samples were adjusted to the optimum pH value measured in the first experiment step.

7. The concentration of PACl (20 g/L) in waste glycerol was adjust from 6 g/L to 1 g/L.

8. The removal efficiencies of COD, TSS and soaps in the different PACl concentrations were measured.

9. The optimum PACl concentration was ascertained by comparing the removal efficiencies of these parameters.

3.3.4 Coagulation process with PACl and four types of PAMs

1. Reprocess PACl coagulation treat waste glycerol, and measured the optimum pH value and the optimum PACl concentration.

2. After acidification pretreatment, the pH of treated waste glycerol was adjusted to the optimum pH value. The optimum concentration of PACl was added into these waste glycerol samples.

3. The solutions of PACl and waste glycerol were mixed using a jar test apparatus at 100 rpm for 1 min, and then reduced to 20 rpm for 20 mins until the solutions were separated completely.

4. The appropriate dosage (0.15 g/L) of cationic PAM (C-8385), cationic PAM (C-8800), anionic PAM (A-9770) and anionic PAM (A-9934) were added into waste glycerol (Zhao et al., 2008).

5. The effects of these four types of PAMs on removal COD and TSS in waste glycerol were compared, and then select the one of these PAMs, according to the removal efficiencies of COD and TSS, as the coagulant aid to treat waste glycerol.

6. The concentration of the selected PAM was adjusted from 0.07 g/L to 0.005 g/L in waste glycerol.

7. The solutions were mixed at 100 rpm for 1 min, and the rate reduced to 50 rpm for 2 mins.

8. Removal efficiencies of COD, TSS, glycerol and soaps were measured. The optimum concentration of selected PAM was determined.

9. The remove effect of PACl and selected PAM at the optimum conditions will compare with electotreat C-7123.

3.4 Inclusion process of glycerol by β-CD

This experiment step uses β-CD to include pure glycerol and residual glycerol from treated waste glycerol with PACl and selected PAM. The value of glycerol included by β-CD was measured with X-ray Diffractometer.

1. Put 20 g of β-CD into 100 mL water, and heat the water at 50 ℃ until the β-CD dissolve into the water. And then let the water cool down to room temperature. The β-CD will precipitate from the water, since 100 mL water can dissolve 1.85 g of β-CD at maximum.

2. Separate the β-CD from water, the impurities of CD was removed. Then the clean β-CD was dried by oven at 105℃.

3. Put 10 g dry clear β-CD into 100 mL of pure glycerol and treated waste glycerol, respectively. Heat the solution at 50℃, and mix it for 3 hours.

4. Cool down the solutions at room temperature until the β-CD precipitates from solution.

5. Separate β-CD from solution, and put the two β-CD sample into oven to dry for 1 hour.

6. The β-CD samples inclusion pure glycerol and waste glycerol was shown in **Figure 3.2**. The left one is the pure glycerol included by β-CD, the right one is the treated waste glycerol included by β-CD. Take the dry β-CD samples to measure the value of included glycerol with X-ray Diffractometer

Figure 3.2 The β-CD samples inclusion pure glycerol and residual waste glycerol

3.5 Production of gelatinous waste glycerol

3.5.1 Production of gelatinous waste glycerol with NaOH and stearic acid

1. The 4 g (0.015 mol) of stearic acid was put into 50 mL of waste glycerol in 250 mL round-bottom flask with reflux condenser. The solution was heated at 60℃ until the stearic dissolved into the waste glycerol

2. The 3 g (0.074 mol) of solid NaOH was mixed in 23.5 mL water, and then add 25 mL waste glycerol into the NaOH solution.

3. The solution from step 1 was mixed with the solution from step 2. The mixed solution was heated for 15 mins.

4. Stop heating the mixed solution, and put the mixed solution into refrigerator (about 4℃) for 10 mins.

3.5.2 Production of gelatinous waste glycerol with NaOH, stearic acid and methanol

1. The 4 g (0.015 mol) of stearic acid, 50 mL of waste glycerol and 5 mL methanol (> 93%) were put into 250 mL round-bottom flask with reflux condenser. The solution was heated at 60℃ until the stearic acid dissolved in waste glycerol.

2. The 3 g (0.074 mol) of solid NaOH was mixed in 23.5 mL water. And then added 25 mL methanol (>93%) into the NaOH.

3. The solution from step 1 was mixed with the solution from step 2, and then was heated for 15mins.

4. Stop heating the mixed solution, and put the mixed solution into refrigerator (about 4℃) for 10 mins. And then the gelatinous waste glycerol was produced and it can be kept gelatinous form at room temperature.

3.5.3 Production of gelatinous waste glycerol with NaOH, HPMC, and methanol

1. The 9 g of Hydroxypropyl methylcellulose (HPMC), 50 mL of waste glycerol and 5 mL methanol (>93%) were put into 250 mL round-bottom flask with reflux condenser. The solution was heated at 60 ℃ until the HPMC dissolved into the solution.

2. The 3 g (0.074 mol) of solid NaOH was mixed in 23.5 mL water. And then added 25 mL methanol (>93%) into the NaOH.

3. The solution from step 1 was mixed with the solution from step 2, and then was heated for 15mins.

4. The mixed solution was put into the refrigerator (about 4℃) for 10 mins.

5.   The heating values of the three types of gelatinous waste glycerol were measured with Proximate Analyzed method by NMP spectrometer. Their heating values will be compared with the heating value of fossil fuels.

Chapter 4

Results and discussion

4.1 Separation of oily sludge and glycerol from waste glycerol by coagulation process using electotreat C-7123

The purpose of this research is to reduce the water pollution from waste glycerol by using a coagulation process and discussing the possibility of waste glycerol reuse. The electotreat C-7123 (20 g/L), which was composed of cationic polyamine (PA) 6% and polyaluminium chloride (PACl) 94% (w/w), was used as coagulant to treat waste glycerol. The results showed that after acidification and coagulation process, most of the chemical oxygen demand (COD), biochemical oxygen demand (BOD$_5$), total suspended solids (TSS) and oily sludge (such as fatty acid, methyl ester, methanol and soaps) in raw waste glycerol were removed, except glycerol.

4.1.1 Introduction

With global warming and the price of fossil fuel rising, biodiesel is becoming favored as a kind of carbon neutral fuel (Topaiboul and Chollacoop, 2010). During the biodiesel production process by transesterification, oils/fats (triglycerides) are mixed with methyl alcohol and alkaline catalysts to produce esters of free fatty acid, with glycerol as a primary by-product. In general, production of 100kg of biodiesel yields approximately 10kg of raw waste glycerol, which is impure and of low economic value (Chi et al., 2007; Dasari et al., 2005).

Raw waste glycerol contains a variety of harmful compounds, such as 12-16% of the alkali especially in the form of alkali soaps and hydroxides, and 8-12% of methanol which may cause water pollution and environmental problems. Moreover, the cost for disposal of raw waste glycerol is quite expensive (Yazdani and Gonzalez., 2007; Silva et al., 2008). In order to reduce the cost for disposal of raw waste glycerol, it has been suggested to use some methods to convert waste glycerol into some valuable products. One application that has been evaluated is

the conversion of crude glycerol into propylene glycol and acetone (Chiu et al., 2006). Another application being investigated is the fermentation of glycerol to 1,3-propanediol, which is an intermediate compound for the synthesis of polymers used in cosmetics, foods, lubricants, and medicines (Zong et al., 2008).

Coagulation is a process by which small particles are separated from a solution in a reasonable amount of time using simple or pre-hydrolyzed metal salts, such as alum and PACl, polyelectrolytes, or long chain polymers like PA as the primary coagulation. This process is not only simple and economic, but can also effectively reduce levels of COD, BOD_5, TSS, color and organic compounds (Yue et al., 2008). In addition, the coagulation process can remove organic compounds effectively but not good for glycerol removal (Wang et al., 1996).

The reason that electotreat C-7123 (PACl blend with PA) was selected as the first coagulant to treat waste glycerol is PACl and PA are frequently used to treat various wastewater. Choo et al. (2007) used PACl and PA to treat textile wastewater. More than 97% of turbidity was removed during coagulation process. In addition, Yue et al. (2008) used PACl and PA to treat dye wastewater. At the optimum conditions of coagulation process, the removal efficiencies of color and COD were 90% and 89%, respectively.

In this study, the raw waste glycerol was pretreated by acidification with hydrochloric acid (HCl), since Chi (2007) used HCl to pretreat waste glycerol in acidification process. After pretreatment, the waste glycerol was taken to be treated by PACl blend with PA in the coagulation process. The effect of acidification process and the optimum conditions of coagulation process were examined.

4.1.2 General characteristics of raw waste glycerol

As is evident from the **Table 4.1**, there were high concentrations of COD, BOD_5, TSS and organic matters in raw waste glycerol. The ratio rate of BOD_5: COD had a value of 0.53, which was difficult for biological treatment process. From this value of BOD_5: COD ratio, the raw waste glycerol can be treated by the high dilution ratio with nutrient added (Boonsawang et al., 2008). From other values of organic compounds, the raw waste glycerol can be used as a

carbon resource or compost. However, the impurities include methanol and soaps and the high pH value would affect the anaerobic treatment or coagulation process and utilization of raw waste glycerol.   In addition, because waste glycerol contains 9.3-11.9% water, it has a low fuel value (Peereboom et al., 2007).

It could be concluded that the raw waste glycerol from the biodiesel process is impure and of low economic value. The pH value needs to be reduced, and soaps also need to be removed from the raw waste glycerol before the coagulation process.

Table 4.1 Selected characterizations of raw waste glycerol

Characterizations	Units	Concentration
pH		9.6
COD	g/L	1,757
BOD_5	g/L	930
TSS	g/L	387
Total glycerol	g/L	412
Soaps	ppm	265,607
Methanol	g/L	202
Water	% by weight	9.3-11.9

4.1.3   The effect of acidification on treatment of waste glycerol

The relation of HCl volume and pH changing of waste glycerol:

The pH is an important factor on pre-treatment of waste glycerol. To study the effect of pH on removal efficiency of TSS, COD, BOD_5, oil and grease, and other organics, the relation of HCl volume and pH changing is the first thing need to be studied.

The curve of pH changing in 400 mL waste glycerol was showed in **Figure 4.1**. Because there were a large amount of organic and inorganic matters in waste glycerol, so the curve of pH changing was not a smooth curve. At the beginning, as the addition of 0.8 M HCl into raw waste glycerol, the pH was reduced from 9 to 8 quickly, because HCl reacted with KOH

and NaOH in waste glycerol. When pH reduced to 7, the HCl destroyed the oil-in-water emulsion and reacted with soaps in waste glycerol. Thus, the pH was reduced from 7 to 5 slowly. When pH was 5, most of oil-in-water emulsion was destroyed, and the soaps converted into free fatty acid and salts. The free fatty acid and methyl ester floated into the upper layer, as shown in **Figure 4.2**. The upper layer is like oil, and lower layer is water. It believe that the upper layer contains high concentrations of fatty acid and methyl ester, but their concentration need to be test by thin layer chromatography (TLC). If it is proved there are concentrations of fatty acid and methyl ester, the recovering and reuse methods of them will be study.
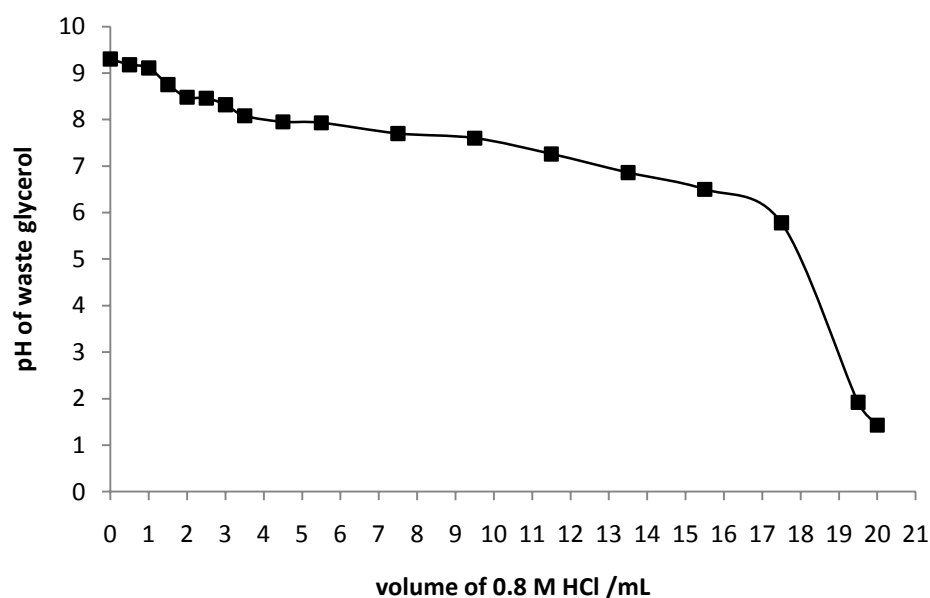
Figure 4.1 The curve of pH changing in 400 mL waste glycerol

Figure 4.2 The appearance of waste glycerol in pH range from 9 to 3

The effect of pH on COD, BOD_5 and TSS removal:

It was found that the appearances of waste glycerol with different pH values varied. When the pH value was 8, an emulsion was produced in the waste glycerol. An emulsion is an intimate mixture of two liquid phases, such as oil and water (Kemmer, 1987). Since the emulsion in the waste glycerol was an oil-in-water emulsion with a positive charge (Gi et al., 1992), the emulsion absorbed the soaps with negative charge.

When pH values were between 6 and 7, the emulsion with solid particles was separated from the solution in the upper and lower layers. When pH values were in a range of 5 and 3, the soaps were converted into free fatty acids and salts and the emulsion was broken. The upper layer solution contained mainly free fatty acid and methyl ester, and the lower layer solution was water, glycerol, and methanol.

When pH values were from 7 to 3, the lower layer samples were taken from the pretreated solution to measure the COD, BOD_5 and TSS.

The concentrations of COD, BOD_5, and TSS are shown in **Figure 4.3**. The COD

and BOD_5 of waste glycerol decreased with the reduction of pH from 9 to 5. The TSS rapidly increased from pH 9 to pH 8, and then slowly reduced from pH 7 to pH 5. This is because when the pH was 8, the waste glycerol began to produce an emulsion that absorbed solid particles at the oil/water interface. And then, as pH value was reduced, the neutralization charge and emulsion were broken. In addition, when the pH values were between 3 and 5, the values of COD and BOD_5 decreased slightly, while TSS remained stable.
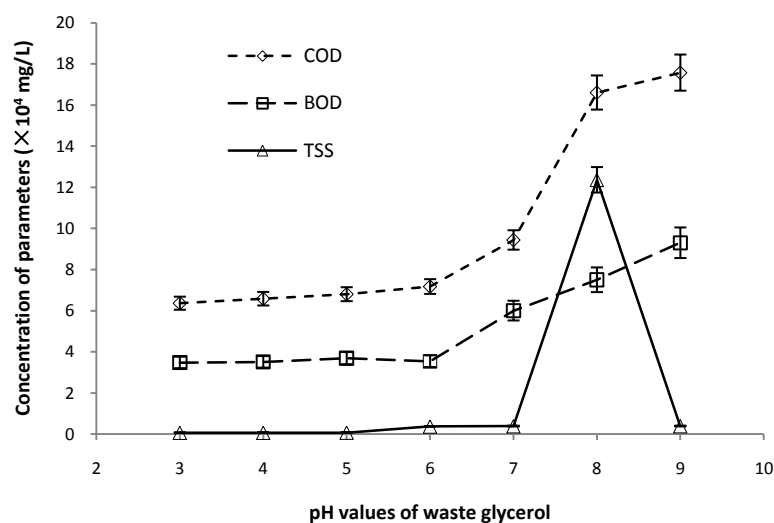
Figure 4.3 The variation of parameters in different pH values (in lower layer)

The effect of pH on oil and grease removal:

The concentration of oil and grease in upper layer were showed in **Figure 4.4**. As the pH of waste glycerol decrease, the concentration of oil and grease in upper layer increase. Because during the pH of waste glycerol decrease, the more soap in waste glycerol was reacted and produced more fatty acid in solution. Thus, the oil and grease concentration in upper layer is increasing.
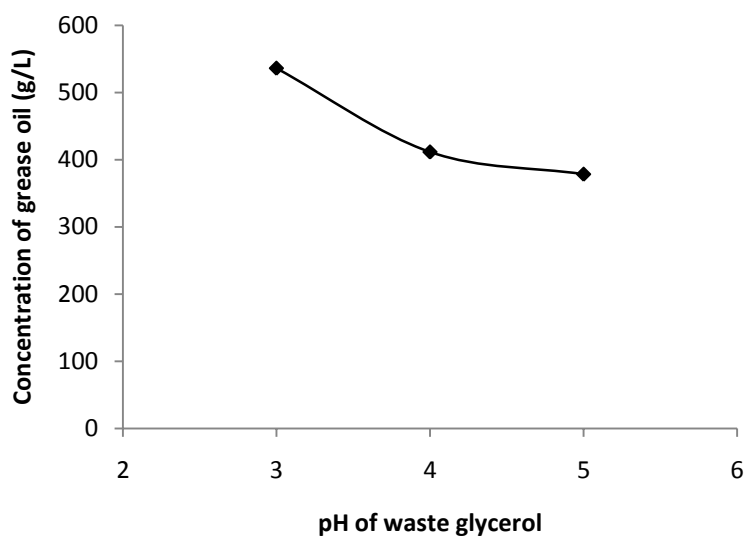
Figure 4.4 Oil and grease concentration of different pH of waste glycerol

The effect of pH on soaps removal:

Samples were taken from both layers of solution to measure the concentration of soaps. When the pH values were between 5 and 3, the upper layer solutions were used to measure the concentration of free fatty acid, methyl ester, and impurities.

The concentrations of soaps in two layers and total solution, and the mass fraction of fatty acid in the upper layer solution are shown in **Figure 4.5** and **Figure 4.6**. When the pH value was reduced, the concentration of soaps in the two layers and total solution also decreased, but the mass fractions of free fatty acid and methyl ester increased. This indicates that the soluble soaps were converted into salts and insoluble free fatty acids. In addition, most of the soaps were in the upper layer as shown in **Figure 4.5**. This shows that most of the soaps with negative charge were absorbed by oil-in-water emulsion.

It was found that when pH values were from 5 to 3, the mass fractions of fatty acid and methyl ester were 78.8%, 85.9%, and 89.8%, respectively. The upper layer solution can be recovered and reused as a raw material in biodiesel production processes (Gumpon et al., 2007).

The pH value of waste glycerol should be adjusted below 5 in acidification pretreatment because when pH value was 5, the most of soaps converted into free fatty acid and

salts, and the free fatty acid and methyl ester floated to the upper layer.

It could be concluded that as a pretreatment, the pH values should be adjusted to 5 and the upper layer solution should be removed from waste glycerol. The acidification process can reduce the COD, BOD_5, TSS and soaps in raw waste glycerol effectively.
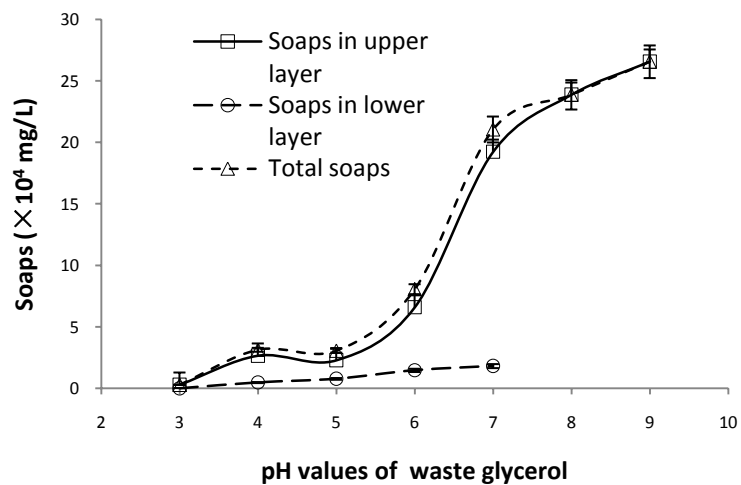
Figure 4.5 The variation of soaps concentrations in different layers of waste glycerol
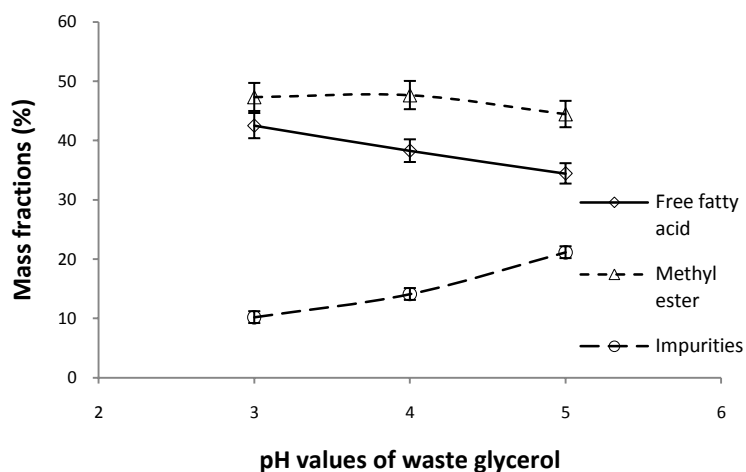
Figure 4.6 The variation of compositions for mass fractions in different pH values (in upper layer solution)

The effect of pH on glycerol and methanol removal:

The concentration of glycerol and methanol in different pH of waste glycerol are showed in **Figure 4.7**. The glycerol and methanol concentration were fluctuated as the pH change. It was because the acidification made the volume of waste glycerol change, but the concentrations of glycerol and methanol were not removed in acidification process.
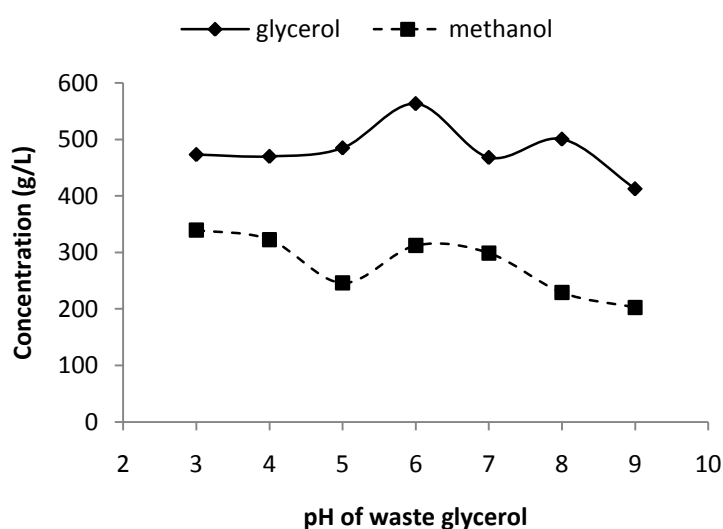
Figure 4.7 Glycerol and methanol concentrations of different pH of waste glycerol

4.1.4 The effect of the electotreat C-7123 dosage on parameters removal

The removal efficiencies of parameters in different concentrations of electotreat C-7123 are shown in **Figure 4.8**. When the concentration of the electotreat C-7123 was 5 g/L, the removal efficiencies of TSS, COD and BOD_5 were maximum value, $92.3\% \partial 2.2\%$, $75.5\% \partial 4.4\%$ and $87.9\% \partial 3.0\%$ respectively. After this concentration, the removal efficiency of COD decreased, and the removal efficiencies of BOD_5 and TSS changed slightly. This can be explained by the influence of excessive PACl on the coagulation (Gordana et al., 2008). 5 g/L of the electotreat C-7123 was the optimum concentration of the electotreat C-7123 and was selected to carry out the following experiment.

The cost of electotreat C-7123 is 40 Baht/kg (Electronics Chemical Co. Ltd,

2009). Thus, the cost calculation of electotreat C-7123 for treating waste glycerol was shown as follow:

(1) 40 Baht/kg =0.04 Baht/g

(2) 0.04 Baht/g $\times$ 5 g/L = 0.2 Baht/L = 200 Baht/m^3

The open market value of crude glycerol may be eventually stabilize at low price of 150 Baht/m^3, but the cost to refine this crude glycerol will cost approximately 600 Baht/m^3 (USDOE, 2004). The cost of electotreat C-7123 (200 Baht/m^3) is still higher than the price of raw waste glycerol. It needs to find cheap other coagulant instead of electotreat C-7123.
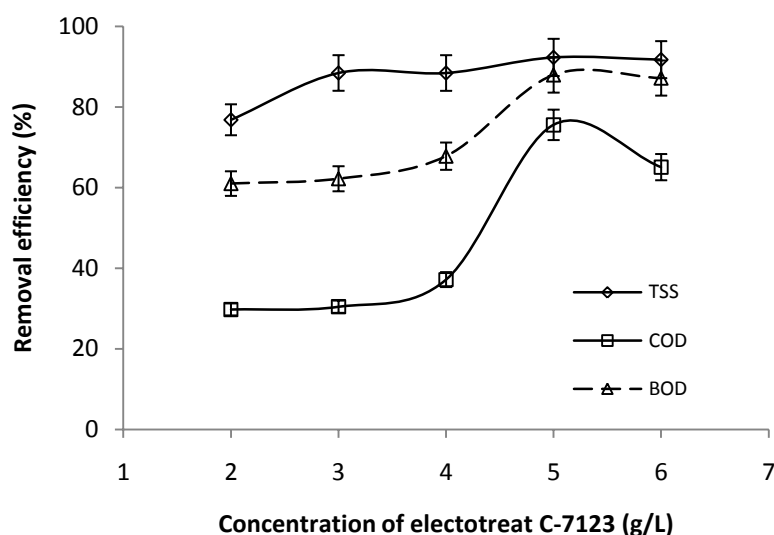
Figure 4.8 The variation of parameters in different concentrations of polymer (pH values is 8)

4.1.5   The effect of pH on coagulation

The removal efficiencies in different pH values of waste glycerol are shown in **Table 4.2**. Because the charge of the PA blended with PACl is a cation that cannot charge neutralization with hydrogen ions and form particle-polymer-particle bridges (Avci et al., 2002), it cannot react with waste glycerol of low pH values of 3, 4 and 5.

The removal efficiencies of waste glycerol from pH 6 to 9 showed that, when the

pH value of waste glycerol was 7, the removal efficiencies of TSS, COD, BOD_5 reached the maximum value, and the removal efficiencies of TSS, COD, BOD_5, methanol and glycerol were 98.1%±1.5%, 96.2%±0.7%, 93.3%±1.2%, 85.8%±2.9 and 65.4%±2.0% respectively. Moreover, when the pH value was 7, the soaps and other impurities were removed by coagulation process. The organic and inorganic matters were removed effectively, except glycerol. The residual glycerol can be recovered by distillation (Gerpen, 2005), since the solution separated from coagulation mainly contains water and glycerol, or can be recovered by cyclodextrin (CD) inclusion complexation from the solution (Song et al., 2008).

In addition, when the pH value was 7 and the concentration of the electotreat C-7123 was 5 g/L, the concentrations of TSS, COD, BOD_5, methanol and glycerol in the wastewater separated from the coagulation were 0.01 g/L, 2.3 g/L, 2.2 g/L, 17 g/L and 147 g/L respectively. The BOD_5: COD ratio had a value of 0.96, which is higher than the ratio rate in raw waste glycerol (0.53). It means that the pretreatment and coagulation process can improve the biodegradability of waste glycerol.

The heating value of coagulation production is 2,967 kcal/kg, which is closed to the heating value of cane trash, rice husk, leaves and vegetable waste (3,000 kcal/kg) (Indian portal calorific value of fuels, 2002). It means that the coagulation production can be used as a biomass fuel. The heating value of coagulation production is not quite high, because the coagulation production contained water about 24 % by weight.

It can be concluded that the optimum conditions of the PA blend with PACl coagulating waste glycerol were as follows: (1) the optimum concentration was 5 g/L; (2) the optimum pH value of waste glycerol for coagulation process was 7; (3) in the conditions of this research, the TSS, COD, BOD_5 and methanol were removed effectively; (4) the coagulation production which contained large amount of organic compounds which could be used as a biomass fuel. In addition, the biodegradability of waste glycerol was improved by acidification and coagulation process.

Table 4.2 The removal efficeincies of parameters in different pH values

pH values	TSS (%)	COD (%)	BOD$_5$ (%)	Glycerol (%)	Methanol (%)
6	97.3±2.0	64.9±3.4	65.7±4.2	78.6±2.9	92.1±3.9
7	98.1±1.5	96.2±0.7	93.3±1.2	65.4±2.0	85.8±2.9
8	98.9±0.6	82.7±1.6	84.0±2.9	66.9±1.2	83.4±2.8
9	96.1±1.1	95.9±0.9	90.2±1.6	76.3±2.1	39.5±4.0

4.1.6 Summary

The raw waste glycerol needs to be pretreated by acidification process to remove soaps. When pH value was adjusted below 5, the soaps converted into free fatty acid which can be separated and recovered from waste glycerol. And then, the treated waste glycerol was adjusted its pH value and treated by electotreat C-7123 coagulation. The optimum conditions of coagulation process were measured according to the results of different pH values and electotreat C-7123 concentrations.

On the basis of operation from a laboratory scale model of PA and PACl coagulation treatment of raw waste glycerol, the following conclusions can be stated: (1) raw waste glycerol needs to be pretreated by 0.8M HCl to adjust the pH value and remove parts of the soaps, fatty acid and methyl ester; (2) in optimum conditions, the removal efficiencies of COD, BOD$_5$, TSS and organic compounds were considerable. However, there was still a certain amount of residual glycerol (147.5g/L) in the solution separated from coagulation; and (3) the oily sludge produced by the coagulation process of waste glycerol and the electotreat C-7123, contains abundant organic matters, which may be used as an energy resource or a fuel.

Additionally, these methods can be used as a pretreatment for the free fatty acid, methyl ester and glycerol recovered from waste glycerol, which can be purified and sold, and bring economic benefits for biodiesel facilities in future.

However, the cost of electotreat C-7123 for treat waste glycerol is quite

expensive (200 Baht/m^3); and the concentration of electotreat C-7123 is quite high, which is about 5 g/L; it produces a large amount of wastewater after coagulation process. It needs to find other coagulant to replace electotreat C-7123, which can reduce water pollution effectively and remain more glycerol after coagulation process. The PACl and cationic PAM were used to treat waste glycerol, because electotreat C-7123 is composed by PACl and cationic PA. In addition, PACl and PAM are cheap and not easy to flocculate small organic compounds, such as glycerol.

Table 4.3 The concentrations of characterizations in raw waste glycerol, after acidification and after coagulation with electotreat C-7123 at optimum conditions

Characterization	Unit	Total waste glycerol	After acidification	After coagulation
pH		9.6±0.6	5.0±0.5	7.0±0.5
COD	g/L	1,757±96	67.0±9.0	2.3±0.2
BOD$_5$	g/L	930±70	37.0±8.0	2.2±0.2
TSS	g/L	387.0±74	1.7±0.45	0.01±0.007
Total glycerol	g/L	412±65	420±30	147±10
Soaps	ppm	265,607±800	7,819±87	0
Methanol	g/L	202±68	104±46	17±4

4.2 Improvement of coagulation process with four types of PAMs for oily sludge separation from waste glycerol

In this study, polyacrylamide (PAM) flocculant was used as a coagulant aid to enhance the PACl coagulation process. This process can separate oily sludge and reduce water pollution. The effects of four types of PAM flocculants, such as cationic PAM (C-8385), cationic PAM (C-8800), anionic PAM (A-9770) and anionic PAM (A-9934), on removal of COD and TSS have been compared. The residual glycerol in treated waste glycerol will be recovered by CDs. The different of four types of PAMs is that they are cationic and anionic polymer, and their molecular weight is different.

4.2.1   Introduction

Biodiesel is gaining more and more importance as an attractive fuel due to the depletion of fossil fuel resource. During the biodiesel production process by transesterification, oils/fats (triglycerides) are mixed with methyl alcohol and alkaline catalysts to produce esters of free fatty acids, with waste glycerol as a primary by-product (Nur et al., 2009). Waste glycerol contains a high level of glycerol (50% by weight) and other oily sludge, including 1% – 3% oil and grease, 15% – 18% methyl esters and 12% – 16% soaps. This oily sludge may become an environmental problem, since it cannot be disposed of in the environment (Paulo et al., 2009). For the treatment of waste glycerol by conventional methods such as aerobic or anaerobic digestion, the ratio of BOD_5 to COD should be > 0.6 (Chian and Dewalle, 1997). However, waste glycerol from biodiesel industries through a transesterification method, usually has a BOD_5/COD ratio around 0.5. In addition, the waste glycerol is alkaline (having a pH of more than 9) with a high content of oil and grease, and a low content of nitrogen and phosphorus. As such, biological treatment of the waste glycerol is expected to be very difficult (Sridhar et al., 2002).

In Thailand, typical treatments of oily wastewater employ a dissolved air floatation technique (DAF), an oil and grease trap unit or other commercial oil and grease removal units to separate oil and grease prior to biological treatment. However, these

conventional flotation techniques are not satisfactory for removing emulsified oils in waste glycerol without chemical pretreatment (Chavalparit and Ongwandee, 2009). It has been reported that the addition of aluminum or ferric salts, highly charged cations, can enhance the destabilization of an oil-in-water (O/W) emulsions when applying DAF (Al-Shamrani et al., 2002). The chemical treatment aspects of DAF are extremely important with respect to the removal of colloid or emulsified oil (Zeng et al., 2007). Coagulation appears to be effective in removing oil and grease from oily wastewater, but it allows easy formation of smaller flocs with a low setting rate making flocs removal harder (Tzoupanos et al., 2009).

The trend in coagulation-flocculation field nowadays is the preparation of new, composite coagulants by the introduction of several additives to produce pre-polymerized coagulants, in order to improve their efficient than the commonly applied organic polymers. The pre-polymerized coagulants such as polyaluminium chloride (PACl), developed during the last 25 years, have shown better coagulation performance than the conventional coagulants, such as alum or $FeCl_3$, and are now applied in increasing quantities for water or wastewater treatment (Renault et al., 2009). There are a number of different mechanisms involved in the coagulation process, including ionic layer compression, absorption and charge neutralization, inter-particle bridging, and sweep coagulation (Liu et al., 2003). These mechanisms are very important in forming micro-flocs of oily sludge, such as O&G and soaps, and suspended solids which can easily float and be removed (Zeng and Park et al., 2009; Srivastava et al., 2005). Therefore, destabilizing charge neutralization and demulsification via the addition of PACl has been shown effective as a coagulant to pretreat oily wastewater (Wong et al., 2006). Bridging the micro-floc particles together by the addition of a flocculant additive forms large, denser flakes that are easier to separate. A simple separation step then eliminates the flocs. The flocculants frequently used are synthetic polymers such as PAMs.

Polyacrylamide (PAM) is a commonly used polymeric flocculant because it is possible to synthesize polyacrylamide (PAM) with various functionalities (cationic, nonionic and anionic) which can be used to produce a good setting performance at a relatively low cost (Yang et al., 2010). These polymers, usually referred to as polyelectrolytes, are synthetic compounds that tend to absorb the particles on the surface and form bigger and more compacted flocs (Zeng, 2007). The use of high molecular weight of PAM-C and PAM-A has resulted in tremendous

performance improvement for industrial separation processes (Yang et al., 2010). The coagulation-flocculation process with PACl and PAMs for treatment of wastewater has been researched, because it is effective, low cost, easy to handle and available (Zeng, 2007).

O/W emulsions are stabilized mainly by electrostatic interactions and/or adsorption of macromolecules or solid particles at the interface (Yang, 2007). As soaps are surfactant in waste glycerol, they can form complexes with oil to be micelle which can be oil emulsified in water (O/W) (Reynolds et al., 1996). Coagulants are wasted when raw waste glycerol is directly mixed with them, the O/W emulsion coagulates and floats from the liquid, and thus the coagulants are also removed with the O/W emulsion (Zeng et al., 2007). The destabilization or demulsification of O/W can be achieved with reducing electric forces or destroying electrical double layers in acidification process (APHA, AWWA and WEF, 1998). The raw waste glycerol should then be pretreated through acidification before coagulation.

In this research study, waste glycerol samples were taken to a coagulation-flocculation process after an acidification process. The efficiency of acidification pretreatment and coagulation-flocculation process with PACl and two types of PAMs in the treatment of raw waste glycerol was investigated.

4.2.2   Characteristics of Raw waste glycerol

As shown in **Table 4.4**. The characteristics of raw waste glycerol are not the same as the characteristics of raw waste glycerol sample which was collected at first time on October 2009.

Waste glycerol has a high pH value (> 9.7) and consists of high concentrations of oil and grease and other organic matters. For example, oil and grease was around 3.77-5.35 g/L, glycerol was 413- 477 g/L and has high content of soaps. The other values of organic compounds, including 1,700-1,900 g/L of COD, 900-1,200 g/L of BOD_5 and high concentrations of TSS (see detail in **Table 4.4**). The ratio rate of BOD_5: COD had a value of 0.53, which was a rather low value for the biological treatment process (Sperling and Oliveira, 2009; Kobayashi et al., 2009). However, the high pH value and impurities could cause problems for biological treatment or

coagulation processes and utilization of raw waste glycerol. In addition, waste glycerol contains 9.3 – 11.9% of water and has a low fuel value.

It can be noted that raw waste glycerol from the biodiesel process is impure and of low economic value. The pH value and soaps need to be reduced and removed before coagulation process.

Table 4.4 Selected characterizations of raw waste glycerol

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

4.2.3   Effect of acidification on oily sludge separation

As the high O/W emulsion affect the coagulation process, waste glycerol need to be demulsified through acidification process. The results show that the change of emulsion and coalesce of oil drops was observed when the pH value decrease to 5. It was due to the electric charge was closed to the isoelectric point, the electrical double layers of O/W was destroyed, and then the demulsification was occurred (Sharma et al., 2008). When pH value was lower than 5, the oil and grease (O&G) floated to the upper layer, and the lower layer was mainly water, glycerol, methanol and soaps.

The pictures of oil drops coalescence at pH 3 and pH 5 are shown in **Figure 4.9 (a)**. It can be seen that the accumulation of oil drop coalescence increased with a decrease in pH

value. Increasing of oil drop coalescence made more O&G separate from the solution and float to the surface water, which is simulated in **Figure 4.9 (b)**.

The concentrations of soaps in the solutions of both layers are shown in **Figure 4.9 (c)**. The concentrations of soaps in both upper and lower layer solutions decreased due to reduction of pH value. This indicates that the soluble soaps were converted into salts and insoluble free fatty acids which floated to the upper layer (Wang et al., 1996). Therefore, most of the O/W emulsion which was absorbed by soaps was destabilized (Reynold et al., 1996).

In addition, when the pH value was below 5, more than 80% by weight of the upper layer solution was comprised of free fatty acids and methyl ester, which was measured with gas chromatography (EN 14103, 2003). The upper layer solution can be recovered and reused as raw material in the biodiesel processing (Israel et al., 2008).

Therefore, acidification is a necessary pretreatment of the coagulation-flocculation process. When the pH value of waste glycerol was adjusted below 5, the O&G, free fatty acids and methyl ester and some soaps separated to the upper layer solution. Moreover, when pH values are lowered, most of the O/W emulsion is destabilized thus showing the necessity of acidification. The lower layer solution, which contains water, soaps, glycerol, methanol and a small amount of O&G, was taken to the coagulation-flocculation process.

(a)

(pH 5)

(pH 3)

(b) —△— O&G in upper layer   —✕— O&G in lower layer

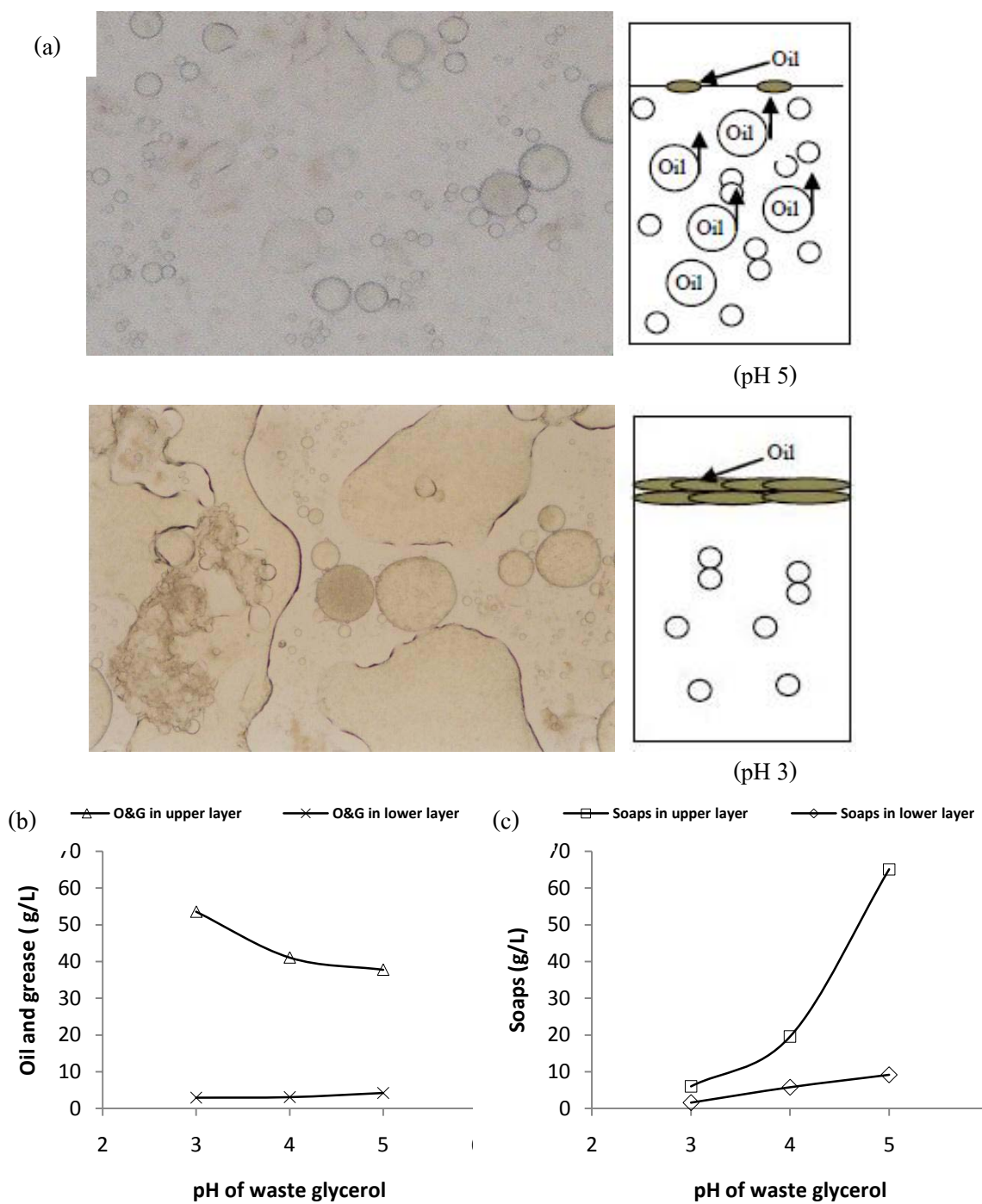(c) —☐— Soaps in upper layer   —◇— Soaps in lower layer

Figure 4.9 Acidification on separation of oily sludge: (a) coalescence of oil droplet in upper layer solution; (b) oil and grease concentrations in two different layer solutions; (c) soaps concentrations in two different layer solutions.

4.2.4   The effect of pH on PACl coagulation

After adjusting the pH of lower layer waste glycerol samples from 9 to 3 with 0.8 M HCl and 6 M NaOH, a moderate concentration of PACl (20 g/L) was added into the same volume of waste glycerol of different pH values. Then, the total solutions of waste glycerol and PACl were mixed with a jar test apparatus. The samples were taken from the wastewater and removal efficiencies of COD, BOD_5, TSS, and glycerol were measured. The results of total removal efficiencies of different pH values are shown in **Figure 4.10**.

Figure 4.10 indicates that when the pH values of waste glycerol were 4 and 7, the total removal efficiencies of the parameters were quite high. When the pH value of waste glycerol was 4, the total removal efficiency was highest. The removal efficiencies of the COD, BOD5, TSS, and glycerol were 78%, 66%, 97%, and 31%, respectively. When the pH value of waste glycerol was 7, the total removal efficiency of parameters was slightly less than that when the pH value was 4. Thus, the pH values of 4 and 7 for waste glycerol were carried over to the next experiment.

Generally, the optimum pH value for PACl coagulation is 7. However, in waste glycerol the PACl destabilizes the particles and organic matters through the compression of electrical double layers. The charges are neutralized and adsorbed, and coagulations are formed (Kemmer, 1987). When the pH value of waste glycerol is 4, the soaps that have a negative charge in the lower layer solution can have a neutralized charge with PACl. Therefore, binding particles and organic matters becomes agglomerate.
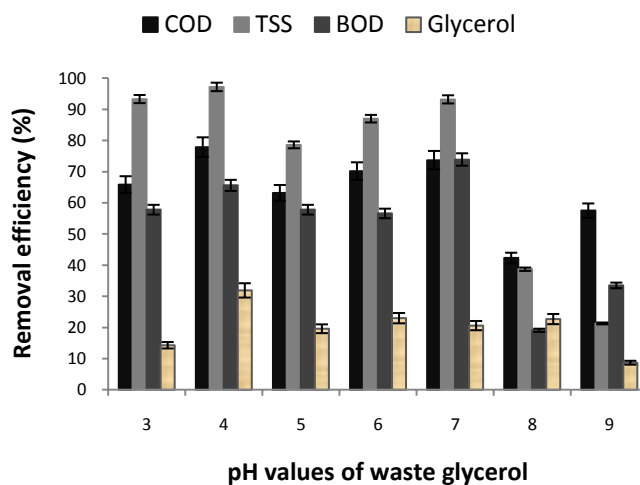
Figure 4.10 Effect of PACl on removal efficiency of parameters at different pH

4.2.5   The effect of PACl concentration on parameters removal

The pH values of lower layer waste glycerol samples were adjusted to 7 and 4; the different concentrations of stock solution PACl (20 g/L) were added to waste glycerol to adjust concentrations of PACl in solutions of waste glycerol and PACl. The solutions of waste glycerol and PACl were mixed with a jar test apparatus. The samples were taken from the wastewater separated from coagulation, and removal efficiencies of the COD, TSS, soaps, and the concentration of glycerol were measured.

Results of the removal of COD, TSS and soaps in the lower layer waste glycerol solution at pH 4 and 7 are shown in **Figure 4.11**. It was evident that the average total removal efficiency at pH 4 was higher than at pH 7. When the PACl concentration was 2 g/L, the total removal efficiency of COD, TSS, and soaps was highest at pH 4; the removal efficiencies of COD, TSS, and soaps were 82%, 97%, and 100%, respectively. When the PACl concentration was 4 g/L, the total removal efficiency of parameters was highest at pH 7; the removal efficiencies of COD, TSS, and soaps were 69%, 94%, and 88%, respectively. Moreover, when the PACl concentration was 2 g/L and the pH value was 4, the concentration of glycerol in the sample was 224.3 g/L. When PACl concentration was 4 g/L and the pH value was 7, the concentration of

glycerol in the sample was 205.6 g/L. In order to save chemicals, reduce wastewater production, and retain more glycerol in wastewater, the optimum PACl concentration of 2 g/L and a pH value of 4 in waste glycerol were taken to the next experiment steps

It can be concluded that the optimum conditions of PACl coagulating waste glycerol for this study are as follows: (1) the optimum pH value of waste glycerol for the coagulation process is 4; (2) the optimum PACl concentration is 2 g/L.
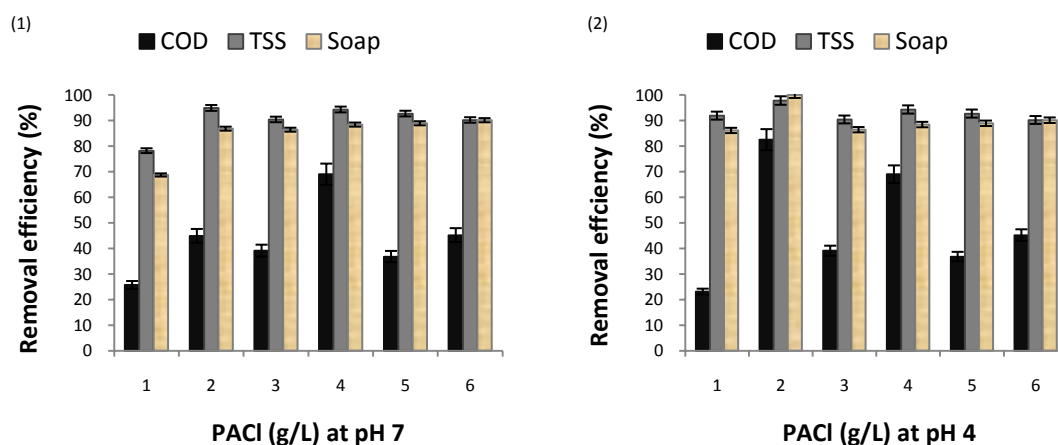
Figure 4.11 Removal efficiency of parameters in different PACl concentrations.

(pH value of 7 and 4)

4.2.6 Effect of four types of PAM on removal COD and TSS

The PACl coagulation process needs to add PAM flocculants to flocculate flocs particles in a net, since the PACl coagulation flocs are small and easily broken. Thus, after PACl coagulation process at the selected conditions (pH value of waste glycerol was 4, PACl concentration was 2 g/L), the appropriate dosage of cationic PAM (C-8385), cationic PAM (C-8800), anionic PAM (A-9770) and anionic PAM (A-9934) was added into the solution.

The results of four types of PAM on removal COD and TSS are shown in **Figure 4.12**. It was observed that the cationic PAM (C-8800) and anionic PAM (A-9934) were effective on removal COD and TSS. The removal efficiencies of COD and TSS in flocculation

with PAM (C-8800) were 74% and 97%, and with PAM (A-9934) were 80% and 97%, respectively. It is because they have larger molecular weight than other two types of PAM, so that they can form larger flocs and reduce the turbidity of waste glycerol, which is shown in **Figure 4.13**.

Thus, the PAM (C-8800) and PAM (A-9934) were selected as coagulant aids in next step.

Figure 4.12 Removal efficiency of four kinds of PAM

Figure 4.13 The appearance of treated waste glycerol with four types of PAM

4.2.7 The effect of PAM-C (C-8800) as a coagulation aid

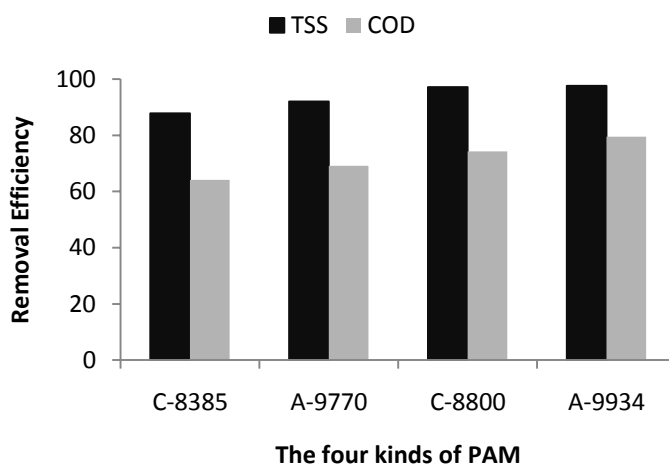PAM-C (C-8800) was chosen as a coagulation aid because of the following advantages: (1) it is cheap and non-toxic; (2) usually the dosage used to treat wastewater is very small (Zeng et al., 2007); (3) it can flocculate all kinds of organic matters in waste glycerol, except glycerol (Wang et al., 1996).

When the lower layer of waste glycerol samples had a pH value of 4, 2 g/L of PACl was added. The solutions of waste glycerol and PACl were mixed with a jar test apparatus. Different concentrations of PAM-C (1 g/L) were added into the solution of waste glycerol and PACl to adjust concentrations of PAM-C. The solutions were mixed with a jar test apparatus, as well. The samples were taken from the wastewater separated from coagulation to measure the concentrations of COD, BOD_5, TSS, and glycerol. Then, they were compared with the concentrations of these parameters after dilution with HCl, PACl, and PAM-C to measure the removal efficiencies of these parameters.

The results of the removal efficiencies are shown in **Figure 4.14**. When the concentration of PAM-C was 0.01 g/L, the removal efficiencies of COD, BOD_5, and TSS were highest at 80.2%, 67.9%, and 96.6%, respectively. Moreover, the concentrations of glycerol in different samples are shown in **Figure 4.15**. It was found that when the concentration of PAM-C was 0.01 g/L, the concentration of glycerol had a maximum value of about 288 g/L. As the concentration of PAM-C increased, the removal efficiencies of parameters and the concentrations of glycerol decreased slightly. In order to save the chemicals, the concentration of PAM-C chosen as the optimum concentration when adding it to PACl was 0.01 g/L. Comparison of parameters on removal efficiencies of the PACl and PAM-C in conjunction with PACl in optimum conditions is shown in **Figure 4.16**. It was evident that the parameter removal efficiencies of PAM-C in conjunction with PACl were not higher than the removal efficiencies of PACl, except BOD_5, the PAM-C folliculated PACl flocs particles into large agglomerates and was not easily broken. After adding PAM-C to PACl as a coagulation aid, the ratio rate of BOD_5: COD increased to 0.87, which was higher than the ratio rate when adding PACl into waste glycerol (0.62) and raw waste glycerol (0.53). This implies that PAM-C in conjunction with PACl can

improve the biodegradability of wastewater.

    Thus, after treating waste glycerol with PACl at optimum conditions, 0.01 g/L of PAM-C should be added to the solution of PACl and waste glycerol to flocculate flocs particles into large agglomerates. After PAM-C was added with PACl to treat waste glycerol in optimum conditions, the biodegradability of wastewater separating from coagulation was improved.
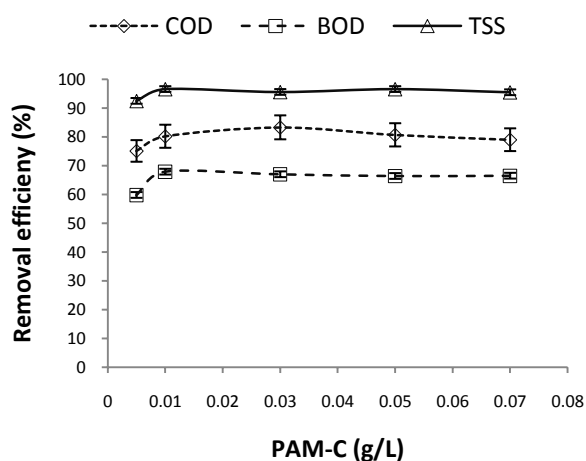
Figure 4.14 Removal efficiencies of parameters in different PAM-C concentrations
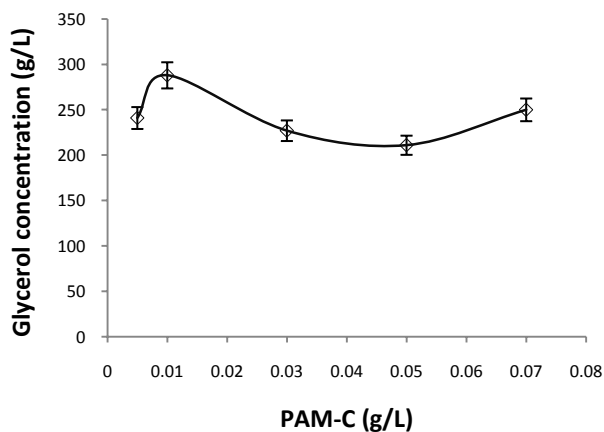
Figure 4.15 Concentration of glycerol in different PAM-C concentrations
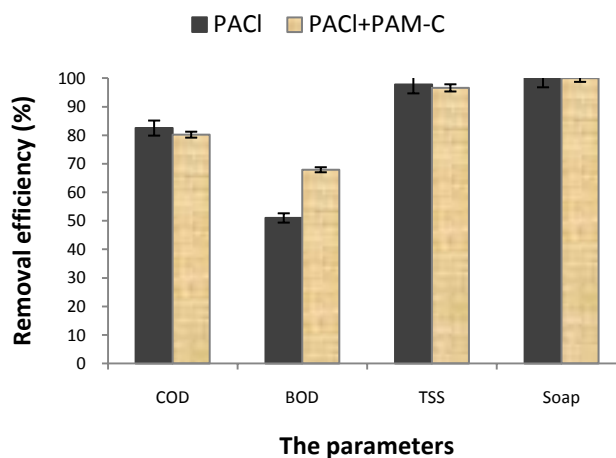
Figure 4.16 Comparison of parameters removal efficiencies before and after adding PAM-C into

PACl

The price of PACl is 5400 Baht/ton (Electronics Chemical Co. Ltd. 2009), and the PAM-C (C-8800) is 45000 Baht/ton (Electronics Chemical Co. Ltd. 2009). The cost calculation of PACl and PAM-C for treating waste glycerol was shown as follow:

(1) PACl

$$5400 \text{ Baht/ton} = 5.4 \text{ Baht/kg} = 5.4 \times 10^{-3} \text{ Baht/g}$$

$$5.4 \times 10^{-3} \text{ Baht/g} \times 2 \text{ g/L} = 10.8 \text{ Baht/m}^3$$

(2) PAM-C

$$45000 \text{ Baht/ton} = 45 \text{ Baht/kg} = 4.5 \times 10^{-2} \text{ Baht/g}$$

$$4.5 \times 10^{-2} \text{ Baht/g} \times 0.01 \text{ g/L} = 0.45 \text{ Baht/m}^3$$

(3) PACl and PAM-C

$$10.8 \text{ Baht/m}^3 + 0.45 \text{ Baht/m}^3 = 11.25 \text{ Baht/m}^3$$

The prices of PACl with PAM are cheaper than commercial polymers at 11 Baht/m^3 of waste glycerol, rather than the commercial polymer price of 200 Baht/m^3. This indicates that using PACl with PAM to coagulate waste glycerol is cheaper than commercial polymers and reduces the amount of wastewater generated.

The characteristics of waste glycerol after treatment with the PACl and PAM-C

at optimum conditions compared with raw waste glycerol are shown in **Table 4.5**. The COD, BOD_5 and TSS are above the oil terminal and industrial effluent standards of Thailand (PCD, 2004). Thus the treated waste glycerol cannot be discharged outside in the environment. However, the glycerol can be recovered more easily from treated waste glycerol compared to raw waste glycerol by certain methods. When organic matters existing in waste glycerol are coagulated with PACl and PAM-C, the sample obtained consists of glycerol (~280 g/L) and methanol (~3.8 g/L).

Table 4.5 Selected characteristices of waste glycerol after treatment with PACl and PAM-C at optimum condition

Characterizations	Units	After Treatment	Oil Terminal Effluent Standards of Thailand (PCD, 2004)
pH		5.0 ± 0.5	5.5-9.0
COD	g/L	17 ± 1.6	0.2
BOD_5	g/L	15 ± 1.2	0.06
TSS	g/L	0.06 ± 0.01	0.06
Oil and Grease	g/L	$0.4\times10^{-3}\pm 0.06\times10^{-3}$	0.015
Total glycerol	g/L	300 ± 20	⸺
Soaps	ppm	0	⸺
Methanol	g/L	3.8 ± 0.3	⸺
Water	% by weight	99.3 ± 0.2	⸺

The oil and grease and soaps, which were toxic matters for the microorganisms, were removed in coagulation process (Lopez et al., 2009). Moreover, the ratio rate of BOD_5: COD increased to 0.87, which was higher than the ratio rate of raw waste glycerol (0.53). This implies that coagulation process with PACl and PAM-C can improve the biodegradability of waste glycerol. The treated waste glycerol can probably be used as a carbon source or compost for biological treatment process.

4.2.8   Comparison PAM-C (C-8800) with PAM-A (A-9934) on separation of oily sludge

At the selected conditions in coagulation process, the results of parameters removal efficiencies in coagulation-flocculation process with PACl blend with different concentrations of PAM-C and PAM-A are shown in **Figure 4.17**. It was found that the removal efficiency in coagulation-flocculation process with PACl and PAM-A was slight different with PACl and PAM-C. The removal efficiencies of parameters were highest, when both PAM-C and PAM-A were 0.01g/L. The removal efficiencies of COD, BOD_5, and TSS in coagulation-flocculation process with PACl and PAM-C at selected conditions were 80%, 68% and 98%, respectively. However, the removal efficiencies of COD, BOD_5, and TSS in this process with PACl and PAM-A were 85%, 75% and 99%, respectively.

The effect of PAM-A on removal COD, BOD_5 and TSS is slightly higher than that of PAM-C. This is because PACl is a cationic coagulant, when PACl in combined with anionic PAM, a synertic effect can be observed due to charge neutralization (Yang et al., 2010). Moreover, the molecular weight and size of anionic for aggregating action is larger than that of canonic. Thus, PAM-A enables larger agglomerates of PACl flocs to form than PAM-C.

In generally, the optimum pH value of PACl coagulation should be achieved between pH 6 to pH 7 in water supply. However, the optimum pH value of PACl coagulation in waste glycerol is pH 4. Normally, there is no alkalinity in solution when pH value is below 4.5. Thus, the PACl cannot form $Al_n(OH)_mCl(3n-m)$ which can coagulate the organic compounds with waste glycerol. However, the removal efficiencies of organic compounds at pH 4 are higher than that at pH 7. It is because the waste glycerol still remains about 311 mg/L of O&G and 4,838 ppm of soaps in the lower layer waste glycerol after acidification at pH 4. The lower layer contains O/W emulsion, but PACl can destroy the O/W emulsion. This is destruction of the emulsifying properties of the surface active agent or neutralization of the charged oil droplets. The soaps and oil were floated into the upper layer. The upper layer is fat and oil, which heating value is 7750 kcal/kg. The salts were absorbed by Al^{3+} and precipitate to the bottom. That was the reason that the treated waste glycerol with PACl contained 570 ppm of Al^{3+}. There was about 666 ppm of Al^{3+} in PACl solution. However, the concentration of Al^{3+} was reduced to 97 ppm after PAM-C

flocculation, and to 20 ppm after PAM-A flocculation. This is because PAMs flocculate the flocs of Al^{3+} and salts into large flocs, and the large flocs float to the upper layer, so that there is no precipitation in the lower layer. Moreover, PACl is positive charge, when PACl in combined with PAM-A a synertic effect can be observed due to charge neutralization (Yang et al., 2010). Thus, the effect of PAM-A on removing Al^{3+} is better than PAM-C.

The concentrations of glycerol in treated waste glycerol with PAM-C and PAM-A are shown in **Figure 4.18**. When both of the concentrations of PAM-C and PAM-A were 0.01 g/L, the concentration of glycerol had a maximum value of 258 g/L and 230 g/L, respectively. As the concentrations of PAMs increased, the concentration of glycerol decreased. The influence of excessive PAM-C and PAM-A reducing concentration of glycerol and breaking the neutralization charge can explain this reaction (Kemmer, 1987). The glycerol can be recovered more easily from treated waste glycerol than raw waste glycerol by distillation if it needs to be purified (Israel et al., 2008).

The concentration of glycerol in treated waste glycerol with PAM-C is slightly higher than that with PAM-A. However, the PAM-A can form larger agglomerates flocs than PAM-C (Wong et al., 2006). In addition, the effect of PAM-A on the removal of COD, BOD_5 and TSS is slightly higher than PAM-C. Thus, the PAM-A was selected as a coagulation aid for PACl to treat waste glycerol.

Comparisons of parameter removal efficiencies of the PACl and PAM-A in conjunction with PACl in optimum conditions are shown in **Figure 4.19**. It was evident that the parameters removal efficiencies of PAM-A in conjunction with PACl were higher than the removal efficiencies of PACl, the PAM-A folliculated PACl coagulation particles into large agglomerates and was not easily broken. After adding PAM-A to PACl as a coagulant aid, the ratio rate of BOD_5: COD increased to 0.87, which was higher than the ratio rate when adding PACl into waste glycerol (0.60). This implies that PAM in conjunction with PACl can improve the biodegradability of treated waste glycerol.

The increase of ratio rate of BOD_5: COD is because the oil and grease which is the toxic matters for the microorganisms was removed in PACl and PAM-A coagulation process. The removal efficiency of oil and grease is 97% which is shown in **Table 4.7**. However, the

glycerol which is as the food for the microorganisms was remained in treated waste glycerol. Thus, the removal efficiency of BOD_5 is less than that of COD. And the ratio rate of BOD_5: COD was increased.

The cost of PACl is 10.8 Baht/m^3 which was calculated in **Section 4.2.7**. The price of PAM-A (A-9934) is 58000 Baht/ton (Electronics Chemical Co. Ltd, 2009). The cost calculation of PACl and PAM-A was shown as follow:

(1) PACl = 10.8 Baht/m^3

(2) PAM-A

58000 Baht/ton = 58 Baht/kg = 5.8×10^{42} Baht/g

5.8×10^{42} Baht/g $\times 0.01$ g/L = 0.58 Baht/m^3

(3) PACl and PAM-A

10.8 Baht$2$0.58 Baht/m^3 = 11.38 Baht/m^3

The cost of PACl and PAM-A is slightly higher than that of PACl and PAM-C (11.25 Baht/m^3); but it is still much cheaper than the cost of electotreat C-7123 (200 Baht/m^3). The prices and costs of electotreat C-7123, PACl, PAM-C (C-8800) and PAM-A (A-9934) were shown in **Table 4.6**.

Removal efficiencies of oil and grease (O&G) and soaps are parameters used to study the destabilization of dilute emulsion, since the dispersed O&G collide and form bigger oil droplets at high oil content to deviate the optical behavior of the emulsion from that of a real solution (Yang, 2007); and soaps with negative charge can absorb O/W emulsion at their interface (Rios et al., 1998). After the coagulation-flocculation process with PACl and PAM-A at optimum conditions, most of the O&G and soaps were separated from treated waste glycerol; with their removal efficiencies of 97% and 100%, respectively. The results indicate the coagulation-flocculation can destabilize the O/W emulsion in waste glycerol.

The main organic compounds in treated waste glycerol were glycerol (230 g/L) and methanol (4.3 g/L) which cannot form emulsion, but can dissolve in water. The glycerol and methanol are not easy to be removed by coagulation-flocculation process because PAM-A can

flocculate high molecular weight organic matter, but it is not effective with low molecular weight organic matters (Wang et al., 1996).

Table 4.6 The prices and costs of electotreat C-7123, PACl, PAM-C and PAM-A

Chemicals	Price	Dosage	Cost
Electotreat C-7123	40 Baht/kg	5 g/L	200 Baht/m^3
PACl	5.4 Baht/kg	2 g/L	10.8 Baht/m^3
PAM-C (C-8800)	45 Baht/kg	0.01 g/L	0.45 Baht/m^3
PAM-A (A-9934)	58 Baht/kg	0.01 g/L	0.58 Baht/m^3

Table 4.7 Characterizations and their removal efficiencies after treatment with PACl and PAM-A at optimum conditions

Characterization	Removal efficiency	Units	After Treatment	Oil Terminal Effluent Standards of Thailand (PCD, 2004)	Optimal range for biological treatment (Jose et al., 2009)
COD	85%	$\times 10^3$mg/L	15.4	0.2	—
BOD_5	75%	$\times 10^3$mg/L	13.8	0.06	—
TSS	99%	$\times 10^3$mg/L	0.05	0.06	—
Oil and Grease	97%	$\times 10$ mg/L	0.4	1.5	—
Total glycerol	31%	$\times 10^3$mg/L	230	—	—
Soaps	100%	$\times 10^5$mg/L	0	—	—
Methanol	60%	$\times 10^3$mg/L	4.3	—	—
pH	—		7.7	5.5-9.0	6.8-7.7
Alkalinity	—	mg $CaCO_3$/L	800	—	1000-3000
VA	—	mg acetic/L	80	—	50-5000
BOD_5/COD	—		0.8	—	>0.6
VA/Alkalinity	—		0.1	—	<0.4

However, as shown in **Table 4.7**, the COD and BOD_5 of treated waste glycerol were 15.4 g/L and 13.8 g/L , while the COD and BOD_5 in the oil terminal and industrial effluent standards of Thailand were 0.2 g/L and 0.06 g/L (Pollution Control Department, 2004), therefore, the treated waste glycerol cannot be discharged into the environment. But after the pH value of treated waste glycerol was adjusted from 4.8 to neutral range with NaOH, the volatile acidity (VA), BOD_5/COD and VA/alkalinity are around 80 mg acetic/L, 0.8 and 0.1, respectively. These parameters are favorable for anaerobic conditions (Lopez et al., 2009). In addition, the O&G, which is toxic matter for micro-organisms, was removed from waste glycerol. The treated waste glycerol can then be used to produce biogas and/or be treated by biological treatment process until it meets the Oil Terminal and Industrial Effluent Standards of Thailand.
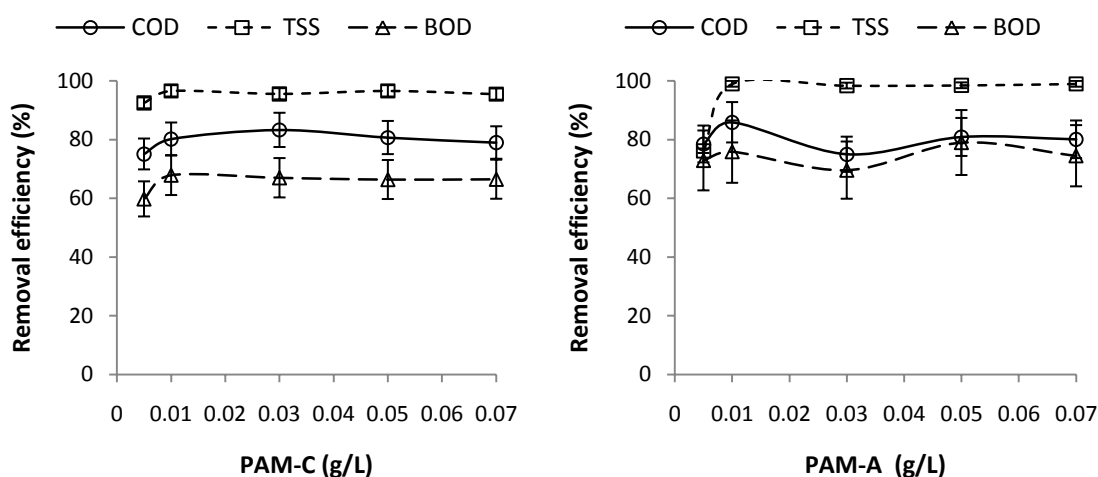
Figure 4.17 Effect of PAMs on the COD, BOD_5 and TSS of waste glycerol after acidification to pH 4 with PACl addition (2 g/L)
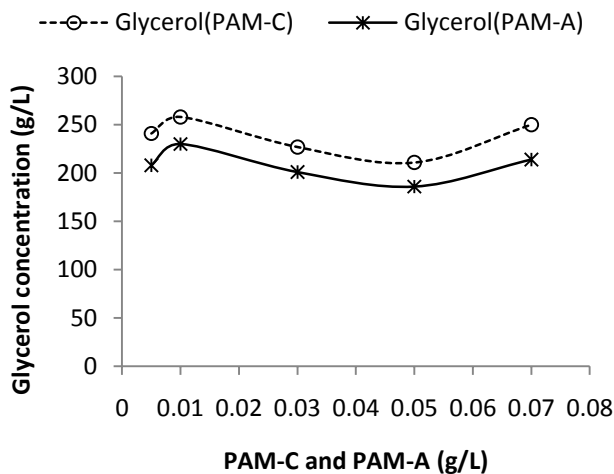
Figure 4.18 The concentration of glycerol in treated waste glycerol with PAM-C (C-8800) and

PAM-A (A-9934)
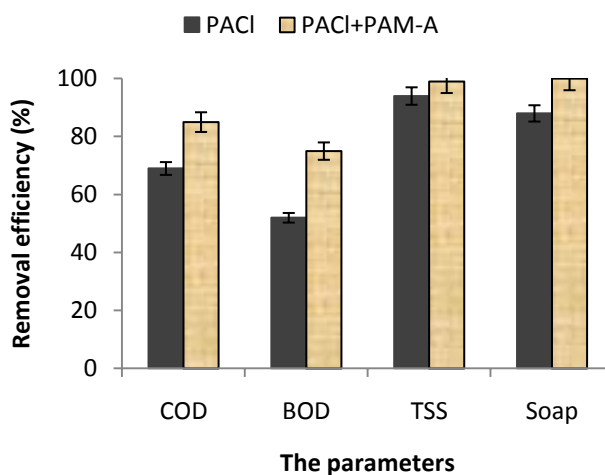
Figure 4. 19 Comparison of parameters removal efficiencies before and after adding PAM-A

(A-9934) into PACl

4.2.9 Comparison PACl and PAM-A with electotreat C-7123

Before this study was conducted, a commercial polymer was used to treat waste glycerol after the acidification pretreatment. A commercial polymer is a kind of cation polymer produced by Sunolin Company in Thailand; it is widely used in the wastewater treatment process. The results of treatment with PACl and PAM-A were compared with the commercial polymer.

It was found that the optimum concentration of the commercial polymer for waste glycerol coagulation was 5 g/L, and the optimum pH value was 7. At these conditions, the removal efficiencies of TSS, COD, and BOD_5 were 98.1%, 96.2%, and 93.3%, respectively (Xie et al., 2010).

Figure 4.20 shows that the concentrations of COD, BOD_5, and TSS in the wastewater sample after coagulation with the PACl and PAM-A, were 15,400 mg/L, 13,800 mg/L, and 50 mg/L, respectively. The concentrations of these parameters are over the oil terminal effluent standards of Thailand (COD: 120 mg/L, BOD_5: 60 mg/L and TSS: 50 mg/L). In the wastewater sample after coagulation with the commercial polymer, the concentrations of COD, BOD_5, and TSS were 2,331 mg/L, 2,241 mg/L and 12 mg/L, which less than with PACl and PAM-A. They should also be reduced until the oil terminal effluent standards are reached. However, the concentration of glycerol in the wastewater sample by coagulation with PACl and PAM-A was higher than in commercial polymers. This implies that more glycerol can be recovered from wastewater treated with PACl and PAM-A. In addition, the optimum concentration of the commercial polymer is 5 g/L, for PACl it is 2 g/L, and for PAM-A it is 0.01 g/L.

When organic matters existing in waste glycerol are coagulated by PACl with PAM-A, the sample obtained consists of glycerol (230 g/L), methanol (4.3 g/L), and impurities (0.3 g/L). This glycerol can be recovered by distillation (Gerpen, 2005) or by treatment with cyclodextrins (CD) inclusion complexation (Song et al., 2009). The glycerol in waste glycerol after treatment with electotreat C-7123 was 147 g/L. The concentration of glycerol in the treated waste glycerol with electotreat C-7123 was so small that it might be not included by CDs inclusion complexation.

It is possible to use the commercial polymer coagulation process to treat waste glycerol, since this polymer can reduce the water pollution of waste glycerol effectively. The PACl with PAM-A coagulation process can be used to pretreat waste glycerol and recover the sediment, which contain great amount of organic matters and glycerol. The wastewater can be treated again until it reaches the oil terminal effluent standards for Thailand after pretreatment.
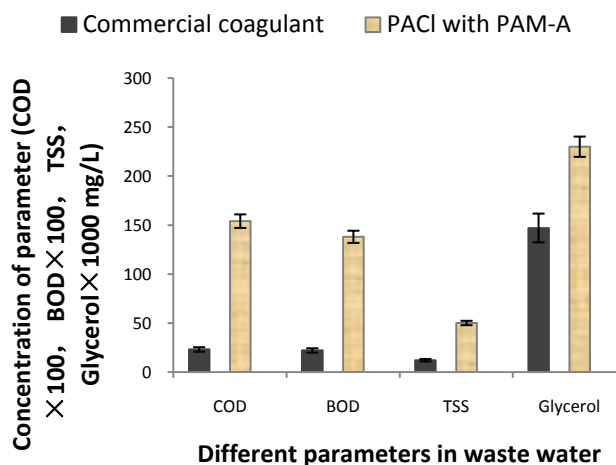
Figure 4. 20 Comparison of coagulation effect for commercial polymer and PACl with PAM-A

4.2.10 Summary

This study demonstrates that the raw waste glycerol needs to be pretreated by acidification process to adjust the pH value, convert soaps into free fatty acids, and destabilization of O/W interface in waste glycerol. When pH value was adjusted below 5, the insoluble free fatty acids and methyl ester can be separated and recovered from waste glycerol. After the acidification pretreatment, the treated waste glycerol was adjusted its pH value and coagulated by PACl coagulation. And then the PACl coagulation was improved by four types of PAM flocculation. The appropriate PAM and the optimum conditions of PACl and PAM coagulation-flocculation were measured according to the results of different pH values, different PACl dosages and different PAM dosages.

The results showed that the PAM-A was selected as the appropriate PAM flocculant to improve PACl coagulation. The PACl coagulant and PAM-A flocculant can destabilized the O/W emulsion in waste glycerol by charge neutralization. The coalesced oil drops attach to soaps and float to the top of the solution where they are eventually adsorbed by coagulant. More than 97% of O&G, soaps and TSS were effectively separated from waste glycerol in this process. However, the COD and BOD_5 are above the Oil Terminal and Industrial

Effluent Standards of Thailand due to less significant removal of glycerol and methanol. Therefore, this process is possibly suitable for a primary treatment of glycerol recovery process. In addition, the coagulation-flocculation process can enhance the biodegradability of waste glycerol. The pretreatment with coagulation-flocculation followed by a biological treatment process seems feasible and competitive compared with evaporation or physicochemical treatment. It requires less energy consumption, more cost efficient, and it is effective and easy to handle. In addition, the coagulation with PACl and PAM-A is cheaper and can remain more glycerol than the coagulation with electotreat C-7123.

Table 4.8 The concentrations of characterizations in raw waste glycerol, after acidification, PACl coagulation and PAM-A flocculation at the optimum conditions

Characterization	Units	Raw waste glycerol	After acidification	After PACl coagulation	After PAM-A flocculation
pH		9.8	4.0	4.0	4.0
COD	g/L	1,795	102	30.6	15.4
BOD_5	g/L	966	56	18.8	13.8
TSS	g/L	217	5	0.3	0.05
Oil and grease	$\times 10$mg/L	535	13.3	1.3	0.4
Total glycerol	g/L	477	330	224	230
Soaps	g/L	218	7.4	0.8	0
Methanol	g/L	203	10.7	6.1	4.3

4.3 Preliminary study of β-CD include glycerol from treated waste glycerol after PACl and PAM-A coagulation

4.3.1 Introduction

The treated waste glycerol contains about 230 g/L of glycerol (the raw waste glycerol contains 423 g/L of glycerol) after PACl and PAM-A (A-9934) coagulation treatment. At present, due to its properties, pure glycerol has more than 2000 different applications (Lopez et al., 2009). The recovery of glycerol can make economic benefit for biodiesel plants. Song et al., (2008) found that the β-CD can include glycerol. The rate of β-CD include glycerol is 1:1; it means that one β-CD can include one molecule of glycerol. This is because of its structure characteristics. The CDs have the shape of a hollow truncated cone. The intra-cavity of CDs is hydrophobic while the exterior of the cavity is hydrophilic (Song et al., 2008). CDs can form host-guest inclusion complexes by weak intermolecular interaction with a wide variety of guests including organic molecules, inorganic ions, coordination compounds and even rare gases (Song et al., 2008).

4.3.2 Results and discussion

The results of β-CD including the pure glycerol and the treated waste glycerol after PACl and PAM-A coagulation process were shown in **Figure 4.21** and **Figure 4.22**. The concentration of glycerol in pure glycerol was 99.5% by weight, and in treated waste glycerol was 23% by weight.

It was found that the peak of β-CD absorption of pure glycerol was at position of 12.5, which is the highest peak in the **Figure 4.21**. The position of 12.5 is the value of glycerol included by β-CD. Thus, at the same position in **Figure 4.22**, the peak value is not as high as the peak value in **Figure 4.21**. It means that the β-CD can include residual glycerol from treated waste glycerol, but the amount of residual glycerol included by β-CD is not as much as the amount of pure glycerol. It is because the concentration of residual glycerol in treated waste

glycerol is less than the concentration of glycerol in pure glycerol; and there is an amount of methanol (4.3 g/L) and a slight amount of impurity matters in treated waste glycerol, which could affect the β-CD absorption of glycerol (Song et al., 2008).
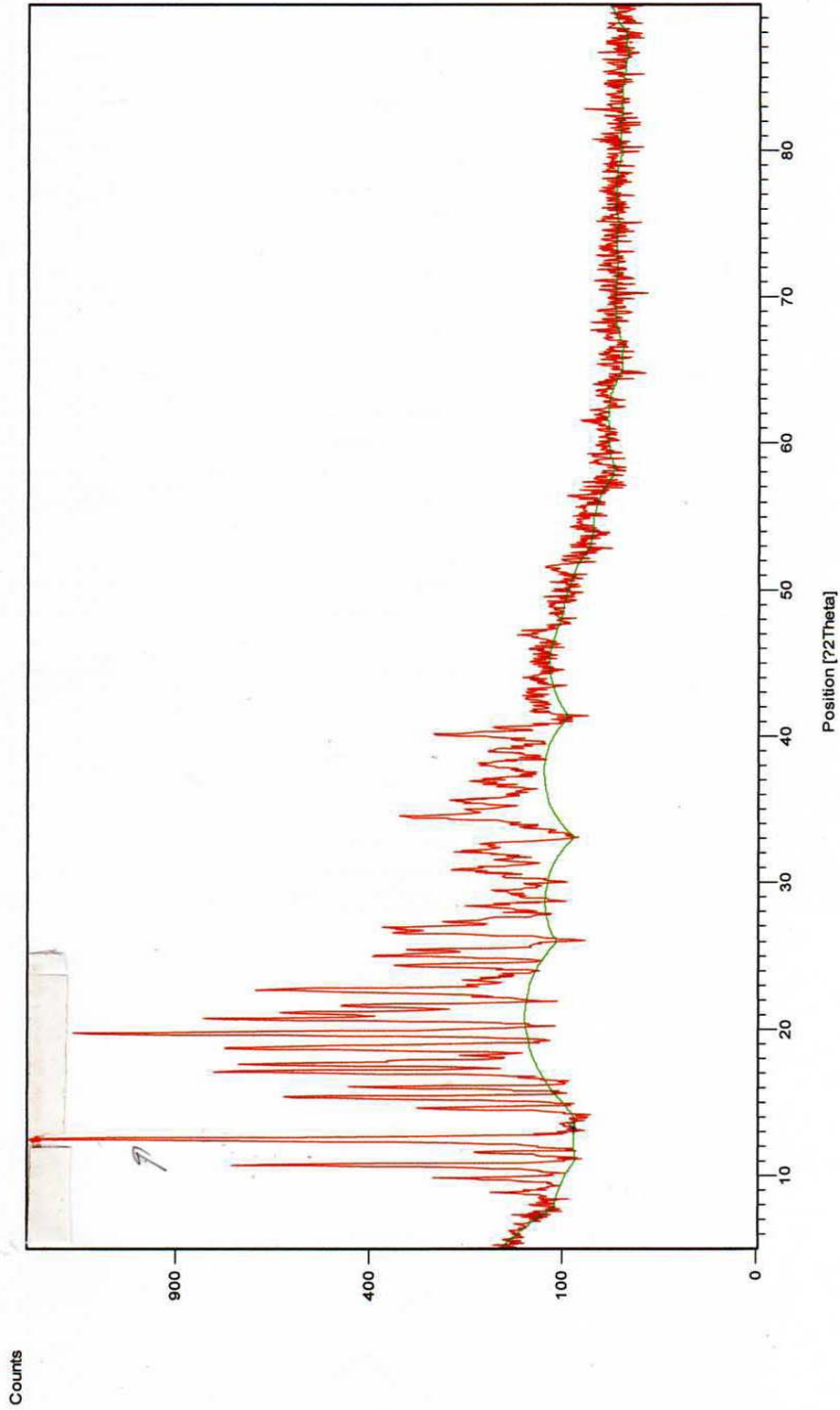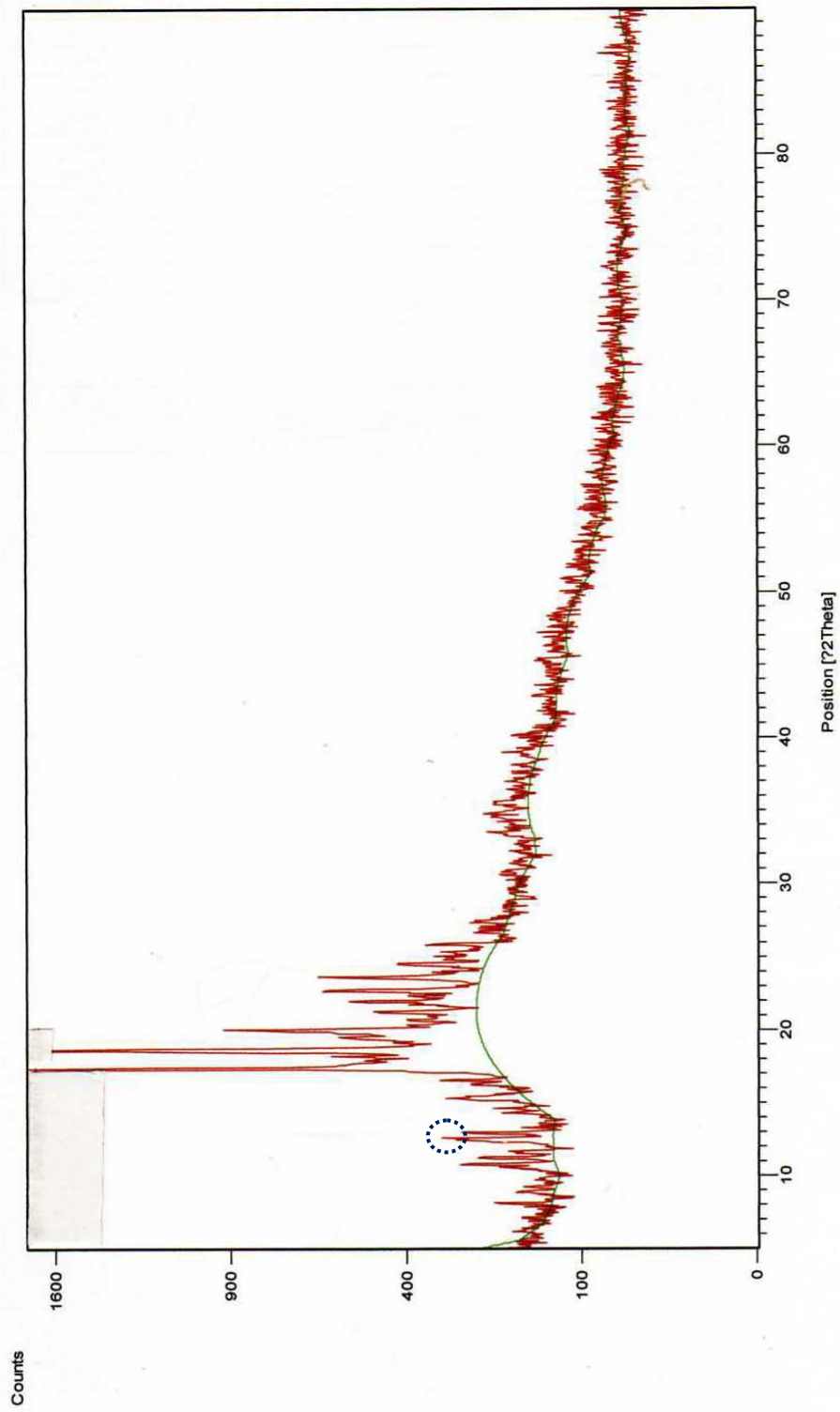
Figure 4.21 The results of β-CD including pure glycerol

Figure 4.22 The results of β-CD including residual glycerol from treated waste glycerol

4.3.3   4.3.3 Summary

It can conclude that the β-CD can include the residual glycerol from treated waste glycerol, but the amount of included glycerol is small. If the methanol and impurity matters can be removed from treated waste glycerol, and the purity of residual glycerol can be improved by distillation, the amount of included glycerol by β-CD may increase.

4.4 Gelatinous production from raw waste glycerol

4.4.1   Introduction

With the growing capacity in biodiesel production and the resulting glut of the glycerol by-product, there is increasing interest in finding alternative uses for raw waste glycerol. One option may be to burn it locally for combined process heat and power, replacing fossil fuels and improving the economics of biodiesel production. However, due to its low energy density, high viscosity, and high auto-ignition temperature, raw waste glycerol is difficult to burn. Additionally, the composition of the raw waste glycerol can change dramatically depending on the biodiesel feedstock (e.g., vegetable oils or rendered animal fats) (Bohon et al., 2011).

The raw waste glycerol from biodiesel production by transesterification with waste oil and palm oil contains oil-in-water emulsion, glycerol, alcohol, catalyst and a mixture of other organic material (soaps and unreacted fats and oils). The raw waste glycerol is difficult to burn, mainly due to its water content. The energy density of raw waste glycerol can be improved by adding methanol (Bohon et al., 2011).

Yin (2003) used hydroxypropyl methylcellulose (HPMC) and stearic acid to transform liquid methanol into solid methanol. The HPMC, stearic acid and methanol may be able to be used to transform raw waste glycerol into gelatinous waste glycerol which can be used as a fuel, and save cost of disposing raw waste glycerol (Silva et al., 2008).

Hydroxypropyl methylcellulose (HPMC), a so-called polymeric emulsifier, is able to absorb at liquid polymeric emulsifier, is able to absorb at liquid interfaces and to lower the

interfacial tension. The formation of stabilizing interfacial layers requires, first, the diffusion of the polymer from the solution bulk to the interface and, second, its adsorption at the layers may be described according to the train-loop-tail model: lipophilic segments along the polymer chain attach to the interface and form trains, which are separated by hydrophilic loops and tails, that extend into the aqueous phase. The properties of the interfacial layers, especially the ratio of train: loop and tail segments, and the elasticity of the layer, determine the emulsion stability, particularly the coalescence stability of oil droplets.

Stearic acid is used to harden soaps, particularly those made with vegetable oil (Wootthikanokkhan and Tunjongnawin, 2002). Batte et al., (2007) used stearic acid to transform vegetable oily water into oil-water gels.

The principal aims of this study are: (1) transform liquid raw waste glycerol into gelatinous waste glycerol with stearic acid, stearic acid blend with methanol and HPMC blend with methanol; (2) compare the three type of gelatinous waste glycerol.

4.4.2   Results and discussion

The three types of gelatinous waste glycerol are shown in **Figure 4.23**. The left one is the gelatinous waste glycerol made with waste glycerol, stearic acid and NaOH. The middle one is made with waste glycerol, stearic acid, methanol and NaOH. The right one is that made with waste glycerol, HPMC, methanol and NaOH.

It was found that the gelatinous waste glycerol made by waste glycerol, stearic acid and NaOH transform into solution when it was set at the room temperature for about two hours. However, when methanol was added into waste glycerol, the stearic can easily dissolve in the solution, and the gelatinous waste glycerol can keep gelatinous form at room temperature for a long time. The gelatinous waste glycerol made with waste glycerol, HPMC, methanol and NaOH can keep gelatinous form at room temperature for a long time also. However, the price of HPMC is higher than stearic acid.

The price of stearic acid is about 25,300 Baht/ton, but the price of HPMC is 96,000 Baht/ton (Alibaba, 2009). The price of methanol is 12.88 Baht/L (Alibaba, 2009); and the

volume of methanol production gelatinous waste glycerol is 25 mL. The dosage of stearic acid for making 50 mL waste glycerol into gel is 4 g, and the dosage of HPMC for making 50 mL waste glycerol into gel is 9 g. Thus, the prices of stearic acid and HPMC for making 1 m^3 waste glycerol into gel are as follow:

(1) The price of stearic acid:

25,300 Baht/ton = 2.53×10-2 Baht/g

2.53×10^{-2} Baht/g×4 g÷50 mL = 2.02 Baht/L = 2.02×10^3 Baht/m^3

(2) The price of HPMC:

96,000 Baht/ton = 9.6×10^{-2} Baht/g

9.6×10^{-2} Baht/g×9 g÷50 mL = 17.2 Baht/L = 1.72 × 10^4 Baht/m^3

(3) The price of methanol:

12.88 Baht/L = 1.288×10^{-2} Baht/mL×25 mL= 0.32 Baht

0.32 Baht÷50 mL = 6.4 Baht/L = 6.4×10^3 Baht/ m^3

Thus, the cost of production gelatinous waste glycerol with stearic acid and methanol is 8,420 Baht/m^3, and the cost of production gelatinous waste glycerol with HPMC and methanol is 23,600 Baht/m^3. The price of stearic acid for making 1 m^3 gelatinous waste glycerol is much cheaper than the price of HPMC.

The heating value and water content of three types of gelatinous waste glycerol samples were shown in **Table 4.9**. The heating value of gelatinous waste glycerol made with stearic acid is 6338 kcal/kg, which is closed to the heating value of coke (6500 kcal/kg) in **Table 4.10**. The heating value of gelatinous waste glycerol made with waste glycerol, stearic acid, methanol and NaOH is 8519 kcal/kg; and the heating value of gelatinous waste glycerol made with waste glycerol, HPMC, methanol, and NaOH is 8253 kcal/kg; their heating values are closed to natural gas (8600 kcal/kg). It indicates that the gelatinous waste glycerol made with waste glycerol, stearic acid, methanol and NaOH, and that made with waste glycerol, HPMC, methanol, and NaOH are easy to burn as a fuel. The heating value of gelatinous waste glycerol made with waste glycerol, stearic acid and NaOH is lower than the gelatinous waste glycerol which was

added methanol, because the methanol can improve the heating value of waste glycerol. The heating value of gelatinous waste glycerol made with waste glycerol, stearic acid and NaOH is close to the heating value of raw waste glycerol.

As shown in **Table 4.9**, the water content of gelatinous waste glycerol made with waste glycerol, stearic acid and NaOH is higher than that of the other two types of gelatinous waste glycerol. This is because the other two types of gelatinous waste glycerol content more methanol than the gelatinous waste glycerol made with waste glycerol, stearic acid and NaOH.

4.4.3   Summary

These experiments indicate that the gelatinous waste glycerol made by stearic acid blend with methanol, and HPMC blend with methanol can keep gelatinous form at room temperature for a long time. The heating value of gelatinous waste glycerol made by stearic acid blend with methanol and HPMC blend with methanol are 8519 kcal/kg and 8258 kcal/kg, which can be used as a fuel.

It can be concluded that: (1) stearic acid blend with methanol and HPMC blend with methanol can transform liquid waste glycerol into a gelatinous waste glycerol which is easy for transportation; (2) the production of gelatinous waste glycerol can save waste glycerol treatment cost, and convert waste glycerol into a fuel; (3) the gelatinous waste glycerol can keep gelatinous form at room temperature for a long time, which can make into a candle; (4) the price of stearic acid for making 1 m^3 waste glycerol into gel is cheaper than the price of HPMC.

Table 4.9 The heating value and water content of three types of gelatinous waste glycerol

Gelatinous waste glycerol	Heating value (kcal/kg)	Water content (% by wt)
Made with stearic acid	6338	35.5
Made with stearic acid and methanol	8519	13.3
Made with HPMC and methanol	8253	16.0

Table 4.10 Calorific value of fossil fuels (Indian portal calorific value of fuels, 2002)

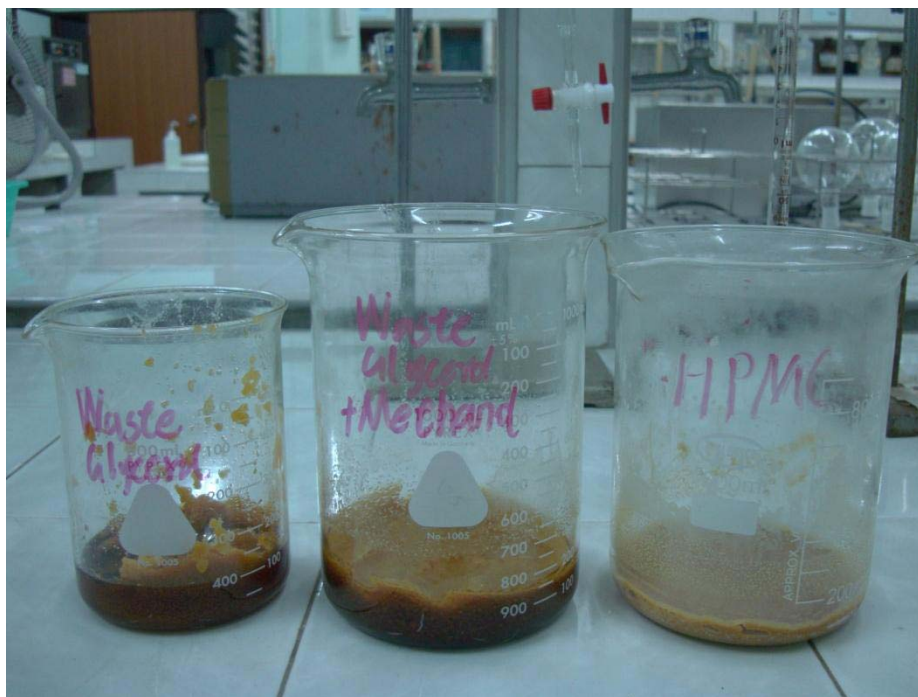| No.	Fossil fuel	Approx heating value (kcal/kg)
1	Coal	4,000-7,000
2	Coke	6,500
3	Charcoal	7,000
4	Carbon	8,000
5	Fuel oil	9,800
6	Kerosene and diesel	10,000
7	Petrol	10,800
8	Paraffin	10,500
9	Natural gas	8,600
10	Coal gas	4,000
11	Electrical (kcal/kw)	860
12	Biogas (kcal/ cu mtr) (12kg of dung produces 1 cu. Mtr gas)	4,700-6,000

Figure 4.23 The appearance of three types of gelatinous waste glycerol

Chapter 5

Summary and future works

This chapter presents the conclusion of the work applying acidification and coagulation processes to treat waste glycerol from biodiesel production process; and production of gelatinous waste glycerol process. It summarizes the advantages and the limitation of these treatment and production. In addition, it presents the discussion of this work and suggests some future works.

5.1 Conclusion

The aim of this research was to study the treatments of waste glycerol by acidification process and coagulation process with electotreat C-7123, polyaluminium chloride (PACl), cationic PAM (C-8385), cationic PAM (C-8800), anionic PAM (A-9770) and anionic PAM (A-9934). It also studies the production of gelatinous raw waste glycerol to transform waste glycerol solid fuel.

5.1.1   Coagulation of waste glycerol with electotreat C-7123

The results show that in acidification pretreatment process, the pH value of waste glycerol should be adjusted below 5. The COD, BOD_5, TSS and soaps were reduced in this process. The upper layer mainly contains free fatty acid and methyl ester can be recovered from waste glycerol and reused as raw materials for biodiesel production; the lower layer was taken to coagulation process.

In the coagulation process with electotreat C-7123, the optimum pH value of waste glycerol is 7, and the optimum concentration of electotreat C-7123 is 5 g/L. In the optimum conditions, the removal of COD, BOD_5, TSS, soaps and methanol was effective, but the removal efficiencies of glycerol is low. Residual glycerol (147 g/L) can be recovered from waste glycerol.

However, the concentration of electotreat C-7123 is quite high, and the cost of this electotreat C-7123 is quite expensive (about 200 Bath/t). In addition, the concentration of residual glycerol is not very high. Thus, it needs to find other coagulant, which is cheaper and can separate glycerol from waste glycerol more effectively, to treat waste glycerol.

5.1.2 Coagulation of waste glycerol with PACl and four types of PAMs

It found that in the cationic PAM (C-8385), cationic PAM (C-8800), anionic PAM (A-9770) and anionic PAM (A-9934), the cationic PAM (C-8800) can remain more glycerol than anionic PAM (A-9934). But the anionic PAM (A-9934) improves PACl coagulation the most effectively. More than 97% of oil and grease (O&G), soaps and TSS were effectively removal from waste glycerol in this process. The demulsification of O/W was achieved during the acidification and coagulation process. The concentration of residual glycerol was 230 g/L. The COD and BOD_5 in treated waste glycerol are above the Oil Terminal and Industrial Effluent Standard of Thailand due to low removal efficiencies of glycerol and methanol. However, the biodegradability of waste glycerol was enhanced; thus, the treated waste glycerol can be sent to biological treatment.

Therefore, the coagulation process with PACl and PAM-A can be used as a primary treatment of glycerol recovery and a pretreatment following a biological treatment.

This method can be applied to the type of biodiesel plants which use alkali-catalyzed transesterification to produce biodiesel from waste oil and palm oil. The free fatty acid, methanol and glycerol can be recovered from treated waste glycerol and bring economic benefit to biodiesel facilities in the future.

5.1.3 The preliminary study of β-CD include glycerol from treated waste glycerol after PACl and PAM-A coagulation

The results show that β-CD can absorb the residual glycerol from treated waste glycerol, but the amount of including residual glycerol by β-CD is smaller than the amount of

including pure glycerol. If the purity of glycerol in treated waste glycerol can be improved, the amount of including glycerol may increase.

5.1.4   Production of gelatinous waste glycerol

The study provides another method to treat waste glycerol. Because the waste glycerol contains approximately 10% water, its fuel value is quite low. Thus, it can be added a certain amount of methanol and make into gelatinous waste glycerol, since the gelatinous waste glycerol is easier for transportation than liquid waste glycerol. Moreover, the gelatinous waste glycerol can be used as a fuel; the heat value of gelatinous waste glycerol made with waste glycerol, stearic acid, methanol and NaOH is 8519 kcal/kg; the heat value of gelatinous waste glycerol made with waste glycerol, Hydroxypropyl methylcellulose (HPMC), methanol and NaOH is 8258 kcal/kg. Their heating values are closed to heating value of nature gas.

5.1.5   Schematic diagram

There are two methods to treat raw waste glycerol. One method is treating waste glycerol by acidification and coagulation processes; another one is transforming raw waste glycerol into gelatinous waste glycerol which can be used as a fuel.

As shown in **Figure 5.1**, the steps in the method of treating waste glycerol by acidification and coagulation processes are shown as follow: (1) the raw waste glycerol is pretreated by acidification process. The oil-in-water emulsion can be destroyed in the process; the soaps can be converted into free fatty acid and salts; the free fatty acid and methyl ester can be recovered in the process. (2) After acidification process, the waste glycerol can be coagulated with PACl and PAM-A or electotreat C-7123. (3) The treated waste glycerol by electotreat C-7123 coagulation contains glycerol 147 g/L (the raw waste glycerol contains glycerol 412 g/L); the cost of treating 1 m^3 waste glycerol with electotreat C-7123 is about 200 Baht. (4) The treated waste glycerol by PACl and PAM-A contains glycerol 230 g/L (the raw waste glycerol contains glycerol 423 g/L); the cost of treating 1 m^3 waste glycerol with PACl and PAM-A is about 11

Baht. (5) The residual glycerol in treated waste glycerol can be recovered by CDs inclusion or distillation.

The steps in the method of production raw waste glycerol into gelatinous waste glycerol are shows as follow: (1) The raw waste glycerol can be made into gel with stearic acid and methanol or HPMC and methanol. (2) The heating value of gelatinous waste glycerol produced by stearic acid and methanol is 8519 kcal/kg; the cost of producing gelatinous waste glycerol with stearic acid and methanol is 8,420 Baht/m^3. (3) The heating value of gelatinous waste glycerol produced by HPMC and methanol is 8258 kcal/kg; the cost of producing gelatinous waste glycerol with stearic acid and methanol is 23,600 Baht/m^3.

The method of waste glycerol treatment can be managed by biodiesel plants, which produce biodiesel with palm oil and/or waste oil, according to the conditions of these plants.
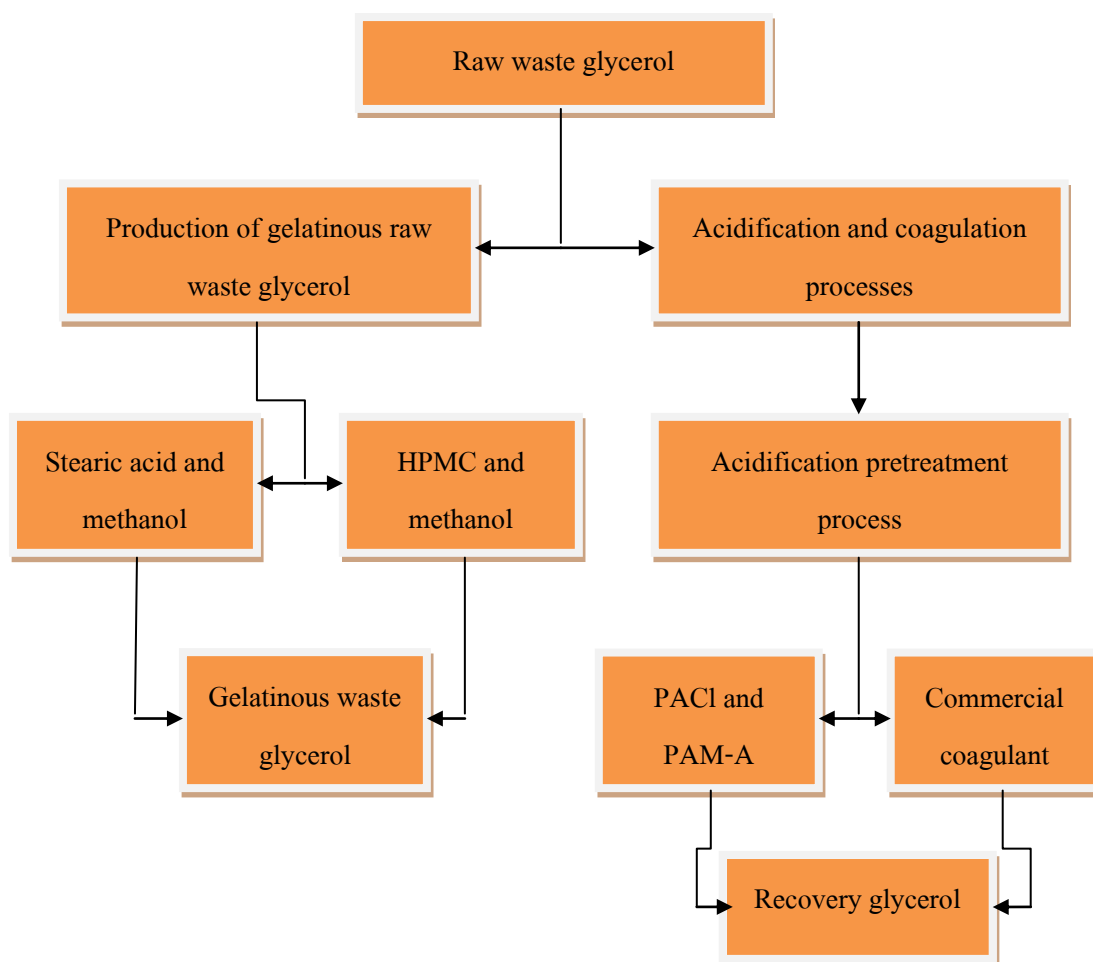
Figure 5.1 Schematic diagram of treatment of raw waste glycerol

5.2 Advantages and limitations

The results of this study produce several benefits. However, there are many limitations which require improvement. This part discusses the benefits and results from this work.

5.2.1   Advantages

1. The coagulation processes and production process of gelatinous waste glycerol is cheap, easy to hand and can be applied in the different types of biodiesel plants which use alkali-catalyzed transesterification to produce biodiesel from waste oil and palm oil.

2. After the coagulation processes, the upper layer solution which mainly contains free fatty acids and methyl ester can be reused as a raw material for biodiesel production process; The residual glycerol can be recovered from treated waste glycerol; the treated glycerol also can be used as a carbon source or compost; the coagulation production, which contains a large amount of organic compounds, can be used as a fuel.

3. The production of gelatinous waste glycerol can save waste glycerol treatment cost, and convert waste glycerol into a fuel which has high heat value and easy to transportation;

4. The coagulation processes and production process of gelatinous waste glycerol can reduce water pollution and/or reuse waste glycerol, and bring economic benefits for biodiesel plants.

5.2.2   Limitations

1. The Al remains in the treated waste glycerol after coagulation process, which may have potential risks to public health.

2. The amount of coagulants which are used to treat waste glycerol is still high. It can find some methods to reduce the amount of coagulants that are used to treat waste glycerol, such as electrocoagulation process.

5.2.3 Future works

1. The recovery methods of glycerol from treated glycerol need to be study in future.

2. In order to reduce the concentration of Al remain in the treated waste glycerol, it needs to find other coagulants to replace PACl, which can reduce water pollution of waste glycerol and remain glycerol after coagulation process.

3. In order to reduce the concentration of coagulant, it needs to find other high molecule weight of coagulants to treat waste glycerol.

4. The methods of production biogas with treated waste glycerol need to be studied in future.

5. In order to increase the amount of including glycerol by CDs, the purity of glycerol in treated waste glycerol need to improved first, and then the glycerol can be included by CDs.

6. In order to keep gelatinous waste glycerol at room temperature for a long time and reduce the amount of chemical, the production process of gelatinous waste glycerol needs to be test with different adhesives, such as nitrocellulose and calcium acetate.

7. The methods to make gelatinous waste glycerol into a candle can be studied in future works.

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List of Publication and Proceedings

[1] Qiao-guang Xie, Chaisri Suksaroj, Wirach Taweepreda and Charonpun Musikavong, "Removal of Oily Sludge in Waste Glycerol from the Biodiesel Production Process by Coagulation", *Proceedings of the 4th International Congress of Chemistry and Environment*, Thailand, 21-23 January 2009.

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