Faculty of Resource Science and Technology

Solubilization of Residual Oil in Palm Oil Mill Effluent (POME) Using Mixture of Anionic (GE-460) and Non-ionic Surfactants (Brij 35)

Muhammad Mirza bin Ariffin (31416)

Bachelor of Science with Honours
(Resource Chemistry)
2014

UNIVERSITI MALAYSIA SARAWAK

Grade: ____________

Please tick (√)

Final Year Project Report ☑

Masters ☐

PhD ☐

DECLARATION OF ORIGINAL WORK

This declaration is made on the ....25.......day of....JUNE.......2014.

Student's Declaration:

I MUHAMMAD MIRZA BIN ARIFFIN /31416/ FSTS

(PLEASE INDICATE STUDENT'S NAME, MATRIC NO. AND FACULTY) hereby declare that the work entitled ~~RE~~ SOLUBILIZATION RESIDUAL OIL USING MIXTURE SURFACTANTS is my original work. I have not copied from any other students' work or from any other sources except where due reference or acknowledgement is made explicitly in the text, nor has any part been written for me by another person.

20/6/2014
Date submitted

MUHAMMAD MIRZA ARIFFIN (31416)
Name of the student (Matric No.)

Supervisor's Declaration:

I--- (SUPERVISOR'S NAME) hereby certifies that the work entitled --(TITLE) was prepared by the above named student, and was submitted to the "FACULTY" as a * partial/full fulfillment for the conferment of -- (PLEASE INDICATE THE DEGREE), and the aforementioned work, to the best of my knowledge, is the said student's work.

Received for examination by: ____________________ Date:____________________
(Name of the supervisor)

I declare that Project/Thesis is classified as (Please tick (√)):

☐ **CONFIDENTIAL** (Contains confidential information under the Official Secret Act 1972)*
☐ **RESTRICTED** (Contains restricted information as specified by the organisation where research was done)*
☑ **OPEN ACCESS**

Validation of Project/Thesis

I therefore duly affirm with free consent and willingly declare that this said Project/Thesis shall be placed officially in the Centre for Academic Information Services with the abiding interest and rights as follows:

- This Project/Thesis is the sole legal property of Universiti Malaysia Sarawak (UNIMAS).
- The Centre for Academic Information Services has the lawful right to make copies for the purpose of academic and research only and not for other purpose.
- The Centre for Academic Information Services has the lawful right to digitalise the content for the Local Content Database.
- The Centre for Academic Information Services has the lawful right to make copies of the Project/Thesis for academic exchange between Higher Learning Institute.
- No dispute or any claim shall arise from the student itself neither third party on this Project/Thesis once it becomes the sole property of UNIMAS.
- This Project/Thesis or any material, data and information related to it shall not be distributed, published or disclosed to any party by the student except with UNIMAS permission.

Student signature ____________________ (Date)

Supervisor signature ____________________ (Date)

Current Address:

____

____

Notes: * If the Project/Thesis is **CONFIDENTIAL** or **RESTRICTED**, please attach together as annexure a letter from the organisation with the period and reasons of confidentiality and restriction.

[The instrument is duly prepared by The Centre for Academic Information Services]

ACKNOWLEDGEMENTS

First of all, I would like to thank my supervisor Madam Amira Satirawaty binti Mohamed Pauzan who has provided me with non-stop excellent help, discussions and support throughout this research. I would like to thank Dr. Azham Zulkharnain for guidance and support on conducting bacterial test.

I would also like to thank my fellow lab mates for guidance and help whenever I was face difficulties while conducting my research. I would like to thank the students in Virology Lab and Environmental Lab for providing us with necessary materials for bacterial test.

Lastly, I would like to thank my family for their endless support.

DECLARATION

I declare that this thesis entitled "Solubilization of residual oil in POME by using mixture of anionic (GE 460) and non-ionic (Brij 35) surfactants" is the result of my own research except as cited in the reference. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Muhammad Mirza bin Ariffin (31416)

Resource Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

Table of Contents

List of Abbreviations

BOD	Biochemical oxygen demand
Brij 35	Polyoxyethylene (23) lauryl ether
CMC	Critical micelle concentration
COD	Chemical Oxygen demand
CPO	Crude palm oil
DMSO	Dimethyl sulfoxide
DOE	Department of Environment
EFB	Empty fruit bunches
EQA	Environmental Quality Act
FT-IR	Fourier Transform Infrared
GE-460	Glycolic acid ethoxylate lauryl ether
KBr	Potassium bromide
O/W	Oil in water
POME	Palm oil mill effluent
W/O	Water in oil

List of Tables

List of Figures

Solubilization of Residual Oil in Palm Oil Mill Effluent (POME) Using Mixture of Anionic (GE-460) and Non-ionic Surfactants (Brij 35)

Muhammad Mirza bin Ariffin

Resource Chemistry Programme
Faculty of Science and Technology
Universiti Malaysia Sarawak

ABSTRACT

Palm oil mill effluent (POME) is oily wastewater produced during the processing of palm oil. Although POME is not toxic, the organic compounds such as residual oil have high oxygen depleting ability which will harm the aquatic ecosystems when released into the environment. Thus, effective treatment methods should be applied on POME before it is discharged into the streams. In this study, the residual oil in POME was removed by solubilisation using mixture of anionic (GE-460) and non-ionic (Brij 35) surfactants. Three experimental parameters were studied to obtain maximum solubilization of oil which were critical micelle concentration (CMC) of GE-460, optimum concentration of GE-460 and temperature. The results obtained shows that the CMC of GE-460 is 0.25 mM while maximum amount of oil solubilized occurred at concentration of 0.5 mM with 0.25 g oil solubilized and at temperature of 75 °C with 0.09 g oil solubilized. Fourier Transform infrared (FT-IR) spectroscopy was used for quantitative analysis of interaction between residual oil and surfactants. The spectrum showed peak at 2924 cm^{-1} which suggested that the oil components in POME combined with hydrophobic part of the surfactant. The shifting of O-H, C=O and C-O stretches also indicated the interaction between the oil and surfactants. The surfactants used were not toxic to aquatic organisms and readily degradable by microorganisms.

Keywords: Palm oil mill effluent, residual oil, anionic (GE-460), non-ionic (Brij 35), solubilization

ABSTRAK

Sisa kumbahan kilang kelapa sawit (POME) ialah sisa berminyak dari pemprosesan kelapa sawit. Walaupun tidak toksik, kandungan sebatian organik akan mengurangkan kandungan oksigen terlarut dalam air yang boleh mengancam hidupan akuatik. Oleh itu, kaedah rawatan kumbahan yang efektif perlu dijalankan ke atas POME sebelum dilepaskan ke dalam sungai. Dalam kajian ini, sisa minyak dirawat dengan menggunakan campuran surfaktan anionik (GE-460) dan bukan ionik (Brij 35). Tiga parameter dikaji bagi mendapatkan kadar minyak terlarut tertinggi seperti kepekatan kritikal misel untuk GE-460, kepekatan optimum untuk GE-460 dan suhu. Keputusan menunjukkan kepekatan kritikal misel untuk GE-460 ialah 0.25 mM dan kadar minyak terlarut tertinggi dicatatkan pada kepekatan 0.50mM dengan 0.25 g minyak terlarut dan pada suhu 75 °C dengan 0.09 g minyak terlarut. Spektroskopi inframerah (FT-IR) digunakan bagi analisis interaksi antara minyak dan surfaktan. Spektra menunjukkan puncak pada 2924 cm^{-1} menunjukkan sisa minyak dalam kumbahan terikat pada bahagian hidrofobik surfaktan. Peralihan puncak regangan O-H, C=O dan C-O juga menandakan berlaku interaksi antara sisa minyak dan surfaktan. Surfaktan yang digunakan juga tidak toksik terhadap hidupan akuatik dan boleh didegradasi oleh mikroorganisme.

Kata kunci: Sisa kumbahan kilang kelapa sawit, sisa minyak, anionik, bukan ionik, terlarut

CHAPTER 1: Introduction

Palm oil has been widely used across the continent for several decades for the production of household products as well as biofuels (Greenpeace, 2013). In Malaysia, the palm fruit species harvested is mainly *Elaeis guineensis* which gives a high yield. Until the year 2011, around 56 palm oil refineries have been built throughout the country (Malaysian Palm Oil Board, 2014). The palm oil industry undeniably helps to increase the economy sector of Malaysia but at the same time, the processing of palm oil brings a lot of adverse effects to the environment such as air pollution, water pollution and soil pollution. The release of huge amount of palm oil mill effluent (POME) into the streams has gain major concern from many parties as this activity is known to be one of the main reasons for the destruction of aquatic ecosystem. POME is not toxic but it is rich in organic compound which will greatly deplete the dissolved oxygen content in the water source, harming the aquatic organisms. The high composition of residual oil in POME is not favourable due to its low water solubility and not readily biodegradable thus several treatment methods of POME have been introduced to overcome this problem. One of the treatment methods is by using surface active agent or surfactant which helps to solubilize the oil in the effluent so that it can be kept mobilized and increase availability for biodegradation by microbes (Pauzan & Aziz, 2013). Surfactants are classified based on the nature of their head group either anionic, cationic, non-ionic or amphoteric but the most widely used is non-ionic surfactant because they are stable at high temperatures and resistant to harsh environment. Mixed surfactant system which is made by mixing of two single surfactant systems (usually ionic and non-ionic) is gaining more attention for POME treatment nowadays due to its low critical micelle concentration value thus making it more effective in solubilizing oil compared to single surfactant system. In this study, mixture of anionic (GE-460) and non-ionic (Brij 35) was used to solubilize the oil

The objectives of this study are:

i) to solubilize the residual oil in POME by using the mixture of anionic and non-ionic surfactant.

ii) to study how several parameters such a critical micelle concentration (CMC), concentration and temperature affect the solubilization of residual oil.

iii) to determine the optimum conditions for solubilization of residual oil in POME.

iv) to evaluate the toxicity of the surfactants used

v) to determine the biodegradability of the surfactants used

CHAPTER 2: Literature Review

2.1 Palm Oil Processing Industry

The fresh fruit bunches harvested from the plantation will be sent to the palm oil mill to be processed into crude palm oil and palm kernel. The kernel will later be crushed and undergo few more processes such as extraction to form kernel palm oil. However, the kernels will be processed at separate palm kernel crushing plants since only a few palm oil mills have this facility included in their plants.

The extraction of crude palm oil involves several technical processes which starts from transferring fresh fruit bunches from the plantation to the mill. Next, the fruit bunches will be sterilized to facilitate the stripping of the fruit from the spikelet and prepare the fruit mesocarp for subsequent processing. After that, the fruit bunches will be stripped and digested where they will be mashed in order to rupture the oil-bearing cells lying within the mesocarp. Later, the mashed fruit bunches will move through the twin screw presses machine in order to squeeze out the oil content in the fruit. Figure 2.1 summarizes the overall processes of crude palm oil extraction including the production of palm kernel.

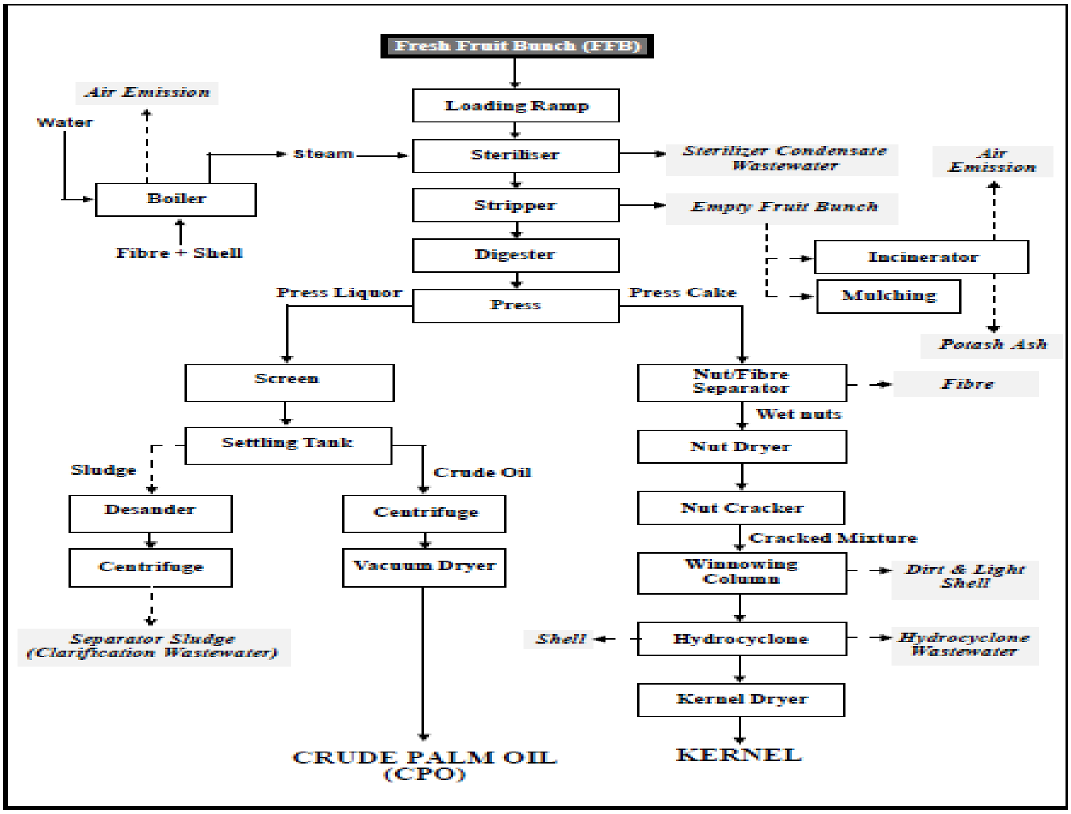

Figure 2.1: Crude palm oil extraction and palm kernel production processes (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999).

2.1.1 Generation of waste and environmental issues

The palm oil industry releases huge amount of waste into the environment. About more than half of the leftover fresh fruit bunches are discharged in the form of empty fruit bunches, fibres and shells as well as liquid effluent (Zafar, 2013). Other than that, partial combustion of solid waste materials as a fuel to heat the boilers releases smoke and dust to the atmosphere (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999).

The establishment of this industry commercially since 1911 (Basiron & Chan, 2004) has created many environmental issues as mentioned in Industrial Processes and The Environment-Crude Palm Oil Industry (1999) such as:

- Pollution of water due to improper discharge of untreated or partially treated palm oilmill effluents into public watercourses
- Unsuitable land application techniques or practices for solid and/or liquid wastes
- The use of boilers and incinerators for empty bunches cause air pollution
- Poorly managed effluent treatment systems, especially if the mill is located near to residential areas cause odour pollution
- Noise pollution due to the milling processes

2.1.2 Palm Oil Mill Effluent (POME)

The extraction of crude palm oil also produces wastewater which is termed as palm oil mill effluent (POME). POME is generated through combination of several primary processes which are sterilization, hydrocyclone separation of cracked mixture of kernel and shell and clarification of extracted crude oil (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999) which are summarized in Table 2.1.

Table 2.1: Processes that generate POME and their respective composition

Type of Process	Composition in POME (%)
Sterilization	36
Hydrocyclone separation of cracked mixture or kernel and shell	60
Clarification of extracted crude oil	4

These processes require tremendous amount of water ranging from 5-7.5 tonnes and 50 % of the water used will be discharged as POME (Ahmad *et al*., 2003a). In average, about 0.6-0.7 tonnes of POME is generated for every one ton of fresh fruit bunches processed (Zafar, 2013). In 2004, 381 palm oil mills throughout Malaysia generated about 30 million tonnes of POME (Yacob *et al*., 2006)

1 tonne POME has a biochemical oxygen demand (BOD) of 27 kg and carbon oxygen demand (COD) of 62 kg which are 10 times higher than raw domestic sewage in a municipal (Zafar, 2013). It also contains substantial amount of total solids (40,500 mg L^{-1}) and oil and grease (4000 mg L^{-1}) with pH between 4 to 5 (acidic) and temperature of 80-90 ºC (Ma, 2000). Table 2.2 shows several characteristics of typical palm oil mill effluent.

Table 2.2: Characteristics of typical palm oil mill effluent (Ma, 2000)

Parameter	Concentration (mg dm^{-3} except pH)
pH	4.7
Oil and grease	4000
Biochemical oxygen demand (BOD)	25 000
Chemical Oxygen Demand (COD)	50 000
Total solids	40 500
Suspended solids	18 000
Total volatile solids	34 000
Ammonia nitrogen	35
Total nitrogen	750

POME consists of high amount of oils which usually exist in complex form that contains significant amount of triacylglycerides, di- and monoacylglyceridesand monoglycerides and some derivatives of fatty acids (Alias & Tan, 2005). Some of the major fatty acids present in POME are palmitic, oleic and linoleic acid (Hilditch & Williams, 1964). POME is considered as non-toxic because during the whole processes of extracting crude palm oil, no chemicals are added at all. However, due to its high organic and nutrient content, it might pose environmental threat to the aquatic ecosystem as it has a very large oxygen depleting capability (Zafar, 2013). Fortunately, it is rich in essential nutrients for plant growth such as N, P, K, Mg and Ca (Habib *et al*., 1997) thus making it suitable to be used as fertilizer to provide adequate mineral requirements. Other than that, Pb is also found in the effluent due to contamination from plastic and metal pipes, tanks and containers which are either glazed or painted with Pb-containing materials (James *et al*., 1996)

2.1.3 Pollution load of POME discharge

According to Malaysia Palm Oil Board (2014), there is an increase in the production of crude palm oil in 2003 (13.35 million tons) as compared to in 2002 (11.91 million tons). This means that 46 000 m^3 of oil is produced daily and based on this amount, the average amount of effluent discharged is approximately 161 000 m^3 with BOD of about 4025 tons. From this figure, we can estimate the population equivalent (PE) which refers to the equivalence between the polluting potential of an industry (expressed in terms of biodegradable organic matter) and a population which generates similar polluting load by using the formula

$PE = \frac{\text{BOD load from industry } (\frac{\text{kg}}{\text{day}})}{0.054\ (\frac{\text{kg}}{\text{inhabitant.day}})}$ (Sperling & Chernicharo, 2005). The PE for the year 2003 is estimated to be 74 537 037 persons. This pollution statistic points out that the raw effluent discharged by the palm oil mill has the same polluting effect on the waste-receiving watercourse as a city of 74 537 037 people discharging untreated sewage.

2.1.4 Oxygen-depleting capability of POME

When POME is discharged untreated or semi-treated into the receiving water source, it will undergo natural decomposition which requires oxygen, thus depleting the available dissolved oxygen inside the water source. Besides that, the oily effluent may float on the water surface and form wide-spread film, causing declination of the amount of atmospheric oxygen dissolving into the water (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999). When the water source is completely lacking of dissolved oxygen, anaerobic processes by the aquatic organisms will take place, releasing hydrogen sulphide and several other malodorous gases into the atmosphere resulting in unpleasant odours (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999). If this condition is left without any proper actions taken, it will cause destruction of aquatic lives.

2.2 Regulatory control for effluent discharge

The Environmental Quality Regulations emphasizing on POME discharge standards was enacted on 1978. The key parameter of this standard is biochemical oxygen demand (BOD) and initially, the allowable BOD in untreated POME is set to 25 000 ppm and after several amendment on the standards, the present allowable amount is reduced to 100 ppm (Malaysian Palm Oil Berhad, 2012). The Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations, 1977 enacted under the enabling powers of Section 51 of the EQA are the regulations meant for the crude palm oil industry which ensure the comprehensive and systematic control of this industry (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999). The regulations contain the effluent discharge standards and other regulatory requirements to be enforced on palm oil mills through conditions of license. Some of main requirement and element of regulatory control are:

- Application for annual license
- Reporting of effluent discharge information to the Department of Environment on quarterly basis

Table 2.3 shows the effluent discharge standards which are implemented on all crude palm oil mills throughout Malaysia.

Table 2.3: Effluent discharge standards for crude palm oil mills (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999)

PARAMETER		PARAMETERLIMITSFOR CRUDEPALMOILMILLS (SECOND SCHEDULE)	REMARKS
Biochemical Oxygen Demand (BOD; 3-Day, 30°C)	mg/L	100	
Chemical Oxygen Demand(COD)	mg/L	*	
Total Solids	mg/L	*	
Suspended Solids	mg/L	400	
Oil and Grease	mg/L	50	
Ammoniac Nitrogen	mg/L	150	Value of filtered sample
Total Nitrogen	mg/L	200	Value of filtered sample
pH	-	5-9	
Temperature	°C	45	

2.3 Treatment of POME

The discharge of POME into the environment brings about various destructive effects. Thus, it is very important to treat the effluent efficiently in order to minimize the impacts upon discharging. For more than two decades, numerous treatment methods and technologies for POME have been introduced and applied by palm oil mills in Malaysia (Lim *et al*., 1984). Normally, the effluent treatment involves the combination of various physical and biological processes.

2.3.1 Physical treatment

The physical treatments or primary treatment involve pre-treatment steps in typical wastewater plants such as screening and sedimentation in order to remove the suspended solid particles while oil is removed via sand trap and/or oil trap. These steps are prerequisite to the biological treatment which is the secondary treatment. The residues removed from the processes are normally disposed-off onto the plantation land (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999).

2.3.2 Biological treatment

Biological treatments are usually based on anaerobic and aerobic processes which uses microorganism such as bacteria and algae to degrade organic matter into simpler products. There are few known biological treatment methods which are widely used in palm oil mill industries (Industrial Processes and The Environment-Crude Palm Oil Industry, 1999) such as:

- Anaerobic-cum-Facultative Lagoon System
- Anaerobic-cum-Aerated Lagoon System
- Anaerobic Reactor-cum-Aerated Lagoon System
- Anaerobic Lagoon-cum-Land Application System
- Anaerobic Reactor-cum-Land Application System

Since POME is mostly composed of organic compound, anaerobic process is considered the best treatment method (Perez *et al.*, 2001). This is due the fact that microorganism will speed up the degradation process of organic compound. In Malaysia, ponding system which is composed of combination of anaerobic, aerobic and/or facultative ponds or lagoons has been used in palm oil mills since 1982 (Onyia *et al*., 2001). This method is sought-after by more than 85% of mills due to low cost and operating systems.

Unfortunately, biological treatment methods require proper maintenance and monitoring due to the fact that they rely literally on microorganisms which are very sensitive to the changes in the environment (Ahmad *et al*., 2003b). Therefore, to ensure these methods to operate smoothly, it is crucial to maintain conducive environment for the microorganism to grow in the processes.

2.3.3 Removal of residual oil in POME

Presently, few studies have been conducted to remove residual oil in POME. A study by Ngarmkam *et al*. (2011) utilized activated carbon prepared from palm shell to remove residual oil in POME. The activated carbon was prepared by the impregnation of zinc chloride ($ZnCl_2$) into the shell followed by subsequent physical and chemical activation under carbon dioxide flow at 800°C. The study showed that almost 85 % of residual oil in 50 ml of POME can be removed by the activated carbon.

Another studies by Shavandi *et al*. (2012) used fixed bed column packed with natural zeolite (clinoptilolite) to remove maximum of 100mg/g of residual oil while Ahmad *et al*. (2005b) managed to remove 99 % of residual oil in POME by using chitosan at 100 rpm and mixing time of 30 minutes. Another experiment by Ahmad et al. (2005c) utilized rubber powder to adsorb residual oil from POME.

2.4 Surfactants

Surfactants or commonly termed as “surface active agents” are organic molecules which are able to imbibe themselves at the interfaces of low concentration solvent thus modifying the physical properties of those interfaces. Interfaces are actually the partition in ‘liquid and liquid’, ‘liquid and solid’ and ‘gas and liquid’ systems (Eastoe, 2003). Surfactants act by decreasing the surface tension of a liquid by imbibing at the gas and liquid system interface, as well as reducing surface tension between two liquids by imbibing at the liquid-liquid interface (Makkar & Cameotra, 2002). Surfactants are very efficient in increasing the aqueous solubility of hydrophobic compound and under favourable conditions, they are able to solubilize generous amount of palm oils (Lim *et al*., 2005).

Surfactants are amphiphilic molecules in which they have two major components; a hydrophilic (water soluble) head group and a hydrophobic (water insoluble) tail group, all combined in a single molecule. When mixed with water-oil system, this unique properties cause the surfactant to imbibe at the interfaces in order to keep the hydrophobic group away from the strong water interactions and the hydrophilic part away from interacting with water molecules. This mechanism will eventually reduce the interfacial energies in the system (Rosen, 1989).

Surfactant can exist in various forms depending on their structure of both the head and tail group. The head may exist as charged or neutral molecules while the tail group may contain single or double bond, straight or branched hydrocarbon chain and aromatic groups (Eastoe, 2003). Figure 2.2 shows typical structure of surfactant.