

EFFECT OF CHEMICALS ON THE FORMATION OF TAR BALLS FROM OVERBOARD WATER DISCHARGES AN ANALYSIS OF ENVIRONMENTAL VIEW

R. Desrina

“LEMIGAS” R & D Centre for Oil and Gas Technology

Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, P.O. Box 1089/JKT, Jakarta Selatan 12230 INDONESIA

Tromol Pos: 6022/KBYB-Jakarta 12120, Telephone: 62-21-7394422, Faxsimile: 62-21-7246150

First Registered on July 7th 2012; Received after Corection on August 27th 2012

Publication Approval on : August 31th 2012

ABSTRAK

Rasio antara air terproduksi dengan hidrokarbon yang dihasilkan meningkat seiring dengan umur suatu sumur minyak. Adalah hal yang biasa bahwa fluida yang dihasilkan oleh sumur minyak dalam reservoir yang sudah tua pada akhirnya terdiri dari air sebanyak 90% atau lebih dan hanya mengandung minyak hanya 10% bahkan kurang. Setelah melalui proses pemisahan dari fluida-fluida tersebut, air terproduksi masih mengandung padatan terdispersi dan hidrokarbon. Air terproduksi ini harus di injeksikan kembali ke bawah permukaan atau dibuang ke permukaan misalnya ke laut. Ambang batas dari air terproduksi di atur oleh peraturan pemerintah. Kandungan minyak di dalam air terproduksi di tetapkan dalam suatu Keputusan Menteri Lingkungan Hidup dengan nilai tidak melebihi 50 mg/L. Berbagai zat-zat kimia telah dikembangkan sebagai sarana membantu mempercepat proses pemisahan antara minyak, air, dan zat-zat padat. Bahan-bahan kimia ini umumnya dikenal sebagai *de-emulsifier* dan *clarifier*. Zat-zat kimia lainnya misalnya zat pencegah karat akan mempengaruhi proses pemisahan fluida ini (minyak dan air). Dalam beberapa tahun terakhir ini, terjadi permasalahan dengan adanya bola-bola tar dan *chocolate mousse* yang terdapat di daerah pantai di Indonesia misalnya Pulau Seribu dan Pantai Timur Kalimantan. Walaupun, bola-bola tar ini tidak sering terjadi, namun masalah ini telah memberikan dampak terhadap masyarakat sekitarnya terutama para nelayan. Tulisan di dalam makalah ini bertujuan untuk memberikan suatu pandangan analisis lingkungan dari berbagai faktor yang dapat menyebabkan terbentuknya bola-bola tar dan *chocolate mousse* dari pembuangan air terproduksi yang berasal dari ladang-ladang minyak tua.

Kata kunci: air buangan, air terproduksi, *de-emulsifiers*, zat pencegah karat, lingkungan laut, bola-bola tar, *chocolate mousse*

ABSTRACT

The ratio of produced water to produced hydrocarbons increases over the lifetime of an oil well. It is common that oil well production fluids in the old reservoirs are eventually composed of 90% or more of water and only 10% or less of hydrocarbons. After the initial separation of the bulk produced fluids, the produced water still contains finely dispersed solids and hydrocarbons. It must either be re-injected underground or discharged to surface waters, such as oceans. Strict overboard discharge limits are set by the government regulation. The oil content of overboard water is limited by the Ministry of Environment to be less than 50 mg/L. Various chemicals have been developed as proprietary chemical separation aids to effect and accelerate the separation of oil, water, and solids from each other. These chemicals are commonly referred to as de-emulsifiers and water clarifiers. Other chemicals, for example corrosion inhibitors, have properties that are contradictory to de-emulsifier and clarifier. These non-separation aid chemicals will absolutely affect the fluid (oil and water) separation. In the last couple of years, there were problems with the tar balls and chocolate mousse found in the coastal regions of Indonesia, such as at Pulau Seribu and Eastern Coast of Kalimantan. Although these tar balls do not frequently happen, these problems have given nuisance to the surrounding communities especially the fishermen. This paper is intended to give an analysis of environmental view of the possible factors that might contribute to the formation of tar balls and chocolate mousse from the overboard water discharges from the old oil fields.

Keywords: overboard water, produced water, de-emulsifiers, corrosion inhibitors, oceanic environment, tar balls, chocolate mousse.

I. INTRODUCTION

The production of petroleum hydrocarbons from underground formations produces various amounts of formation or connate water. The ratio of this produced water to produced hydrocarbons increases over the lifetime of a well. It is common that oil well production fluids in the old reservoirs are eventually composed of 90% or more of water and only 10% or less of hydrocarbons⁽¹⁾.

After the initial separation of the bulk produced fluids, the produced water still contains finely dispersed solids and hydrocarbons. It must either be re-injected underground or discharged to surface waters, such as rivers, streams, or oceans. Besides contributing lost production, excessive residual oil in the discharged water can damage human health, local eco-systems, or the broader environment. Strict overboard discharge limits are set by the government regulation. The oil content of overboard water is limited by the Ministry of Environment to be less than 50 mg/L⁽²⁾.

The oil industry has an interest in the separation of crude oil-water emulsions for two main reasons: i) the emulsified water add significant volume to the crude oil; this will cause corrosion in the pipelines and increase the cost of transportation and refining. ii) In case of accidental oceanic spill, water-in-crude oil emulsions are very stable and the oil phase is difficult to recover. Due to their color and semisolid consistency, they are often named as chocolate mousse⁽³⁾.

The process and equipment to separate oil in water once produced, are generally designed for optimal separation of the oil. The systems to remove oil from the produced water often end up undersized when there are increases of flow rates. In the beginning of the production process generally there has been no problem with the production of sludge. When there is an increasing of solid particles, eventually increases the sludge formation, adequate treatment of the water, physically or chemically, has to be re-evaluated. This treatment will depend on some calculation of economic consideration. Generally, chemical treatments are less expensive to apply than the capital and operational costs of new equipment.

Various chemicals have been developed as proprietary chemical separation aids to effect and accelerate the separation of oil, water, and solids from each other⁽⁴⁾. Those used to remove water and solids from oil are commonly referred to as de-emulsifiers, those used to remove oil and solids from water are commonly referred to as water clarifiers. When applied with appropriate expertise, they assist in separating the produced fluids to meet the required specifications.

Other chemicals, for example corrosion inhibitors, have properties that are contradictory to de-emulsifier and clarifier. These are typically film type inhibitors, and these are designed to form a barrier on the metal walls to prevent contact with water. These non-separation aid chemicals will absolutely affect the fluid (oil and water) separation. Other additives can also affect the fluid separation. These substances, in particular are: (i) dispersants to prevent the deposition of asphaltenes, paraffins, gas hydrates, or scales; (ii) foamers to enhance gas lifting; and (iii) cleaners for removing solids that can be active at the oil/water interface.

In the last couple of years, there were problems with the tar balls and chocolate mousse found in the coastal region of Indonesia, such as at Pulau Seribu and Eastern Coast of Kalimantan. Although these tar balls do not frequently happen, these problems have given nuisance to the surrounding communities especially the fishermen. The local authority assumes that these tar balls might come from the nearby oil production activities. Nevertheless, the oil production companies state that they have complied with the existing regulation issued by the local environmental legislator as well as the Ministry of Environment. Beside, forensic investigation often fails to proof that these tar balls were resulted from the nearby oil activities, since these tar balls had changed significantly in their properties due to weathering effects.

This paper does not intend to discuss the environmental impacts of those tar balls nor the forensic investigation, but rather to give an analysis of environmental view of the possible factors that might contribute to the formation of tar balls and chocolate mousse from the overboard water discharges from the old oil fields.

II. CHEMICALS USED IN CRUDE OIL-WATER SEPARATION PROCESSES

A. Water-Crude Oil Emulsion Stability Phenomenon

During oil production and transportation, the water and oil phases are co-produced, and thereby exposed to sufficient mixing energy to form dispersions of water droplets in oil and, conversely, oil droplets in the water. Unfortunately, the crude oil contains a number of components, which in nature have interfacial properties. These components especially are asphaltenes, resins and naphthenic acids. These components may accumulate at the water-oil interface and inhibit the oil droplets to a separate phase. Among these components, asphaltenes are the major material involved in emulsion stabilization.

Asphaltenes tend to adsorb at water-in-crude oil interfaces to form a rigid film surrounding the water droplet, and protecting the interfacial film from breaking during droplet collisions. Hence, the formation of extremely stable water-in-crude oil emulsions is facilitated. This stable water-in-crude oil emulsion results in a demand for expensive separation equipment such as separators, water treaters and coalescers. Chemical destabilization is a very common method for destabilizing emulsions. Also, the capital cost of implementing or changing a chemical emulsion-breaking program is relatively small and can be accomplished without a shutdown.

The type and amount of chemicals employed will contribute in reducing the oil content in the offshore produced water. Commercial de-emulsifiers are typically mixtures of several components, which have various chemical structures and cover a wide molecular weight distribution. De-emulsifiers with equal partitioning between the aqueous and oil phase, give the best destabilizing efficiency.

In some situations the de-emulsifier is injected before the emulsification process has taken place. This gives the de-emulsifier the chance to compete with the emulsifying agent in the process of covering the interface as the emulsifying process occurs, and thereby prevent the formation of a stabilizing film.

It should be noted, however, effects of the concentration of the injected chemicals on the emulsion stability. As too much chemicals injected may result in an over-treat where the emulsion is

actually stabilized, or a new emulsion type is created. Also, the injected de-emulsifiers should be checked to be compatible with other chemicals (such as corrosion inhibitors and scale inhibitors) used in the stream.

B. Building-up of Solid Particles in Oil

Solid particles may increase during production period due to characteristic changes of the oil, such as increase in sediment content. Solid particles may also increase due to corrosion of the pipelines in a form of iron-sulfides (ferro- or ferri sulfides), compounds that are insoluble in water.

These solid particles have a tendency in absorbing the oil. During separation process of oil and water, these solid particles that have adsorbed the oil will settle down. In the mean time, oil adsorbed by the solid particles will be released and replenished to the water column. This is a common case in sorption phenomenon, where adsorption and desorption process will occur concurrently depending on the environmental condition of the media, such as pressure, temperature, pH, and the present or absence of surface active agents. The present of oil adsorbed particles will result in increasing of sludge, while oil release by the solid particles will cause in higher oil content in water.

In attempt to reduce the adsorbed oil content in water, several physical methods could be applied using sedimentation process. Sedimentation is the process of removing particulate solids from a liquid by the effects of gravity. This can provide for higher density solids to be removed from water through settling and for lower density solids to be removed from water through flotation. However, the settling velocity for particles is greatly affected by the diameter of the particles. As particle size drops to 10-micron diameter or less, the time required to settle is so long. It is not feasible to construct a settling area large enough to allow the particles time-to-settle by gravity alone⁽⁵⁾.

A special of chemical additives commonly referred to as water clarifiers has been developed and marketed commercially. Water clarifiers assist in optimization of treating system efficiency and help to purify the produced water to meet water specifications. Water clarifiers consist of special blends of polymers, coagulants, surfactants and

metal salts which work in conjunction with process systems to remove oil, solid particles, and water soluble organics from the water.

C. Corrosion Phenomenon

The oil industry has an interest in water-crude oil emulsions for several main reasons. One of which is that the emulsified water causes corrosion in the pipelines and increases the cost of transportation and refining.

There are various ways of overcoming the problem of corrosion. The most efficient one is using inhibitors. Inhibitors are chemical compounds which reduce and inhibit the contact of metals with their corrosive environment. Corrosion inhibitors can effectively work in small concentrations. The corrosion affects all stages in the exploitation of crude oil ranging from drilling of wells through the separation process, export pipelines, storage tanks, and refineries.

A corrosion inhibitor acts as a barrier preventing the corrosive materials from coming into contact with the metal. However, corrosion inhibitors can form more stable emulsions, thus making oil-water separation less efficient.

Partitioning of a single compound between two phases is normally defined. Many commercial corrosion inhibitors, however, are not single compounds but complex mixtures of many compounds, each with its own unique partitioning coefficient. Thus a commercial corrosion inhibitor has no unique partitioning coefficient but rather one for each of the multiple components. Organic inhibitors are generally more soluble in aromatic hydrocarbons than aliphatic ones and more soluble in long chain aliphatic than short chain ones.

Steel is particularly very susceptible to attack by acids. As pH falls below neutrality corrosion rates increase sharply. Acidity that causes the corrosion comes from the hydrolytic conversion of the magnesium and calcium salts to form hydrochloric acid, and also from acid gases such as hydrogen sulfide, carbon dioxide which come from organic fatty and naphthenic acids. At pH values above seven, steel is generally stable with increasing pH up to values as high as 13 or greater. Practically neutralization of acid to pH 6-8 can be adequate to

slow down corrosion. By adding the inhibitors the protection can take place at pH 5-6.

Petroleum production activities nowadays use various film forming inhibitors. These filming amines are surfactants that align themselves between the metal surface and the oil, where the polar head of the film is oriented towards the metal surface, and the non-polar tail is oriented towards the oil.

Most of the inhibitors used nowadays are long chain nitrogenous compounds which include the following⁽⁶⁾:

- i. Aliphatic fatty acid derivative:
 - Primary monoamine $C_{18}H_{37}-NH_2$
 - Secondary monoamine $C_{36}H_{64}-NH$
 - Tertiary monoamine $C_{18}H_{37}-N(CH_3)_2$
 - Diamines $C_{18}H_{37}-NH-CH_2CH_2CH_2-NH_2$
 - Amides $R-CONH_2$
 - Polyethoxylated amines, amides and Diamines
- ii. Imidazolines and derivatives
 - Quaternaries
 - Rosin derivatives
 - Acetic, oleic, acid phosphate salts
 - Amphoteric compounds.

III. ANALYSIS OF ENVIRONMENTAL VIEW

It is normal that during the first couples of years of oil production there has been no problem with the chemicals used for de-emulsification and clarification purposes as well as for corrosion inhibition process. Nevertheless, it is common that concentration ratio of these chemicals has to be re-evaluated, since the hydrocarbon composition, including its sediment (BS&W) content, may change to the old oil fields.

Corrosion inhibitors usually have been selected on the basis of their ability to form a protective film on the surface of a test coupon in a flowing side stream of the actual production fluids at actual process conditions, including temperature, turbulence, and surface to volumetric flow ratios. This experiment is normally conducted in the field.

This paper do not attempt to discuss the effectiveness of the corrosion inhibiting process, since all of the chemicals are considered having their proper properties. Corrosion inhibitor, besides its

function in preventing corrosion by forming a film on the metal surface, acts also as dispersant which stimulates the dispersion of oil in water. Upon addition of the corrosion inhibitor the emulsion of oil in water persists longer.

Corrosion inhibitors in fact are surfactants in nature, hence surfactant properties of the corrosion inhibitors are also followed. These fundamental properties of surfactants are: (i) phenomenon according to which a molecule comes from the bulk of a solution to place itself at the interface with some specific orientation which is called adsorption, and (ii) surfactant molecules in solution exhibit a tendency to self associate to produce aggregation polymer which is called micelles.

Surfactants are substances whose molecule consists both a polar and a non-polar part. Such substances have been called *amphiphile* which is derived from latin word *amphi* that means duality or “both sides”, and *philos* that indicates affinity or attraction. Generally speaking, these affinities are referred to as hydrophilic and lipophilic (or hydrophobic) respectively since the polar solvents are in most cases aqueous solutions and the non-polar phases are organic “oils”⁽⁷⁾.

It is worth remarking that the polar interaction are typically ten times stronger than the non-polar ones. This is why the polar group is in general unique while the non-polar part is made of a long hydrocarbon chain which contains ten or more carbon atoms. The actual surfactant thus has the shape with a bulky polar “head” and an elongated non-polar “tail”.

When a surfactant molecule goes to the interface (liquid-solid) and locates itself there with some preferential orientation, it is said that the molecule is adsorbed. At a liquid-solid interface, the relative polarity of the solid with respect to the liquid would decide whether the surfactant adsorbs by the head or by the tail.

Water contains both H^+ and OH^- ions which are likely to adsorb at any solid interface. The relative adsorption of H^+ or OH^- depends on both the solid nature and the ionic concentrations, for example pH of the solution. As a matter of fact solid surfaces are always charged when in contact with water.

The most effective corrosion inhibitors are typically hydrophobic amines, such as fatty imidazolines. These corrosion inhibitors are all

cationic surfactants. Their heads are attracted to the anionic hydrous metal oxide or sulfide surface and their tails are attracted to oil (repulsive to water); see Figure 1.

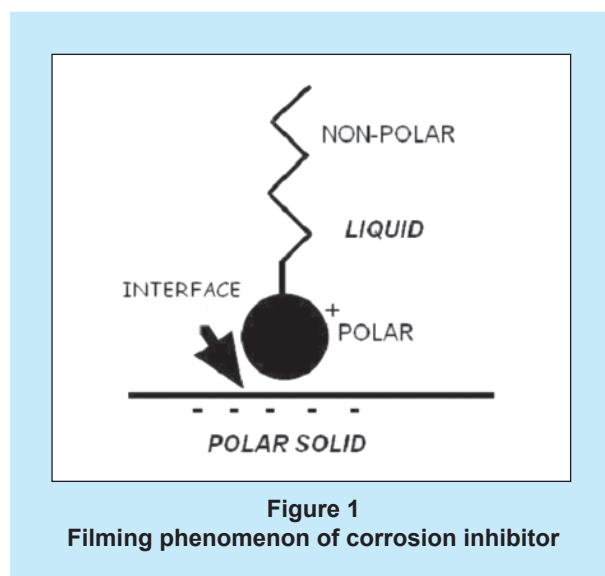


Figure 1
Filming phenomenon of corrosion inhibitor

Since the surfactant molecule has a lower free energy when it is adsorbed at interface than in the solvent bulk phase, the equilibrium is very much displaced toward the adsorbed state. Hence, the interface (metal surface) is very rapidly covered by a monolayer of surfactant molecules. When a monolayer is formed, the interface were coated with a thin layer or film of a new material. Such monolayer of corrosion inhibitor molecules will produces hydrophobic properties of the metal surface, as if it were covered by a thin coating of grease. Such phenomenon is of first importance in chemical processes of corrosion inhibition.

However, when the surfactant concentration in the aqueous phase increases, the surfactant molecules first saturate the interface, and then accumulate in the solution. Each time a new surfactant molecule is added to the solution, the unfavorable interaction between the surfactant hydrophobic tail and the water molecules that poses hydrophylic properties is increased. At some point the surfactant molecules start aggregating into the so-called micelles, a self-association structure in which the hydrophobe tail is removed from the aqueous environment.

The concentration at which the first micelles are formed is called the Critical Micelle Concentration (CMC). The CMC is the concentration at which the

factors which favor the formation of the micelle is start dominating the effects which oppose to a film formation.

Micellar solutions are able to solubilize different kinds of substance. Hydrophobic substances such as oils can be solubilized inside the micelles core. Once the CMC is formed it will gives the opposite effect to the de-emulsification process due to the oil solubilization of the micelles. This phenomenon gives increases of oil in water as dispersed oil. (see Figure 2).

It is clearly recognized, in which the more concentration of corrosion inhibitor added to the water, the more stable emulsion is. The stability of the emulsion or the dispersed oil is caused by the repulsion energy among the droplets. And as stated above, oil that is produced by the old fields will contain more asphaltenes. These compounds may accumulate at the water-oil interface and inhibit the oil droplets to a separate phase. These asphaltenes are also the major material involved in emulsion stabilization.

However, upon addition of de-emulsifier there will be a chemical reaction in which polar head of the micelle will react or will interact with the polar head of the de-emulsifier. This interaction process causes micelle “soluble” in the de-emulsifier and releases the oil that previously solubilized inside the micelle.

The separation of oil from the micelle will also occurs upon dilution with sea water. This phenomenon can be explained as follows. When the surfactant (in this case the corrosion inhibitor) molecules form micelles, it involves cohesion force between the

surfactant molecules. This force is called Van der Waals intermolecular forces. In case of micelle, there are cohesive forces between non-polar or tail groups of the surfactant.

There are three kinds of Van der Waals forces: (i) Keesom forces which are produced by the interaction of a permanent dipole with another permanent dipole. (ii) Debye forces which result from the interaction of a permanent dipole with an induced dipole. and (iii) London or dispersion forces which have no specific direction of action and are said to be non-polar interactions. The two first forces involve polar molecules and binding energies in the few Kcal/mol range, whereas the third one occurs in all kind of molecules, specially non-polar ones, with a much lower interaction energy, typically ten times lower. This kind of energy is possessed by micelle molecules, where non-polar tails of the micelle molecules are binding among other.

Upon dilution with sea water there will be competition between cohesive forces among the non-polar (tail) groups of surfactant and adhesive forces which occurs between polar (head) groups of surfactant and water molecules that are polar in nature. Nevertheless, it should be noted that since an entropy decrease can not happen spontaneously, this mechanism can occur only at the expense of the cohesive/adhesive forces that will opposes each other.

The cohesion/adhesion forces are the ones that determine the attractive forces between droplets particles dispersed in a continuous liquid phase. These forces tend to produce the aggregation of the dispersed phase fragments, and thus they are driving forces behind the dispersion instability mechanisms of the dispersed oil.

We can easily understand, that when an overboard waters containing dispersed oil is discharged into the ocean, it does not spontaneously result in the separation of oil. The separation of the dispersed oils will be influenced by many factors. If, for example, the wave of the ocean is great

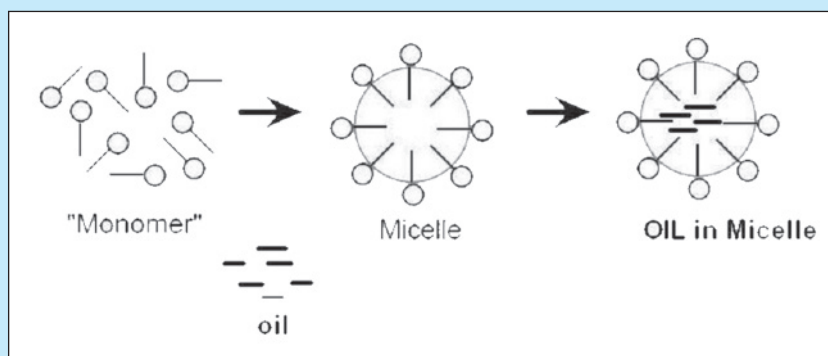


Figure 2
Micelles formation of surfactant molecules and “dissolution” of oil into the micelles

enough, such as in a wet seasons, the binding energy of the micelle would be eliminated and thus producing separate oils that would promote tar balls formation.

When an overboard water is discharged to the ocean, the separation of dispersed oil might be caused by many kind of chemicals present in the receiving water. These chemicals could be in a form of de-emulsifier or polymer in nature. The destruction of the emulsifying properties of the surface-active agent (i.e. corrosion inhibitors and asphaltenes) can be effected by polymer products. A polymer or combination of polymers will destabilize the electrical bond between oil and water allowing oils to free themselves, creating droplets and a distinct layer or flocculated mass. Flocculation refers to the collisions that occur when the destabilized particles (i.e. oil) are agglomerated via a bridging effect due to these polymers.

These kind of chemicals and polymers might come from water discharges of any other sources, such as other industries surrounding the oil industries. In many cases these chemicals are not oftenly identified in the environmental monitoring program. The monitoring program only emphasizes on the parameters that included in the regulation. Once these chemicals react or solubilize the micelle molecules, the separation of the dispersed oil occurs, and this will promote the formation of tar balls or chocolate mousse.

The analysis of view in this study and the discussions that follow can be used as arguments. These arguments are: (i) even the oil content in the overboard water has complied with the regulation (i.e. 50 mg/L), there would be no guarantee that it would not create a problem to the environment; (ii) depending on the conditions of the ocean where the overboard water is discharged, the oil separation of the discharged water might occurs and might promote the formation of tar balls or chocolate mousse; (iii) the formation of the tar balls is very much likely caused by great ocean wave during wet seasons and the presence of chemicals that could destabilize oil dispersion; and (iv) once the oil has been separated, the cohesion/adhesion forces are the ones that determine the attractive forces between bubbles, droplets or solid particles. These forces tend to produce the aggregation of the dispersed phase

fragments (oils), and thus they are driving forces behind the formation of the tar balls or chocolate mousse.

Referring to the Article 5, Point 1 of the Environmental Ministerial Regulation No. 19-2010, the local authority can add additional parameters, which are not listed in the national regulation. These parameters, for example, would be surface active agents. In addition, according to the Article 7 and 8 of the regulation stating the Environmental Impact Assesment (EIA), it is worthy to recommend that the oil content of the overboard water discharge has to be re-evaluated. This re-evaluation is based on the recent EIA studies of the receiving water where tar balls and chocolate mousse frequently happen. Even when oil content of the overboard water discharge has complied with the recent regulation (i.e. 50 mg/L), depending on the receiving water condition, such as climate and the present of chemical waste, the separation of the dispersed oil from the overboard discharge water might occur. This oil separation would creat what is so called tar balls or chocolate mousse.

IV. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

As conclusions it can be drawn several remarks as follows:

When an overboard waters containing dispersed oil is discharged into the ocean, it does not spontaneously result in the separation of oil. The separation of the dispersed oils will be influenced by many factors, such as ocean waves and the presence of chemicals and polymers which acts as de-emulsifiers.

Once the oil has been separated, the cohesion/adhesion forces are the ones that determine the attractive forces between bubbles, droplets or solid particles. These forces tend to produce the aggregation of the dispersed phase fragments (oils), and thus they are driving forces behind the formation of the tar balls or chocolate mousse.

B. Recommendations

Even when the oil content in the overboard water has complied with the recent regulation (i.e. 50 mg/L), there would be no guarantee that it would not

create a problem to the environment; the separation of the dispersed oil might occur. These separated oils would create what is so called tar balls or chocolate mousse. It is worthy to recommend to re-evaluate the oil content of the overboard water, which is based on the recent EIA studies of the receiving water where tar balls and chocolate mousse frequently happen.

REFERENCES

1. **Anonymous**, 2010, Environmental Ministerial Regulation No. 19-2010 describing Waste Water Quality Standard for Oil and Gas and Geothermal Activities, signed by the Minister of Environment, Prof. DR. IR. Gusti Muhammad Hatta, MS., Jakarta, 30 November 2010.
2. **Auflem , I. H.**, 2002, Influence of Asphaltene Aggregation and Pressure on Crude Oil Emulsion Stability, Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of DOKTOR INGENIØR, Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway.
3. **Anonymous**, 2012, Oil & Gas Production - Demulsifiers - Emulsion Breakers, http://www.bakerhughes.com/bakerpetrolite/oilgas/emulsion_breakers.htm.
4. **Hennessy, T**, 2004, Theory of Water Clarification, The Analyst, the Voice of the Water Treatment Industry, Vol. XI, Number 1, http://www.awt.org/members/publications/analyst/2004/2004_issues.htm.
5. **Hart, P, Towner, J, and Cheng, J**, 2009, Water Clarifier Improves Throughput, Oil Quality, and Overboard Water All, Integrated Petroleum Environmental Consortium (IPEC) Conference, http://ipec.utulsa.edu/Conf2003/Papers/hart_towner_cheng_55.pdf.
6. **Anonymous**, 2012, Nurchemicals oil and water treatment chemicals, http://www.nurchemi-cals.com/Products_Chemicals/water_treatment.htm
7. **SALAGER, Jean-Louis**, 1994, Interfacial Phenomena in Dispersed Systems, FIRP BOOKLET # E120-N, Teaching aid in Surfactant Science & Engineering in English, Universidad de Los Andes, Facultad de Ingeniera, Escuela de Ingeniera Quimica, Mérida-Venezuela.