DEVELOPMENT OF NEW GREEN DEMULSIFIER COMPOSITION FOR OIL PRODUCTION

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Masters of chemical Engineering with Entrepreneurship

UNIVERSITI MALAYSIA PAHANG

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Dissertation submitted in partial fulfilment of the requirements for the award of the degree Master of Chemical Engineering with Entrepreneurship

Faculty of Chemical and Natural Resources Engineering

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EXECUTIVE SUMMARY

Among the most critical aspects of petroleum production today no matter what the production system, is the separating the produced crude from water and basic sediment. Doing this in an efficient and environmentally sustainable way constitutes one of the more challenging problems in petroleum industry.

About 90% of world's produced crude is in form of oil-in-water emulsions which caused predominant problems in exploration, processing and transportation, as the presence of water with oil increases transportation cost and corrosion problem in pipe lines and vessels

Today, the call for safer and greener environment has grown exponentially, creating a demand of chemicals that could be use effectively and in an environmental benign manner in the petroleum industry.

Consequently the company **D®-Oil Chemicals VENTURES** will launch an operation infrastructure with novel production system to address the aforementioned problems and take the full advantages of the challenges associated with breaking of emulsions in an environmental friendly manner. The company has completed the design, development and testing of a novel and proprietary green product with a view to provide an everlasting solution at competitive price.

This Dissertation will show how a total investment of RM 1,705,000 in a novel production system could generate a cumulative net profit of RM 37,000,000 over a five year period while maintaining sufficient level of liquidity. It is our objectives to secure an additional funding to finance the start-up as the financial projections promises a brighter and encouraging performance with estimated pay back periods of only 1.5 years.

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THESIS STATUS VALIDATION

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CHAPTER I

INTRODUCTION

1.1 Background

The current state of environmental conditions on planet Earth is a substantial basis for modification in the cleaning and disposal of waste and emissions, and fundamental changes in processes and technology industries. An increasing need to limit the use of chemicals used in oil production and to search for safer products mainly due to more severe environmental constraints necessitated a continuous research and development in the field of Demulsifiers (Zhukov and Zaripov, 1998)

Among the most critical aspects of petroleum production, no matter what the production system, is separating produced crude from water and basic sediments. Your profits depend on doing so efficiently. But at the same time, dealing with produced water in an efficient and environmentally sustainable way is equally important. The most important objective of any oil production facility is the separation of water and other foreign materials from the produced crude. The breaking of these crude oil and water emulsions constitutes one of the more challenging problems in today's petroleum industry (Laurrier, 1992)

In oil production today, water is an inevitable bye product. In fact, nearly 90% of crude contains oil and water emulsions. The gradual encroachment of water in to oil-bearing formations and the advent of secondary and tertiary recovery methods have led to the development of new technologies to break crude oil and water emulsions (Hanafi et.al, 2006)

After decades of research and encouraging results, the breaking of water-in-petroleum emulsions is not yet completely understood, particularly as far as the added chemical Demulsifiers role is concerned, and much research is still required (Miguel et al., 2006). Thus Demulsifiers performance has to therefore be improved, from the application as well as from the environmental point of view. New formulations must be less toxic and at least as efficient as classical chemical families.

Petroleum is most often produced as a water-in-oil emulsion and the water must be removed (down to a level of <1%), in a process that is usually called Demulsification or dehydration, which consists of forcing the coalescence of water droplets and producing their separation by settling (Miguel et al., 2006).

Demulsifiers are used as process aids in crude oil production to separate the emulsified water from produced oil. Breaking of these emulsions is carried out by using synthetic surfactants (Demulsifiers) which are added to oil emulsion. Role of Demulsifiers consists in Demulsification and prevention of its repeated formation due to decrease of mechanical strength of the protective shells which are formed on surface of water drops. The reagent is injected into emulsion and mixed with it. After that water is removed from oil by sedimentation (Koshelev et al., 2000).

Conventional Demulsifiers are typically polymeric and interfacial active. Unfortunately, existing demulsifiers may have disadvantages, for example;

I. In complete water removal from the emulsion,leaving the problem of environmentally disposing of oil-containing water residues at sea
II. Many are toxic to the environment, traces of which are left behind in the discarded water residue
III. Many requires huge amount of mixing energy and thus take a long time to accompolish the separation of water from the crude
IV. Most are specifically design to treat a particular crude and thus not effective in most other case and stuation.

The breaking of the water-in crude emulsion is still a technical challenge in the petroleum industry. Having an effective Demulsifiers treatment process can save millions of dollars every year in operation cost, increasing water content in oil at 1% of transportation costs increase by 3-5% for each transfer. In addition to costs directly in the oil industry, large volumes of water extracted along the way during transport cause the destruction of oilfield corrosion and environmental problems due to accidents of pipelines (Loumer, 1992)

Consequently, creating a "green" brands Demulsifiers is justifiable not only due to environmental concern, but also with the economic position as a biodegradable agent does not require, or at least reduces the cost of clean-up and disposal of waste containing it. So the desire to create “environmentally friendly” chemicals is a step in a right direction as it can actually lead to significant cost savings (Christine and Christine, 2001).

1.2 Product Overview

1.2.1 An overview of Emulsion and Demulsification

We live in what has been called the Petroleum Age. This hydrocarbon-rich mixture of crude oil and gases runs our factories, our cars, heats homes and has changed the face of life on the earth since it’s discovery on 1901(Manar,2012)

Crude oil is an extremely versatile, naturally occurring, flammable liquid consisting of a complex combination of various molecular hydrocarbons weights and other organic liquid compounds that are found in geologic formations beneath the Earth's surface.Petroleum is recovered principally as an emulsion through oil drilling(Miguel et.al., 2006).

If two immiscible liquids are mixed together in a container and then shaken, examination will reveal that one of the two phases has become a collection of droplets that are dispersed in the other phase; an emulsion has been formed (Figure 1.1). Emulsions have long been of great practical interest because of their widespread occurrence in everyday life. Some important and familiar emulsions include those occurring in foods (milk, mayonnaise, etc.), cosmetics (creams and lotions), pharmaceuticals (soluble vitamin and hormone products), and agricultural products (insecticide and herbicide emulsion formulations). In addition to their wide occurrence, emulsions have important properties that may be desirable, for example, in a natural or formulated product, or undesirable, such as an unwanted emulsion in an industrial process (Laurrier,1992).

Petroleum emulsions may not be as familiar but have a similarly widespread, long-standing, and important occurrence in industry. Emulsion may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions). Crude oils consist of, at least, a range of hydrocarbons (alkanes,naphthenes,and aromatic compounds) as well as phenols, carboxylic acids, and metals. A significant fraction of sulfur and nitrogen compounds may be present as well. The carbon numbers of all these components range from 1(methane) through 50 or more (asphaltenes). Some of these components can form films at oil surfaces, and others are surface active. It is perhaps not surprising, then, that the tendencies to form stable or unstable emulsions of different kinds vary greatly among different oils. Because of the wide range of possible compositions, crude oils can exhibit a wide range of viscosities and densities, so much so that these properties are used to distinguish light,heavy, and bituminous crude oils (Laurrier,1992)

During heating, as part of an oil recovery process such as hotwater flotation or insitu steam flooding, emulsions having a wide range of viscosities can be formed, particularly if they are of the water dispersed in oil type. When these different kinds of oils are emulsified, the emulsions may have viscosities that are much greater than, similar to, or much less than the viscosity of the component oil , all depending on the nature of the emulsion formed.emulsion may be desirable or undesirable defending on its nature and type, infact An emulsion may be desirable in one part of the oil production process and undesirable at the next stage, however, many kinds of emulsions pose difficult problems wherever they may occur. For example, crude oil when spilled on the ocean tends to become emulsified in the form of "chocolate mousse" emulsions, so named for their color and semisolid consistency. These water-in-oil emulsions with high water content tend to be quite stable due to the strong stabilizing films that are present. Mousse emulsions increase the quantity of pollutant and are usually very much more viscous than the oil itself (Manar, 2012)

1.2.2 What is an Emulsion?

The widespread importance of emulsions in general and scientific interest in their formation, stability, and properties have precipitated a wealth of published literature on the subject. Colloidal droplets (or particles or bubbles), as they are usually defined, have at least one dimension between about 1 and 1000 nm. Emulsions are a special kind of colloidal dispersion: one in which liquid is dispersed in a continuous liquid phase of different composition. The dispersed phase is sometimes referred to as the internal (disperse) phase, and the continuous phase as the external phase. Emulsions also form a rather special kind of colloidal system in that the droplets often exceed the size limit of 1000 nm. In petroleum emulsion one of the liquids is aqueous, and the other is hydrocarbon and referred to as oil (Laurrier,1992).

Not all emulsions exhibit the classical " milky " opaqueness with which they are usually associated. A tremendous range of appearances is possible, depending upon the droplet sizes and the difference in refractive indices between the phases. An Emulsion can be transparent if either the refractive index of each phase is the same, or alternatively, if the dispersed phase is made up of droplets that are sufficiently small compared with the wavelength of the illuminating light. Thus an O/W microemulsion of even a crude oil in water may be transparent. If the droplets are of the order of l-μπι diameter, a dilute O/W emulsion will take on a somewhat milky-blue cast; if the droplets are very much larger, the oil phase will become quite distinguishable and apparent. The rheological properties of an emulsion are very important High viscosity may be the reason that an emulsion is troublesome, a resistance to flow that must be dealt with, or a desirable property for which an emulsion is formulated(Laurrier,1992). .

Two types of emulsion are now readily distinguished in principle, depending upon which kind of liquid forms the continuous phase (Figure 1.1),

- Oil-in-water (O/W) for oil droplets dispersed in water
- Water-in-oil (W/O) for water droplets dispersed in oil

However, Emulsions do not always occur in the idealized form of droplets of one phase dispersed in another. The occurrence of multiple emulsions, of the types O/W/O and W/O/W, has already been identified and widely discused. Petroleum emulsions may also occur within another type of colloidal dispersion((Laurrier,1992).

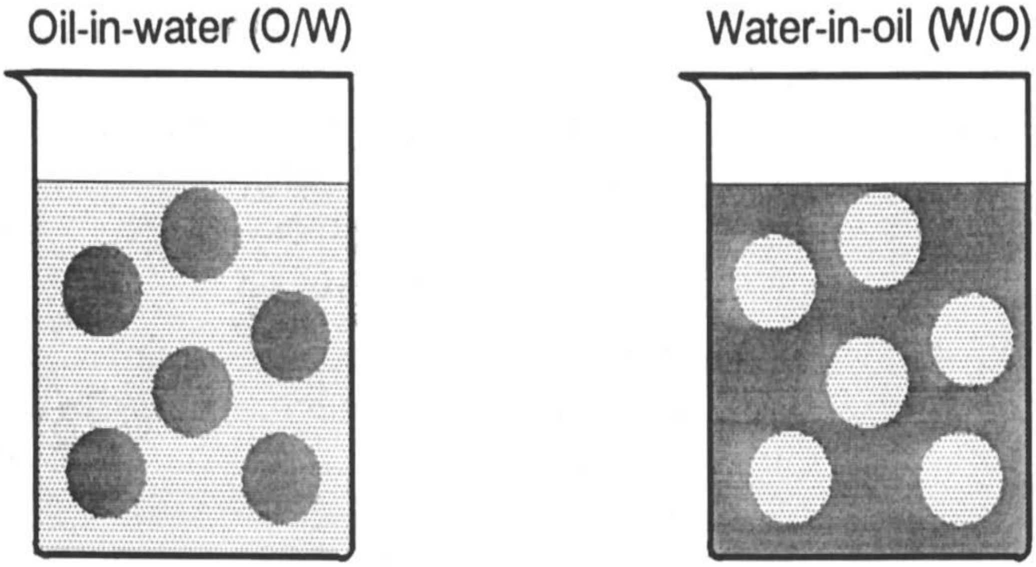

Figure 1.1:- An illustration of the simplest type of emulsions

1.2.3 Demulsification

When many of the present-day oil fields were established, the produced crude contained little or no water, allowing operators to ship the crude oil directly to the refinery using very little in the way of sophisticated emulsion breaking equipment and chemical technology.

The natural emulsifiers contained in crude oils have a complex chemical structure, so that, to overcome their effect, petroleum emulsion demulsifiers must be selectively developed. As new oil fields are developed, and as the production conditions change at older fields, there is a constant need for demulsifiers that lead to a rapid separation into water and oil, as well as minimal-residual water and salt mixtures (Grace, 1992).

The emulsion must be separated by the addition of chemical demulsifiers before the crude oil can be accepted for transportation. The quality criteria for a delivered crude oil are the residual salt content and the water content. For the oil to have a pipeline quality, it is necessary to reduce the water content to less than approximately 1.0% (Koshelev et al., 2000)

The presence of water-in-oil emulsions often leads to corrosion and to the growth of micro organisms in the water-wetted parts of the pipelines and storage tanks.At the refinery, before distillation, the salt content is often further reduced by a second emulsification with freshwater, followed by demulsification. Crude oils with high salt contents could lead to break downs and corrosion at the refinery. The object of using an emulsion breaker, or demulsifier, is to break the emulsion at the lowest possible concentration and, with little or no additional consumption of heat, to bring about a complete separation of the water and reduce the salt content to a minimum (Manar,2012)..

Demulsification or emulsion breaking of water-in-crude oil emulsion is carried out by using either four methods such as mechanical, thermal, chemical and electrical

(Gafonova, 2000). The knowledge of the properties and characteristics of the emulsion and the mechanisms that are taking place during coalescence of water droplets are required for fast separation (Ese et al., 2006).

- There are many kinds of mechanical separation tools that are typical equipment used in destabilization the crude oil emulsion such as cyclones, gravity settling tanks, centrifugal separators and many materials had been suggested to be used as porous coalescers such as fiberglass, glass, Teflon. Other materials such as clay, magnesium silicate, or silica gel had been used as a filter aid in conventional filter press (Auflem, 2002).

- Thermal method is carried out by the addition of heat to enhance emulsion breaking in oil field. An increase in temperature above the paraffin melting point ranging between (50-65) °C may completely destabilize an emulsion. So, the optimum operating temperature at refinery is (65) °C. The application of heat alone is insufficient to break emulsion and often require the addition of chemicals (demulsifires) (Grace, 1992).

- Electrical method is the principle of electrostatic dehydration in demulsification for oil-field production. This process does not typically resolve emulsions completely by itself, although it is an efficient and often require the addition of chemicals or heat (Grace, 1992).

- Chemical demulsification is the most widely applied method of treating water-in-oil and oil-in-water emulsions and involves the use of chemical additives (demulsifiers) to accelerate the emulsion breaking process. The stability of emulsions is largely affected by the nature of the interface/film and surfactant adsorption mechanisms. The most common method of demulsification in both oil-field and refinery application is the combination of heat and application of chemical design to neutralize and eliminate the effects of emulsifying agents (Grace, 1992). Chemical demulsification is a dynamic process since it is a phenomenon that occurs under non- equilibrium conditions. This demulsification activity promotes coalescence of the water droplets in the emulsion, which in turn causes separation of water and lowering of viscosity. Since the stability of emulsions can be traced to the presence of surfactant films at the water/oil interface, the rupture of the thin film separating droplets in a water-in-oil emulsion is affected primarily by the demulsifier. The role of the demulsifier is the suppression of the interfacial tension gradient in addition to the lowering of interfacial viscosity, thus causing accelerated film drainage and coalescence (Fiocco, 1999).

1.2.4 Demulsifiers

Demulsifiers, or emulsion breakers, are a class of specialty chemicals used to separate emulsions (e.g. water in oil). They are commonly used in the processing of crude oil, which is typically produced along with significant quantities of saline water. This water (and salt) must be removed from the crude oil prior to refining. If the majority of the water and salt are not removed, significant corrosion problems can occur in the refining process (Christine and Christine, 2001).

Demulsifiers are typically based on the following chemistry:

- Acid catalysed phenol-formaldehyde resins
- Base catalysed phenol-formaldehyde resins
- Epoxy resins
- Polyethyleneimines
- Polyamines
- Di-epoxides
- Polyols

Demulsifiers speed up water droplets coalescence by;

a. Decreasing and cancelling out the electrostatic forces of repulsion between water droplets
b. Briging well-dispersed water droplets closed together through flocculation

c. Decreasing surface tention between the water droplets speeding up coalescence and formation of bigger droplets thus increasing the speed of separation.

1.3 Market Overview

In 2010, world oil consumption was 3.2% over 2009, totaling 87.4 million barrels/day. The oil was more consumed in the region of Asia-Pacific, with a total of 27.2 million barrels/day or 31.2% of the total. Consumption growth was 5.3% over 2009, especially to China which, after the United States was the country with the second largest consumer in the world, 9.1 million barrels/day, 10, 4% more than last year, according to the B.P statistical review of world energy survey 2013.

Demand and production of oil will have a direct impact on the demand for oilfield process chemicals.Significant branch of the modern chemical industry is the manufacture of products used in the processes of the oil and oil transportation. Each year the requirements for this kind of reagents increasingly tightened (Presh,2011)

In recent years, many deposits are opened in the late stage of development which has significant water content of the output. As a result, commercial facilities pose serious technological challenges associated with the need to handle large quantities of water extracted simultaneously. Formation of emulsions during oil production is the main cause for large losses of oil, cost of transportation and preparation for recycling(Zukhov and Zaripor, 1998)

The growing demand for more efficient methods and sophisticated chemicals in the exploitation and processing of oil is intensified as producers push to tap more oil from the existing reserve. The escalation and volatility in crude oil prices has generated the right economic conditions for further investment in reseach and development of high technology oilfield chemicals. The design and development of such chemicals can reduce the capital investment to produce oil, thus making the market of oilfield chemicals more lucrative now than ever before. Nevertheless, intence competition between a large number of European and Americans companies for a market share renders it exteremely challenging as well (Presh,2011)

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1.4 Resources And Raw Materials

The company primary raw materials is a natural protein obtained from the non edible animals waste **“**the Gall Bladder **“** which is dispense in an appropriate solvent.

The products of sloughter houses include a number of non edible materials which can be processed in to valuable and useful secondary materials. In fact, in developed countries, processing of sloughter house non edibles is a large industry accaunting for substantial part of sloughter house income (Marlina, 2010).

In malaysia,there are over 300 sloughter houses which their non edible products except hide and skin are by far not utilised(Marlina 2010) Similarly, there are a large number of sloughter houses for cattles,Buffaloes,small ruminants and Pigs in member countries of Animal production and Health Commision for Asia and the pacific(APHCA) in which south east asian countries are registered members(fao.org) Accordigly indonesia top the list with over 800 sloughter house,500 in philipenes, 450 in thailand and about 250 in singapore. All these guaranteed the steady supply of the basic raw material required for our production.

Suitable solvent for our operation could be selected from the group consisting of glycol,glycol ethers,alcohols,water,hydro carbons,aromatics solvents, fatty acids methyl esters and combination thereof. This leaves us with a wide range of choices for the solvent and thus ensure the security of this second most important raw materials.

CHAPTER 2

MARKET ANALYSIS

2.1 Global Market

Soaring oil prices and perpetually increasing global demand for energy are creating a ripe environment for the oil and gas exploration and production (B.P statistical review of world energy 2013).

The global oilfield chemical market is projected to increase at a compound annual growth rate (CAGR) of 5.7% between 2010 and 2015 as the drilling activities returns and production rates are simulated and new wells brought online. The market grew to nearly USD 16 Billion in 2010 and is expected to increase to almost USD 19 Billion by 2015 according to IHS chemical global market study 2012.

Though the industry will be faced with the restraints of proving the effectiveness of some new chemicals, over caring environmental concern and confronting a weak global economy, the oilfield chemical market is likely to provide substantial growth opportunities for potential investors the report added.

The market was particularly strong in the US and Canada which accounted for more than $8Billion or 52% as shown in figure 2. Latin America, particularly Brazil is the second largest consumer with 11% in 2010 or nearly $1.8Billion of sales revenue. Russia and Africa follow with 8% each slightly more than $1Billion. Middle East, Asia Pacific and European regions each contributed 7% of global market demand or roughly close to $1Billion each in market share the report further clarified.

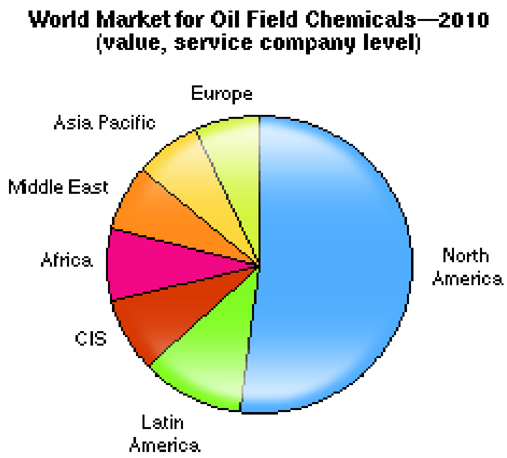


Figure 2.1: Global consumption of oil field chemicals in 2010

World demand for these chemicals is expected to grow during the next five year despite economic uncertainties, particularly in the developing countries which the demand is expected to overtake that in industrialised countries for the very first time. This is driven particularly by strong demand from china, India and other developing Nations across Asia which continues to see strong economic growth according to the IHS global chemical market report 2012. Figure 2.2, depict the past trend and expected future projection to year 2015.

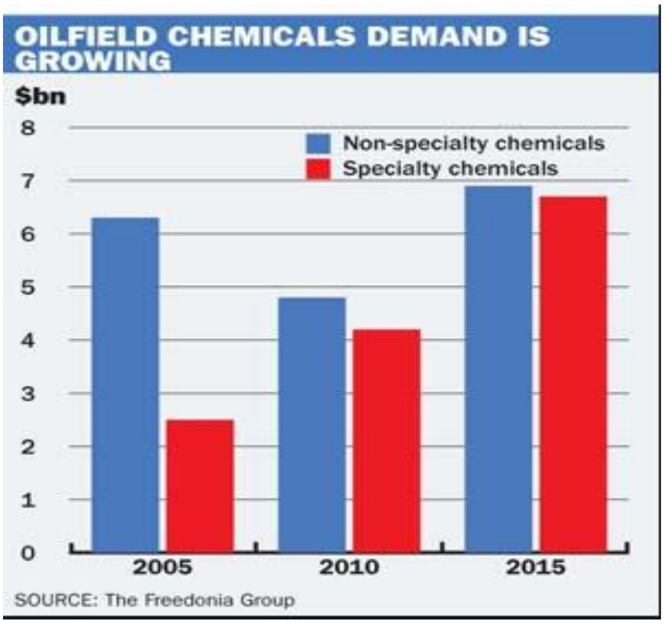
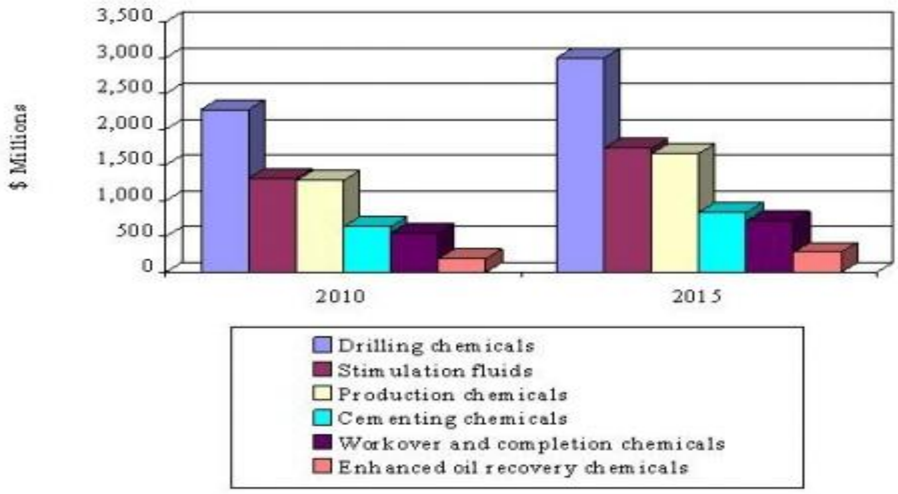


Figure 2.2 : Oilfield chemical demand 2010-2015

Oil field chemicals typically fall under three categories; drilling fluids, cementing and simulation, and oil production. Oil production are use at all stage from oil production at the wellbore to the delivery of crude to the refinery.products includes corrosion and scale inhibitors, biocides and Demulsifiers With technologically challenging oil exploration in deep water the world over,new emulsion breaking formulation to process oil quickly and cost effectively are in increasing demand (IHS report 2013).

Demand of various chemicals used in the oilfield by application will continue to rise through 2015 .The largest growth rate by process application Figure 2.3, is expected in drilling applications which is mostly has to do with enhance oil recovery (EOR) applications. Europian oilfield production is mostly in the North Sea, aging wells have been accompanied by corrosion and scales. In addition European environmental concerns have led to restriction or outright bans on many chemical formerly employed. Accordingly, production chemical sector will continue to grow strongly.Asia pacific market for production chemicals are likely to grow slowly due to the fact that much development is coming from shale gas field and thus favouring the demands of drilling, cementing and simulation sector (IHS report 2013)..

Value of Oilfield Chemicals by Application, 2010 And 2015 (Millions USD)



Source: BCC

Figure 2.3 : Value of Oilfield Chemical by Application 2010 And 2015

2.2 Target Market

Demulsifier market is growing, the consumption is estimated at 40 million barrel annually with 70-75% of this used in oil production. Global market of demulsifier in petroleum industry is put at USD585 Million in 2010,.refresenting 45% of the global demand of oilfield production chemicals. This trend is expected to grow annually and is expected to reach USD 743 Million by 2015 according to the report by Brazilian petroleum agency,2011.

Asia pacific account for 13% of the global demulsifier consumption, figure 2.4, which translate to about USD76 Million in revenue based on the year 2010 estimate to reach an average of USD 97 Million by 2015 accoding to the report.

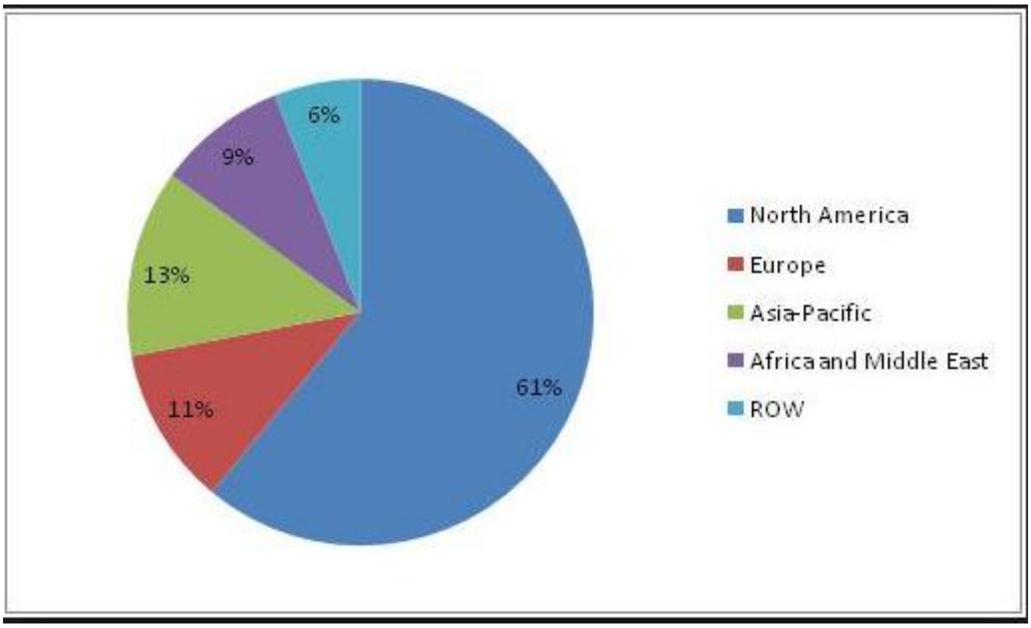


Figure 2.4: Year 2010 Global Demulsifier Consumption by Geography