Journal of Applied Science and Agriculture, 9(18) Special 2014, Pages: 245-248

AENSI Journals

Journal of Applied Science and Agriculture

ISSN 1816-9112

Journal home page: www.aensiweb.com/JASA

Application of Different Groups of Demulsifier In Water-In-oil Emulsion

Krittika Chandran, Smita Krishnan and Chandra Mohan Sinnathambi

Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS Malaysia.

ARTICLE INFO

Article history:
Received 25 July 2014
Received in revised form
8 July 2014
Accepted 15 September 2014
Available online 17 October 2014

Keywords:
Crude oil Demulsifier Emulsion

ABSTRACT

Crude oil is always produced with water. This association causes many problems during oil production, arising from the formation of emulsion. To overcome this issue, a synthetic surfactant, *aka* demulsifiers, is formulated to break the emulsion. Emulsion, a mixture of liquids with no mutual solubility between them is usually present as droplets of one liquid distributed in other continuous phase. Demulsifiers acts as an emulsion breaker, where they are able to separate the water-oil emulsions to their respective phases. There are many types of demulsifiers formulation where they may be divided into four main type of group for the oil and gas industries. This include; polymer, amines, alcohol and polyhydric alcohol. Demulsifier main function is to reduce the interfacial tension properties of the emulsion. This in turn helps break the emulsion into their respective phases. Demulsification formulation is also dictated by the properties of the crude oil. Demulsification formulation is tailor made for individual type of crude. Therefore, choosing the right demulsifiers formulation is important to give an effective separation of emulsion in crude oil processing. The objective of this review is to examine the different groups of demulsifiers used as surfactant for the removal/breakdown of emulsion from crude oil processing. Polymeric demulsifiers are found to be more suitable for water-in-oil emulsion, while the other 3 mention above are suitable for oil-in-water emulsion.

To Cite This Article: Krittika Chandran., Smita Krishnan and Chandra Mohan Sinnathambi., Application of different groups of demulsifier in water in oil emulsion. ***J. Appl. Sci. & Agric.,*** *9(18): 245-248, 2014*

INTRODUCTION

Crude oil is natural and unprocessed oil found under the earth's surfaces. During the production of crude oil, water will be produced along with the oil in the form of an oil-and-water emulsion (Abdel-Azim *et al.*, 2010). Emulsion is defined as the mixture of liquids that have no mutual solubility between them, where one liquid is present as droplets and distributed throughout the other (Abdurahman, H.N., and M. Nuraini, 2010). Emulsion is an undesirable substance, which increases the operational and capital cost in pipelines and processing equipment. Consequently, an effective and efficient demulsifier is needed to separate the oil and water, destabilize and break the emulsion to produce oil without any water. The demulsifiers need to be analyzed and formulated precisely to ensure it meets the requirements in separating the emulsion. Demulsifiers acts as an emulsion breaker, where they are able to separate the water-in-oil into their respective phases (Adel, S.H., *et al*., 2003).

However, it has been found that the interfacial barrier (boundary between the oil and water phase) is the main cause of the formation of the water-oil emulsion. The interfacial boundary divides the oil and water phases. Due to its close proximity reaction between oil and water takes place. This creates interfacial barriers which prevent the coalescence between the oil and water phase from taking place. As a result, oil-water emulsion is formed. Adding the demulsifier will interrupt this interfacial barrier by destabilizing and breaking the emulsion to segregate the oil and water phase. Addition of demulsifiers needs to be carefully administrated as wrong formulation might make the emulsion more stable and difficult to break. A correct formulation is a must to ensure it meets the necessary requirements in breaking the emulsion.

Development of different groups of demulsifier:

Before the 1940's, the chemicals that were obtained from condensation, such as sulphuric acid, sulphated caster oil, polyamines and polyhidric alcohols were used directly as demulsifiers (Auflem, I.H., 2002). However, in the early 1940's, with the development of the condensation of alkylene oxide technology, majority

Corresponding Author: Chandra Mohan Sinnathambi, Universiti Teknologi PETRONAS, Department of Fundamental and Applied Sciences, Bandar Seri Iskandar, Malaysia.
E-mail: chandro@petronas.com.my

of the demulsifier components were made up of condensation products such as ethylene-, propylene- and butylene- oxides, which are derived from the alkoxylated polymer group.

After 1950, new classes of nonionic detergents were developed through condensed polyether, which were made possible by the large-scale production of ethylene and propylene oxides (Amir Mosayebi, Reza Abedini., 2013). The condensation products of ethylene oxide were found to be water-soluble (hydrophilic), whereas propylene oxide gave poly condensation products that tended to be oil soluble (hydrophobic).

At present, the polymer widely used in demulsification industry is a surfactant which consists of both the hydrophilic and hydrophobic groups. This means that the polymeric surfactant has both a hydrophilic and hydrophobic group. The hydrophilic part is able to locate itself to the water molecule and the hydrophobic to the oil molecules present at the interface. Alkoxylated material was found to be the best polymeric surfactant.

In water-in-oil emulsion, the most effective demulsifiers are oil-soluble or hydrophobic demulsifiers. This is because; oil is the continuous phase while water is the dispersed phase. Therefore, the surfactant will absorb directly into the continuous phase without any resistance in its optimum temperature. Oil soluble demulsifiers are usually formulated only in the organic solvents, such as toluene, xylene, dioxane, or even in co-solvents comprising of organic solvents and water, where the organic solvent usually consists of ethylene diamine, diethylene triamine or ethanolamines (Becker, J.R., 1997).

Objective:

The objective of this review is to investigate the different groups of demulsifiers that have been used as surfactants for breaking water-oil emulsion from crude oil.

RESULTS AND DISCUSSION

Most common groups of demulsifiers used in oil and gas industries is either water-in-oil or oil-in-water. The main surfactant species can be basically be divided into 4 groups namely; amine, polymeric, alcohol and polyhydric alcohol. The grouping of the different surfactant species are summarized in Table 1 below

Table 1: Grouping of demulsifiers based on surfactant species

Amines	Pentylamine Hexylamine Octylamine Dioctylamine
Polymeric	Polyethylene Oxide Polyethylene block
Alcohol	Methanol Ethanol Propanol Butanol
Polyhydric Alcohol	Polyethylene glycol Ethylene glycol Propylene glycol

The separation rate of water-in-oil emulsion is influenced by the addition of a chemical breaking agent *aka* demulsifier, into the emulsion. Demulsifiers are strained from a wide range of chemistries. With the right formulation, the demulsifiers are able to treat all kinds of emulsions under the most challenging field conditions, such as in high turbulence or high water content. This is due to its ability, affinity and properties to locate the interfacial section of the oil-water emulsion. Apart from its swift action, a successful demulsifier formulation needs to have a water separation efficiency of 80% separation, a sharp and clear interface, and the separated water phase must be clear to the naked eyes.

According to previous study done by (Kim, Young-Ho, 1995), polymer group demulsifiers give drier oil, cleaner water and a sharper interface. Moreover, the polymer group demulsifiers provide outstanding performance in heavy oils and low temperatures. This is because the polymeric molecule has high molecular weight, and is able to flocculate the large number of sub-micron water droplets dispersed in the crude oil. Therefore, water droplets are concentrated at the base of the oil column due to the coalescence action, and the oil is dehydrated above the settling level of the flocculated water droplets.

Amine group demulsifiers are frequently used in crude oil emulsion studies because it provides good results in separating the emulsion. According to the study of Nuraini *et al* (2011), oil soluble demulsifiers are the best for water-in-oil emulsion. Amines are highly surface active and are able to absorb on the oil-water interface, because it will directly absorb into the continuous water phase. However, the disadvantage of the amine group demulsifiers is that they are capable of changing the pH or salinity of the aqueous phase of the emulsion. This property will enhance emulsion stability and decreases the demulsification efficiency of the applied demulsifiers (Merchant, Jr. and M.L. Sylvia, 1988).

The influence of alcohol and polyhydric alcohol demulsifiers towards water-in-oil emulsion was also studied. The efficiency of this group of demulsifiers depends on the water solubility and the molecular weight of the demulsifier. Alcohol is a low molecular weight demulsifier, which is also known as a water-soluble demulsifier. In general, demulsifiers with lower molecular weight chemistries cause increase in the interfacial adsorption rate and decrease in the interfacial activity. Therefore, lower molecular weight demulsifiers have a faster initial effect, but it will not be effective in the overall demulsification.

Producing a workable demulsifier formulation for a demulsification purposes is a complicated process/method. The most important challenge in producing a novel demulsifier to match the characteristics of the crude oil investigated. This is because, not all the crude oil has the same composition or properties. One demulsifier formulation suitable for one type of crude might be risky for another. In the water-in-oil emulsion system, the key factor of a demulsifier mechanism is breaking the stable interfacial film (Mosayebi, A., Abedini., R., 2013). The mechanism of the demulsification process should be examined carefully in order to understand the molecular interaction between the demulsifiers and interfacial active agents, such as asphaltenes, resins and waxes, which exist in crude oil. It is likely that the demulsifier interacts differently with some crude oil components, which causes differences in the demulsification performance. Demulsifier bases give outstanding performance in resolving a range of crude oil emulsions and are mostly effective when used in heavy crude formulations (Monson, L.T., 1969). This is because as the density of the crude increases, its density approaches the density of water. The interface attraction between the water and oil molecules increases as a result a correct demulsifier formulation at an optimum temperature is able to increase the thinning of the interface barrier, resulting in better separating of the two phases.

If the demulsifier is prepared based on the needs of the particular emulsion, it will ensure that the excess water in the oil be removed or treated before disposal. Further work in selection of the surfactant for a particular application is essential to provide a better understanding of the mechanisms involved, in order to help in the development of a demulsifier formulation that could serve its applicable in the industry.

To further illustrate the above statement, experiment conducted by Mosayebi is given in Figure 1. The experiment investigates the amount of water separated from water-in-crude oil emulsion versus time using different demulsifiers on artificially prepared water-in-oil emulsions. All the demulsifiers were used under similar condition and matrix, at different solvent concentration. Results shows that in the first 200 minutes, the amount of water separated by EO/PO Block Copolymer (polymer group) hexyle amine, pentyl amine (amine group) and ethylene glycol (polyhydric alcohol group) was 7, 7, 2, and 0 % respectively. There was no water separation from 1000 minutes until 2200 min. After 2200 minutes, EO/PO Block Copolymer had separated the highest percentage of water which was approximately 55 %, followed by hexyle amine with 34 %, pentyl amine with 29 %, and ethylene glycol at 22% respectively (Kim, Young-Ho, 1995).

Thus, the polymer-group (EO/PO) demulsifiers provided a better result in separating the emulsion in crude oil. This is because the polymer-group demulsifier is able to decrease the interfacial tension gradient, and accelerates the coalescence of crude efficiently. This occurs when the displacement of the natural stabilizers (from demulsifier), which is present in the interfacial film around the water droplets occurs, creates an interfacial tension gradient, whereby it is high on the inside of the film and low on the outside the film. Subsequently, when the demulsifier molecules are adsorbed, the interfacial tension is decreased, causing an increase in the rate of film thinning by inducing sharper interface resulting in droplet coalescence and better separation (Salam, K.K., *et al.*, 2013).

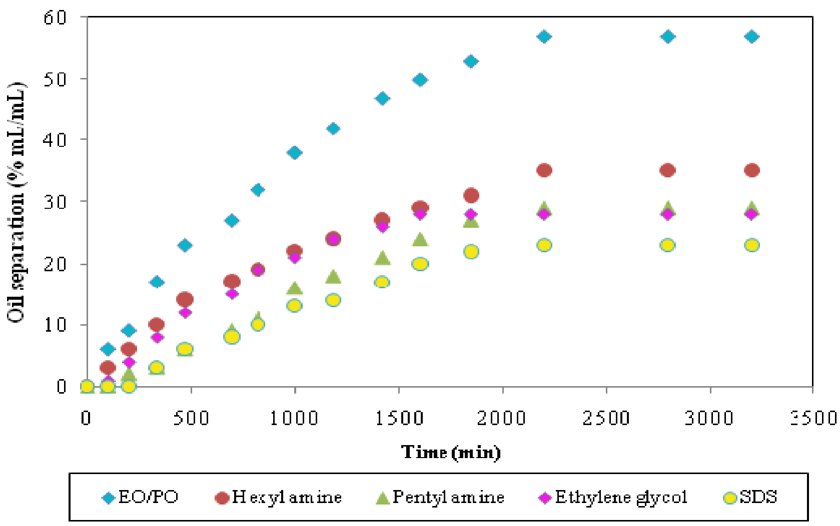

Fig. 1: The effect of polymer and amine demulsifiers on crude oil emulsion (Kim, Young-Ho, 1995)

Conclusion:

The results from the findings demonstrate that the stability of the crude oil emulsion depends on the type or group and concentration of surfactant and solvent used. For oil-in- water, water soluble demulsifier such as amine and alcohol surfactant group are favored. For water-in-oil, polymeric surfactant group is recommended as the continuous phase is oil. Properties of the crude also play an important part in breaking oil-water emulsion. Therefore, having selected surfactant group laboratory and industrial experiments need to be carried out to select the best group, solvent and their optimal concentrations.

ACKNOWLEDGMENTS

The author would like to thank Universiti Teknologi PETRONAS for the encouragement & studentship from the Enhance Oil Recovery, mission oriented research division and MyBrain 15 for its tuition fees support. The author would also like to express her sincere and honest gratitude to colleagues from UTP and PRSB, who have given guidelines and assistance throughout the study.

REFERENCES

Abdel-Azim, Abdel-Raouf, Abdul Raheim, Maysor, 2010. Sugar- based Ethoxylated amine surfactants as demulsifiers for crude oil emulsion: 2- demulsification of different types of crudes., *Brazillian journal of petroleum and gas*., pp: 155-165.

Abdurahman, H.N., and M. Nuraini, 2010, Chemical Destabilization on Water in Crude Oil Emulsions., *World Academy of Science, Engineering and Technology*.,4 0000-00-00.

Adel, S.H., Hamadi, R.F. Hamidillin, O.N. Shibayva, E.E. Diyarov, 2003."New Composition of Chemical Reagents for Improvement the Rheological Properties for Heavy Crude Oils", (in Russian), Science and Technology of Hydrocarbon, Moscow.

Auflem, I.H., 2002. Influence of Asphaltene Aggregation and Pressure on Crude Oil Emulsion Stability. Norwegian University of Science and Technology. Phd Thesis.

Amir Mosayebi, Reza Abedini., 2013. Using demulsifier for phase breaking of water/oil emulsion., *Petroleum & Coal*., 55(1): 26-30.

Becker, J.R., 1997. Crude Oil Waxes, Emulsions, and Asphaltenes. PennWell Publishing Company. Oklahoma., pp: 126-129.

Kim, Young-Ho, 1995. A Study Of Dynamic Interfacial Mechanisms For Demulsification Of Water-In-Oil Emulsions. Illinois Institute Of Technology: PhD Thesis.

Nuraini., M., A.H.N. Abdurahman and A.M.S. Kholijah, 2011. Effect of chemical breaking agents on water-in crude oil emulsion system., *International Journal of Chemical and Environmental Engineering*.

Merchant, Jr. and M.L. Sylvia, 1988. Water Based Demulsifier Formulation and Process for Its Use in Dewatering and Desalting Crude Hydrocarbon Oils. (US Patent 4,737,265).

Mosayebi, A., R. Abedini., 2013.Using demulsifier for phase breaking of water/oil emulsion., *Petroleum & Coal* 55 (1) 26-30.

Monson, L.T., 1969. Chemical Resolution of Petroleum Emulsions. Surface Operations in Petroleum Production. American Elsevier Publishing Company Inc. New York. pp: 46-64.

Salam, K.K., A.O. Alade, A.O. Arinkoola and A. Opawale, 2013. Improving the Demulsification Process of Heavy Crude Oil Emulsion through Blending with Diluent, pp: 1-6.

Schramm, L.L., 2005. Emulsions, foams and suspensions; fundamental and applications. Weinheim : Wiley-VCH Verlag GmbH & Co.

Selvarajan Radhakrisnan, Anantha-subramaniam Sivakumar and A.M. Robert, 2001. "Aqueous Dispersion of an Oil Soluble Demulsifier for Breaking Crude Oil Emulsions", US Patent No. 6,294,093.

Sjöblom, J., L. Mingyuan, A.A. Christy and H.P. R¬nningsen, 1992. Water-in- Crude Oil Emulsions from the Norwegian Continental Shelf. – 7. Interfacial Pressure and Emulsion Stability. *Coll. Int. Sci*., 66: 55-62.

Qu, G., Gong, X., and Liu, Y. (2014). New research progress of the demulsification of produced liquid by polymer flooding. *Journal of Chemical and Pharmaceutical Research*, 6(1): 634-640.