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Simplified Formulation of Demulsifier from Locally Sourced Materials Using Saponification Method

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ABSTRACT

Conventional demulsifier (chemical) are still been used until now in many oil industries with the attendant formulas been both expensive and harmful for the environment. In this research, the new formula of local demulsifier has been tested with palm oil, glycerin, and Potassium Hydroxide (KOH). These materials are friendly for the environment and contain hexane group and octadecenoic acid which are basic composition in plants that can break the emulsion. The method of formulation of the demulsifier used is saponification is fundamental. Other methods currently available for demulsification can be broadly classified as chemical, electrical and mechanical. In this paper, the first experiment was carried out without any emulsion breaker. This was to certify that there was no natural demulsifier available in the crude oil. The second experiment was carried out using surphuric acid (H2S04) as demulsifier. There was little separation of water from the emulsion. The third experiment was carried out using the local demulsifier that was formulated, which show a high level of water separation from the oil emulsion. The results indicated that there is better level of separation when using local demulsifier than sulphuric acid. Also the density of crude oil emulsion before local demulsifier was added are 1.086 for BET-SCS and 0.982 for OREDO-4ST and after the local demulsifier was added, the density of crude oil increased to 1.141 for BET-SCS and 1.053 for OREDO-4ST. The research is fundamental to local content development, policy formulation and quality decision-making driven by adequate and verifiable data for sustainable development.

Keywords: Local Materials; Demulsifiers, Crude Oil Emulsions, Saponification

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INTRODUCTION

Crude oil is a complex mixture of saturates (paraffin/waxes) aromatics, naphthalene, asphaltenes and resins (Lee, 2008). In petroleum industry, emulsion is the crucial part to investigate. Emulsion is a system with dispersion of a liquid phase into another. Water is normally present in crude oil reservoirs or is injected to stimulate oil production and pipelining, and the types of emulsions include those of Water-in-Oil (W/O), Oil-in-Water (O/W) and more complex Oil-in-Water-in-O il (O/W/O) emulsions. An oil-in-water emulsion is a mixture of two immiscible liquids where oil phase is dispersed into the water continuous phase. Oil-in-water emulsions are very rare, deliberately produced to reduce the viscosity of highly viscous crude oil so that they can be transported easily through pipelines (Zaki, 1997). The oil-in-water emulsion reduces the viscosity of heavy crude oils and bitumen and may provide an alternative to the use of diluents or heat to reduce viscosity in pipelines (Langevin et al., 2004). The crude oil emulsion is one of the major obstacles in crude oil production. Water in the crude oil emulsion can contain gas hydrates and salts such as NaCl, $MgCl_2$, $CaCl_2$, and KCl which are responsible for corrosion of production equipment and pipelines. They also decrease the quality of petroleum distillates, especially by the reactions of heavy components such as boiler fuel, the raw material for catalytic cracking and others. In addition, the crude oil emulsion increases transportation cost as it occupies extra spaces and increases the viscosity of the crude oil. Therefore, the demulsification of crude oil emulsion is one of the most important processes in all oil fields. Demulsification is the basic process used to separate water from the crude oil emulsion. The demulsification can be classified into electrical, mechanical, and chemical methods. Chemical demulsification is the most common method in the industry due to its applicability. This method involves the use of chemical additives to enhance emulsion separation processes, of which surfactants are commonly used. Demulsifiers being used in the petroleum industry are usually petroleum-based or polymer-based surfactants. The petroleum-based surfactant is less environmental-friendly, while the polymer-based surfactant costs higher as raw materials are not easily available. The development of demulsifier by palm oil-based surfactants is of necessity considering the use of abundant biomass materials(agricultural crops and waste), hence zero carbon emission, as the Republic of Indonesia produced 35 million tons of CPO (chief product officer) from a total plantation area of 12 million ha in 2017 .In this study, a formula of a demulsifier was developed to break emulsion in crude oil using palm oil-based surfactants, diethanolamine (DEA) and Sodium Methyl Ester Sulphonate (SMES).

Separation of water from oil before transportation or refining is very essential for economic and operational reasons. Several methods in use have suffered from drawbacks such as high costs of production and environmental concerns. The need to develop a cost effective and efficient demulsifier in treating crude oil emulsions without compromising quality and environmental safety is a major concern. In this study, new of local demulsifier are formulated to minimize the negative impact of commercial demulsifier both in reduce the high cost and minimize the negative impact of using chemical on the environment. The new local demulsifier formula will be formulated using palm oil, glycerin and KOH compounds. Palm oil contain hexane group and octadecenoic acid. Those compositions are two main plant components that can break the emulsion (Yaakob and Sulaimon, 2017). Emulsions are also classified by the size of the droplets in the continuous phase. When the dispersed droplets are larger than 0.1 μm, the emulsion is a macro-emulsion. (schramm and Schubert 1992), Emulsions of this kind are normally thermodynamically unstable (i.e., the two phases will separate over time because of a tendency for the emulsion to reduce its interfacial energy by coalescence and separation). However, droplet coalescence can be reduced or even eliminated through a stabilization mechanism. Most oilfield emulsions belong in this category. In contrast to macro-emulsions, there is a second class of emulsions known as micro-emulsions. These emulsions form spontaneously when two immiscible phases are brought together because of their extremely low interfacial energy. Micro-emulsions have very small droplet sizes, less than 10 nm, and are considered thermodynamically stable. Micro-emulsions are fundamentally different from macro-emulsions in their formation and stability. For the result, those local and commercial demulsifiers will be compared base on the temperature, concentration of separation, and the time of separation. Several investigative case studies have been reported for understanding the causes of tight emulsions (Kokal and Wingrove 2000) (Kokal and Al-Juraid 1999) (Kokal et al. 2001) and optimizing demulsifier usage.

MATERIAL AND METHODS

3.1 Apparatus and Equipment

The apparatus/equipment used for laboratory study of emulsion and demulsification include but not limited to the following; Centrifuge machine; heater and stirrer; beakers; Viscometer etc.


Figure 1: (a) Centrifuge machine (b) viscometer

Production Materials, Methods and Procedures

For the production of local demulsifier, we used a commercial palm oil, potassium hydroxide (KOH), glycerin, oil emulsion sample:- BET-SCS (sample A), OREDO-4ST (sample B), hydrogen Sulphate (H_2SO_4). Local demulsifier was formulated using the following step; a) 50ml of palm oil commercial was added to a beaker and heated at 80^oC for 30 minutes. b) 12.5g of KOH add into breaker along with 25 ml glycerin and then heated until homogenous .c) Add KOH + Aqueous into palm oil and stir it with heater and stirrer in 80^oC, 800 rpm, for 1 hours and 30 minutes.(d) For the last add 50 ml of glycerin and stir for 5 minutes, then wait the formula for 24 hours until the formula become liquid. Two samples of Oil emulsion was added into the test tubes (three test tubes were filled with sample A up to 10ml and the remaining test tubes were also filled with sample B up to 10ml), then two test tubes of sample A and B were picked and no demulsifier was added, another two test tubes both of sample A and B was picked and commercial demulsifier (H_2S0_4) was added, then the remaining two sample of both sample A and B was picked and then local demulsifier was added, tall the six test tubes were inserted into the centrifuge machine and then the machine was set at 600rpm for 5 minutes, after the time elapsed, the test tubes were removed and the sample separated into three layers, the down layer was water, the middle layer was BS&W and the upper layer was oil, the separation was recorded for each case(that is for no demusifier, for adding commercial demulsifier and for adding of local demulsifier). The above steps were repeated but at 1000rpm for 5 minutes, and also the separation were recorded.

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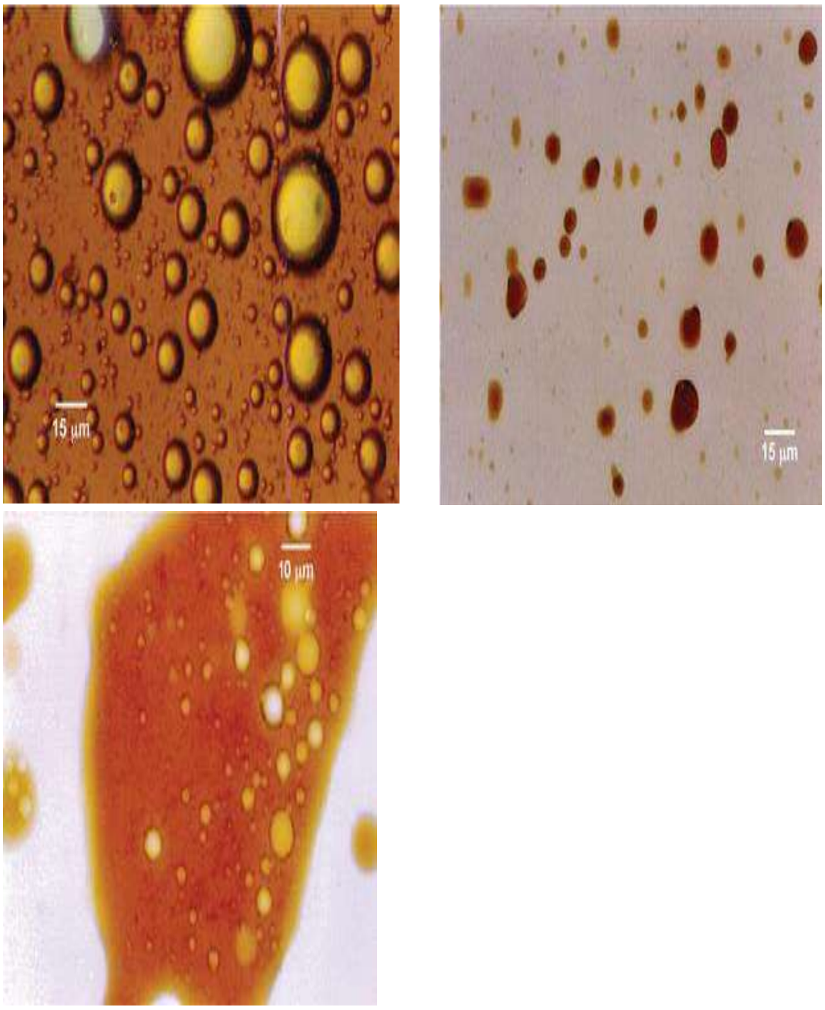

Figure 2: (a) – Photomicrograph of a water-in-oil emulsion, (b) Photomicrograph of an oil-in-water emulsion and (C) Photomicrograph of a water-in-oil-in-water emulsion.

RESULTS AND DISCUSSIONS.

Table 1: Emulsion with commercial demulsifier (sulphuric acid) (600rpm and 1000rpm)

Sample	Rpm	Time (min)	Emulsion (ml)	Sulphuric acid (drop)	Water level (ml)	Crude oil (ml)	Basic sediment of water
A	600	5	10	Xx	Xx	Xx	Xx
B	600	5	10	Xx	Xx	Xx	Xx
A	1000	5	10	Xx	Xx	Xx	Xx
B	1000	5	10	Xx	Xx	Xx	Xx

Table 2: Emulsion with local base demulsifier (600rpm and 1000rpm)

Sample	Rpm	Time (min)	Emulsion (ml)	Local demulsifier (drop)	Water level (ml)	Crude oil (ml)	Basic sediment of water
A	600	5	10	Xx	Xx	Xx	Xx
B	600	5	10	Xx	Xx	Xx	Xx
A	1000	5	10	Xx	Xx	Xx	Xx
B	1000	5	10	Xx	Xx	Xx	Xx

Table 3: Properties of crude oil used before adding demulsifier

S/N	CRUDE OIL SAMPLE	VISCOSITY (cp)	DENSITY (g/cm^3)	SPECIFIC GRAVITY	API
1	BET-SCS	2.3	1.086	0.839	37.113
2	OREDO-4ST	1.8	0.982	0.759	40.0

Table 4: Emulsion without demulsifier (RPM 600 and 1000)

Sample	RPM	Time(min)	Emulsion (ml)	Water level (ml)	Crude oil (ml)
A	600	5	10	1.0	8.4
B	600	5	10	0.3	9.6
A	1000	5	10	1.7	8.0
B	1000	5	10	0.4	9.5

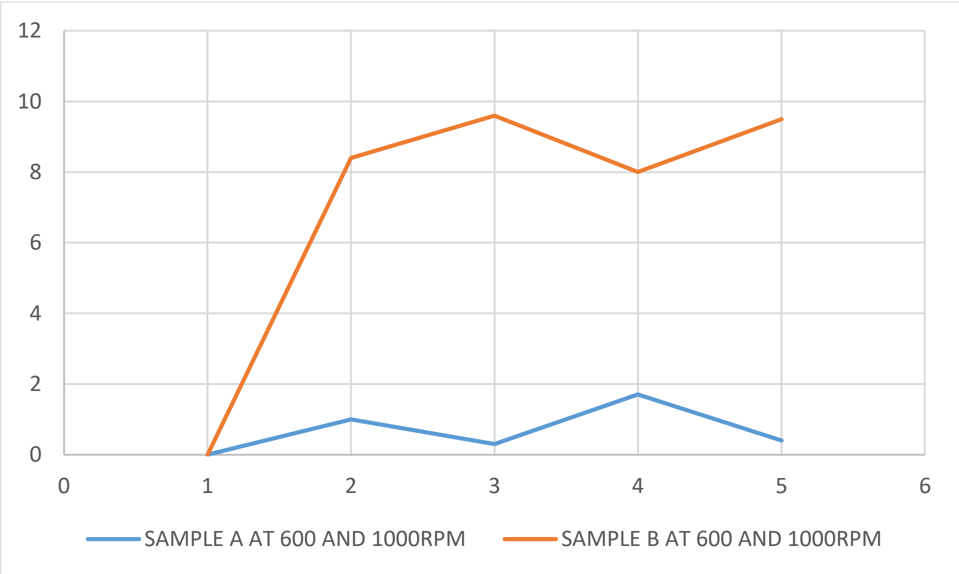

Table 3: showed the result of crude oil emusion without the application of any demulsiers, in which the emulsion was agitated in the centrifuge machine at 600rpm and 1000rpm, where the water separation level was the point of discussion, where water level of sample A and B are 1.0 and 0.3 at 600rpm and 1.7 and 0.4 at 1000rpm, this shows that the water separated at 1000rp/m is higher than that of 600pm with no demulsier added.

Table 5: Emulsion with commercial demulsifier (Sulphuric acid) (RPM 600 and 1000)

Sample	RPM	Time (min)	Emulsion (ml)	Sulphuric acid (drop)	Water level (ml)	Crude oil (ml)	Basic sediment and water
A	600	5	10	3	1.5	8.0	0.5
B	600	5	10	3	0.3	9.6	0.1
A	1000	5	10	3	0.7	8.6	8.6
B	1000	5	10	3	0.3	9.6	9.6

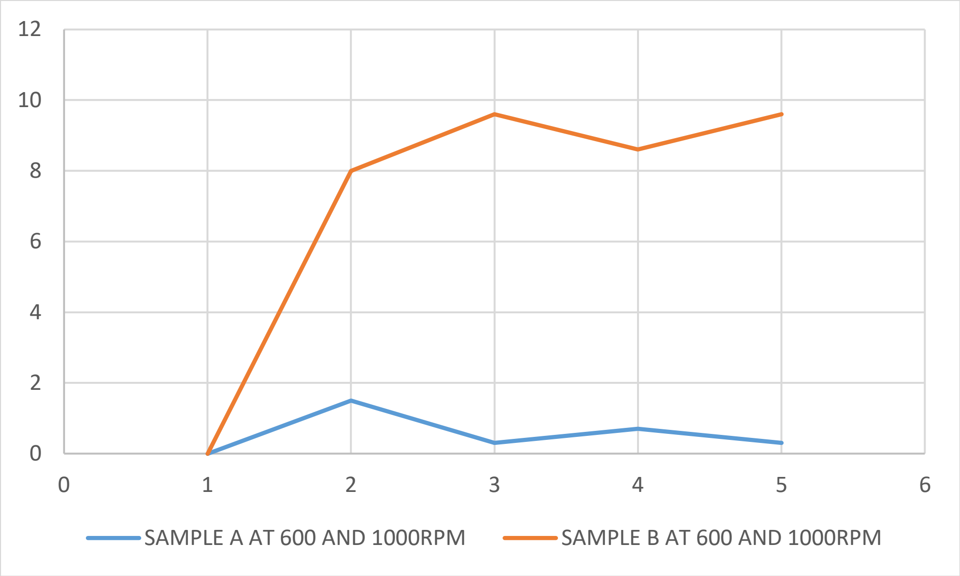

Table 4: shows the result of using commercial based demulsifer and locally sourced demusifier which was tested using the two sample of oil emulsion which are BET-SCS (sample A) and OREDO-4ST (sample B). the experiment conducted to test the influence and performance of demulsifier on crude oil emulsion stability. The stability of the emulsions was determined visually by measuring the water and oil separation from emulsion as a function of rpm. The amount of water separated from the emulsion for sample without demulsifier is higher than the amount of water separated using sulphuric acid which 1.5 and 0.3 for 600rpm, 0.7 and 0.3 for 1000rpm respectively.

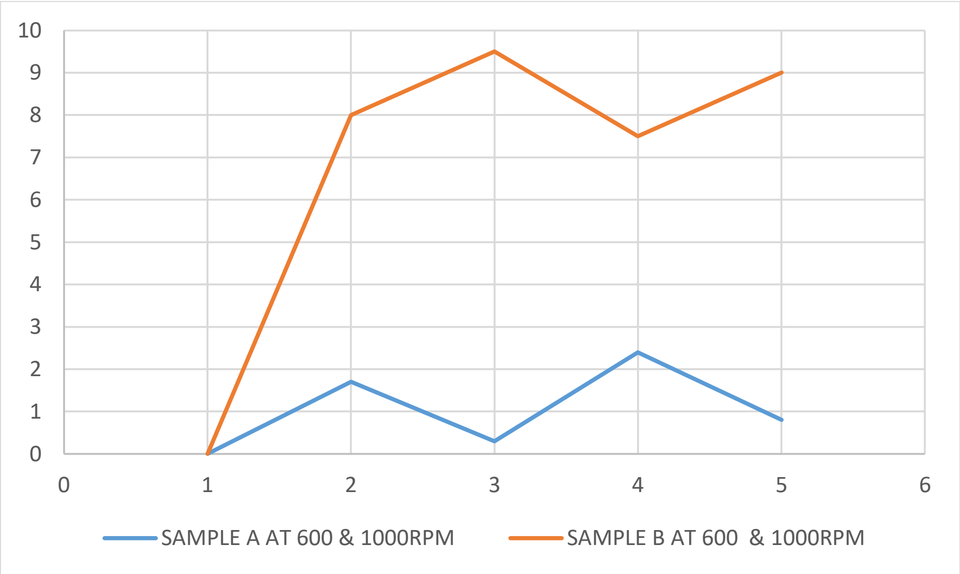

Fig.5 shows that sample A contain high amount of water compared to sample B, which from all the three experiment, the level of water separation of sample A is higher than sample B, though sample A is a heavy crude oil as indicated from its API (37.113) while sample B is a light crude oil as indicated from its API (54.979).

Also this prove that agitating crude oil emulsion in higher revolution per minutes(1000rpm) gives higher separation than agitating at lower reolution per minutes(600rpm).

It appears that the use of sulphuric acid as a demulsifier led to a decrease in emulsion stability, as evidenced by the lower emulsion index values (0.7 and 0.3) compared to the values obtained without a demulsifier (1.7 and 0.4). This suggests that the sulphuric acid was effective in breaking down the emulsion and separating the components. However, it is worth noting that the emulsion index values obtained without a demulsifier are still relatively low, indicating some degree of separation and instability in the emulsion. This could be due to a variety of factors, such as the composition of the emulsion, the mixing conditions, and the presence of other contaminants or impurities.

It is also important to consider the potential risks associated with the use of sulphuric acid as a demulsifier. Sulphuric acid is a highly corrosive and reactive substance that can be dangerous to handle and requires careful handling and disposal procedures. Overall, the results suggest that the use of sulphuric acid as a demulsifier can be effective in breaking down emulsions. Furthermore, when the centrifugal machine operates at high speed, the water molecules and crude oil experience stronger centrifugal force. The force act radically outward and cause the high density water molecules to move towards the outer edge of the emulsion, while the less dense crude oil molecules tends to stay closer to the center. This differential movement allows for the separation of water from the emulsion. At lower agitation speed, such as 600rpm, the centrifugal force may not be sufficient to overcome the interfacial force between the water and crude oil molecule. As a result the water separation levels are relatively low. The increased centrifugal force at the higher speed helps to overcome the interfacial forces and separate the water molecules from the emulsion. However, even at the higher speed, the water separation levels are still relatively low in the absence of demulsifier. This is the fundamental advantage of developing locally sourced materials for the effective demulsification of crude oil in this paper.

CONCLUSIONS AND RECOMMENDATION

The successful formulation of demulsifier using locally sourced materials is a viable contribution to local content development in the oil and gas industry in Nigeria. The formulated demulsifiers were tested on crude oil samples and showed promising results in terms of separating water from the oil. From the experiment, it was established that the separation of water from the base case (no demulsifier added) 1.0 and 0.3 at 600rpm and 1.7 and 0.4 at 1000rpm ratio respectively separated. Again, for emulsion with commercial demulsifier (sulphuric acid), 1.5 and 0.3 for 600rpm and 0.7 and 0.3 for 1000rpm ratio was recorded. Finally, for emulsion with local demulsifier, 1.7 and 0.3 for 600rpm and 2.4 and 0.8 for 1000rpm was recorded. The result clearly shows the effectiveness of the local demulsifier by separating high amount of water. Also the densities of crude oil emulsion before the addition of demulsifier were 1.086 for BET-SCS and 0.982 for OREDO-4ST and 1.141 for BET-SCS and for OREDO-4ST 1.053 respectively, after the addition of the locally formulated demulsifiers. This indicated an increase in the density of the oil emulsion after demulsifier was added. The use of locally sourced materials not only reduced the cost of production but also promotes sustainability by reducing the reliance on imported chemicals. Further optimization and testing of the demulsifiers through a pilot scheme would enhance the industrial application of the process and thus recommended to fully evaluate their effectiveness and potential for commercial use. Overall, this method contributes to the development of more environmentally friendly and cost-effective solutions for the oil and gas industry and it is recommended that: A pilot scale study process to conduct further optimization and enhance the effectiveness of the demulsifiers to reduce production costs is fundamental to industrialization and commercialization of the products. There is a stronger need to explore potential partnerships with local oil and gas companies to promote the use of these environmentally friendly and cost-effective demulsifiers through public private partnerships. Furthermore, there is need to consider conducting life cycle assessments to fully evaluate the sustainability benefits of using locally sourced materials in demulsifier production at the commercial scale in the Nigeria's oil and gas industry. More industrial scale investigation on the potential of applying this approach to other chemical products used in the oil and gas industry to promote sustainability and cost-effectiveness is recommended. Overall, these recommendations can help to further develop and promote the use of locally sourced materials in the oil and gas industry, contributing to a more sustainable and cost-effective future, add to volume of existing knowledge as well as influence quality decision making based on verifiable data for economic development.

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