

Laboratory Experiment on high performance of locally produced demulsifiers over conventional imported demulsifier on crude oil emulsion demulsification

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ABSTRACT

A laboratory experimental work was carried out to produce local demulsifiers using local materials. An experimental investigation was carried out to ascertain the produced local demulsifiers effectiveness and efficiency in breaking crude oil water emulsion. Materials used included locally made Palm oil, KOH compound, Lemons, Glyserin, for sample A, locally made liquid soap, starch, camphor, alum, castor oil, and distilled water for sample B and the combination of sample A and B make up sample C demulsifier. The three different demulsifier formulations made were tested on a crude oil emulsion sample from a Niger Delta field and subjected to a temperature of 30°C. A commercially available demulsifier, CAD, of the same quantity and under the same laboratory experimental condition, served as a basis for comparison (validation).

The result of the treatment was a successful separation of oil and water using the sample Alpha, Beta, and Mega, produced demulsifier. The maximum separated water volume by the local demulsifier was 72%, while that separated by commercially available imported demulsifier, CAD was 35%. This showed that locally formulated demulsifiers had better water separation capability than the commercially available (imported) demulsifier.

Key words; *Emulsion, local materials, Temperature, Concentration, Niger Delta, Demulsifiers, Separation.*

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I. INTRODUCTION

Emulsion is defined as a system in which one liquid is relatively distributed or dispersed, in the form of droplets, in another substantially immiscible liquid. Emulsions have long been of great practical interest due to their widespread occurrence in everyday life which occurs due to reliance of the behaviour of the emulsion on the magnitude and range of the surface interaction. They may be found in important areas such as food, cosmetics, pulp and paper, biological fluids, pharmaceutical, agricultural industry, and petroleum engineering. In production and flow assurance, the two commonly encountered emulsion types are water droplet dispersed in the oil phase and termed as water-in-oil emulsion (W/O) and if the oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion. When there is dispersion (droplets) of one liquid in another immiscible liquid is called emulsion. The phase that is present in the form of droplets is the dispersed or internal phase, and the phase in which the droplets are suspended is called the continuous or external phase. For produced oilfield emulsions, one of the liquids is aqueous and the other is crude oil. The amount of water that emulsifies with crude oil varies widely from facility to facility. It can be less than 1% and sometimes greater than 80%.

In a true emulsion, either the drop size must be small enough that forces from thermal collisions with molecules of the continuous phase produce Brownian motion that prevents settling, or the characteristics of the interfacial surfaces must be modified by surfactants, suspended solids, or another semisoluble material that renders the surface free energy low enough to preclude its acting as a driving force for coalescence.

Problem Statement

In crude oil production from brown fields or heavy oil, there is production of water in oil emulsions which can either be controlled or avoided. This emulsion resulted in an increase in viscosity which can seriously affect the production of oil from sand phase up to flow line. Failure to separate the oil and water mixture efficiently and effectively could result in problems such as overloading of surface separation equipment, increased cost of pumping wet crude, and corrosion problems. Because of inadequacy and water separation incapability of the long term existing demulsifier; commercially available imported demulsifiers the research to formulate and apply local demulsifier to separate water in oil crude oil emulsion with high efficiency and effectiveness is proposed. Commercially available (imported) demulsifiers CAD are very expensive with low efficiency and effectiveness on crude oil emulsion separation and with environmental hazards. Formulation of local demulsifiers from local materials with high efficiency and effectiveness on separating crude oil emulsion and with no environmental

hazards is an alternative option and also a local content policy and initiative. This research is focus on formulation and application of local demulsifier to separate crude oil emulsion.

1.3 Objectives of Study

This research is focused primarily to formulate and apply local demulsifier from locally sourced raw materials to break water-in-oil emulsion.

SPECIFIC OBJECTIVES

1. Laboratory characterization of local materials and commercially available (imported) demulsifier
2. Formulation of local demulsifier using local materials
3. Application of local demulsifiers and commercially available demulsifier on the crude oil emulsion.
4. Comparison and validation of the efficiency and effectiveness on the rate of separation of crude oil emulsion by the formulated local demulsifiers and commercially available (imported) demulsifier.

II. Literature

Water-in-oil crude oil emulsions may be encountered at all stages in the petroleum production and in processing industry. With presence of water, they are typically undesirable and can result in high pumping costs and pipeline corruptions and increase the cost of transportation (Hanapi, Ariffin, Aizan, & Siti, 2006). Reduced throughput is needed to introduce special handling equipment, contribute to plugging of gravel pack at the sand phase (Espinoza & Kleinitz, 2003) and affect oil spill cleanup (Fingas & Fieldhouse, 2003).

Despite the success of enhanced oil recovery (EOR) process, one of the problems associated with the process is emulsion problem. Efevbokhan, Akinola, & Hymore (2010) observed that physical factors that enhance oil recovery can also greatly contribute to the formation of very stable emulsions because EOR-induced emulsions are established by surfactant/polymer (SP) and alkaline/surfactant/polymer (ASP) processes which makes breaking of emulsion different from naturally occurring emulsions which are stabilized by asphaltenes and resins (Efevbokhan et al., 2010). Traditional demulsifiers are often not effective on emulsions created by chemical floods; therefore, the performance of demulsifier in surfactant/polymer-flooding-induced emulsion depends on the selection of the best demulsifier with respect to the system under consideration (Nguyen & Sadeghi, 2011). In breaking of surfactant/polymer-flooding-induced emulsion with the use of surfactant, Oseghale, Akpabio, & Udotong (2012) worked on separation of oil-water emulsions expected during chemical enhanced recovery operations using crude oil from a field in Niger delta during surfactant/polymer flooding operation. Surfactant N-octyltrimethyammonium bromide (C8TAB) was used as the demulsifier and a dosage between 200 and 300ppm was the optimum dose that yielded oil and water phases with oil content reduction from 550 to 70 ppm after 4 h. Microscopy test confirmed that addition of N-octyltrimethyammonium bromide (C8TAB) produced significant coalescence shortly after it was added to the emulsion, which is in agreement with an increase of the oil droplet size in the presence of the demulsifier. Their findings show that this investigation worked with the principles of using cationic surfactants as demulsifier (Oseghale et al., 2012).

Early petroleum industry operators used condensed chemicals such as sulphuric acid, sulphated castor oil, polyamines and polyhydric alcohols directly as demulsifier (Auflem, 2002). Later in the early 1940, the alkoxyated polymer group derivatives such as ethylene-, propylene-, and butylene-oxides were used (Chandran, 2014). A decade after, as a result of a large scale production of ethylene and propylene oxide, a new classes of non atomic detergents developed through condensed polyether were used as demulsifiers (Mosayebi & Abedini, 2013).

Presently, a polymer based hydrophilic and hydrophobic surfactants are used as demulsifiers this is to enable the demulsifier to permeate and destabilize the interfacial barrier between the crude oil and water in the emulsion. Hence it is expedient for the designed demulsifier to contain both oil soluble (hydrophobic) and water soluble (hydrophilic) solvents. (Daaou & Bendedouch, 2012) in their study on the effect of pH on Algerian crude oil emulsion, confirmed the fact that neutral medium is more efficient in stabilizing the emulsions compared to the acidic and basic solutions.

The surfactants used in the petroleum industry can be grouped into four groups namely, the amines, polymeric compounds, alcohols and polyhydric alcohols (Chandran, 2014). While oil soluble demulsifiers such as polymeric demulsifier give outstanding performance for water in oil emulsion, water soluble demulsifiers such as amine group, alcohol and polyhydric alcohol based demulsifiers are prefer for oil in water emulsion (Nurainia, Abdurahmanab, & Kholijaha, 2011).

Amines are surface active with high solubility in the continuous water phase. However, the amine group demulsifier has an ability to alter the pH or salinity of the aqueous phase of the emulsion thereby stabilizing the emulsion (Nurainia et al., 2011).

2.1 Emulsion identification and Characterization

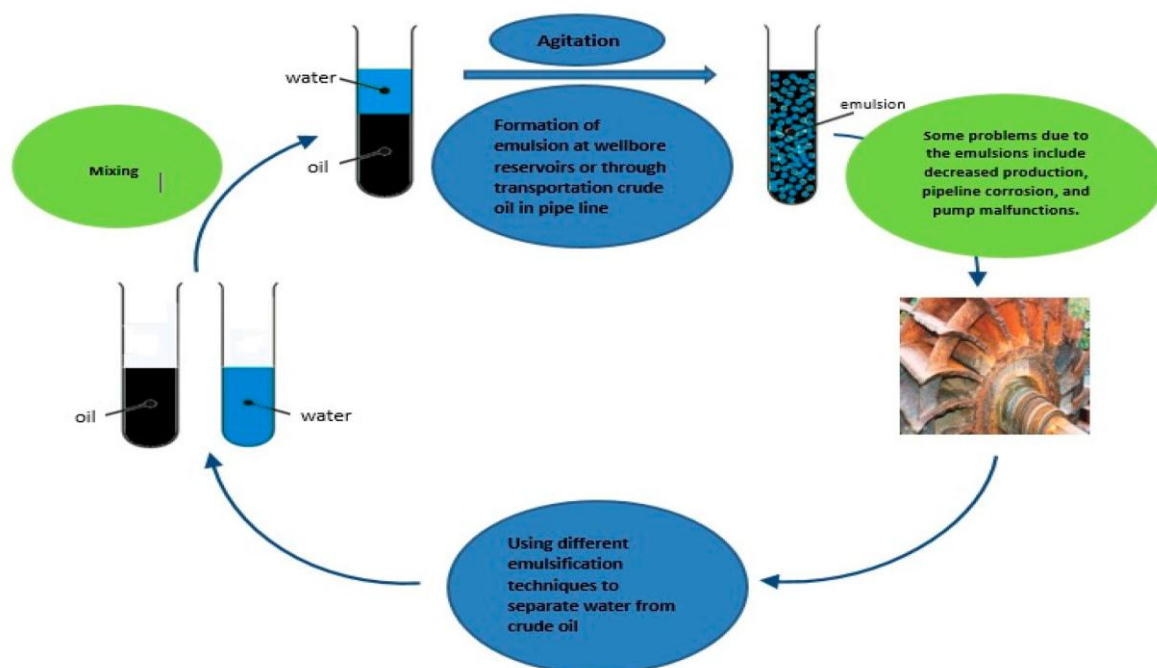


Figure 2.1 cycle of emulsion

Figure 2.1 cycle of emulsion is the complete phase of emulsion formulation to emulsion demulsification.

The most important objective of any oil production facility is the separation of water and other foreign materials from produced crude. Emulsions of oil and water are one of many problems directly associated with the petroleum industry, in both oil-field production and refinery environments (Grace, 1992),

Whether these emulsions are created inadvertently or are unavoidable, as in the oil-field production area, or are deliberately induced, as in refinery desalting operations, the economic necessity to eliminate emulsions or maximize oil-water separation is present. Emulsion problems in crude oil production and transportation requires expensive emulsion separation equipment such as water treaters, separators and coalescers. Hence, chemical demulsification is the most suitable method from both operational and economic point of view to break the crude oil emulsion (Auflem, 2002). Among chemical agents, interfacial-active demulsifiers, which weaken the stabilizing films to enhance droplets coalescence, are preferred due to lower addition rates needed. However, these demulsifiers are costly and pose significant threat to the environment. It becomes imperative to develop cheap and environmentally friendly demulsifiers from locally source raw material.

3.1 Materials

Local Materials A:

- i. Palm oil
- ii. Glyserin
- iii. Lemons
- iv. 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).

Local Materials B:

- i. ALUM
- ii. Castor Oil
- iii. Starch
- iv. Local Soap
- v. Camphor

(i) Imported Materials

Amine group Demulsifiers

3.2.2 Formulation of local demulsifier using local materials

3.2.2.1 Formulation of local demulsifier 'A'

- (a) A measured 45ml of palm oil was heated with 90°C for 25mins

- (b) 12g of KOH along with 20ml distilled water was heated till homogeneous
- (c) The solution of (b) above was added to the solution (a) and stir it with heater for 90°C, 800rpm for 70mins
- (d) 50ml distilled water was added for the last time and stir for more 5mins
- (e) The formulation was observed until it become liquid after 24hrs

This was called local demulsifier 'A' ALPHA

3.2.2.2 Formulation of local demulsifier 'B'

- (a) A prepared 5ml solution of Alum was added to a mixture of 5g of starch and 30ml of liquid soap in a beaker
- (b) A dissolved solution of 10g of camphor in 30ml of castor oil was stirred and heated to achieve homogeneity
- (c) the solution (a) and (b) above was added to each other, stirred and heated for 90mins
- (d) sediments and precipitates settlement will be removed after 24hrs

This was called local demulsifier 'B' BETA

3.2.2.3 Formulation of local demulsifier 'C'

- (a) A mixture of produced local demulsifier 'A' and local demulsifier 'B' was stirred and slightly heated to obtain homogeneity
- (b) It was observed for 72hrs for any change possible.

This was called local demulsifier 'C' MEGA

3.2.3 Application of local demulsifiers and commercially available demulsifier on the crude oil emulsion for water separation.

The local demulsifier formulated and commercially (imported) demulsifier were contacted with the crude oil samples in the different ratio of the crude oil emulsion samples.

- i. Demulsification of crude oil emulsion using local demulsifier 'A'
- ii. Demulsification of crude oil emulsion using local demulsifier 'B'
- iii. Demulsification of crude oil emulsion using commercially available demulsifier (imported)
- iv. Demulsification of crude oil emulsion (crude oil tight emulsion like tar) using the combined local demulsifier 'A' and 'B'

3.2.4 Comparison and validation of the efficiency and effectiveness on the rate of separation of crude oil emulsion by the formulated local demulsifiers and commercially available (imported) demulsifier.

Comparison and validation of the efficiency of temperature, concentration of separation and the time of separation.

- i. Comparison and validation of local demulsifier 'A' with commercially available demulsifier (imported)
- ii. Comparison and validation of local demulsifier 'B' with commercially available demulsifier (imported)
- iii. Comparison and validation of combined local demulsifier 'A' and 'B' with commercially available demulsifier (imported)
- iv. Comparison and validation of local demulsifier 'A' with local demulsifier 'B'

IV. Results and Result discussion

The demulsification results using the three locally formulated demulsifiers (ALPHA, BETA and MEGA) and Commercially Available Demulsifier CAD at a different treatment temperature of room temperature, 30°C to 70°C and at time intervals of 1-10 minutes after heating, are summarized in tables and plots respectively. Before carrying out any analysis, all samples were drained of free water after aging for a week. This allowed the water to settle out by gravity. The Basic Sediment and Water (BS&W) and the API of a sample before and after treatment were determined.

Results

Specific Results:

4.1.1 Demulsification efficiency and effectiveness of locally formulated demulsifiers 'ALPHA', 'BETA', and 'MEGA' respectively on crude oil water emulsion demulsification was determined.

Temperature (30°C), 500RPM

Vol. of demulsifier (ml) ALPHA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.10	0.10	0.15	0.2	0.2
1.0	0.25	0.3	0.3	0.3	0.3
1.5	0.3	0.5	0.9	1.5	2.0
2.0	0.3	0.5	1.0	2.8	3.5
2.5	0.3	0.6	1.10	3.5	5.2
3.0	0.3	0.8	1.15	4.7	5.6

Table 4.1.1 demulsification result on ALPHA at 30°C (500rpm)

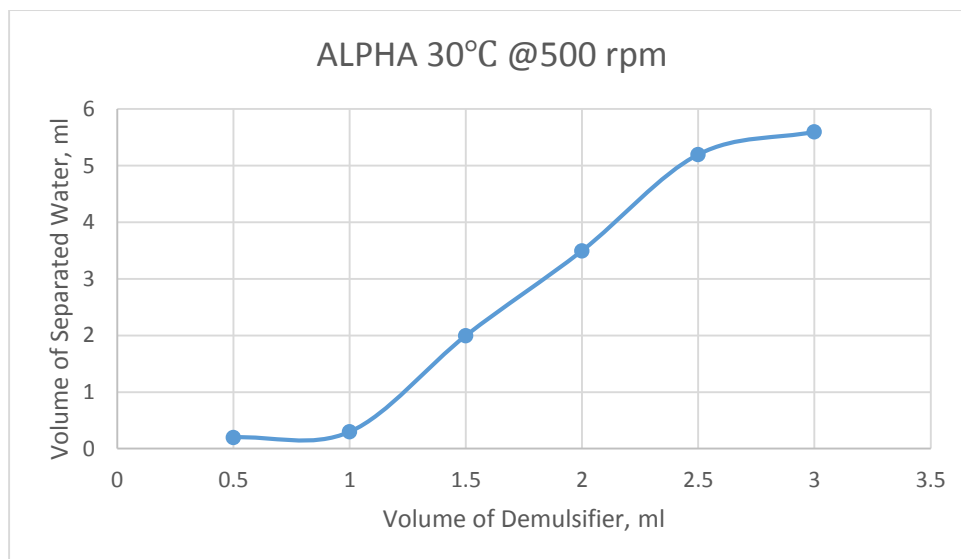


Fig 4.1.1 demulsification result on ALPHA at 30°C (500rpm)

Temperature (30°C), 500RPM

Vol. of demulsifier (ml) LDFii	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.3	0.4	0.4	0.5	0.5
1.0	0.6	0.8	1	1.1	1.1
1.5	0.6	1.0	1.5	1.5	1.5
2.0	1.5	1.5	1.8	1.8	1.8
2.5	1.8	3.0	4.2	4.6	4.6
3.0	2.9	4.2	7	7	7

Table 4.1.7 demulsification result on BETA at 30°C (500rpm)

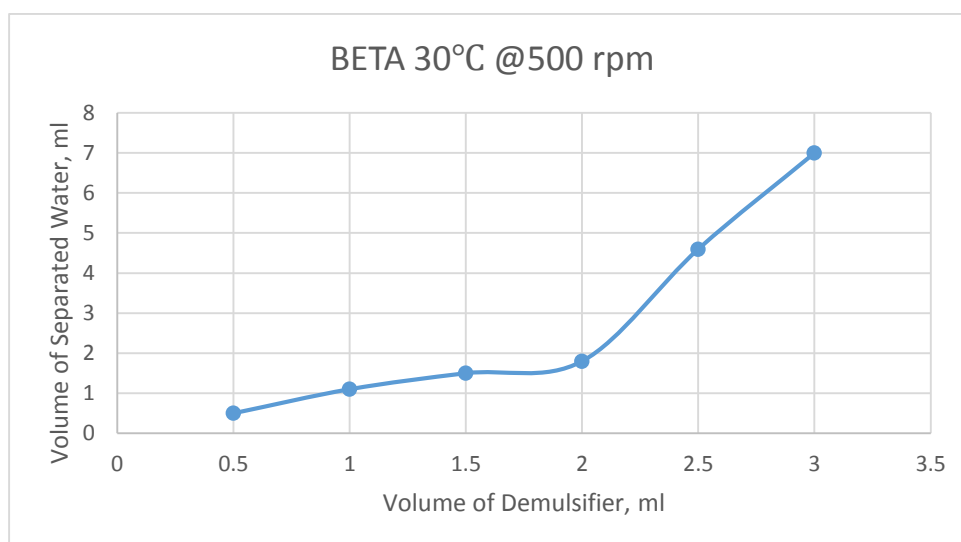


Fig 4.1.7 demulsification result on BETA at 30°C (500rpm)

Temperature (30°C), 500RPM

Vol. of demulsifier (ml) MEGA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.7	0.75	0.8	0.8	0.8
1.0	0.8	0.95	1.2	1.3	1.5
1.5	2.0	2.2	2.4	2.9	3.0
2.0	2.5	2.6	2.9	3.1	3.5
2.5	3.0	3.2	4.0	4.6	5.0
3.0	2.1	3.8	6.5	7	7.2

Table 4.1.13 demulsification result on MEGA at 30°C (500rpm)

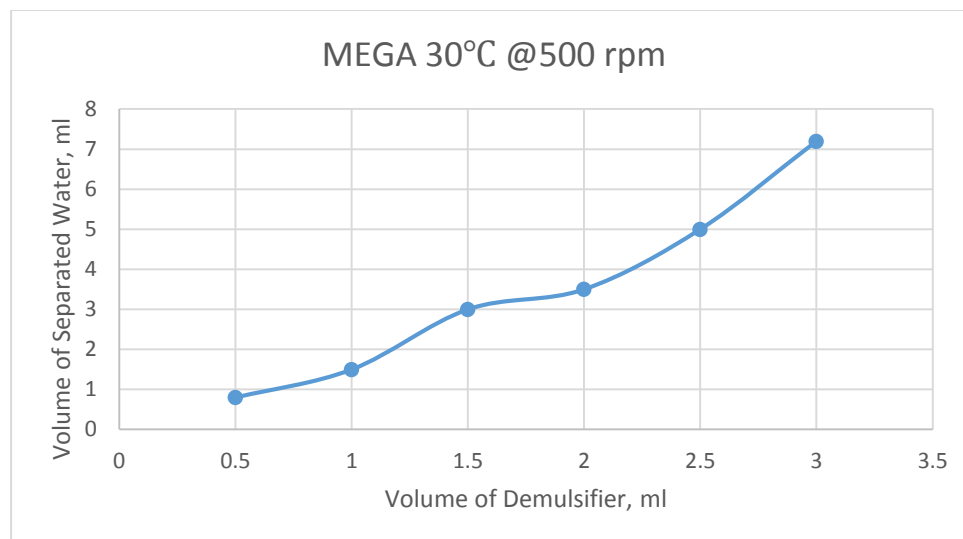


Fig 4.1.13 demulsification result on MEGA at 30°C (500rpm)

Temperature (30°C), 500RPM

Vol. of demulsifier (ml) CAD	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0	0	0	0	0
1.0	0.1	0.2	0.5	0.9	1.4
1.5	0.2	0.5	0.7	1.0	1.5
2.0	2.0	2.2	2.5	2.5	2.5
2.5	2.3	2.5	2.7	2.7	3.0
3.0	3.0	3.1	3.3	3.5	3.5

Table 4.1.2.1 demulsification result on CAD at 30°C (500rpm)

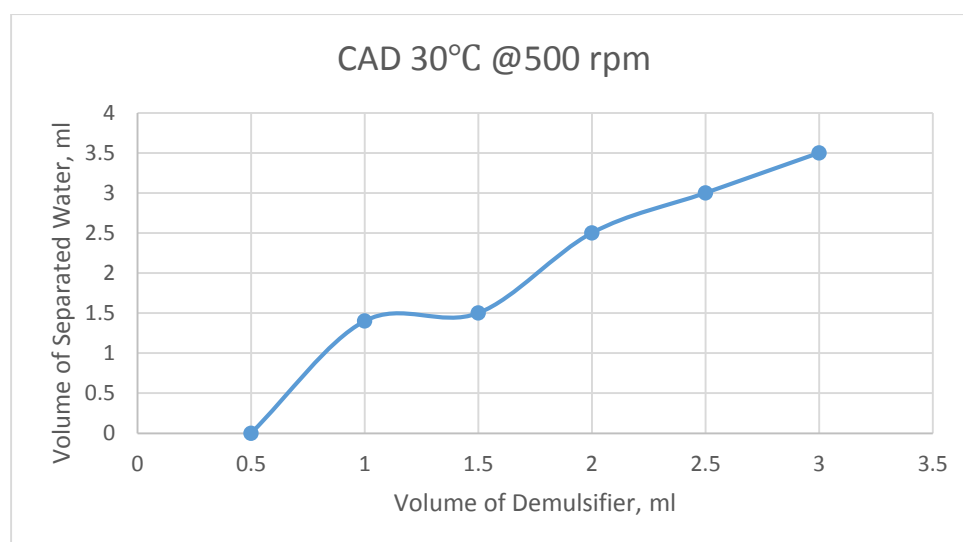


Fig 4.1.2.1 demulsification result on CAD at 30°C (500rpm)

4.1.1 Comparison and validation of water crude oil emulsion rate of separation from local demulsifier 'ALPHA', 'BETA', and 'MEGA' to commercially available demulsifier CAD (imported) Result

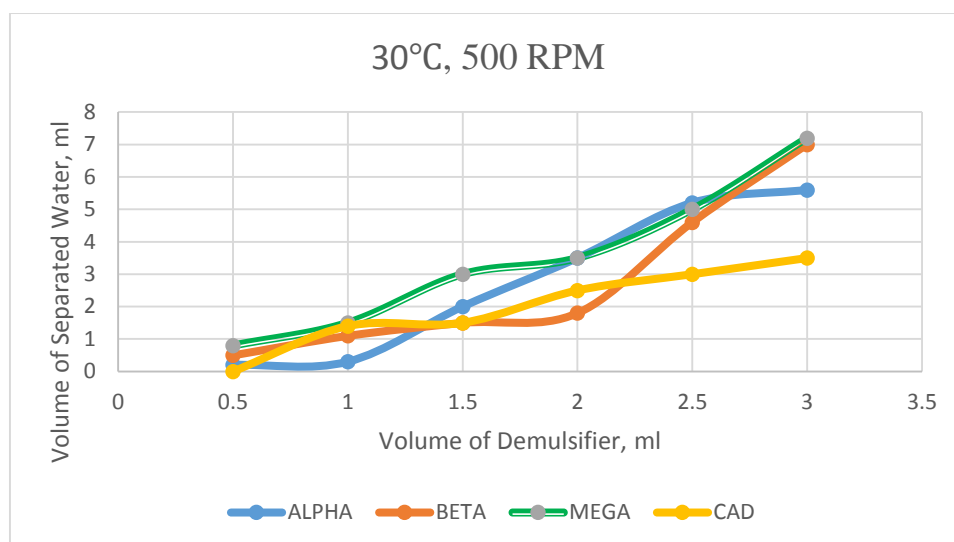


Fig 4.1.3.1 comparison demulsification result on ALPHA, BETA, MEGA & CAD at 30°C (500rpm)

V. Conclusion

The three key factors to work dependently on during crude oil emulsion demulsification are:

1. Concentration of the demulsifier
2. Operating Temperature
3. Settling/Separating Time

In this research, low concentration of the formulated demulsifier from locally sourced raw materials; ALPHA, BETA, and MEGA yielded high rate of demulsification efficiency with a low operating temperature employed in order not to lose the lighter end of the crude. Minimum settling/separating time was used to achieve the required BS&W needed in making a crude oil emulsion (non sellable crude) to sellable crude.

This work was a birth from Nigeria Local content policy thereby a local material was sourced to formulate local demulsifiers for demulsification of crude oil emulsion to enhance crude oil productivity. Three different local demulsifiers ALPHA, BETA, MEGA were formulated and were all tested on crude oil emulsion (tight emulsion) and subjected to range of temperature, 30°C, to 70°C

There was a successful treatment resulted in separation of the oil emulsion sample into oil and water. The separation water volume by the locally formulated demulsifiers ALPHA, BETA, & MEGA were high in different temperature range than that of commercially available imported demulsifier, CAD.

The results clearly demonstrated that cheap local materials with demulsification properties as determined with laboratory characterization can be used to successfully break crude oil emulsions and enhance the quality of the produced crude. The Demulsifiers contained no organic chloride, bromides, iodides, or lead, hence will not cause any refining problems.

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