FORMULATION AND PRODUCTION OF CRUDE OIL DEMULSIFIERS FROM LOCALLY SOURCED MATERIALS

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ABSTRACT

The presence of crude oil emulsions in the production and processing systems is of great concern to the oil industry worldwide. This is because of their huge cost to the oil industry and hence the global economy in terms of the risk of corrosion of export and subsea pipelines and refining equipment, possible catalyst poisoning, increased crude oil pumping costs and other associated problems. However, chemical demulsifiers have been favourably applied in the treatment of these emulsions and most of them are produced overseas and imported. Consequently, in this work,demulsifiers were formulated using locally sourced materials, their effectiveness was ascertained by contacting with five emulsion samples from different Shell pumplines and comparing their water removal abilities with commercially available once. For sample A, CD-Z (local demulsifier) gave at 250 minute, 11 ml compared to 10.5 ml for CD-A (commercial) For sample B CD-Y (local) gave 6ml against 8.5 for CD-C (commercial), for sample C, CD-X gave 20ml against 15.5 for CD-C (commercial) and for sample D, CD-X (local) gave 19ml compared to 16ml for CD-C (commercial). The result shows that these demulsifiers from local materials if properly worked on will not only give good water recovery but also help reduce our dependence on imported ones.

Keywords: Crude oil, water, Emulsion, demulsifiers, local, commercial.

INTRODUCTION

In today's science and technology driven world, the global oil and gas industry is compelled to witness tremendous improvement in the production and treatment of crude oil to meet the ever increasing global demand for fuel and its derivatives without compromising quality and environmental safety. However, during crude oil production and transportation, oil and water are co-produced. The water and oil phases are immiscible but they are exposed to sufficient mixing energy to form dispersions of water droplets in oil i.e. form water –in-oil emulsions. Crude oil emulsions are found in reservoirs, wellbore and wellhead, crude oil storage facilities and during petroleum processing [1]. There are essentially three conditions necessary for emulsion formation: the liquids must be immiscible, sufficient agitation is required to disperse one liquid in the other and there is usually the presence of an emulsifying agent. The energy input for the formation of crude oil emulsion in oil production is provided by vigorous agitation of oil-water mixture at points such as perforations, gas lift mandrels, wellbore valves/chokes, bends along flow line, separators and pumps . In order to meet the desired crude oil market high quality demand, it is necessary to treat crude oil emulsions to remove the water involved in emulsion formation. Failure to properly dehydrate water-in-oil emulsions involves a number of problems including [2] :

- increased cost of pumping
- significant flow line or tubing pressure resulting from high viscosity emulsion.
- high pressure drops created in flow lines

These problems can result potentially in huge economic costs and possible environmental damage. However, the mechanisms and factors governing the emulsion formation process are still not yet fully understood. Crude oil emulsions are thermodynamically unstable. The process of stabilization/destabilization of water–in- oil emulsions is a complex field with great implications for petroleum processing. The destabilization process can be achieved by using one or a combination of the following methods: gravity settling (centrifugation), application of heat, electrical methods and chemical methods involving application of chemical demulsifiers. The hardware involved in the use of settling tanks, cyclones, centrifugal separators and other kinds of mechanical separation tools in the destabilization of crude oil emulsions is considerably voluminous as well as expensive to install on offshore platforms and even on land operation station [3]

Therefore, Chemical destabilization method is consequently a common method for destabilizing emulsions [5]. Thus, the major objective of this study is to produce chemical demulsifiers using locally sourced materials that are environmentally friendly and make a comparative analysis of the produced ones with some commercially available demulsifiers to establish their effectiveness in the destabilization of crude oil emulsions. With reliable information concerning the crude oil and its emulsifying properties, appropriate steps can be taken I n the treatment of crude oil with such chemical demulsifiers to avoid formation of emulsion of enhance thorough management of the formed emulsions [6,7]. It is hoped that this knowledge will lead to the development of more effective and environmentally friendly chemical demulsifiers.

MATERIALS AND METHODS

Experimental material and Equipment

The materials and equipment used are in tables below.

Table 2.1: Experimental material and equipments

Materials/equipment	Comment
Crude oil emulsion samples	Dark brown viscous liquids from Shell Petroleum Development Company, Warri pipelines at Otorogun and Ughelli East.
Demulsifier CD-A	A commercial demulsifier from the Warri refinery.
Camphor	White crystals obtained from local source.
Olive oil	Yellow oil obtained from local source.
Candle wax	White, waxy solid obtained from local source.
Liquid soap	White jelly like liquid obtain from local source.
Starch	White solid cassava starch obtained from local source
Distilled water	Colourless, odourless and tasteless liquid obtained from local source
Polyoxyalkylene copolymers	White powder from Stanley chemicals, Warri, Delta, State.
Benzalkonium chloride	White granules from Stanley chemicals, Warri, Delta, State.
Acetone	Colourless and highly volatile liquid from Stanley chemicals, Warri, Delta, State.
Polyol	Colourless liquid from Stanley chemicals, Warri, Delta, State.

Gas Chromatographer	To check for the presence of Alcohol and Benzene
Weighing Balance	Scout pro, Ohaus, London. For weighing
25ml Measuring cylinders	Simax Kavalier Stanbil. For measuring
Thermometer	Pyrex, England. For measuring temperature
Plastic containers	For storage
Syringe	Axojet syringe set, China. For suction
Magnetic stirrer	Optichem by Chemglass, New Jersey. For heating and mixing
Water bath	Dargatz, China. For indirect heating at constant temperature
Hot plate	Gallenkamp, England. For heating.
Beakers	Pyrex, England. For weighing and storage
Stop watch	For timing.
Oven	For heating at a constant temperature

The functions of the material used in the production are as given in the table 2.2.
Table 2.2: Materials used and their specific function [7,8,9,10]

Materials	Functions
Camphor	This forms the lipophillic end of the demulsifiers from local sources
Olive oil	It acts as a solvent for the camphor and also increases the lipophillic properties of the crude oil.
Candle wax	This served as the bulking agent in the locally sourced demulsifier.
Starch	This forms the hydrophilic end of the locally sourced demulsifier because of its strong affinity for water.
Liquid soap	This served as the binder demulsifier formulation from locally sourced material to bind the lipophillic and the hydrophilic end.
Distilled water	This was used as solvent for the starch solution.
Polyoxyalkylene copolymers	Known chemical demulsifier.
Benzalkonium chloride	Known chemical demulsifier.
Acetone	Served as solvent in the chemical demulsifiers preparation.
Polyol	Served as performance enhancer to demulsifiers.

PRODUCTION OF DEMULSIFIER FROM LOCALLY SOURCED MATERIALS

The production of the demulsifier involved three steps. First, formation of the lipophillic end, then the hydrophilic end, and lastly, the addition of the binder to bind the above two ends. 10g of the solid camphor was measured and poured into a beaker containing 30g olive oil and placed on the magnetic stirrer- heater at a regulated temperature of 40^oC to dissolve the camphor. The olive oil became camphorated. 10g of the candle wax was then added to the hot camphorated olive oil. Next, 4.86g of the starch was weighed and first dissolved in cold water, water was boiled to change it to the jellylike state, the total weight of the starch and water was then taken and it was noted that the total weight of water (hot and cold) required to prepare the 4.86g of starch was 25.14g. The starch and water mixture (30g) was then added to the mixture from the first step. Finally, 20g of the liquid soap was then added to obtain a homogenous blend at a temperature of 40^{o}C for about 60 minutes. The same procedure was used for formulation CD-Y and CD-Z while the olive oil and camphor concentration were varied. Below is a table showing the formulation for the production of demulsifiers using locally sourced materials.

Table2.3: Formulation for demulsifiers from locally sourced materials.

Material	CD-X(g)	CD-Y(g)	CD-Z(g)
Olive oil	30.00	25.00	20.00
Camphor	10.00	15.00	20.00
Candle wax	10.00	10.00	10.00
Starch	4.86	4.86	4.86
Water	25.14	25.14	25.14
Liquid soap	20.00	20.00	20.00
Total	100.00	100.00	100.00

Determination of Alcohol and Benzene Groups in Commercial Demulsifier (CD-A)

The chemical demulsifier sample CD-A was analyzed to confirm the absence of the Alcohol and (or) Benzene groups which were part of the active ingredients for the chemicals used in the enhancing Demulsification process. The alcohol group and benzene tests were performed using the Gas Chromatograph (GS) in Thermosteel Nigeria Ltd, Warri, Delta state. The result clearly indicates the absence of benzene and alcohol.

Preparation of Demulsifiers from Known Active chemicals

20g of the Polyoxyalkylene copolymers was weighed and poured in a beaker containing 80g of Acetone and both were thoroughly mixed to form a homogenous solution. The 20% w/w solution was labelled CD-B. The same process was used for the production of the 30%w/w solution with 30g of the polyoxyalkylene copolymer and also labeled sample CD-C. Acetone was used as the solvent in both cases. 20g of Benzalkonium chloride was weighed and poured into a beaker containing 80g of water to produce the 20%w/w Benzalkonium chloride used and this mixture was labeled CD-D. 30g of Benzalkonium chloride was also weighed and poured into a beaker containing 70g of water to produce the 30%w/w Benzalkonium chloride used and this mixture was labeled CD-E. Water served as the solvent in both cases.

Determination of the Efficiency of the Demulsifiers

The six chemical demulsifiers used are:

1. CD-A (Chemical demulsifier from Warri refinery)
2. CD-B (20% w/w Polyoxyalkylene copolymers)
3. CD-C (30% w/w Polyoxyalkylene copolymers)
4. CD-D (20% w/w Benzalkonium chloride)
5. CD-E (30%w/w Benzalkonium chloride)
6. CD-X (Demulsifier formulated from locally sourced materials)
7. CD-Y (Demulsifier formulated from locally sourced materials)
8. CD-Z (Demulsifier formulated from locally sourced materials)

Test Procedure

The effectiveness of the different chemical demulsifiers was ascertained by contacting them with the crude oil in a ratio 1:50ml. 25ml of the crude oil emulsions sample from Utorogu Flow Station Well 3T (Sample A) was introduced into nine (9) different measuring cylinders. Then, with the aid of a syringe, 0.5ml of each of all the demulsifiers produced was added to eight (8) out of the nine (9) samples and the mixture were thoroughly mixed and left to stand. Nothing was added to the ninth emulsion sample which was labeled as Blank. The initial readings were taken. These mixtures were allowed to stand for 10mins while the amount of water separated was read off and recorded. The process was monitored for one hour at 10 minutes interval then 30 minutes interval for another three hours.

Enhancement of the Demulsifier Performance

Polyol is a known performance enhancer to demulsification process. 0.5ml of polyol was therefore added to each of the mixture to enhance demulsification. After the 240th minute and its effect with respect to time was noted for all samples. These mixtures were allowed to stand for 10mins while the amount of water separated was read off and recorded. The process was monitored for one hour at 10 minutes interval then 30 minutes interval for another two hours.

The above two steps were repeated for the other crude oil samples in the following order.

- Ughelli East Flow Station Well 3S (Sample B)
- Ughelli East Flow Station Well 1T (Sample C)
- Ughelli East Flow Station Well 8T (Sample D)
- Utorogu Flow Station Well 12S (Sample E)

Determination of Effect of Temperature on Demulsification

25ml of blank samples of the five crude oil emulsions were taken in five measuring cylinders and placed in an oven at a regulated temperature of 40^{o}C. These mixtures were allowed to stand for 10mins in the oven while the amount of water recovered was read off and recorded. The process was monitored for one hour at 10 minutes interval then 30 minutes interval for another two hours. Then, 0.5ml of chemical CD-B (the lowest in efficiency amongst all the demulsifiers produced and used at room temperature) was then added to 25ml of all the crude oil emulsions and placed in an oven at 40^{o}C. The rate of demulsification was also taken for the duration of 3 hours at 10minutes interval. Hence, 0.5ml of chemicals CD-Z, CD-C, CD-X and CD-Y (the best in efficiency amongst all the demulsifiers produced and used at room temperature for crude oil emulsion samples A, B, C and D respectively) was then added to 25ml of all the crude oil emulsions and placed in an oven at 40^{o}C. The rate of demulsification was also taken for the duration of 3 hours with 10minutes interval.

RESULT AND DISCUSSION

This section x-rays the experimental outcome of the demulsification of the different crude oil emulsion samples (Otorogun well 3T (A), Ughelli East wells 3S(B), Ughelli East well 1T (C), Ughelli East well 8T (D), Otorogun well 12S (E) using local material based demulsifiers (CD-X, CD-Y, CD-Z) in comparison with other chemical based demulsifiers (CD-A, CD-B, CD-C, CD-D, CD-E). Also, the effect of polyol as a performance enhancer on the demulsifier was examined. Table below gives a summary of the performance results of the demulsifiers in relation to existing and established chemical demulsifiers.

Table 3.1: Summary of performance for selected demulsifiers.

CES	QWR_B	MED	QWR_D	QWR_P	% QWR_P
Sample A	1.00	CD-Z	10.00	15.00	50.00
Sample B	2.00	CD-C	8.50	12.50	47.06
Sample C	4.00	CD-X	19.50	21.00	7.69
Sample D	4.00	CD-X	19.00	21.00	10.53
Sample E	0.00	Nil	0.00	0.00	0.00

QWR_B – Quantity of water Recovered after 180minutes from the blank sample (ml)
MED - Most Efficient Demulsifier
QWR_D - Quantity of Water Recovered with the addition of demulsifier after 180minutes (ml)
QWR_P – Quantity of water Recovered with Polyol addition to demulsifier after 180minutes (ml)
CES - Crude Oil Emulsion Sample

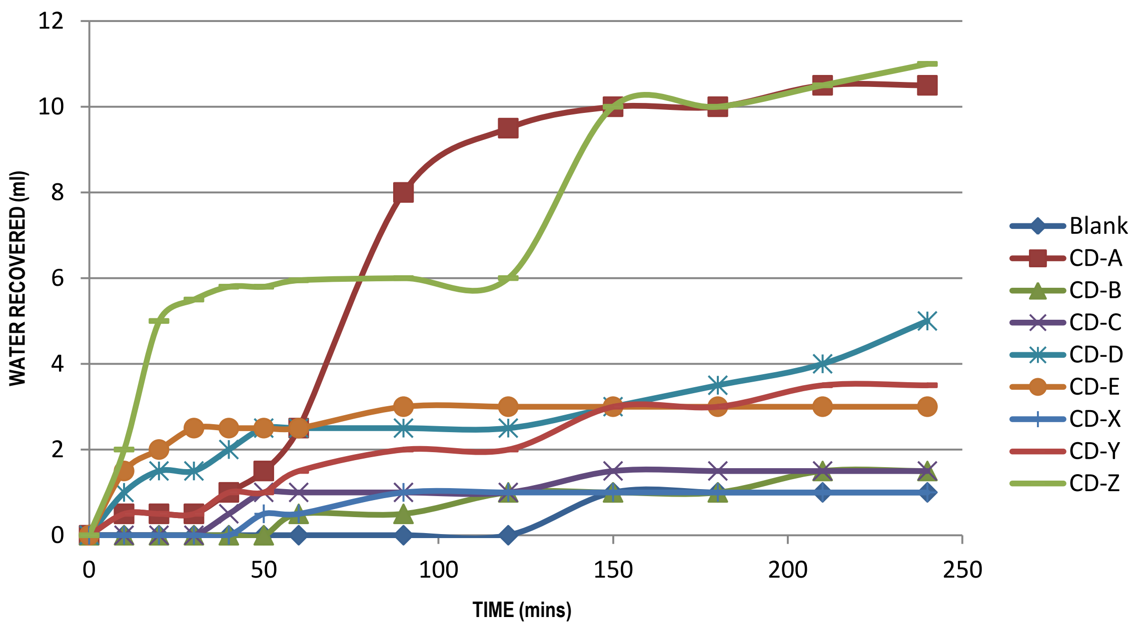

FIGURE 3.1: GRAPH SHOWING AMOUNT OF WATER SEPARATED WITH TIME BY DIFFERENT CHEMICAL DEMULSIFIERS FOR WELL 3T, UTOROGUN FLOW STATION (SAMPLE A)

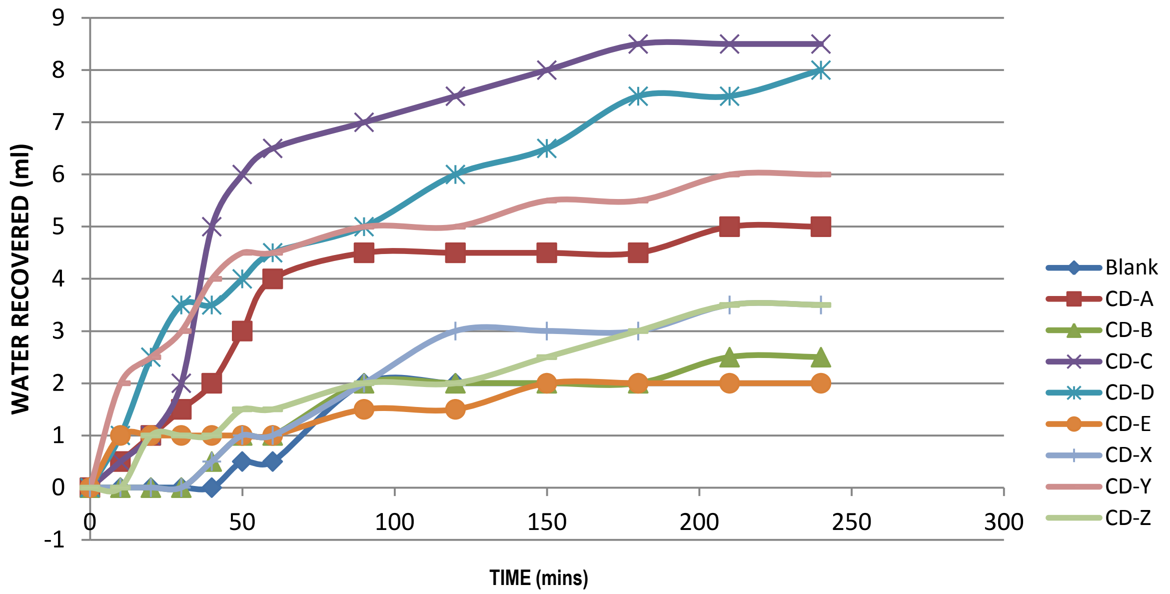

FIGURE 3.2: GRAPH SHOWING AMOUNT OF WATER SEPARATED WITH TIME BY DIFFERENT CHEMICAL DEMULSIFIERS FOR WELL 3S, UGHELLI EAST FLOW STATION (SAMPLE B)

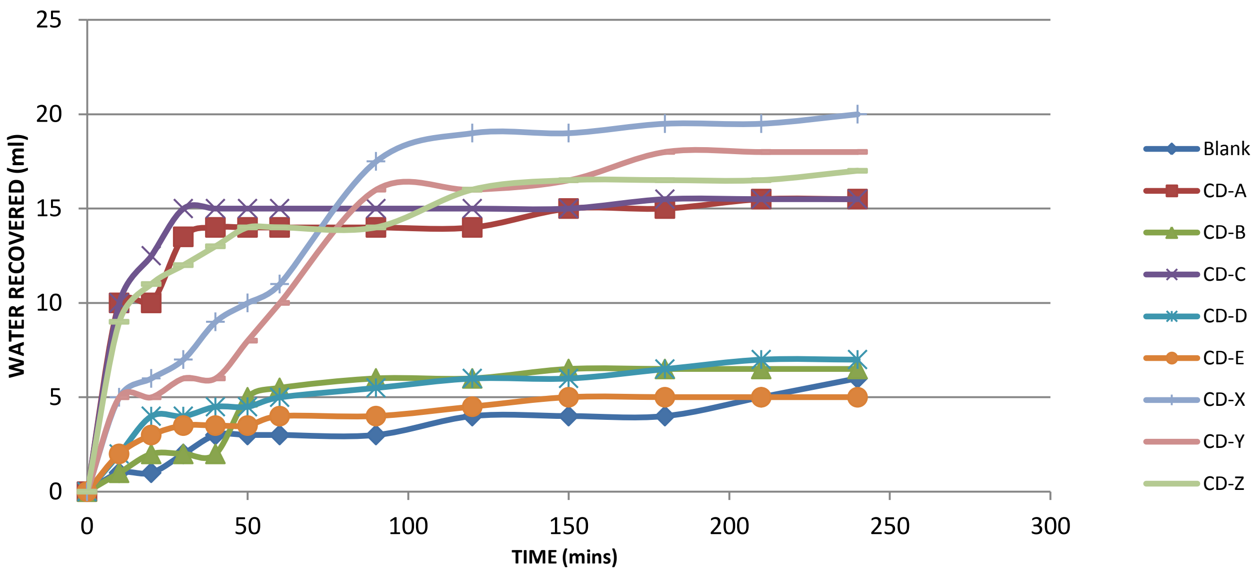

FIGURE 3.3: GRAPH SHOWING AMOUNT OF WATER SEPARATED WITH TIME BY DIFFERENT CHEMICAL DEMULSIFIERS FOR WELL 1T, UGHELLI EAST FLOW STATION (SAMPLE C)

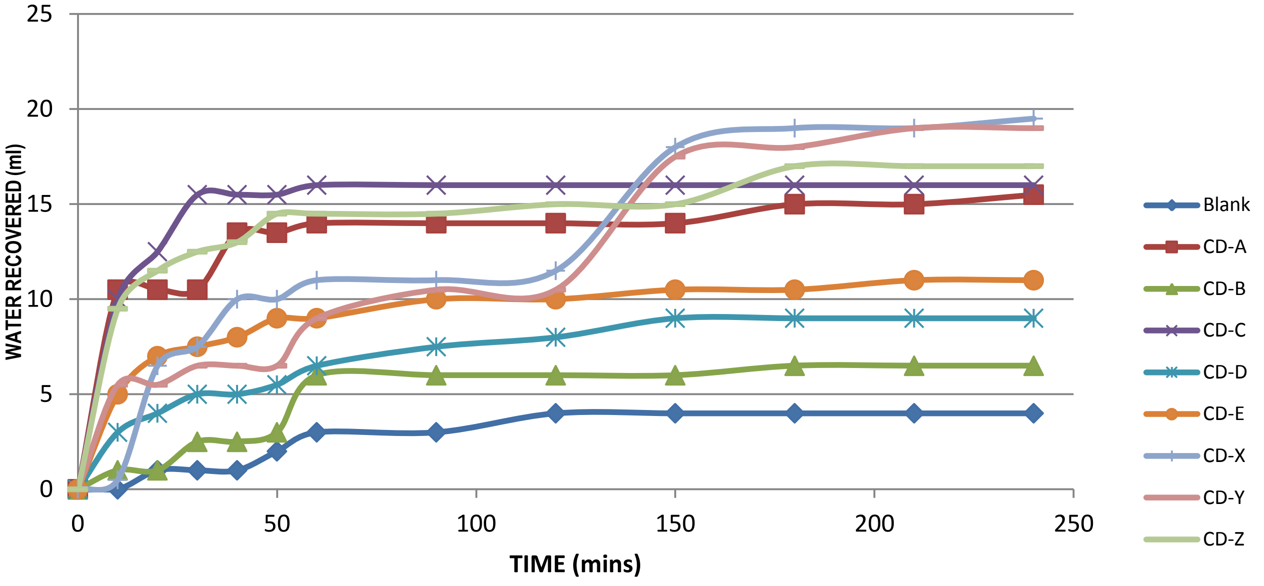

FIGURE 3.4: GRAPH SHOWING AMOUNT OF WATER SEPARATED WITH TIME BY DIFFERENT CHEMICAL DEMULSIFIERS FOR WELL 8T, UGHELLI EAST FLOW STATION (SAMPLE D)

Figure 3.1 shows the performance of the demulsifiers (locally sourced and others) on crude oil emulsion sample A. From the figure, CD-Z (local demulsifier) gave a better result when used on the sample along with other demulsifiers although, CD-A and CD-D also showed remarkable water recovery within the time of analysis. This can be seen from the result as CD-Z gave 6ml within the first 6minutes, remained steady and rose to 10ml after about 150minutes, then 11mlat about 250minutes. While at 250minutes, CD-A and CD-D recovered about 10.5ml and 5ml respectively after 250minutes. For sample B, in figure 3.2, on using all demulsifiers, the performance of the locally sourced material based demulsifiers was also impressive as CD-Y ranked third in the list with CD-C and CD-D producingthe best results in the same order. CD-Y gave 6ml in 250 minutes against 8.5ml and 8ml for CD-C and CD-D respectively. This may have been as a result of the fact that crude oil emulsion properties determine the type of demulsifier to apply for maximum efficiency. While for sample C, the result show remarkable difference from all two considered so far as all the different formulations for the local material based demulsifiers gave better results compared to the others. From the result in figure 3.3, CD-X gave a peak of 20ml of recovered water; CD-Y gave 17.5ml, CD-Z gave 16.5ml at 250minutes while CD-C and CD-A gave 15.5ml each at same time. This performance also is in line with the former showing that demulsifiers from locally sourced materials have the ability to perform as those of known chemical material based or even do better.

In the same vein, analysis on sample D still followed the same pattern as seen before where the local material based demulsifier formulations perform impressively. Figure 3.4 shows CD-X, CD-Y, CD-Z giving 19ml, 18.5ml and 17.0ml respectively compared to 16 and 15.5ml for CD-C and CD-A respectively. This result also confirms the fine performance of the demulsifiers on the emulsion samples.

In the next set of analysis that followed, polyol (an alcohol) was used as a performance enhancer for the demulsifiers. This was to examine how the performance of the demulsifiers could be enhanced for better water recovery.

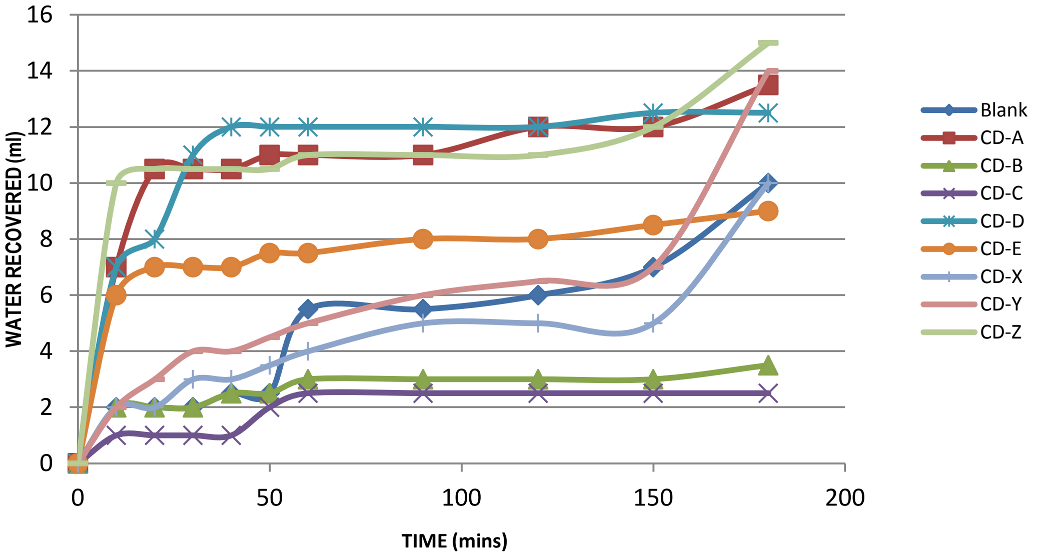

FIGURE 3.5: GRAPH SHOWING AMOUNT OF WATER SEPARATED WITH TIME BY DIFFERENT CHEMICAL DEMULSIFIERS AND POLYOL FOR WELL 3T, UTOROGUN FLOW STATION (SAMPLE A)

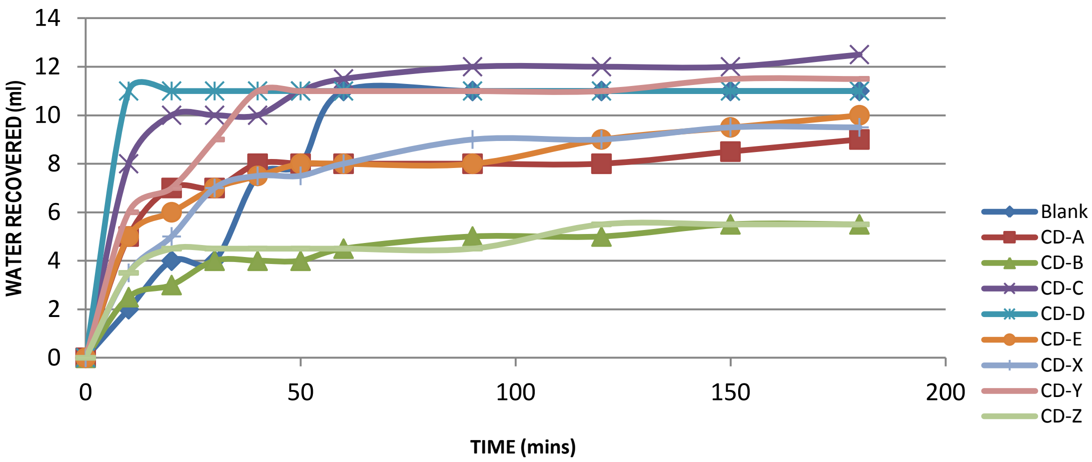

FIGURE 3.6: GRAPH SHOWING AMOUNT OF WATER SEPARATED WITH TIME BY DIFFERENT CHEMICAL DEMULSIFIERS AND POLYOL FOR WELL 3S, UGHELLI EAST FLOW STATION (SAMPLE B)

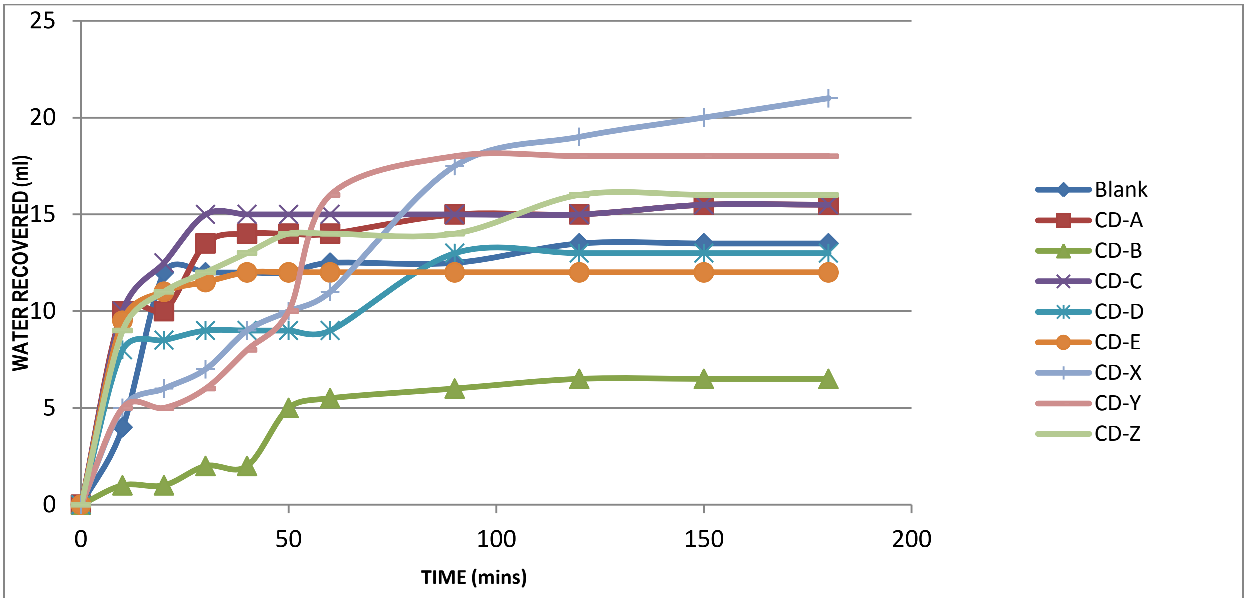

FIGURE 3.7: GRAPH SHOWING AMOUNT OF WATER SEPARATED WITH TIME BY DIFFERENT CHEMICAL DEMULSIFIERS AND POLYOL FOR WELL 1T, UGHELLI EAST FLOW STATION (SAMPLE C)

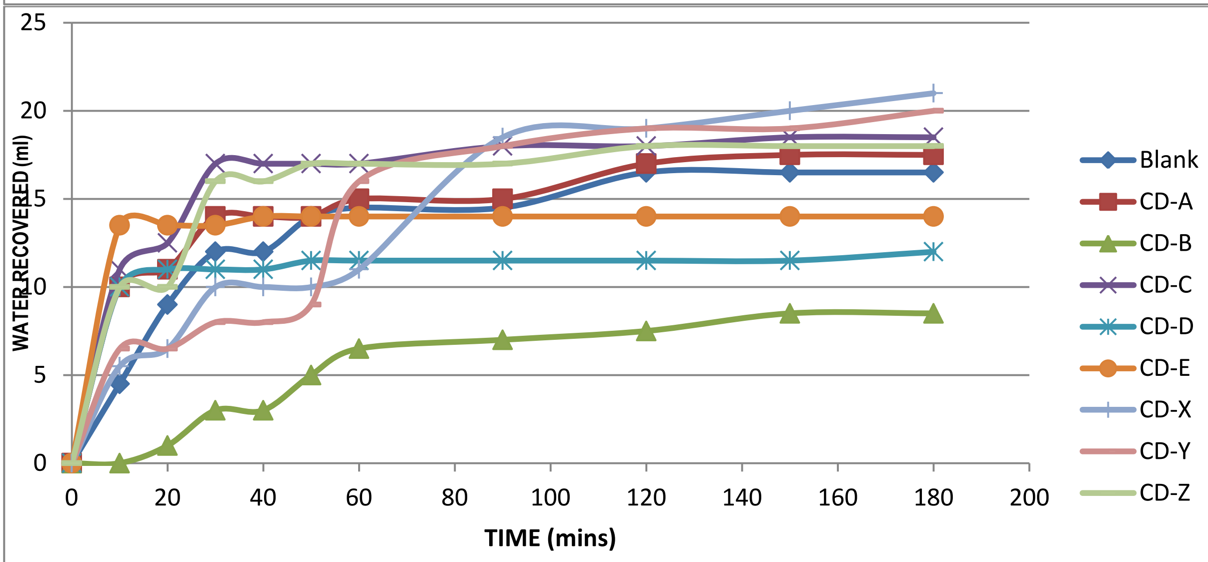

FIGURE 3.8: GRAPH SHOWING AMOUNT OF WATER SEPARATED WITH TIME BY DIFFERENT CHEMICAL DEMULSIFIERS AND POLYOL FOR WELL 8T, UGHELLI EAST FLOW STATION (SAMPLE D)

From figure 3.5 above, the positive effect of the addition of polyol was confirmed here as quantity of water that was recovered upon addition of the polyol increased from 10.00ml to 15.00ml for time duration of 180minutes using CD-Z, while in figure 3.6 amount of water recovered increased to 12.5ml for CD-C as against 8.5ml without the enhancer, and in figure 3.7 with the introduction of polyol, the amount of water increased to 21.0ml. Finally, in figure 3.8, we observe that at a time of 180 minutes, the quantity of water recovered also increased to 21.0ml against the 19.0ml without polyol for the CD-X demulsifier sample. This suggests that polyol, an alcohol can be used in the performance enhancement of demulsifiers including those from locally sourced materials.

CONCLUSIONS

The presence of crude oil emulsion is a common feature in oil production and processing around the world. This investigation involved the study of crude oil emulsions from four different fields using demulsifier produced from locally sourced materials and then compared their efficiency with commercially established ones. Also, the effect of poly (an alcohol) on the performance of the demulsifiers was studied.

A number of conclusions are apparent from the study:

1. Demusifiers can be formulated using locally sourced materials instead of exclusive dependence on high profile chemicals which are expensive and imported.
2. Demulsifiers from these locally sourced materials can perform excellently well in crude oil demulsification (water removal)
3. That crude oil demulsfier ability is field dependent. Thus, demulsification analysis can be performed on the crude oil sample to be demulsified to determine the demulsifier that will be best for it and to optimise water recovery.
4. Those alcohols have the ability to influence demulsifier's water recovery ability.
5. Finally, since we can access local materials with lipophillic and hydrophilic abilities, more work is needed to be carried out to determine their compatibility as demulsifiers thus reducing the dependence on imported chemicals to run our system.

REFERENCES

Mervin F Fingas and Ben Fieldhouse, "What causes the formation of water in oil emulsions", Emergecy science division, Environmental Technology centre, Environmental centre Canada, 3439 River road, Ottawa, Ontario KIA OH3 Canada. Page 1.

HTS Consultants, (2004): "Demulsification" in *Oilfield Production Chemicals and Microbiology* pp 1 – 20 Petroleum Extension Service (PES) (1974) Industrial and Business Training Bureau Division of Extension The University of Texas at Austin *"Treating Oil Field Emulsions"* (3rd Edition) pp 1-10

Petroleum Extension Service (PES) (1974) Industrial and Business Training Bureau Division of Extension The University of Texas at Austin *"Treating Oil Field Emulsions"* (3rd Edition) pp 1-10

Petroleum Extension service "Treating Oil Field Emulsion" 4th edition, Austin Texas, 1990, pages 7-9.

Sunil Kokal, Saudi Aramco, "Crude oil emulsions, a state of art review", SPE Annual technical conference and exhibition, 29th September- 2nd October 2002, San Anthonio, Texas. Pages 2-3

Schramm, L.L. (Ed.), Emulsions: Fundamentals and Applications in the Petroleum industry, Adv. Chem. Ser. 231, ACS, Washington DC (1992). page 1

Rev. O. M. Okorie "Formulation of crude oil emulsion emulsifier from Nigerian Materials" Petroleum Training journal, vol. 4 No. 2. July 2007, Page 69

Mann JC, Hobbs JB, Banthorpe DV, Harborne JB (1994). Natural products: their chemistry and biological significance. Harlow, Essex, England: Longman Scientific & Technical. pp. 309–11. ISBN 0-582-06009-5

International Olive Oil Council. "The Olive Tree, The Origin and Expansion of the Olive Tree".http://www.internationaloliveoil.org/web/aa-ingles/oliveWorld/olivo.html. Retrieved on 2008-07-04

http:/www.search.com/benzlakonium chloride. "Benzalkonium Chloride", accessed on 19th of July 2009

Hayward Walker, A., Ducey, D.L. Gould, J.A. and Nordvik, A. "Formation and Breaking of Water in -in-Oil Emulsions" Workshop Proceedings. Marine Spill Response Corporation, Washington DC. MSRC Technical Report Series 93-018. Nov 1997. Pages 1-2.

H. Vernon, S and Kenneth, E. A. "Crude oil emulsions, Petroleum Engineering handbook, Society of Petroleum Engineers Richardson, Texas, U. S. A.

Francis A. Carey, "Organic Chemistry" 5th edition, 2003 published by McGraw Hill. University of Virginia. Pages 269, 846, 868.

Dr. Sanyi Wang- baker petrolite, "short course in oil field chemistry- chemistry of demulsification" May 26, 2008, Westin hotel, Edmonton, USA. Pages 5.