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Desalting of Crude Oil Using Locally Manufactured Ghanaian Alcoholic Beverage (Akpeteshie) as Demulsifier

Ben Asante[1], Isaac Joseph Cobbinah[2], Yaw Ankomah[3], Solomon Adjei Marfo[4], James Ransford Dankwah[5]

[1]*(Minerals Engineering Department/ University of Mines and Technology, Tarkwa, Ghana)*
[1]*(Electrical and Electronics Engineering Department/ Ghana Communication Technology University, Takoradi Campus, Ghana)*
[2]*(Minerals Engineering Department/ University of Mines and Technology, Tarkwa, Ghana)*
[3]*(Minerals Engineering Department/ University of Mines and Technology, Tarkwa, Ghana)*
[4]*(Chemical and Petrochemical Engineering Department/ University of Mines and Technology, Tarkwa, Ghana)*
[5]*(Minerals Engineering Department/ University of Mines and Technology, Tarkwa, Ghana)*

Abstract:
Background: *Salt in crude oil during refining processes causes problems such as corrosion, fouling of catalysts, etc. Refineries use diverse demulsification methods that are relatively expensive. Sometimes the desalting methods employed by some crude oil refiners have uncertain efficiencies. Because of that, this paper presents economically advantageous and efficient method to demulsify crude oils.*
Materials and Methods*: In this research, the Ghanaian locally manufactured alcoholic beverage (Akpeteshie) was used as a demuslsifier to desalt crude oils. To prepare spilled crude oil, some of the crude was poured into some seawater. The mixture wasleft to sit for two days before the crude was cleaned from the seawater. For desalting, the crude was heated to 110 ^{o}C and hydrolyzed. The mixture was stirred for 4 minutes for emulsification and the breaking of the salt into various ions. The mixture was left to stand for some hours for complete separation before the crude was cleaned from the water. One hundred milliliters of Akpeteshie was added to the spilled crude oil. Then the mixture was shaken for 2 minutes and left to sit for 10 minutes for demulsification. Different volumes of Akpeteshie were used following the same procedure.*
Results*: The electrometric salt testing method using Salt in Crude Analyser showed 89 g/m^3 of salt in the spilled crude oil before desalting. After desalting, testing showed 32.8 g/m^3 of salt left in the crude, which translated, to about 63.15 % salt reduction. The salt test of the unspilled crude oil before and after desalting showed 13.2 g/m^3 and 9.6 g/m^3 respectively. The highest percent reduction of salt in the raw unspilled and desalted unspilled crude oils showed 27.27 % difference.*
Conclusion*: The desalting procedure using Akpeteshie as a demulsifier reduced the contents of salt in the crude oils significantly. The increment of the Akpeteshie in a fixed quantity of crude oil reduced the salt content in the crude consistently. Moreover, prices survey of methanol, popularly used for demulsification by most refineries and Akpeteshie showed that the price of methanol is relatively expensive than Akpeteshie. Hence, Akpeteshie is recommended to refineries for desalting.*
Key Word: *Demulsifier, Akpeteshie, Alcohol, Crude Oil, Desalting*

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I. Introduction

Removal of salts from crude oil before embarking on distillation is an essential step in the crude oil refining industries. This step in the refinery process among other things prevents the corrosion of the downstream refinery equipment such as heat exchangers, fractionators, pipelines, etc., and the fouling of the catalysts (Fajobi *et al*., 2019; Pereira et al., 2015). The desalting of the crude oil saves the manufacturers great amount of money, which otherwise could have been used in repairing the equipment or replacing the equipment and the catalysts (Friedman, 2022; Farzad, 2014; Al-Moubaraki and Obot, 2021). Furthermore, the presence of salts in the crude oil during distillation process causes problems such as decreasing the throughput and increasing plugging, scaling, coking and fouling of heat exchanger and furnace tubes (Esser, 2020; Ibrahim, 2012). Among the major impurities found in the crude oils when received from offshore are salts. Undoubtedly, salts are naturally found in the crude oil when it is drilled (Shah and Przyborowski, 2022) Nevertheless, when crude oil spills into the sea, it picks up additional salts and other impurities such as sulfur and traces of metals, namely, vanadium, nickel, copper, cadmium, lead, arsenic, and others from the sea. The contents of salt in the crude oil received at petroleum refineries range from pounds of salt per thousand barrels of oil(PTB) of 10 to 300 (34 to 1,020 ppm by weight), based on spot samples of many different crude oils delivered to refineries (Abdel-Aal and Aggour, 2003). However, the salt content in crude oil must be lowered to an average of 10 kg/1000 m^3 (3.5 PTP) (Anon, 2010). Researchers have come up with various methods to eliminate this impurity from the crude oil (Abdel-Aal *et al.*, 2018; Nasehi, 2018; Hasan, 2020). Tables 1 and 2 provide the range and the average salt content of crude oil obtained from various locations. The inorganic salts in the crude can decompose in the crude oil pre-heat exchangers and heaters thereby enabling hydrogen chloride gas formation. Then the gas condenses to hydrochloric acid at the overhead system of the distillation column. This may cause corrosion of the equipment. Salt in the crude oil can lead to great undesirable operational problems (Shah and Przyborowski, 2021). However, using corrosion control can assist to avoid corrosion. The byproduct from the corrosion of oil field equipment consists of particulate iron sulfide and oxide. Precipitation of these materials can causeplugging of heat exchanger trains, tower trays, heater tubes, etc. (Trahan, 2010). Moreover, these materials can cause corrosion to any surface on which they are precipitated. Furthermore, if the salt in the crude oil is not desalted before sending it into the fractionating column, it may cause more corrosion in the exchangers, fractionators, pipelines, etc. Desalting can reduce erosion by solids in the control valves, exchanger, furnace, pumps, and save oil from slops of wasted oil (Anon., 2022; Seta, 2019)

Table 1 Properties of Crude Oils Shipped to Refineries

Property	Range	Average
Water in crude, % by volume of crude	0.1 – 2.0	0.3 – 0.5
Salt content in crude, PTB	10 – 250	--
Salt concentration in brine, wt. %	0.4 – 25	--
Salt concentration in brine, ppm	4000 – 250 000	--

Source: (Adel-Aal *et al*., 2016)

Table 2 Average Values for the PTB for some Typical Crude Oils

Source of Oil	Average salt content (PTB)
Middle East	8
Venezuela	11
United States	
Pennsylvania	1
Wyoming	5
East Texas	28
Golf Coast	35
Oklahoma and Kansas	78
West Texas	261
Canada	200

Source: (Adel-Aal *et al*., 2016)

Mohammed (2016) determined the salts (as chloride) in crude oil, diesel, kerosene, and gasoline and turbine oil. Kotona *et al*., (2021) used ASTM D3230, D4929 as standard methods, XRF as alternative technique, and Neutron Activation Analysis as a reference method. Fortuny (2008) conducted analysis of salt content using the classical Mohr's method of titration procedure. (The researchers observed no differences ($p < 0.5$) when comparing the results from the Digital Image-Based (DIB) method with the reference values (The Least Square Support Vector Machine (LSSVM) was used to determine the salt content in a crude oil. (Kamari *et al*., 2015; Holkem, 2021). Electrostatic desalting involves heating the crude oil and passing it through the electrostatic field for demulsification. The creation of emulsion using electrostatic field assists in the desalting process (Wauquier, 2000). The process of desalting crude oil involves emulsification and demulsification. The demulsification step entails using material that is economically advantageous and can perform the task effectively.So far, none of the methods of desalting reviewed involves the use of the locally manufactured Ghanaian alcoholic beverage (Akpketeshie) in the demulsification step. Ethanol, methanol, and other types of alcohol have been used in demulsification of crude/brine mixture by researchers. However, these types of alcohols are not economically advantageous because they are more expensive than Akpeteshie (Igwilo et al., 2017; Atta, 2013; Hajivand and Vaziri, 2013; Nour et al., 2007). Seawater constitutes 96.5 % water, 2.5 % salt, the rest being substances, and the most abundant ions found in it are chloride, sulfate, magnesium, calcium, and potassium (Byme, 2022; Phull, 2010; Ballard, 2021; Chen, 2022; Raj, 2017; William, 2022). Crude oil spilled into the sea emulsifies with the seawater that is known to contain salt as reported by the Transportation Research Board and Research Council of the USA in 2003. Because of that, cleaning the crude oil draws some seawater with it. In this case, much more money will be needed to desalt the crude oil. Figure 1 shows a typical crude oil process flow diagram having double stage desalters.

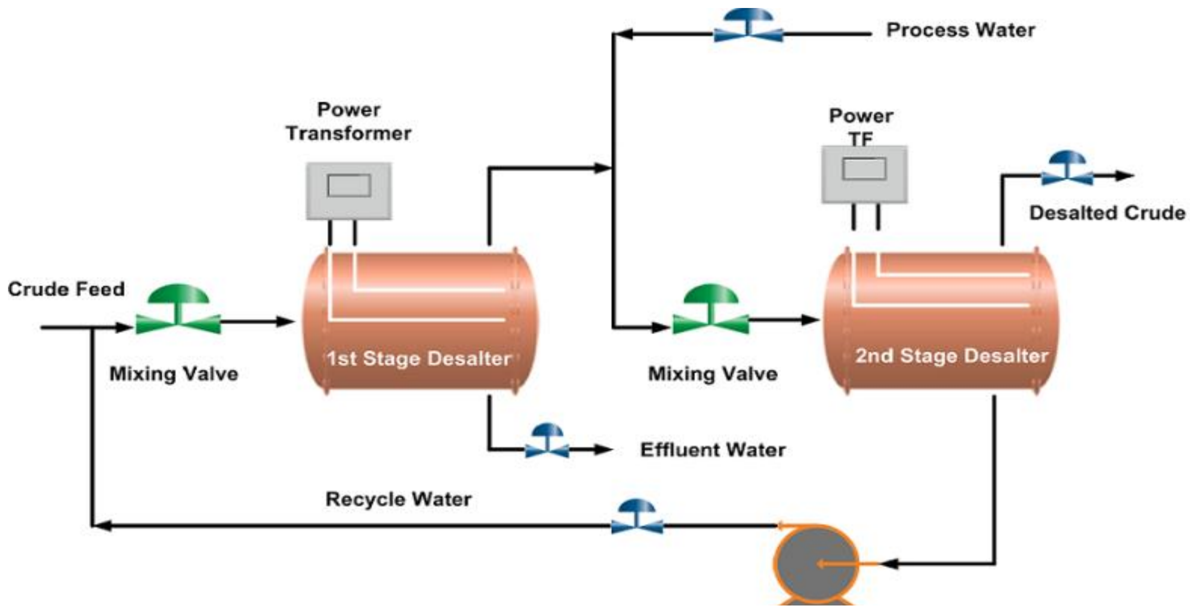

Fig. 1 Double Stage Crude Oil Desalter
Source: (Hussain, 2021)

II. Material And Methods

Before embarking on the desalting of the crude oil, it was necessary to prepare the sample to mimic spilled crude oil. After the sample preparation, a test was done to determine the salt content of it. The following is the procedure employed: Crude oil was pouredinto seawater fetched from New Amanfrom beach, a suburb of Takoradi in the Western region of Ghana. The mixture of the seawater and the crude oil was allowed to sit for two days. The crude oil was cleaned from the surface of the seawater using a foam. Then the electrometric method was used to determine the salt content of the cleaned crude oil. In the commencement of the procedure, fifteen milliliters of xylene was added into the dry 100-mL graduated glass-stoppered mixing cylinder. Then, a 10-mL pipette was used to deliver 10 mL of crude oil sample into the 100-mL graduated, glass-stoppered cylinder. The 10-mL pipette was rinsed using xylene until it was completely free of oil. Then, the mixture in the 100-mL glass-stoppered graduated cylinder was diluted to 50 mL with xylene. After that, the 100-mL glass-stoppered cylinder was stoppered and shaken vigorously for approximately 60 s. Then, the mixture in the glass-stoppered graduated cylinder was diluted again to 100 mL with mixed alcohol solvent. The mixture was then shaken for approximately 30 s and allowed to stand for about 5 min. The 100-mL beaker was placed into the beaker holder before the sample was poured into the beaker until it was leveled the top of the beaker holder. Then, the sensor assembly shown in set up of Fig. 3 was lifted from the sensor assembly holder and placed into the top of the beaker. It was ensured that the plates of the sensor assembly was covered by the sample.Recordings of the salt concentration were made after the upper display was stabilize. The concise method of salt in the crude oil determination process is presented in Fig. 2 below.

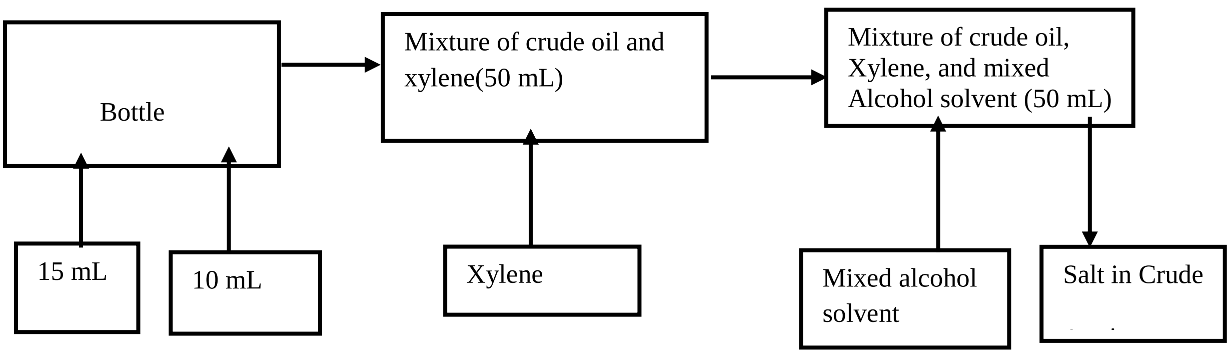

Fig. 2 Block Diagram of the Electrometric Method of Salt Determination

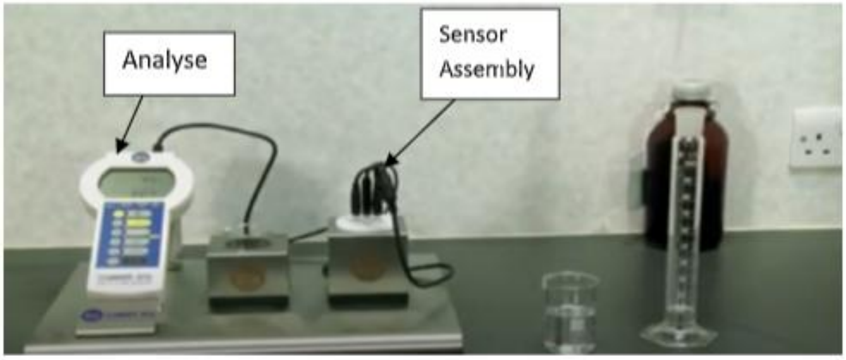

Fig. 3 Set-up of Salt in Crude Analyser

Procedure methodology

The crude oil used in this research was obtained from the Tema Oil Refinery (TOR). The crude was medium dark sour compound having a density of 900.8 kg/m^3. The American Petroleum Institute (API) index of the crude oil was about 25.47^o. The API was calculated using the following equation:

API = 141.4/ (Specific gravity) -131.5 (1)

Like all other crude oils, this contained paraffins, aromatics, naphthenes, and other impurities such as sulphur, nitrogen, salts, mud, nickel, vanadium, iron, oxygen. The average composition of the crude was approximately 84 % carbon, 14 % hydrogen, 1-3 % Sulphur, 1 % nitrogen, 1 % oxygen, 0.1 % minerals and salts (Burruss and Ryder, 2000; Rullkoter and Farrington, 2021; Husen, 2018; Lord, 2014) Before embarking on the desalting process, the raw crude oil was tested for its salt content. The raw crude was subjected to the desalting process as detailed in Fig. 4. The crudewas pouredinto some of the seawater and allowed to sit for two days. After that, it was cleaned from the seawater using a foam. The electrometric method using Salt in Crude analyser was used to determine the salt content of the cleaned crude oil. The salt content in the spilled crude oil was determined to be 89 g/m^3. The crude oil was heated to 110 ^oC and hydrolyzed. Then the mixture was stirred vigorously for about 4 minutes for emulsification and the breaking of the salt into the various ions. The mixture was allowed to stand for about 2.5 hours for complete separation of the water and the crude. Then the crude was cleaned from the surface of the water and poured into the 1.5 L bottle. One hundred milliliters of Akpeteshie was measured and poured into the 1.5 L bottle containing the removed spilled crude oil. The mixture of the crude oil and the Akpeteshie in the bottle was shaken for 2 minutes for mixing. Then the mixture of the Akpeteshie and the crude oil were left to sit for 10 minutes for demulsification. The desalted crude oil was tested for the level of salt using the Salt in Crude Analyser. This process was repeated using 80 mL, 60 mL, 40 mL, and 20 mL of Akpeteshie. Figure 4 shows the flowchart in a concise manner. The following reactions occur when the hot water was added to the salts in crude oil:

$CaCl_2$+ $2H_2O$ = $Ca(OH)_2$ +HCl (2); KCl + H_2O = HCl + KOH (3);NaCl + H_2O = NaOH + HCl (4);
$MgCl_2$ + $2H_2O$ = $Mg(OH)_2$ + 2HCl (5)

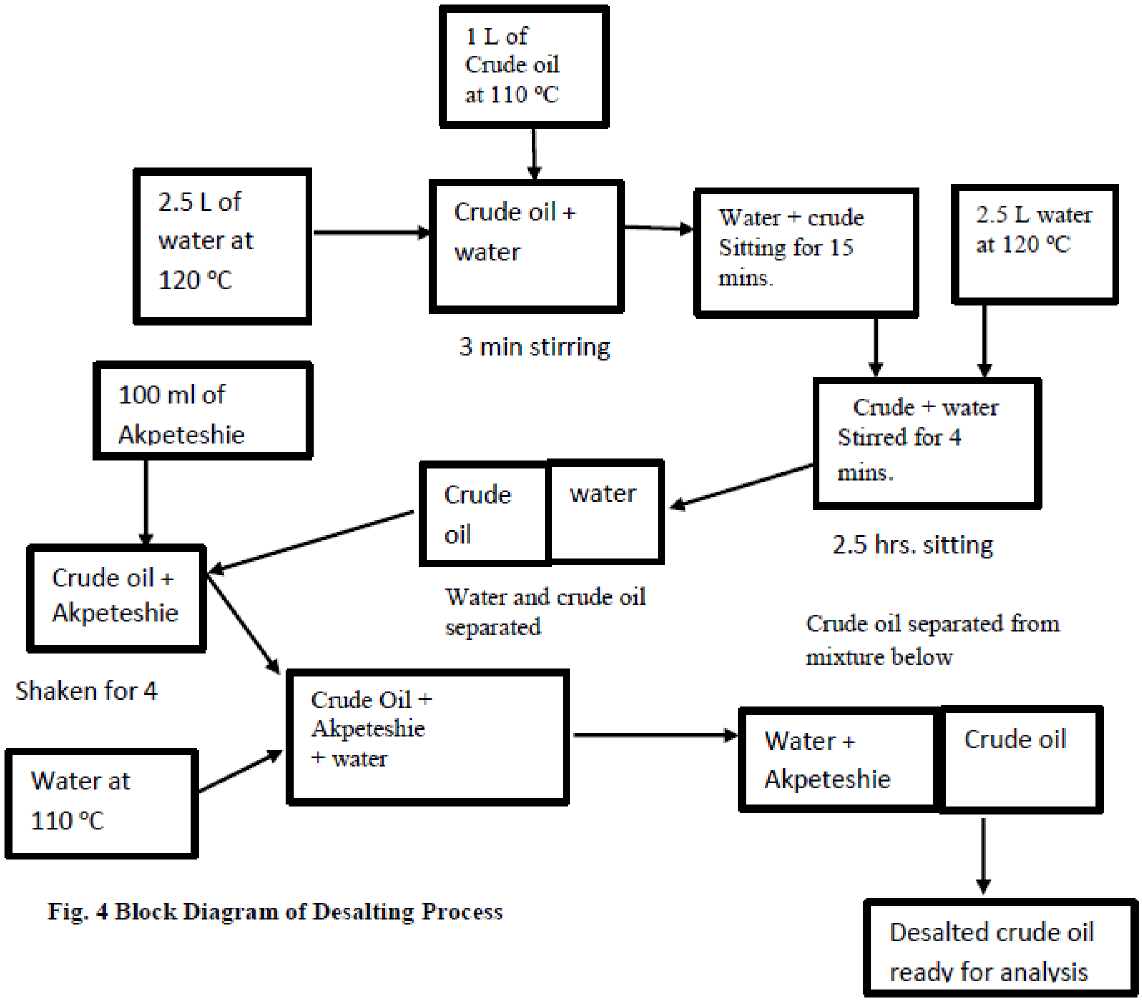

Fig. 4 Block Diagram of Desalting Process

III. Result

This section provides the result obtained from the experiments conducted. Table 3 below presents the summary of the results obtained from testing the salt contents in the crude oils before embarking on the desalting process. Finding the salt contents in the crude oils before desalting assisted the researcher to know how much salt was removed from the crude after desalting so that the effectiveness of the desalting method chosen could be assessed

Table 3: Tests Results of Salt Content in the Spilled and Unspilled Crude Oils before Desalting

Type of crude oil	Density (g/cm3)	Salt content (g/m3)	Salt content (mg/kg)
Spilled	0.9008	89	98.8
Raw crude oil (Unspilled)	0.8719	13.2	15.14

Table 4 and Table 5 show the salt contents found in the various mixtures of the crude oils and Akpeteshies after desalting. The values show that the same quantity of both the spilled and the unspilled crude oils combined with higher amount of Akpeteshie as a demulsifier desalted the crude oil better than the combination of lower amount of Akpeteshie

Table 4: Percent Difference betweenInitial Salt Content (13.2 g/m^3) in Spilled Crude Oil and the Desalted Spilled Crude Oils

Volume of Akpeteshie (mL)	Desalted Spilled crude oil salt content (g/m^3)	Percent (%) Decrease
100	32.8	63.15
80	35.5	60.11
60	39.25	55.90
40	40.2	54.83
20	51.5	42.13

Table 5: TestsResults of Salt Content in the Spilled and UnspilledCrudeOils after Desalting using Different Volumes of Akpeteshie for Demulsification

Volume of Akpeteshie (mL)	Spilled crude oil salt content (g/m^3)	Raw (Unspilled) crude oil salt contents (g/m^3)
100	32.8	9.6
80	35.5	10.1
60	39.25	10.9
40	40.2	11.5
20	51.5	12.3

Table 6 shows the smallest amount of salt found in the desalted crude oils. Table 7 provides the percentage difference computed using the salt found in the original unspilled crude oil 89 g/m^{3}and the salt found in the crude oils after desalting.

Table 6: Tests Results of the Lowest Salt Contents in Desalted Crude Oils

Type of crude oil	Density (g/cm^3)	Salt content (g/m^3)	Salt content (mg/kg)
Spilled	0.9321	32.8	35.19
Raw crude oil (Unspilled)	0.9408	9.6	10.20

Table 7:Percentage Differenceof Salt Content Between the Original Unspilled (89 g/m^3) and Desalting Unspilled Crude oils

Volume of Akpeteshie (mL)	Raw crude oil salt content (g/m^3)	Percent (%) Decrease
100	9.6	27.27
80	10.1	23.48
60	10.9	17.42
40	11.5	12.88
20	12.3	6.82

Figures5 and 6 show the graphs of the relationship between different volumes of Akpeteshie and the amount of salt left in the crude oils after desalting. The abscissa is the volumes of the Akpeteshie and the ordinate is the quantity of salt left in the crude oils after desalting.

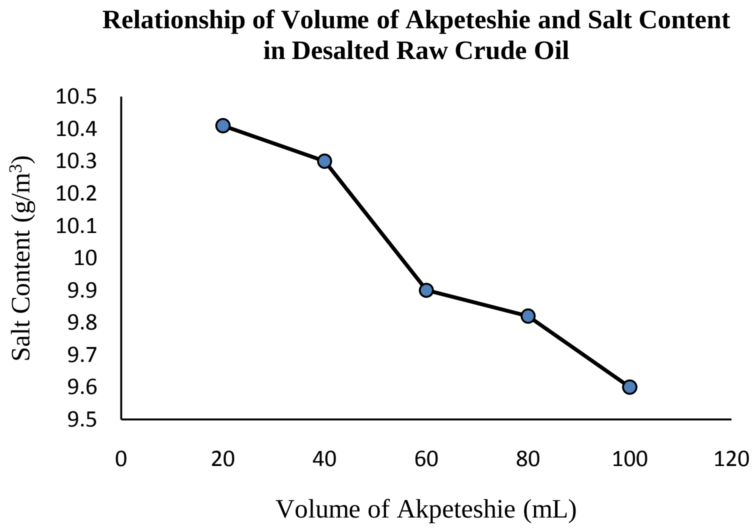

Fig. 5 Salt Contents in Unspilled Crude Oil and Akpeteshie Mixtures after Desalting

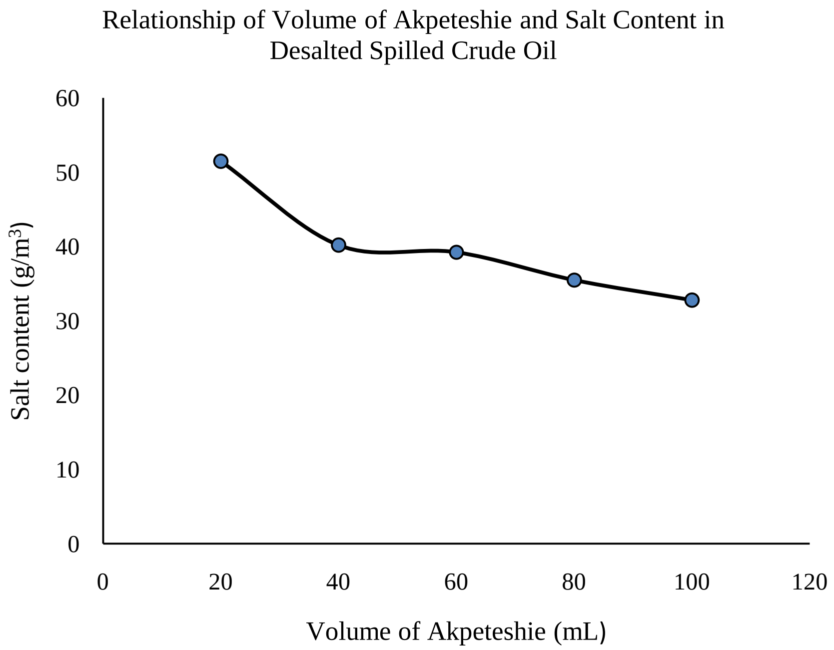

Fig. 6 Salt Contents in Spilled Crude Oil and Akpeteshie Mixtures after Desalting

Tables 8 and 9 show the values of the standard errors derived from desalting the spilled and unspilled crude oil.

Table 8 Standard Error of Unspilled Crude Desalting

Volume of Akpeteshie (mL)	Raw crude oil salt content (g/m^3)	(X-mean)^2
100	9.6	1.6384
80	10.1	0.6084
60	10.9	0.0004
40	11.5	0.3844
20	12.3	2.0164
Sum	54.4	4.648
Mean	10.88	
Standard Deviation	0.9296	
Standard Error	0.415729758	

Table 9 Standard Error of the Spilled Crude Desalting

Volume of Akpeteshie (mL)	Spilled crude oil salt content (g/m^3)	Spilled Crude (X-mean)^2
100	32.8	49.7025
80	35.5	18.9225
60	39.25	0.36
40	40.2	0.1225
20	51.5	135.7225
Sum	199.25	204.83
Mean	39.85	
stadard Deviation	40.966	
Standard Error	18.32055215	

IV. Discussion

Experimental research was adopted for this study. The results presented in Table 3 was instrumental in the computation of the salt contents in the crude oils after the desalting process. Again, the results informed the researcher the effectiveness of the desalting method chosen.Using the Salt in Crude Analyser, the test of salt in the raw crude oil and the spilled crude oil before desalting showed 13.2 g/m^3 and 89 g/m^3 respectively. The effect of Akpeteshie on desalting of the crude oil was careful studied. On different occasions, one liter of crude oil was combined with 100 mL, 80 mL, 60 mL, 40 mL, and 20 mL of Akpeteshie to demulsify the crude oil mixtures in order to check the extent of desalting of the spilled and the raw crude oils (unspilled). The mix ratios of the crude oils to the Akpeteshies were 1000 mL: 100 mL, 1000 mL: 80 mL, 1000 mL: 60 mL, 1000 mL: 40 mL, and 1000 mL: 20 mL. Tables 4 and 5 above show that the same quantity of both the spilled and the unspilled crude oils combined with higher amount of Akpeteshie as a demulsifier desalted the crude oil better than the combination of lower amount of Akpeteshie. The desalted crude oils having the lowest amount of salt was important to present.Again, it was observed that 32.8 g/m^3 was the lowest salt content left in the desalted spilled crude oils among the different volumes of Akpeteshie mixed with the same volume of crude oil. The computation of the salt differences before and after desalting using different quantities of the demulsifier gave 63.15 % as the highest reduction of salt removed from the spilled crude oils. The tests of the spilled crude oils before and after desalting using different volumes of Akpeteshie gave 9.6 g/m^3 as the lowest value. Similarly, computing the difference of the salt found in the unspilled crude oils before and after desalting showed 27.27 % as the highest reduction of salt. The graphs in Figures 5 and 6 show the relationship between different volumes of Akpeteshie and the amount of salt left in the crude oils after desalting. The abscissa is the volumes of the Akpeteshie and the ordinate is the quantity of salt left in the crude oils after desalting. Both graphs give a negative slope indicating that given the same amount of crude oil, using more quantity of Akpeteshie provided better desalting results. It should be noted that the desalting was more pronounced in the spilled crude oil than in the unspilled crude oil.

V. Conclusion

In conclusion, the objective of using the Ghanaian locally manufactured alcoholic beverage (Akpeteshie) as a demulsifier in desalting the spilled and the unspilled crude oils was achieved. Using different amounts of Akpeteshie combined with the same amount of crude oils consistently proved that more Akpeteshie was needed to obtain an efficient result in desalting the crude oils. The standard errors for the spilled and the unspilled crude oils desalting were about 18.32 and about 0.416 correspondingly. This tells that if this research were to be repeated using the same procedures, these will be the error margins that may be obtained. After the desalting processes, the highest reduction of the salt contents in the spilled crude oil and in the unspilled raw crude oil were 63.15 % and 27.27 % respectively. Because of this achievement, it is recommended that more research should be conducted and refineries adopt the use of Akpeteshie as a demulsifier to desalt crude oils. Using Akpeteshie for that will reduce the cost of refining crude oil because survey of the prices popular alcohols used for demulsification and Akpeteshie, showed that the price of Akpeteshie is relatively cheaper.

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