

EFFECTS OF SOME TREATMENT CHEMICALS ON THE QUALITY OF A CRUDE OIL BLEND IN NIGERIA.

*CHIKWE, T.N., OKOLI, I.O.

University of Port Harcourt, Petroleum and Environmental Chemistry Research Group Department of Pure and Industrial Chemistry, PMB 5323 Choba, Port Harcourt, Nigeria.

(phone +234-8035478512; e-mail: templechikwe@yahoo.co.uk)

Received: 30-04-18

Accepted: 19-07-18

ABSTRACT

Quality assurance parameters of untreated and treated samples of a crude oil blend in the Niger Delta area of Nigeria were analyzed with SVM 3000 densitometer, Normalab cloud / pour point test Cabinet, hydrometer and Rotanta 460R petroleum centrifuge using standard methods (American standard for testing and materials). Crude oil samples were treated with chemicals using pour point depressant, wax inhibitor and demulsifier at different concentrations of 10, 20, 30, 40 and 50 ppm respectively with the gross production of the crude as the reference fluid. Results obtained for the treated crude; cloud point (22.0000 - 9.0000 °C), pour point (-12.0000 - 11.0000 °C), specific gravity (0.8222 - 0.8500), API gravity (34.9700 – 40.6000⁰), density (821.8000 – 850.0000 Kg/m³), kinematic viscosity (1.0870 – 4.0000 cSt), wax recovered (5.0000-20.0000 Kg), (BS&W)basic sediment and water (8.0100 – 17.0500 %) compared with those of the untreated crude; cloud point (23.0000 °C), pour point (11.0000 °C), specific gravity (0.8537), API gravity (34.2500⁰), density (853.7000 Kg/m³), kinematic viscosity (4.0102 cSt), wax recovered (35.0000 Kg), basic sediment and water (19.1000 %) showed that all the measured parameters of the crude except the API gravity reduced with increasing concentration of the treatment chemicals used. The increased API gravity of the crude was a reflection of the increased market value of the crude and it is inversely proportional to the other quality assurance parameters considered. The flow characteristics of crude oil diminished as soon as wax crystallization began to occur, this was evident from the cloud point, pour point and the weight of wax recovered after pigging. Treatment with wax inhibitor and pour point depressant reduced these parameters to an acceptable level for the production facility. Demulsifier played an important role in breaking off the water and sediment from the crude which in turn reduces the BS&W, density and specific gravity of the crude thereby optimizing crude production, transportation and delivery. Treatment chemicals in general compliment the production facility in imparting the desired quality on the crude oil.

Key Words: Hydrocarbon, pour point depressant, wax inhibitor, demulsifier, crystallization, pigging, emulsion.

INTRODUCTION

Crude oil is a complex mixture with different hydrocarbons varying in

appearance and composition from one oil field to another. It exists in large quantities beneath the earth surface and is used as a

fuel as well as a raw material in the chemical / petrochemical industry (Deshmukh & Bharambe, 2009). It is formed below the surface of the earth by the decomposition of microbial organisms. Crude oil derives its origin from the organic theory which is based on the accumulation of hydrocarbons from living things in addition to the formation of hydrocarbons by the action of heat on biologically formed organic matter (Osuji, 2011). Crude oil, often called "black gold," is composed of hydrocarbon deposits and other organic materials whose varying viscosity and color depends on its hydrocarbon composition (Abdulkareem and Kovo, 2006). There are more than fourteen commercially available crude oil blends in Nigeria. These include: Bonny light, bonny medium Qua Iboe light, Escravos light, Brass Blend, Pennington light, Focados blends, Amenam blend, Oso condensate, Yoho light, Erha blend, Bonga blends and Agbami light (Ekweozo et al., 1988).

Crude oil in its original state beneath the earth crust has very limited use hence the need for various levels of treatment through the production facility. Chemical treatment is a very important practice during oil production as it complements the facility and the process in boosting the quality of the crude oil produced (Cedre, 2006). Quality Assurance Parameters of crude oil are parameters possessed by the crude certifying its suitability, durability and usefulness for designated purposes. The quality of the crude is also an indicator of the market value of the crude (Speight, 2002). Crude quality has a significant impact on the quality of finished products as well as the amount of resources required to produce petroleum

products. Crude oil assays provide an accurate evaluation of quality parameters and factors in crude selection and optimization of refinery operations (Hafiz and Khidr, 2007). The quality of crude oil directly affects the price of the crude as well as the profitability. Some of the quality assurance parameters of crude oil which affect its market value include density, specific gravity, viscosity, basic sediment and water (BS&W) (Demirbas et al., 2015). Pour point and cloud point affect the flow properties of the crude and they are influenced by the wax and asphalt content of the crude (Kok et al., 1996).

Chemicals such as demulsifier, wax inhibitor and pour point depressant amongst others at standard concentrations can be used to treat the crude in order to achieve the desired quality. The aim of this study is to determine the effects of different concentrations of some treatment chemicals on the quality of a crude oil blend in Nigeria in order to ascertain the concentration needed to obtain the desirable crude quality based on facility / process requirements. Owing to the economic recession currently experienced in most nations of the world especially Nigeria, results obtained from this study could be a veritable tool for cost optimization as regards chemical treatment of crude oil in most production facilities in Nigeria. Further studies will be on the effects of higher concentrations (over injection) of the treatment chemicals as well as other treatment chemicals on the quality of the crude.

MATERIALS AND METHODS

Sample Collection, Preparation and Analyses

Crude oil samples were obtained from an oil producing well in the Niger Delta area of Nigeria with sampling bottles that have been rinsed properly with xylene, air dried and rinsed with the sample. The temperature of the sample was maintained at 43 °C which is exactly the temperature of the export line of the crude. Each of the samples was treated with different concentrations (10, 20, 30, 40 and 50 ppm) of demulsifier, wax inhibitor and paraffin dispersant respectively. Analyses were carried out for the untreated as well as each concentration of the treated sample. Quality assurance parameters such as density, viscosity were measured using SVM 3000 densitometer, while cloud and pour points were measured with Normalab cloud and pour test Cabinet. Specific gravity was measured with the hydrometer while basic sediment and water (BS&W) were determined with Rotanta 460R petroleum centrifuge.

Determination of Density & Kinematic Viscosity

The cells of the equipment were thoroughly cleaned. Then 2 ml of the test sample was introduced into the equipment through the connector installed for filling samples into the measuring cells with the use of a suitable syringe. Density, kinematic viscosity, dynamic viscosity readings were displayed and the readings recorded (ASTM D4052, 2002).

Determination of Cloud Point

The test sample was poured into the test jar to the level mark. The test jar was closed tightly by the cork carrying the test thermometer. Appropriate thermometers

were used depending on the expected cloud points. The test jar was inserted in the jacket of the cooling bath maintained at a temperature of 0 +/- 1.5 °C. At each test thermometer reading that is a multiple of 1°C the test jar was removed from the jacket quickly without disturbing the sample. The cloud point is the temperature at which cloud is observed basically from the bottom of the test jar (ASTM D5771, 2002)

Determination of Pour Point

The test sample was poured into the test jar to the level mark. The test jar was closed with a cork carrying the high-pour thermometer. The appearance of the test sample was examined when the temperature of the test sample was 9 °C above the expected pour point. The pour point is the temperature at which the sample ceased to flow. This was recorded for all the test samples (ASTM D97 – 06, 2012).

Determination of Specific Gravity

The specific gravity of the test sample was determined by the ASTM test Method (D1298/IP 160). A 400 ml graduated cylinder was filled with the sample to be analyzed. A hydrometer with calibrations of 0.80 or 0.85 was submerged into it. Readings were taken as the hydrometer floats on the sample. A thermometer was then inserted into the graduated cylinder for 10 seconds and the temperature recorded. Specific gravity values corresponding to the temperature in °F were read as values for the corrected specific gravity (ASTM D287, 2002).

Determination of Basic Sediment and Water (BS&W)

A 100ml centrifuge bottle was filled with the test sample. A 50ml of the test sample was added into another 100 ml centrifuge bottle and filled up to mark with xylene. Then 0.2ml of demulsifier was added into each of the bottles, stopper the centrifuge bottles tightly and then both bottles were inverted ten times to ensure a homogenous mixture. The bottles were placed in the trunnion cups on opposite sides of the centrifuge to establish a balanced condition. The bottles were spun for 10 – 15 minutes at a minimum relative centrifugal force of 1200 to 1500 rpm. Immediately after the centrifuge came to rest following the spin, the combined volume of water and sediment at the bottom of each tube was read and recorded to the nearest 0.05ml from 0.1 to 1-ml graduations and the nearest 0.1-ml and 1-ml graduation (ASTMD 4007, 2016).

Concentration of Treatment Chemicals:

The concentration of the treatment chemical was derived from the volume of the reference fluid (fluid being treated) and was obtained from the equation below:

$$\text{Concentration (ppm)} = \frac{\text{Volume of Treatment Chemical (litres)} \times 1000}{\text{Gross Production (m}^3\text{)}} \times 1 \dots\dots\dots(1)$$

The reference fluid in this case referred to the gross production which was the crude oil in addition to water and other impurities; often called ‘Total crude’.

Net Production:

This could be defined as the actual production, devoid of water and other physical impurities such as emulsion, mud and sand. This was obtained with the equation below:

$$\text{Net Production (m}^3\text{)} = \frac{(100 - (\text{BS\&W}))}{100 \times \text{Gross Production (m}^3\text{)}} \dots\dots\dots(2)$$

RESULTS

Table 1: Quality Assurance Parameters of Untreated Crude Oil

Parameter	1st Reading	2nd Reading	Average Reading
Cloud Point (°C)	23.0000	23.0000	23.0000
Pour Point (°C)	11.0000	11.0000	11.0000
Specific Gravity	0.8536	0.8538	0.8537
API Gravity	34.1500	34.3500	34.2500
Density (Kg/m ³)	853.8000	853.6000	853.7000
Kinematic Vis. @ 40 °C (cSt)	4.0145	4.0201	4.0102
Wax recovered (Kg)	34.0000	36.0000	35.0000
BS&W (%)	20.0500	18.1500	19.1000

Table 2: Quality Assurance Parameters of Crude Oil Treated with Pour Point Depressant

Parameter	Chemical Concentration (ppm)				
	10	20	30	40	50
Cloud Point ($^{\circ}\text{C}$)	22.0000	20.0000	17.0000	15.0000	11.0000
Pour Point ($^{\circ}\text{C}$)	8.0000	2.0000	-3.0000	-6.0000	-12.0000
Specific Gravity	0.8453	0.8410	0.8364	0.8290	0.8231
API Gravity	35.9000	36.8000	37.7100	39.2000	40.3800
Density (Kg/m^3)	844.8000	840.8000	835.9000	828.5000	822.7000
Kinematic Vis. @ 40°C (cSt)	4.0000	3.7500	3.0000	2.0500	1.9500

Table 3: Quality Assurance Parameters of Crude Oil Treated with Wax Inhibitor

Parameter	Chemical Concentration (ppm)				
	10	20	30	40	50
Cloud Point ($^{\circ}\text{C}$)	20.0000	19.0000	16.0000	13.0000	9.0000
Pour Point ($^{\circ}\text{C}$)	10.0000	8.0000	5.0000	2.0000	-3.0000
Specific Gravity	0.8500	0.8419	0.8388	0.8301	0.8258
API($^{\circ}$) Gravity	34.9700	36.5700	37.2100	39.0100	39.9000
Density (Kg/m^3)	850.0000	841.3000	838.3000	829.5000	825.6000
Kinematic Vis. @ 40°C (cSt)	3.9500	3.6000	2.5600	1.7000	1.2600
Wax recovered (Kg)	20.0000	15.0000	12.0000	9.0000	5.0000

Table 4: Quality Assurance Parameters of Crude Oil Treated with Demulsifier

Parameter	Chemical Concentration (ppm)				
	10	20	30	40	50
Specific Gravity	0.8405	0.8365	0.8295	0.8255	0.8222
API Gravity	36.9000	37.7000	39.1000	40.0000	40.6000
Density (Kg/m^3)	839.8000	835.9000	829.0000	824.7000	821.8000
Kinematic Vis. @ 40°C (Cst)	2.9340	2.6400	2.0130	1.4100	1.0870
BS&W (%)	17.0500	15.5900	12.0100	10.5500	8.0100

Table 5: Correlation of the Quality Assurance Parameters of Untreated and Treated Crude Oil

Parameter	X	Y	X - M _x	Y - M _y	(X - M _x) ²	(Y - M _y) ²	(X - M _x)(Y - M _y)
Cloud Point (°C)	23.0000	9.0000	-99.6140	-98.5400	9922.9960	9710.1120	9815.9770
Pour Point (°C)	11.0000	-3.0000	-111.6140	-121.5400	12457.7380	14771.9470	13565.5830
Specific Gravity	0.8537	0.8222	-121.7610	-108.7180	14825.6280	11819.538	13237.5260
API Gravity	34.2500	40.6000	-88.3640	-68.9400	7808.2380	4752.7100	6091.8220
Density (Kg/m ³)	853.7000	821.8000	731.0860	712.2600	534486.3920	507314.450	520723.2180
Kine. Vis. (cSt)	4.0102	1.0870	-118.6040	-108.4530	14066.9180	11762.0320	12862.9520
Wax (Kg)	35.0000	5.0000	-87.6140	-104.5400	7676.2550	10928.5910	9159.1840
BS&W (%)	19.1000	8.0100	-103.5140	-101.5300	10715.1970	10308.3210	10509.7900

M_x: Mean of X = 122.614, M_y: Mean of Y = 109.540, $\sum(X - M_x)(Y - M_y) = 595966.051$, $\sum(X - M_x)^2 = 611959.363$, $\sum(Y - M_y)^2 = 581367.700$

Pearson correlation coefficient (R) = 0.9992, Coefficient of determination (R²) = 0.9984

Table 6: Pearson's Correlation Coefficient Matrix for the Quality Assurance Parameters of Treated Crude Oil at Various Concentrations.

Parameter	API Gravity (⁰)	BS&W (%)	Cloud Point (⁰ C)	Pour Point (⁰ C)	Wax (Kg)	Kine. Vis. (cSt)	Specific Gravity	Density (Kg/m ³)
API Gravity (⁰)	1.00							
BS&W (%)	-0.96	1.00						
Cloud Point (⁰ C)	-0.94	0.99	1.00					
Pour Point (⁰ C)	-0.90	0.98	0.99	1.00				
Wax (Kg)	-0.99	0.92	0.90	0.85	1.00			
Kine. Vis. (cSt)	-1.00	0.98	0.97	0.93	0.97	1.00		
Specific Gravity	-1.00	0.96	0.94	0.90	0.99	0.99	1.00	
Density (Kg/m ³)	-1.00	0.96	0.94	0.89	0.99	0.99	1.00	1.00

DISCUSSION

Cloud point is the temperature at which haziness is first observed at the bottom of the test jar containing the sample. It can also be said to be the temperature at which wax crystals become visible (ASTM D5771 2002). In Crude oil, cloud point is synonymous to the wax appearance temperature (WAT) and it refers to the solid-liquid phase boundary temperature, which is equivalent to the maximum temperature at which the solid and liquid phases co-exist in

equilibrium at a fixed pressure (Holder and Wrinkler, 1965). The WAT is hugely dependent on the wax concentration, the crystallization habit of the wax, and the shear stability of different wax structures. The flow characteristics of crude oil diminish when wax crystallization starts to occur (Hussain et al., 1999). Most crude oil contain an appreciable amount of wax components. Waxes are complex mixtures of high molecular weight or high carbon number alkanes that consist of straight, branched, and

cyclic chains (Chen et al., 2004). Waxy oils are produced in many countries around the world and the presence of waxes in these oils could cause serious problems to production facilities. Waxy crude oils exhibit Bingham non-Newtonian flow behavior below the cloud point due to wax crystallization (Hussain et al., 1999). The Nigerian Niger Delta crude oil which is the mainstay of Nigeria's economy, exhibits wax deposits in the range of 30-45%. Wax inhibitors are substances capable of penetrating into wax crystals thereby altering the growth and surface characteristics of the crystals. They reduce the cloud / pour point as well as the viscosity of the crude by reducing the tendency to form a three-dimensional network (Pedersen and Ronningsen, 2003).

Another parameter that determines the amount of wax in crude is the pour point. The pour point is the lowest temperature at which movement of the crude is observed. In other words, it is the temperature at which the crude can no longer flow. [Crude oil](#) with high pour points are generally associated with high [paraffin](#) content. Pour point depressants, otherwise known as flow improvers, are chemical additives that reduce the pour point of crude oil (Taraneh et al., 2008). Wax separates out as plate-like crystals or needles at low temperature. These crystals interact to form a three-dimensional network in which the crude oil is trapped, resulting in increased viscosity or even solidification of the bulk oil phase. Pour point depressants affect the crystallization process and prevent the formation of such three-dimensional networks, thereby reducing the pour point (Machado et al., 2001). Pour point depressants are introduced to allow crude oil to efficiently function

at low temperatures, while also keeping the viscosity benefits at higher temperatures (Mahto and Singh, 2013). Anything that changes the formation or the properties of the wax crystal matrix, such as pour point depressants or cloud point depressants, will affect the pour point/cloud point of the crude oil (Pedersen and Ronningsen, 2003). Table 2 and 3 shows that the higher the concentration of the wax inhibitor and the pour point depressants the lower the cloud and pour points of the crude. All pour point depressants are also known as cloud point depressants but not all cloud point depressants act as pour point depressants (Yang et al., 2015). Table 3 shows that the wax inhibitor reduces the pour point of the crude but not as efficient as the pour point depressant as shown in Table 2.

Apart from chemical treatment, an alternative method of getting rid of wax deposits along crude oil export lines is by the process of pigging. However in most cases both operations (chemical treatment and pigging) complement each other (Deshmukh and Bharambe, 2009). Pigging in oil exploration can be defined as the use of devices known as "pigs" to perform various maintenance operations such as cleaning and inspection of the expedition line. This is done without stopping the flow of the product in the pipeline. (Ronningsen et al., 1991; El-Gamal, 1998). Table 1 shows the weight of the wax recovered from untreated crude. Table 3 shows that the higher the concentration of the wax inhibitor, the lower the weight of the wax recovered during pigging. In most production facilities pigging is done once a week or biweekly depending on the waxy nature of the crude. The size of most crude

oil expedition lines are between 12 to 14 inches, but crude that forms gas caps may require export lines of up to 16 inches (Kok et al., 1996). For export lines of 12 inches, a weekly wax recovery of >15Kg is definitely a cause for concern. In such situations chemical treatment is required. Table 3 shows that a wax inhibitor concentration of 30 ppm will be appropriate for the treatment of crude exported along a 12 inch line (Ronningsen et al., 1991).

Kinematic viscosity can also be used to measure the flow characteristics of crude oil. It is a measure of the resistance of a fluid by gravity. It can be determined at various temperatures (preferably 40 °C and 100 °C) by measuring the time it takes a volume of liquid to flow under gravity through a calibrated glass capillary viscometer (Machado et al., 2001). The presence of wax in crude oil could lead to an increase in the viscosity of the crude. The chemical composition of the crude could also be a contributing factor to the viscosity of the crude. For instance, crude oil with high percentage of heavier fractions would be more viscous than those with higher percentage of lighter fractions (El-Gamal, 1998). Tables 2 & 3 shows that the higher the concentration of the wax inhibitor and pour point depressant the lower the viscosity of the crude oil.

The density of crude oil can be defined as the mass per unit volume of the crude, whereas the specific gravity of the crude is the ratio of the weight of a given volume of crude oil to the weight of the same volume of water measured at the same temperature (Machado et al., 2001). Usually, crude oils and their liquid products are first measured on a volume basis before being changed to the

corresponding masses using the specific gravity (Speight, 2002). It is worthy to note that the specific gravity of the crude is a function of the density and a very important parameter that determines the quality of the crude through the API (American Petroleum Institute) gravity. The specific gravity (SG) is related to the API gravity by a mathematical equation shown in equation (3) and both parameters have an inverse relationship (Machado et al., 2001). Crude oil can be classified as light, medium or heavy according to its measured API gravity. Light crude oil is defined as having API gravity higher than 31.1⁰ while medium oil has API gravity between 22.3⁰ and 31⁰. Heavy oil has API gravity below 22.3⁰. The higher the API gravity, the better the quality of the crude in terms of market value (Yasin et al., 2013).

$$API\ gravity = \frac{141.5}{SG} - 131.5 \dots \dots \dots (3)$$

Another factor that increases the specific gravity of crude oil thereby reducing the API gravity is the presence of water and sediments in the crude. Sediments in crude could be in the form of solids or emulsion. Chemical treatment with demulsifier is very important in breaking off water and emulsion from the crude thereby reducing the specific gravity and improving the API gravity (Speight, 2002). Another advantage of exporting oil with an improved API gravity (reduced specific gravity) which is achieved through demulsifier treatment is that it boosts the volume of oil that flows through the expedition line thereby increasing the gross production (El-Gamal, 1998). Results obtained show that chemical treatment generally has a positive impact on the API gravity, as such the higher the concentration of chemical treatment the higher

the API gravity. The basic sediment and water (BS&W) in the crude reduces as the concentration of the demulsifier increases as shown in Table 4. BS&W is used in calculating the net production from the gross. The net production is the actual oil produced while

the gross production is the oil mixed with water and other impurities. The higher the BS&W the lower the net production. This can be deduced from equation 2.

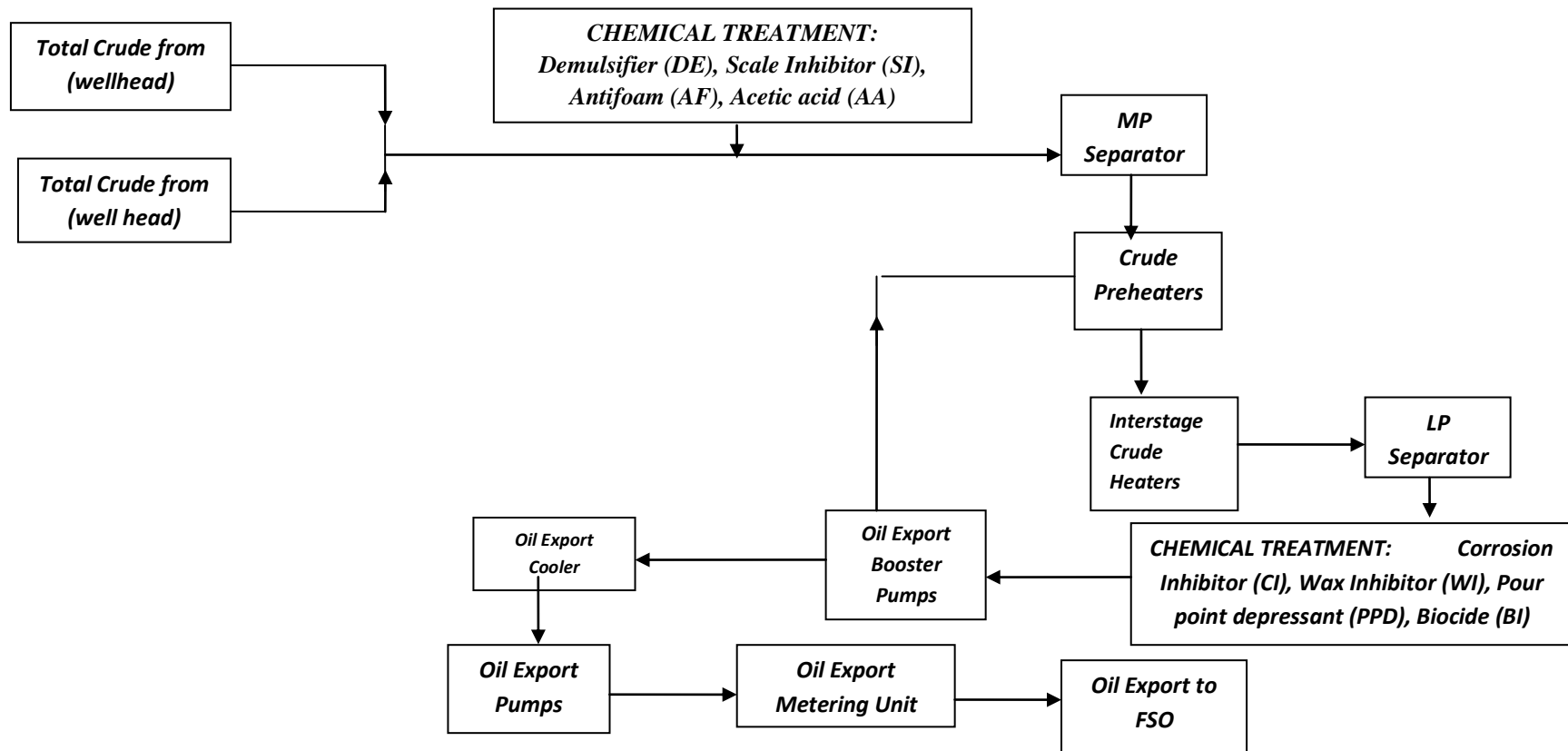


Figure 1: Process flow diagram of an oil phase line

Figure 1 shows a process flow diagram of an oil phase line for a typical oil production facility. Demulsifier treatment with other chemical treatments are done at the inlet of the medium pressure (MP) separator whereas oil treatment with wax inhibitor and pour point depressant as well as other chemicals are done downstream the low pressure (LP) separator. Chemical treatment compliments the process facility in improving the quality of the crude oil that is being exported (Yasin et al., 2013). Further studies will be on the effects of other treatment chemicals on the quality of the exported crude oil.

Pearson's correlation analysis is used to analyze the relationship between the quality assurance parameters of the untreated crude (X) and crude oil treated with 50 ppm of the treatment chemicals (Y) as shown in Table 5, whereas Table 6 illustrates the Pearson's coefficient correlation matrix for the quality assurance parameters of the treated crude at the various concentrations under study. A positive correlation means that a high value on X variable goes with a high value on Y variable and a low value on X variable goes with a low value on Y variable. On the other hand, a negative correlation means that a high value on X variable goes with a low value on Y variable (vice versa).

Table 5 shows that a strong positive correlation was obtained from the statistical analyses carried out which means that a high X variable went with a high Y variable. Pearson's correlation coefficient can be calculated with the equation:

$$R = \frac{\sum(X-Mx)(Y-My)}{\sqrt{\sum(X-Mx)^2\sum(Y-My)^2}} \dots\dots\dots (4)$$

A variety of techniques have been employed in order to reduce problems caused by the crystallization of paraffin during the production and / or transportation of waxy

crude oil. Pour point depressants and wax inhibitors improve the fluidity and extract efficiency of crude oil and this is critical in preventing the production of waxy crystalline clusters, which is evident in the reduction of the cloud point and pour point of the crude (Kok et al., 1996). Demulsifier treatment reduces the BS&W of the crude which in turn results in the reduction of the density, specific gravity and kinematic viscosity of the crude. The quality imparted on the crude through chemical treatment is very important in boosting the market value of the crude by increasing the API gravity, it is also critical in meeting process condition, optimizing the method involved in oil production, transporting, refining and upgrading of the crude oil.

The authors wish to appreciate the management and staff of DIABLOSS Laboratory Limited, No. 25 Liberty Drive, Off Alcon Road Woji Port Harcourt for their support, assistance and response that enabled this work to be completed on schedule.

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