Comparative Precipitation of Heavy Organics from Wellhead, Separator and Flowline Crude Oil Samples using hydrocarbon solvents of different chain length

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Abstract: *The effect of difference in carbon number of the n-alkane precipitants on the precipitation of heavy organics from wellhead, separator and flowline crude oil samples was studied. N-pentane, n-hexane, n-heptane and their corresponding binary mixtures were used to precipitate the heavy organics from the crude oils using the simple or normal laboratory precipitation method. The result obtained showed that n-pentane precipitant yielded the highest precipitate at the three locations of the production system while n-heptane yielded the least precipitate ($nC_5 > nC_6 > nC_7$). Similarly, 1:1 $nC_5:nC_6$ binary mixtures recorded the highest precipitates while 1:1 nC6:nC7 recorded the least (1:1 $nC_5:nC_6 >$ 1:1 $nC_5:nC_7 >$ 1:1 $nC_6:nC_7$). The result is in agreement with previous reports that the lower carbon number n-alkane precipitants yield more precipitate than the higher carbon number. Crude oils from wellhead showed the highest precipitation tendency followed by those from Flowline and Separator.*
Key Words: *Asphaltenes, Binary mixtures, Crude oil, Heavy Organics, Hydrocarbon, Precipitation.*

I.   Introduction

Heavy Organics are high molecular weight complex molecules such as asphaltenes, petroleum resins, saturates(Waxes and Diamondoids), high molecular weight aromatics, Mercaptans and metal carbenes/organometallics present in crude oil heavy fractions or petroleum residuum.The general closed chemical formulae of some heavy organics in petroleum fluids are as follows: asphaltenes - $C_mH_nN_iO_jS_k$,petroleum resins – $C_mH_nN_iO_jS_k$,wax - C_mH_n, diamondoids– $C_{4n+6}H_{4n+12}$andasphaltogenic acids - $C_mH_nN_iO_jS_k$–COOH, where C is carbon, H is hydrogen, N is nitrogen, O is oxygen, S is sulphur and i,j,k=0 or 1.0 ;$18 \leq m \leq 60$ $n \leq 2m+2$[1,2].The proposed chemical structures as reported by Suzuki et al. [3] and Carbognani[4] are shown in fig. 1.

Heavy organic precipitation and deposition on the wellhead, flowline, separator, wellbore, near well bore, safety valves and other petroleum production and transportation facilities is one of the major unsolved problems confronting the petroleum industries. It is known to be responsible for fouling and blockage of tubular production facilities. Flow assurance has often been disrupted by heavy organic precipitation and deposition.

Studies show that changes in temperature, pressure and composition of the fluids as they flow from the reservoir pore spaces to the production facilities are the major causes of heavy organic precipitation and deposition [5, 2, and 6].

These changes in temperature, pressure and composition of the fluid may be induced by a variety of processes including primary depletion of temperature and pressure, injection of natural gas or carbon dioxide, acidizing treatments and commingled production of incompatible fluids, thus leading to heavy organic precipitation and deposition [7,8,9 and10].
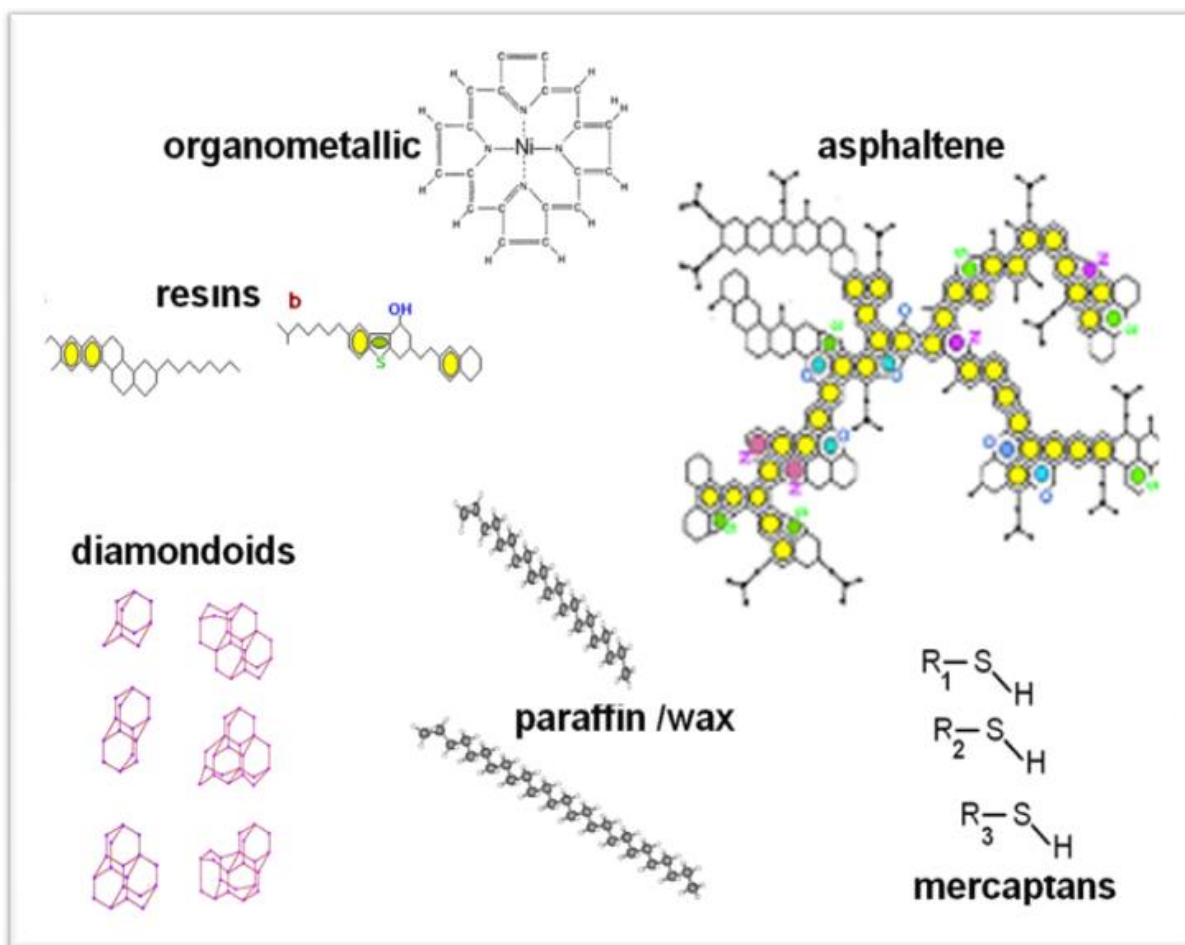
Figure 1: Chemical Structures of some Heavy Organics [3, 4]

Over the years, several studies have been conducted to proffer solution to heavy organic precipitation and deposition problems [5, 2, 6, 11, 12, 13, and 14]. Mansoori [15] reported that the major factors that govern precipitation and deposition of heavy organics from petroleum fluids appear to be: parafin/wax crystallization because of lowering the temperature below the oil cloud point and asphalteneflocculation as initiated through variations in composition of petroleum fluid mixed with the injection (or blending) fluid. Anderson [16] studied South and North American live oils and reported that the precipitation pressure decreases as the temperature increases, requiring a larger pressure change from the original reservoir Pressure-Temperature (P-T) condition to initiate asphaltene precipitation.Chung et al. [17] reported a series of titration experiments in tank-oil samples with liquid alkanes from *n*-pentane to *n*-hexadecane as diluents, to determine the composition, the amount of material precipitated, and the solubility properties of asphaltenes at the onset of precipitation.

Kokal et al. [18] reported the amount of asphaltenes precipitated when two Canadian heavy oils with a high content of asphaltenes (13 and 21 wt %) were titrated with various *n*-alkanes (*n*-pentane to *n*-decane) at different dilution ratios and observed that above a ratio of 10ml solvent/g oil, the precipitation is completed and also a decrease in the amount precipitated at very high dilution ratios was observed, which could be attributed, in part, to a partial redissolution of asphaltenes in the solvent.Buenrostro-Gonzalez et al. [5] measured the precipitation of asphaltene in two Mexican crude oils using a combination of high isothermal expansion and atmospheric titration with n-alkanes and by matching a single titration curve or two precipitation onset points with equation of state (EOS) a good prediction of asphaltene precipitation over wide temperature, pressure and composition intervals was obtained.

In 2015, Achugasim and Ekpo [19] precipitated heavy organics from Nigerian Antai crude oil residue (500˚C AET) using binary mixtures of n-alkane at different ratios and reported that the highest amount of precipitate was obtained at 100% n-pentane solvent, stating that a good understanding of the contribution of different n-alkane solvents in the precipitation of asphaltene is necessary to flow assurance of crude oil in terms of solid precipitation.

Udourioh et al. [20] studied the effects of compositional changes on the phase behavior of heavy organics using binary mixtures of n-alkane precipitants and discovered that heavy organic precipitation is a

three-stage phase transition which includes solid-liquid phase transition, colloidal formations and growth (liquid-solid phase transition) and eventual collapse of the resulting colloids (solid-liquid phase transition).Iroegbu et al. [21] studied precipitation of heavy organics from crude oil using Ternary mixtures of low molecular weight n-alkanes and discovered that varying volume ratios and hydrocarbon type mixtures differently affects heavy organic precipitate yields.Utin et al. [22] studied the composition of heavy organics precipitated by compositional changes with low molecular weight n-alkanes and reported that there is co-precipitation of resins and other solid materials with asphaltene, a justification for the use of the term "Heavy Organics"

The common assumption in all the investigations is that heavy organic is considered to exhibit the same nature, composition and apparently precipitates at the same rate at all locations of the production system.There is scarcely any report on the degree of precipitation on the various locations of the production systems, such as the wellbore, wellhead, flowline, and separator.This work studies the effect of different n-alkane hydrocarbon precipitants chain lengths and their binary mixtures on the quantity of heavy organics precipitated at the wellhead, separator and flowline during petroleum production.A good knowledge of the amount and nature of precipitates obtained at the various locations: Wellhead, Flow line, Separator, Wellbore etc. will be useful in the design of efficient production system and processes devoid of heavy organic precipitation and deposition.

II. Materials And Method

2.1 Sample Collection and Preparation
The crude oil samples were collected at the wellhead, separator and flowline of some oil wells in Niger Delta, Nigeria. The oil samples were separated from the associated water, put into sample bottles and stored in a refrigerator for further analysis.

2.2 Distillation of the crude oil Samples
The crude oil samples were distilled using atmospheric distillation unit to get rid of the lighter fractions. The crude oil samples were heated up to 350˚C atmospheric equivalent temperature (AET) and the residue left to cool and stored in air tight flasks for subsequent analysis.

2.3 Heavy Organic Precipitation
The precipitation of heavy organics from the crude oil samples was carried out by gravimetric titration experiments similar to those implemented by Kokal et al. [18] and Buenrostro-Gonzalez et al. [5] and modified ASTM/IP methods. 30mls of n-pentane (nC_5), n-hexane (nC_6), n-heptane (nC_7) and their corresponding binary mixtures: n-pentane vs n-hexane (nC_5:nC_6), n-pentane vs n-heptane (nC_5:nC_7), n-hexane vs n-heptane (nC_6:nC_7) each was added to about 2g of oil in an appropriate flask.The mixtures were shaken for 30mins using mechanical shaker and allowed to stand for 48hrs. After which the solution of the n-alkanes and deasphalted oil was filtered using a vacuum pump system with a 0.45μm membrane filter fitted in a Buchner funnel/Buchner flask and connected to the vacuum pump. The precipitate was washed with small volumes of the corresponding binary mixtures of n-alkane solvents and poured on the membrane filter to eliminate the residual oil. The membrane filter with the precipitated material was dried in a vacuum oven at 0.1 bar (gauge pressure) and 333k over 2hrs and finally weighed to determine the heavy organic mass precipitate. The weight percent heavy organic precipitate was calculated using the expression:

$$\frac{weight\ of\ HO\ precipitate}{Weight\ of\ crude\ oil}\ x\ \frac{100}{1}$$

III. Results And Discussion
The results of the experiments at room temperature and atmospheric equivalent pressure are presented on tables 1 - 3 and figures 2 - 4.

Table 1: Quantity of Heavy organics precipitated at wellhead, Separator and Flowline for **SAPW1** by different Precipitants
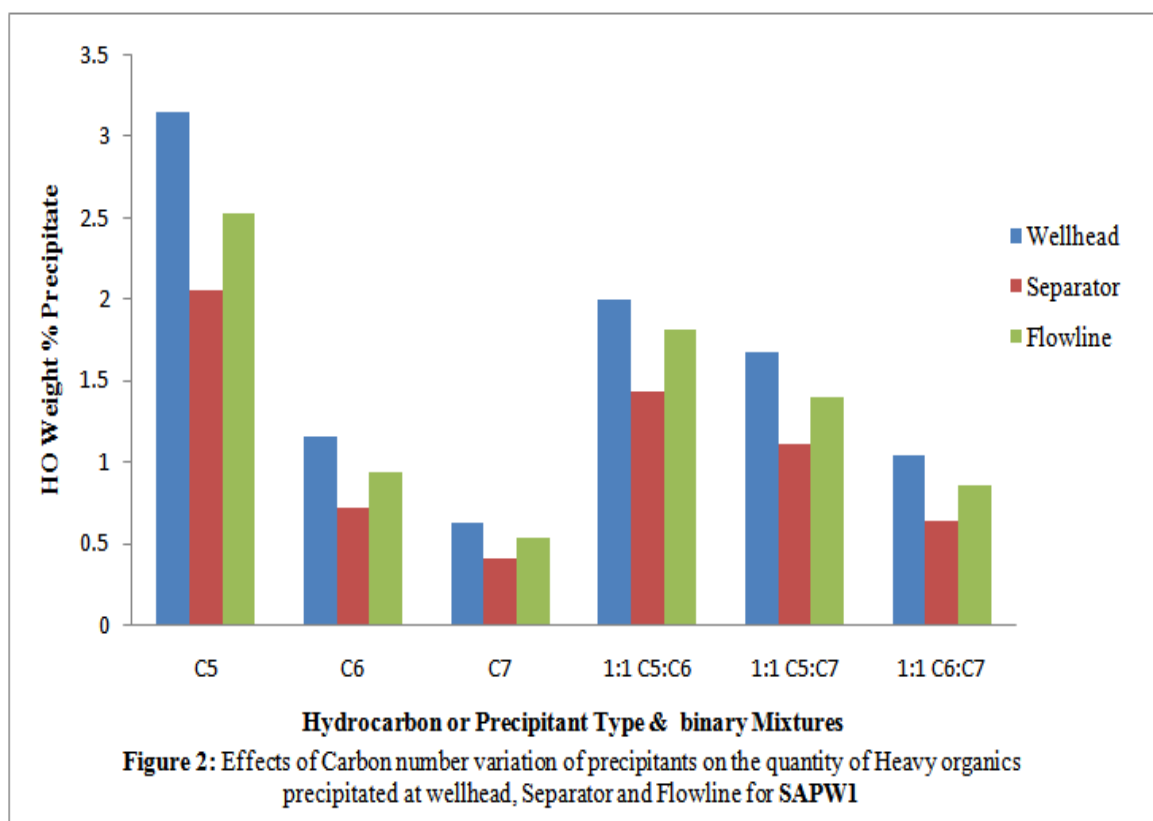
S/N	Hydrocarbon or precipitant type/Binary mixtures	Wellhead (WH)		Separator (SR)		Flowline (FL)	
		Wt. of HO ppt. (g)	Wt. % HO ppt.	Wt. of HO ppt. (g)	Wt. % HO ppt.	Wt. of HO ppt. (g)	Wt. % HO ppt.
1	n-C_5	0.0630	3.15	0.0412	2.06	0.0506	2.53
2	n-C_6	0.0232	1.16	0.0144	0.72	0.0188	0.94
3	n-C_7	0.0124	0.62	0.0080	0.40	0.0106	0.53
4	1:1 C_5:C_6	0.0402	2.00	0.0286	1.43	0.0362	1.81
5	1:1 C_5:C_7	0.0336	1.68	0.0222	1.11	0.0280	1.40
6	1:1 C_6:C_7	0.0208	1.04	0.0128	0.64	0.0172	0.86

Table 2: Quantity of Heavy organics precipitated at wellhead, Separator and Flowline for **SAPW2** by different Precipitants

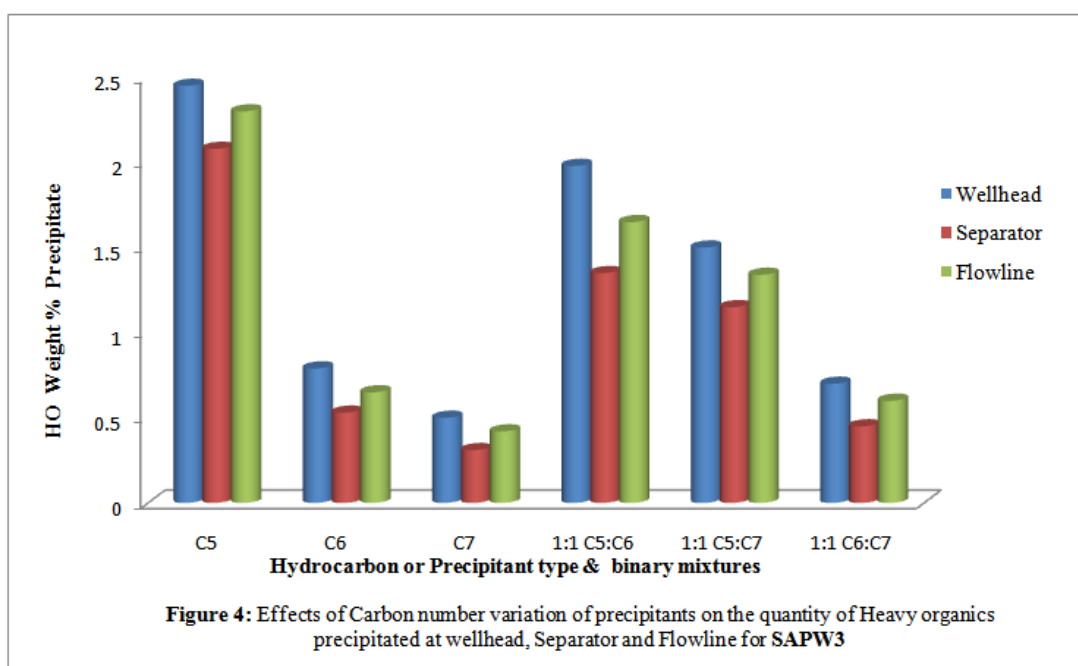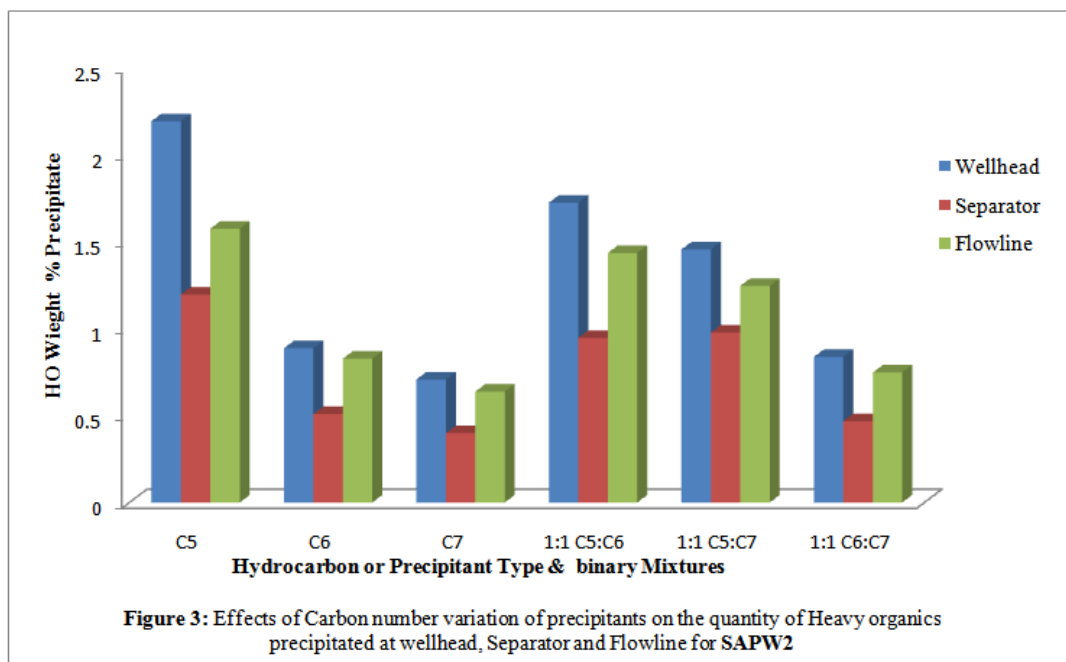| S/N	Hydrocarbon or precipitant type/Binary mixture	Wellhead (WH)		Separator (SR)		Flowline (FL)	
		Wt. of HO ppt. (g)	Wt. % HO ppt.	Wt. of HO ppt. (g)	Wt. % HO ppt.	Wt. of HO ppt. (g)	Wt. % HO ppt.
1	n-C_5	0.0439	2.20	0.0239	1.20	0.0316	1.58
2	n-C_6	0.0178	0.89	0.0101	0.51	0.0166	0.83
3	n-C_7	0.0142	0.71	0.0080	0.40	0.0128	0.64
4	1:1 C_5:C_6	0.0346	1.73	0.0190	0.95	0.0288	1.44
5	1:1 C_5:C_7	0.0292	1.46	0.0196	0.98	0.0250	1.25
6	1:1 C_6:C_7	0.0168	0.84	0.0094	0.47	0.0150	0.75

Table 3: Quantity of Heavy organics precipitated at wellhead, Separator and Flowline for **SAPW3** by different Precipitants

S/N	Hydrocarbon or precipitant type/Binary mixture	Wellhead (WH)		Separator (SR)		Flowline (FL)	
		Wt. of HO ppt. (g)	Wt. % HO ppt.	Wt. of HO ppt. (g)	Wt. % HO ppt.	Wt. of HO ppt. (g)	Wt. % HO ppt.
1	n-C_5	0.0490	2.45	0.0416	2.08	0.0460	2.30
2	n-C_6	0.0158	0.79	0.0106	0.53	0.0130	0.65
3	n-C_7	0.0100	0.50	0.0062	0.31	0.0084	0.42
4	1:1 C_5:C_6	0.0396	1.98	0.0270	1.35	0.0330	1.65
5	1:1 C_5:C_7	0.0300	1.50	0.0230	1.15	0.0268	1.34
6	1:1 C_6:C_7	0.0140	0.70	0.0090	0.45	0.0120	0.60

Figure 2: Effects of Carbon number variation of precipitants on the quantity of Heavy organics precipitated at wellhead, Separator and Flowline for **SAPW1**

Figure 3: Effects of Carbon number variation of precipitants on the quantity of Heavy organics precipitated at wellhead, Separator and Flowline for **SAPW2**

Figure 4: Effects of Carbon number variation of precipitants on the quantity of Heavy organics precipitated at wellhead, Separator and Flowline for **SAPW3**

From the results presented in table 1 and figure 2, the quantity of heavy organics precipitated by n-pentane (nC_5) precipitant at wellhead, flowline and separator are 3.15%, 2.53% and 2.06% respectively. N-hexane (nC_6) precipitantrecorded 1.16% at wellhead, 0.94% at Flowline and 0.72% at Separator. Similarly, n-heptane (nC_7) precipitant recorded 0.62%, 0.53% and 0.40% at wellhead, flowline and separator respectively. These results show that the n- pentane (n-C_5) precipitant produced the highest precipitates irrespective of the location of the production system, followed by n-hexane (n-C_6) and n-heptane (n-C_7). The precipitants precipitation tendency is in the order: n-C_5> n-C_6> n-C_7. The result is in agreement with previous reports that the lower carbon number n-alkane precipitant yielded more precipitates than the higher carbon number [9, 5, 2, and 11].

The results also show that the percentage of heavy organic produced is highest at wellhead, followed by flowline and separator irrespective of the precipitant used. The amount of heavy organics precipitated at the three locations is in the order: Wellhead (WH) > flowline (FL) > Separator (SR).

Furthermore, the 1:1 n-pentane vs n-hexane (1:1 n-C_5:n-C_6) binary mixture of precipitant yielded 2.00% at wellhead (WH), 1.81% at flowline (FL) and 1.43% at the separator (SR). The 1:1 n-pentane vs n-

heptane (1:1 n-C_5:n-C_7) binary mixture recorded 1.68%, 1.40% and 1.11% heavy organic precipitate at wellhead (WH), flowline (FL) and separator (SR) respectively while 1:1 n-hexane vs n-heptane (1:1 n-C_6:n-C_7) binary mixture precipitant produced 1.04%, 0.86% and 0.64% heavy organic precipitate at wellhead (WH), flowline (FL) and separator (SR) respectively. The binary mixture of precipitants produced precipitate in the order: 1:1 n-C_5:n-C_6> 1:1 n-C_5:n-C_7 >1:1 n-C_6:n-C_7 while the degree of precipitation at the three locations is still in the order: Wellhead (WH) > flowline (FL) > Separator (SR).

Two other oil wells: Sapele well 2 and Sapele well 3 (SAPW2 and SAPW3) were tested and similar trends were observed as shown in tables 2 and 3 and figures 3 and 4 respectively.

The significant increase in precipitates at wellhead (WH) may be attributed to the drop in pressure and temperature of the crude oil at wellhead as it is forced through the wellbore [23]. Again, the continuous injection of production chemicals through the wellhead may equally lead to high level of heavy organic precipitation at the wellhead. There is apparently a separation of large asphaltene particles from the petroleum fluid due to high paraffin content thus forming random aggregates which may be micellized by the addition of aromatics or can be colloidally dispersed in the presence of resins [8].N-pentane (n-C_5) precipitant may serve as a better single n-alkane precipitant while 1:1 nC_5:nC_6 precipitant may serve as a better precipitant mixture.

However, it is imperative to use mixtures of precipitating solvents in heavy organic precipitation studies in order to produce results that represent real life precipitation, since crude oil is a complex mixture of hydrocarbons and heteroatomic organic compounds of various molecular weights[24].

IV. Conclusion

Generalized study of heavy organic precipitation without reference to the specific location of the production system such as wellhead, flowline, separator etc. may produce results that are misleading. This is because the temperature, pressure and composition of the petroleum fluids are different at the various locations of the production system.

This study has revealed that the location of the production system does not alter the existing fact that the lower carbon number n-alkane precipitants yield more precipitates than the higher carbon number. The wellhead has the highest precipitation tendency, followed by the flowline and then the separator.

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