

SATURATES IN HEAVY ORGANICS PRECIPITATED FROM CRUDE OIL AT DIFFERENT LOCATIONS OF THE PRODUCTION LINE

Udourioh,^{*1,a} G. A., Achugasim,^{2,b} O., Ofodile,^{3,c} S. E. and Okoye,^{2,d} I. P.

¹ Department of Pure and Applied Chemistry, College of Natural and Applied Sciences, Veritas University, Abuja (The Catholic University of Nigeria), P.O. Box 6523, Garki, Abuja, Nigeria

² Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, P.M.B. 5323, Port Harcourt, Rivers State, Nigeria

³ World Bank African Centre of Excellence in Oilfield Chemicals, Institute of Petroleum Studies (IPS), University of Port Harcourt, P.M.B. 5323, Port Harcourt Nigeria

email: ^{a,*} gadiurioh@yahoo.com; Tel: +2348033770425.

ABSTRACT

The saturate hydrocarbon composition of the nC₅:nC₆ heavy organics precipitated from different locations of petroleum production line were studied. The heavy organics (HOs) were precipitated by gravimetric titration of the crude oils samples from three locations of the production line (wellhead, flowline and separator) with nC₅:nC₆ precipitant binary mixture. The saturate fractions of the HOs were obtained by column chromatography and the hydrocarbon type compositions were analyzed by gas chromatographic-flame ionization detection. The results showed that gas chromatographic-flame ionization detector (GC-FID) has 100% efficiency in quantifying the saturate hydrocarbon composition of the HOs. From one of the wells studied, the wellhead showed the highest total saturate hydrocarbon concentration with 28,497ppm, followed by the flowline with 23,512ppm and separator with 19,346ppm. The order of total saturate hydrocarbon concentration was wellhead > flowline > separator. However, the second well showed an opposite trend: separator (20,686ppm) > flowline (7,580ppm) > wellhead (3,778ppm) while others were completely inconsistent. This may imply that the amounts of saturate hydrocarbon composition at the different locations of the production line do not necessarily translate into the quantity of HOs or wax precipitated at that location of the production line.

Key words: GC-FID, Heavy Organics, Asphaltenes, Precipitation, Saturate hydrocarbons, Crude oil.

INTRODUCTION

Heavy Organics (HOs) deposit on petroleum production system is still an unsolved complex problem confronting the petroleum

industries. Fouling and blockage of reservoirs, wellheads, flow lines and petroleum production facilities are often

attributed to HOs precipitation deposits. Flow assurance disruption, damages of equipment and serious reduction in well productivity are some of the consequences of this. Oil wells have been abandoned in recent times due to HOs precipitates^{1,2,3}.

The complex molecules of HOs: asphaltenes, petroleum resins, saturates C₁₈₊ (waxes and diamondoids), high molecular weight aromatics, mercaptans and metal carbenes or organometallics which are common in petroleum residuum fraction may build up at different locations along the petroleum production line; from wellbore, near wellbore to surface facilities^{4,5,6}. Figure 1 shows some typical locations of heavy organics deposits along the production line⁷.

Studies have shown that the heavy organics precipitated due to compositional changes of the crude oil with single n-alkane solvents or their mixtures consist of mixtures of organic compounds often defined by compound types: Saturates Aromatics, Resins and Asphaltenes (SARA)⁸⁻¹¹. It has also been reported that the total quantity of heavy organics (HOs) do vary with the n-alkane precipitating solvents and volume ratios of their mixture, the location along the petroleum production line and also the crude oil used for the precipitation^{12,13,14}.

Chung *et al.*¹⁵ reported a series of titration experiments in tank-oil samples with liquid alkanes from n-pentane to n-hexadecane as diluents, to determine the precipitation onset composition, the amount of material precipitated, and the solubility properties of asphaltenes. Udourioh *et al.*¹⁶ comparatively studied the effect of single n-alkane solvents and their corresponding binary mixtures on the precipitation of heavy organics from crude oil and concluded that binary mixture experiment has demonstrated real life precipitation problem, hence heavy organic precipitation problem should be approached in the laboratory using mixtures of n-alkane solvents. Iroegbu *et al.*¹² 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.

Udourioh *et al.*¹³ studied the effects of changes in ratios of n-alkane precipitants on the quantity of heavy organics precipitated from different locations of the production line and reported that the wellhead has the highest tendency of HOs precipitation followed by flowline and the separator. Considering these recent reports, it is therefore important to study the concentration of saturates aromatics and possibly resins compositions of the HOs at the different locations of the production

line to determine its individual influence on the quantity of heavy organics (HOs) precipitated at the different locations of the production system.

This work studies only the concentration of the saturate hydrocarbon composition of the

HOs at the three locations using gas chromatography to determine its contribution to the quantity of heavy organics or wax precipitated at wellhead, flowline and separator during petroleum production.

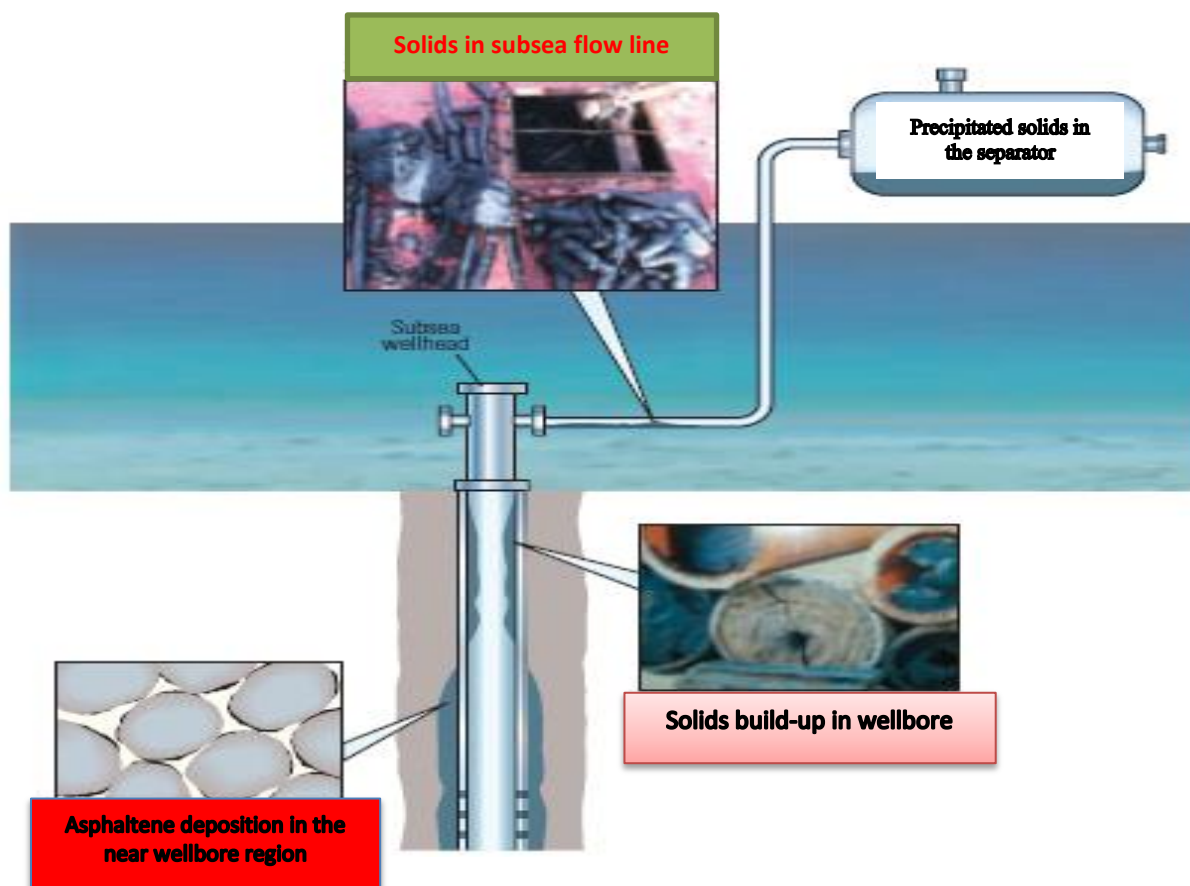


Figure 1: Heavy Organic Precipitate Deposits at Various Locations of the Production System

Source: Akbarzadeh *et al.* ⁷.

MATERIALS AND METHODS

Sample Collection and Preparation

Crude oil samples were taken from wellhead, separator and flowline of different oil wells at Sapele oil field, Niger Delta, Nigeria. The oil samples were separated from associated water using separating funnel, put into sample bottles and stored in the refrigerator for analysis.

Distillation of Samples

The distillation was done using atmospheric distillation unit to get rid of the lighter fractions which boil within the range of 0°C to 349°C. The crudes 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.

Heavy Organics (HOs) Precipitation

Heavy organics (HOs) from the crudes were precipitated using gravimetric titration experiments^{17, 18}. 1:1 volume by volume n-pentane vs n-hexane (C₅:C₆) precipitant at 30mls constant total volume was added to 1gram of sample. Mechanical shaker was used to shake the mixture for 30 minutes. It was allowed to stand for 48hours, filtered, washed, dried and weighed.

Column Chromatographic Fractionation

The maltenes or equilibrium filtrates from the HOs were fractionated by column chromatography (column size: 30 x 1.2cm) using activated silica gel (60-120 mesh size). 0.5g of the maltene was introduced into the column using a syringe. The saturate (n-paraffins, iso-paraffins and naphthenes) fractions were eluted with 50cm³ n-hexane solvent, 70cm³ of 1:1 dichloromethane (DCM)/hexane solvent for aromatic and finally, 60ml (1:2) methanol/DCM for resins. The different fractions were collected and monitored using UV-Visible spectrophotometer to ensure complete separation of each fraction. After which the saturate fractions were taken for GC-FID analysis¹⁹.

GC-FID analysis

The saturate fraction obtained from the column chromatographic fractionations was analyzed by Gas chromatography-coupled with Flame Ionization Detector (GC-FID) to determine the group-type compositions and amounts¹⁹. The gas chromatograph used was Varian model Cp-3800. The saturate samples were injected into the chromatograph using the auto-sampler with a 10μL syringe. For each sample 5.0μL was injected with a fast plunger speed, no sample washes, and three sample pumps. The inlet was run in split

mode at 310°C with a 50:1 split ratio. Hydrogen was carrier gas with air as makeup. The oven was run with a temperature program starting at 50°C for 2 minutes, then ramp at 20.0°C per minute until 300 °C was obtained. The final temperature, 300 °C was then maintained for 7.00 minutes. The total run time was 21.50 minutes and the column used was DB-5MS column model with 0.25mm in diameter, that is, approximately 30m long with a 0.25µm film thickness. The column was at a constant flow of 1.6mL/min. The flame ionization detector temperature was set at 300°C. The flow rate for hydrogen was 30.0mL/min and the makeup flow for air was 25.0mL/min¹⁹.

RESULTS AND DISCUSSION

The n-C₅:C₆ saturate compositions of the heavy organics in crude oil samples from wellhead, flowline and separator of Sapele well two (SAPW2) are presented on Table 1 and Figure 2. The chromatograms of the saturate compositions from the specific locations are presented in Figures 3-5.

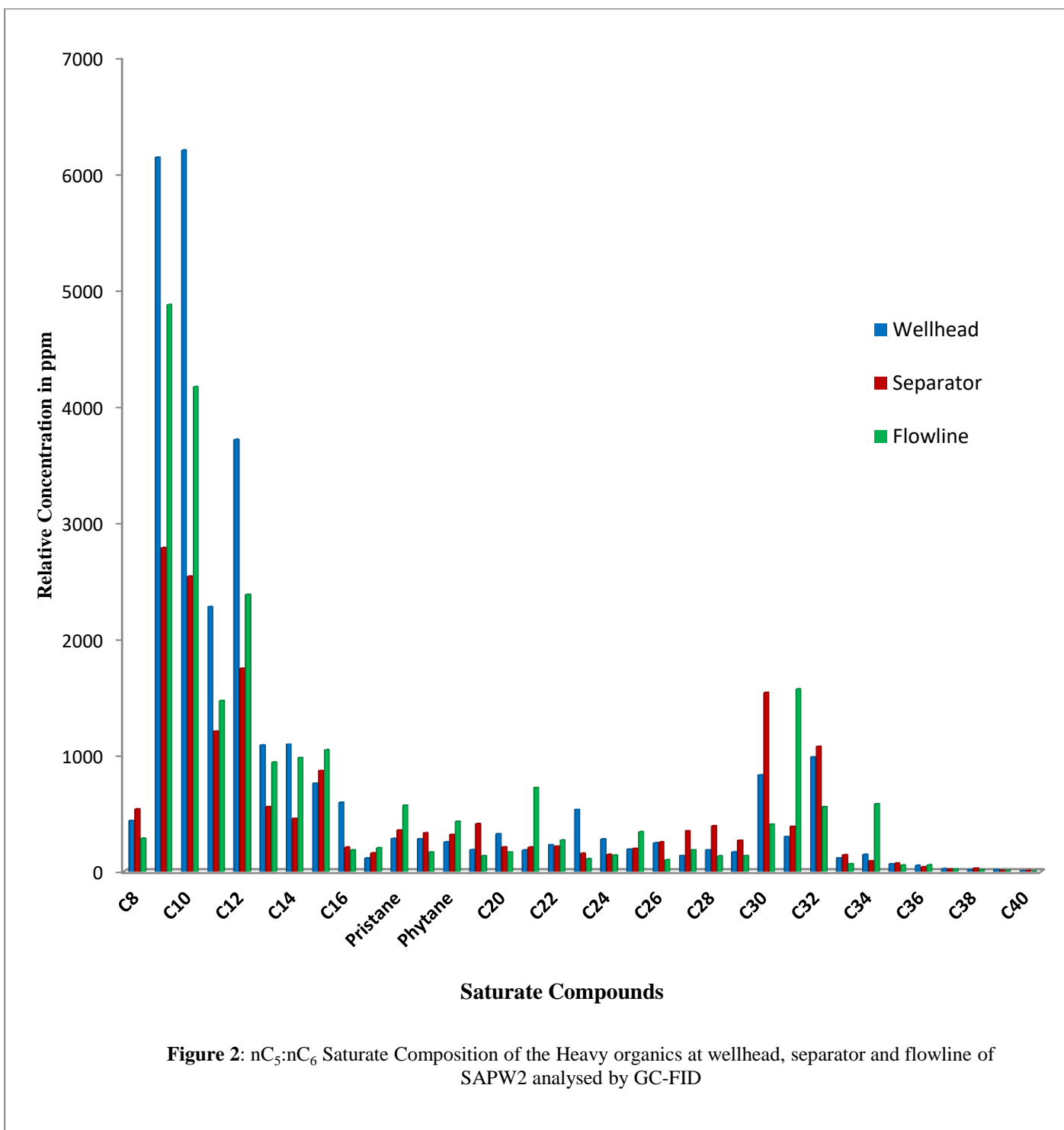
From the results (Table 1 and Figure 2), it was observed that the n-C₅:C₆ heavy organics

showed the highest total saturate concentration at the wellhead with about 28,497ppm, followed by flowline with about 23,512ppm and separator with about 19,346ppm. This is attributed to the increase in concentration of the low molecular weight saturate which might have translated to the increase in wax content in the order: wellhead > flowline > separator as reported by Udourioh *et al.*²⁰.

The lower carbon number saturate C₁₀ (6201ppm) is the most prominent at the wellhead, followed by C₉ (6140ppm). Others include: C₁₂ with 3718ppm, C₁₁ with 2284ppm, C₁₄ with 1097ppm and C₁₃ with 1091ppm. The flowline saturate concentration shows C₉ with 4874ppm as the most prominent, followed by C₁₀ with 4170ppm, C₁₂ with 2387ppm and one higher carbon number saturate C₃₁ with 1572ppm. The lower carbon number saturate C₉ also recorded the highest concentration of 2788ppm at the separator, followed by C₁₀ (2543ppm), C₁₂ (1751ppm) and two higher carbon number saturates, C₃₀ and C₃₂ with 1542ppm and 1079ppm respectively.

Table 1: n-C₅:C₆ Saturate Composition of the Heavy organics at wellhead, separator and flowline of SAPW2 analysed by **GC-FID**

S/N	Saturate Compound	Wellhead (WH) Conc. (ppm)	Separator (SR) Conc. (ppm)	Flowline (FL) Conc. (ppm)
1	C ₈	439.2258	538.5143	284.9236
2	C ₉	6139.9238	2788.3918	4874.3574
3	C ₁₀	6200.6885	2543.3423	4170.1929
4	C ₁₁	2283.7974	1210.1831	1472.1307
5	C ₁₂	3717.9558	1750.6217	2386.9363
6	C ₁₃	1090.7086	558.9276	941.7696
7	C ₁₄	1096.5131	458.1418	981.9200
8	C ₁₅	760.2911	869.9863	1047.7646
9	C ₁₆	594.9592	208.8079	185.1866
10	C ₁₇	115.3873	159.1125	204.1970
11	<i>Pristane</i>	283.5957	357.7971	570.9622
12	C ₁₈	281.3359	333.4398	167.0796
13	<i>Phytane</i>	253.5369	318.3353	430.9031
14	C ₁₉	187.9817	411.7608	134.5449
15	C ₂₀	324.3449	211.5453	168.2198
16	C ₂₁	183.6896	209.1953	723.9913
17	C ₂₂	230.6249	218.7584	270.6129
18	C ₂₃	534.5866	156.8917	108.6926
19	C ₂₄	279.3195	146.1617	140.2826
20	C ₂₅	192.8322	199.4492	341.9622
21	C ₂₆	246.1429	254.0420	100.4135
22	C ₂₇	136.8436	351.1694	186.8270
23	C ₂₈	186.4819	392.5923	133.4189
24	C ₂₉	169.3022	269.0841	137.0291
25	C ₃₀	832.3436	1542.2031	408.1907
26	C ₃₁	301.2075	388.7849	1572.2191
27	C ₃₂	987.4012	1078.4464	558.9957
28	C ₃₃	117.8695	144.1241	67.6076
29	C ₃₄	146.3548	92.6528	582.3583
30	C ₃₅	65.8899	72.6364	55.6646
31	C ₃₆	51.5475	39.7465	56.3874
32	C ₃₇	24.4700	23.0583	22.5650
33	C ₃₈	17.1692	29.5327	13.7576
34	C ₃₉	17.1039	11.1370	6.9419
35	C ₄₀	5.0935	7.4165	3.0291
	Total	28496.5234	19345.9902	23512.0371



All other saturate compounds were present in significant quantities though fewer amounts than those mentioned above, except C_{40} which recorded the least quantity (3.03ppm) at the

flowline, then 5.09ppm at the wellhead and 7.42ppm at the separator. The biomarkers, pristane and phytane were significantly present at all the three locations of the well

under study. Pristane recorded 283.60ppm at the wellhead, 570.96ppm at the flowline and 357.80ppm at the separator. Phytane on the other hand recorded 253.54ppm at the wellhead, 430.90ppm at the flowline and 318.34ppm at the separator.

It could be deduced from the observations on the saturate compositions of the heavy organics from the three different locations of the well's production line that the wellhead recorded the highest total concentrations of saturate compositions of the heavy organics along the production system. This observation is a true reflection of the percentage SARA composition of the bulk oil sample.

However, when a different well (SAPW1) within the same oil field was tested, the opposite observations were noted. As presented in Table 2 and Figure 6, the n-C₅:C₆ saturate composition of the heavy organics for SAPW1 showed the highest total saturate hydrocarbon concentration of about 20686ppm at the separator, followed by the flowline with about 7580ppm and wellhead with about 3778ppm. The total concentration of saturate in this case is in the order: separator > flowline > wellhead. The observation here is a reverse of what was observed on the quantity of HOs precipitated at the three locations of the production system which was in the order: wellhead > flowline >

separator [13]. This may imply that more of saturates were held in solution while asphaltenes precipitated out of the solution.

Within the separator, the lower carbon number saturates: C₉ and C₁₀ showed prominent peak with saturate concentrations of about 3704ppm and 2012ppm respectively, followed by the higher carbon number saturates: C₃₀, C₃₂ and C₃₁ with about 1819ppm, 1718ppm and 1517ppm respectively. C₈ recorded about 1062ppm while C₄₀ recorded the least concentration of about 5.8ppm. Within the flowline, the lower carbon number saturate, C₁₀ recorded the highest concentration of about 994ppm followed by C₉ with about 733ppm, then C₁₂ with about 606ppm. C₃₀ was the only higher carbon number saturate with higher concentration (662ppm). C₃₆, C₃₇, C₃₈, C₃₉ and C₄₀ were almost absent with approximate concentrations of 0.09ppm, 0.16ppm, 0.27ppm, 0.38ppm and 0.07ppm respectively. Within the wellhead, C₉ was prominent with concentration of about 981ppm followed by C₁₀ with about 785ppm. There was almost absence of C₃₇ (0.35ppm), C₃₈ (0.24ppm), C₃₉ (0.75ppm) and C₄₀ (0.43ppm).

In this result, the amounts of total HO precipitates were in the order: wellhead > flowline > separator. This trend was the same as the temperature initiated precipitation of

wax at atmospheric pressure. A casual comparison of the two results may arrive at the conclusion that the wax contents of the different samples are responsible for the trend in the compositional changes induced precipitation because it is well known that the saturates and aromatics compound types are often co-precipitated with asphaltenes and resins ²¹. Hence the preponderance of wax in

the wellhead sample may be assumed to translate to high HOs in the compositional changes induced precipitates.

However, the analysis for the compound types of the HOs show that there is no clear cut trend in the concentration of the individual and total saturates of the heavy organics obtained at the three locations: wellhead, flowline and separator.

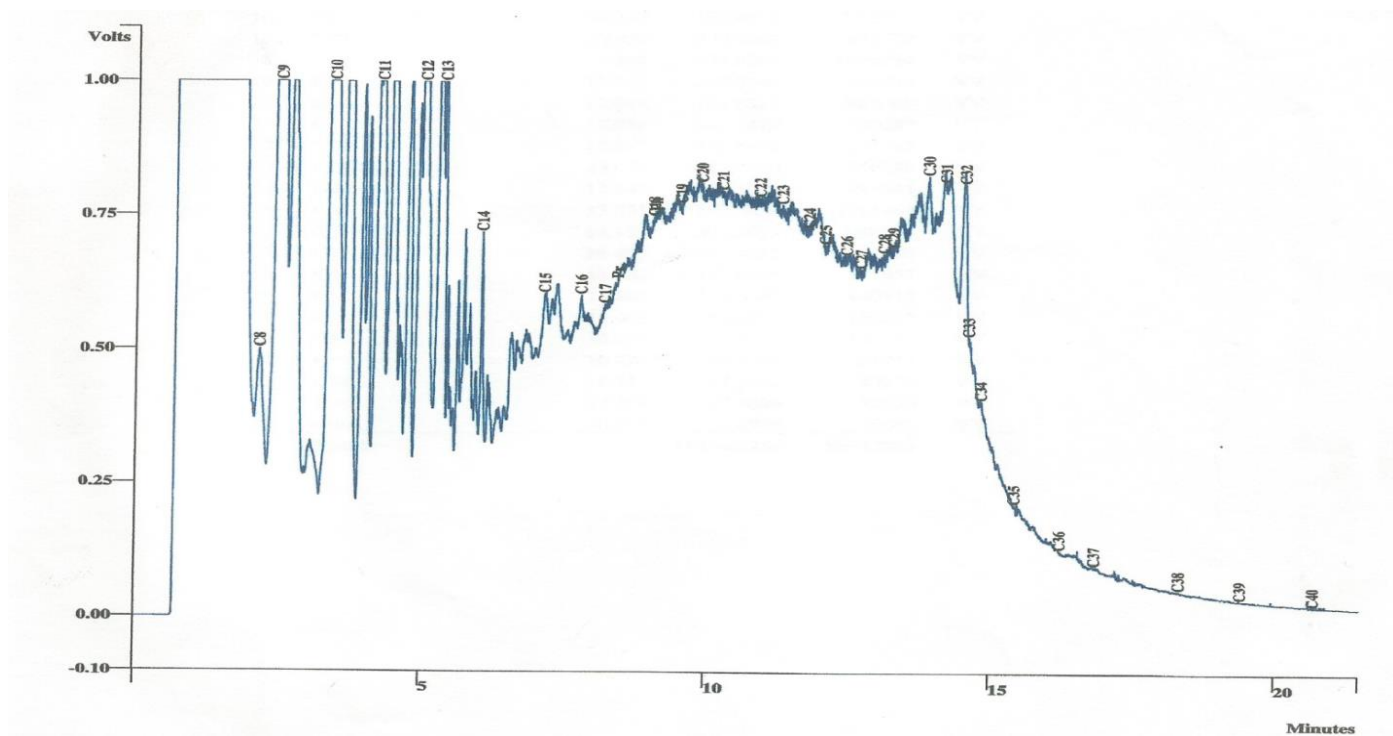


Figure 3: Chromatogram of $nC_5:nC_6$ saturate in HOs precipitated from Wellhead for SAPW2

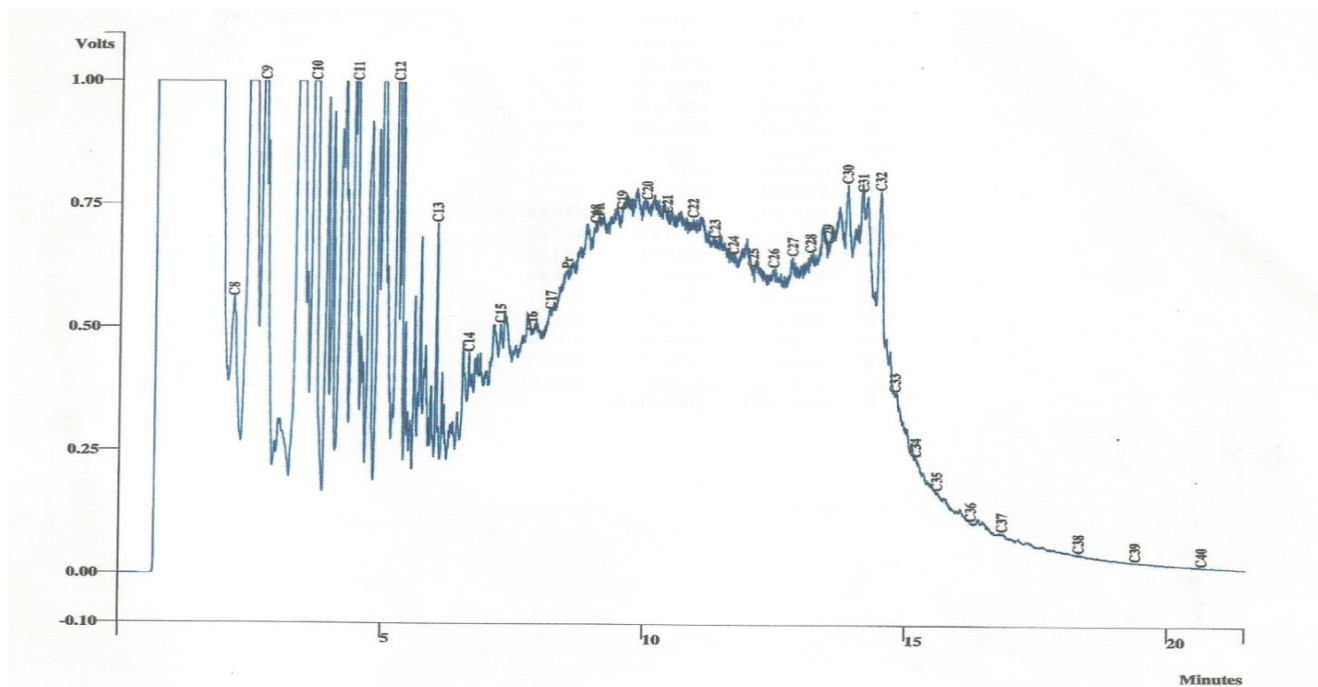


Figure 4: Chromatogram of $nC_5:nC_6$ saturate in HOs precipitated from Separator for SAPW2

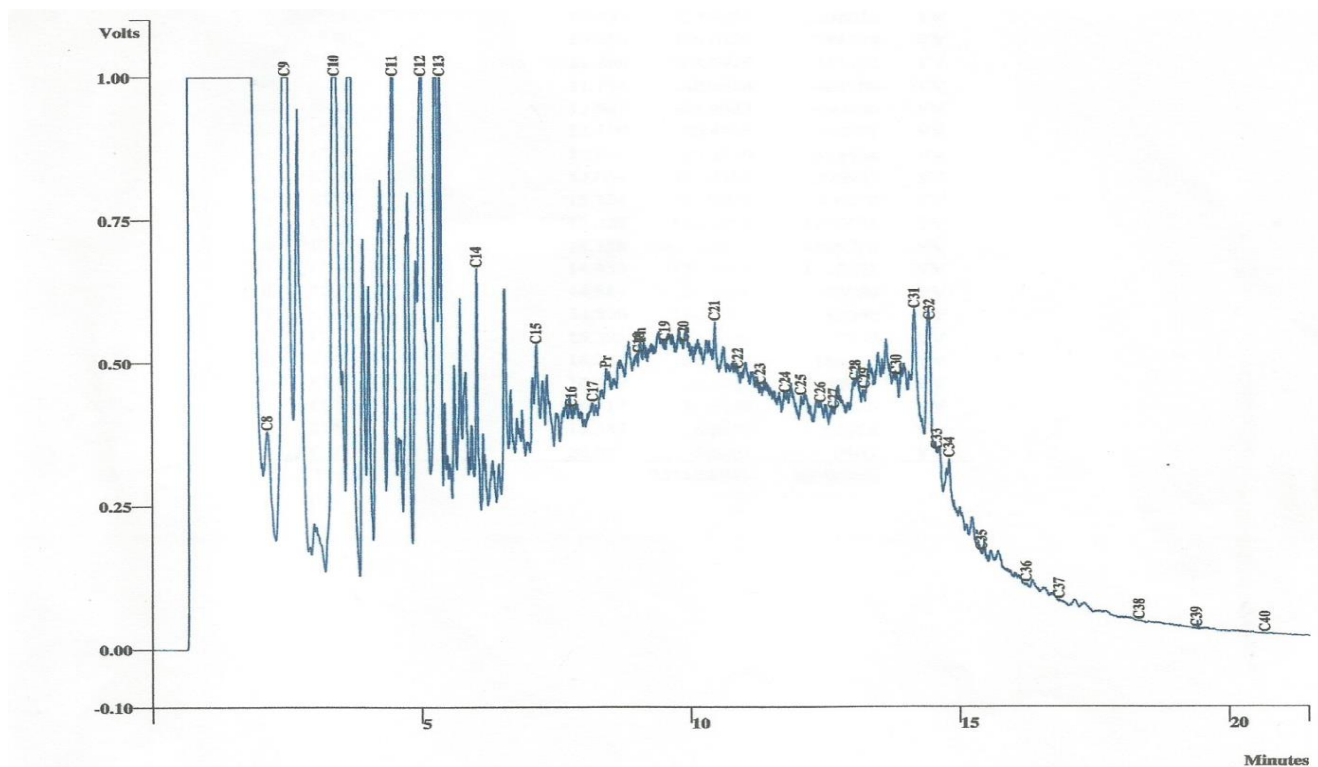
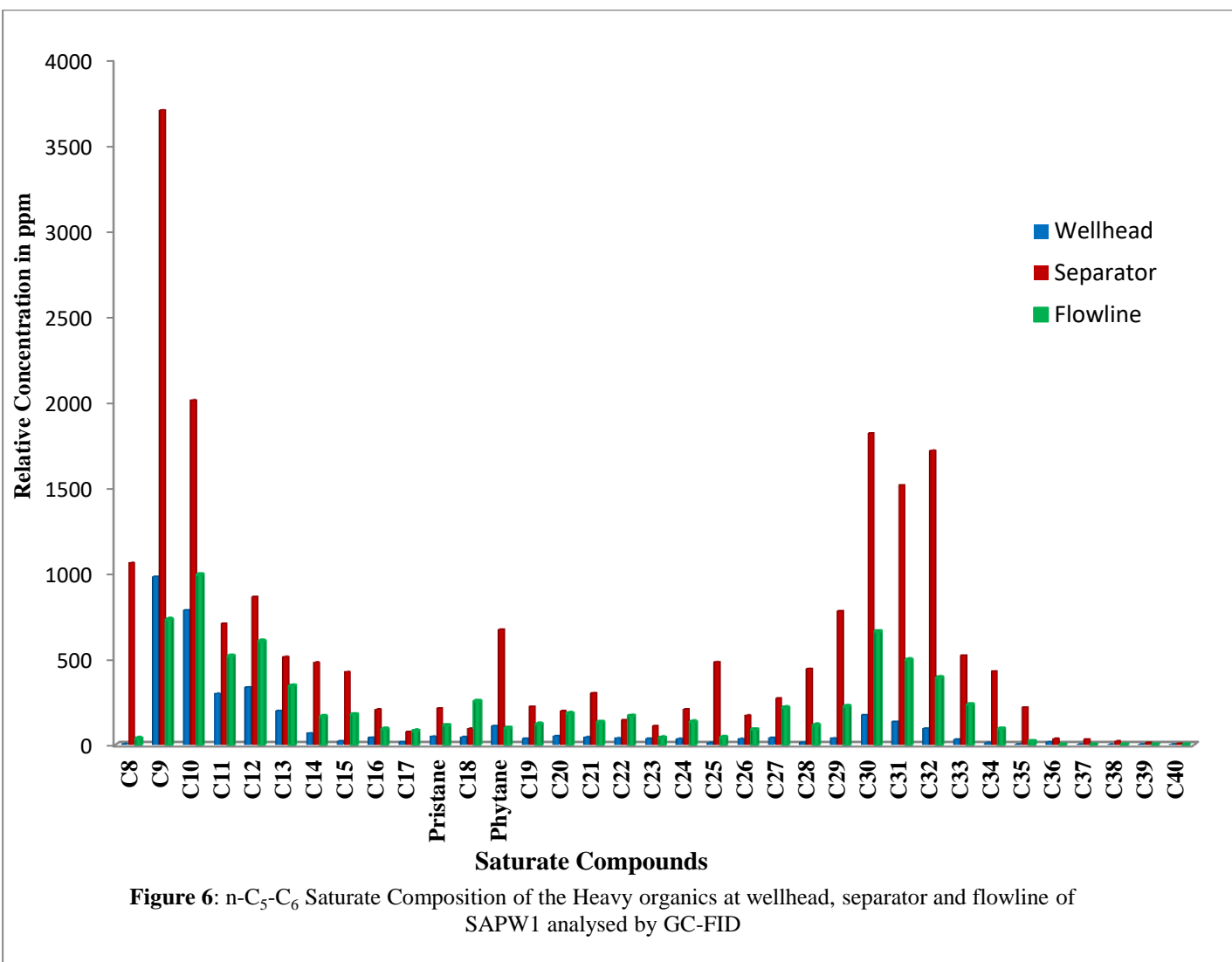


Figure 5: Chromatogram of $nC_5:nC_6$ saturate in HOs precipitated from Flowline for SAPW2

Table 2: nC₅:nC₆ Saturate Composition of the Heavy organics at wellhead, separator and flowline of SAPW1 analysed by **GC-FID**

S/N	Saturate Compound	Wellhead (WH) Conc. (ppm)	Separator (SR) Conc. (ppm)	Flowline (FL) Conc. (ppm)
1	C ₈	3.8875	1061.9482	37.2005
2	C ₉	981.0168	3704.0564	732.7140
3	C ₁₀	785.3117	2012.3416	993.6364
4	C ₁₁	297.7708	707.8850	517.8239
5	C ₁₂	336.1815	863.8522	605.9837
6	C ₁₃	197.6329	513.2810	344.4012
7	C ₁₄	67.1185	479.6607	165.0905
8	C ₁₅	20.5643	424.8654	176.7220
9	C ₁₆	42.3299	205.4346	91.7009
10	C ₁₇	15.8392	75.7540	80.8110
11	<i>Pristane</i>	47.7621	212.9125	113.4530
12	C ₁₈	44.3351	93.0612	254.4052
13	<i>Phytane</i>	109.0149	672.5455	97.8361
14	C ₁₉	35.7155	223.3264	120.6776
15	C ₂₀	49.6240	196.4639	183.4543
16	C ₂₁	43.4423	302.1519	131.6473
17	C ₂₂	38.0396	144.9162	168.2387
18	C ₂₃	34.7307	108.9657	41.2737
19	C ₂₄	33.7626	206.4832	134.3317
20	C ₂₅	9.4591	483.2729	42.9484
21	C ₂₆	33.4816	170.6333	88.7488
22	C ₂₇	39.7181	270.6701	217.4612
23	C ₂₈	12.9107	444.1537	115.4105
24	C ₂₉	37.7523	780.7485	224.2454
25	C ₃₀	173.6962	1819.2743	661.9773
26	C ₃₁	135.1009	1516.6146	496.8441
27	C ₃₂	94.1161	1718.0339	393.6153
28	C ₃₃	30.3238	521.8573	234.6029
29	C ₃₄	9.5496	429.1033	92.5515
30	C ₃₅	1.2662	218.3550	19.3043
31	C ₃₆	14.5290	34.5959	0.0972
32	C ₃₇	0.3494	31.8315	0.1561
33	C ₃₈	0.2345	19.5069	0.2671
34	C ₃₉	0.7525	11.3028	0.3764
35	C ₄₀	0.4341	5.8113	0.0699
	Total	3777.7537	20685.6719	7580.0786



CONCLUSION

There is no trend in the concentration of individual and total saturate composition of the heavy organics along the different locations of the production system.

Therefore, the fact that there was more wax in a sample does not explain the variation of the quantity of heavy organics obtained by the compositional changes precipitation since the

trend in the concentration of saturate at the different locations of the production lines observed here does not correspond to the trend in quantity of HOs and wax precipitate earlier reported. The trend may therefore be attributed to precipitation of asphaltenes and other n-alkane insoluble organic compounds as well as loss of some components along the production line as they flow from the wellhead to the separator.

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