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Minimization of Heavy Organic Deposition by the Application of Binary Mixtures of n-Alkane Solvents in the Oil and Gas Industry

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Abstract

The problem of heavy organic deposition in the production and processing of crude oil in the oil and gas industries is globally known. There had been work done to minimize the problem such as changes in temperature, pressure and composition. This study was designed to investigate how different ratios (v/v) of nC_5:nC_6; nC_5:nC_7; nC_5:nC_8; nC_6:nC_7; nC_6:nC_8 and nC_7:nC_8 affects controlled deposition. The results indicated varying optional (v/v) ratios for the different binary mixtures of Afiesere crude oil; that ***n*C$_5$: *n*C$_6$** binary mixture ratios have a weight % heavy organic precipitation range of 1.02 to 2.42; ***n*C$_5$: *n*C$_7$** binary mixture ratios have a weight % heavy organic precipitation range of 0.15 to 1.88; ***n*C$_5$: *n*C$_8$** binary mixture ratios weight % heavy organic precipitation range of 0.16 to 1.88**; *n*C$_6$: *n*C$_7$** weight % heavy organic precipitation range of 0.85 to 1.19; ***n*C$_6$: *n*C$_8$** weight % heavy organic precipitation range of 0.60 to 1.19 and ***n*C$_7$: *n*C$_8$** binary mixture ratios weight % heavy organic precipitation range of 0.54 to 0.93. Application of the output from this study may minimize deposition problem in the production industries.

Keywords: Heavy organics; Precipitation; Afiesere crude oil; Binary mixtures; Normal alkanes

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Introduction

Crude oil is a complex mixture of hydrocarbons and other compounds of varying molecular weight and polarity. Crude oil can be classified by chemical composition, density, viscosity and distillation characteristics. Heavy organics (fractions) are associated with the problems they cause as solids deposits that obstruct flow in the production system. Heavy organics (fractions) precipitation occurs when there is destabilization of thermodynamic equilibrium in the crude oil. Changes in composition, temperature and pressure have been associated with thermodynamic equilibrium destabilization. Heavy organics (fractions) deposition during oil production and processing is known globally and has been reported to causing several undersea pipeline plugging with substantial economic loss to the oil production operations. The impact of heavy organic (fractions) is felt most in the near-wellbore region where heavy organics (fractions) block pores are difficult to access for remediation. Flocculation and deposition of heavy organics (fractions) can be controlled through a better understanding of the mechanisms that cause its flocculation and deposition in the first place. Production and chemical treatment techniques can be applied to control it [1-7].

In this study, the effect of mixing two *n*-alkane solvents (nC_5, nC_6, nC_7 and nC_8) containing different number of carbon atoms on heavy organics precipitation, the effect of varying ratios of two *n*-alkane solvents on precipitation pattern of heavy organics in crude oil and the relationship in the changes in composition of the petroleum fluids and precipitation of heavy organics will be investigated.

Materials and Methods

The crude oil sample was collected from the Research and Development Division of the Nigerian National Petroleum Corporation (NNPC), Port Harcourt. The precipitation of heavy organics was carried out according to and modified ASTM/IP methods [8]. Approximately, 30 ml of binary mixtures of

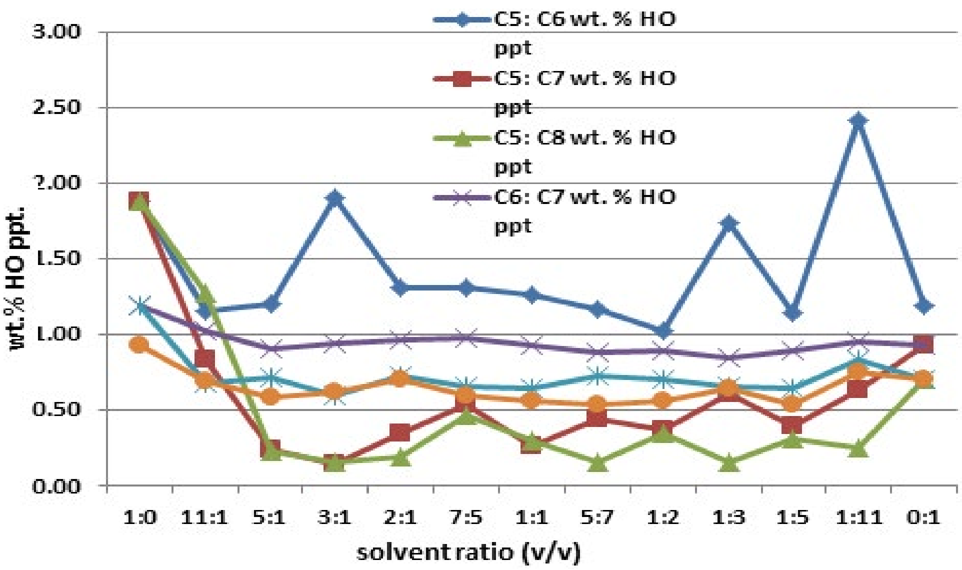

Figure 1 Graphical comparison of weight % heavy organics precipitation for varied ratios of nC_5, nC_6, nC_7 and nC_8 binary solvent mixtures (v/v).

normal alkane solvents were added to 1 ± 0.1 g of crude oil in an appropriate flask. The mixtures were shaken for 30 min using Mechanical shaker and allowed to stand for 48 h. The solution was filtered with a 55 mm diameter Whatman glass microfiber 40-60 µm membrane filter with an initial weight (**W_1**) using vacuum pump fitted in a Buchner flask/funnel. The flask and membrane filter were rinsed with small volumes of the corresponding *n*-alkane binary mixture solvents to eliminate residual oil. The filter paper with the precipitated material was dried in an oven for 2 h at 60°C (333K), weighed (**W_2**) and the difference between **W_2** and **W_1** calculated to determine the heavy organics mass precipitate. The experiment was repeated thrice and a mean value obtained.

Results and Discussion

The percentage weights of the heavy organic precipitate using varying ratios of binary mixtures of *n*-alkane solvents are presented in **Tables 1-6** as well as **Figure 1**.

Results of this study indicate highest precipitation at pure nC_7 and pure nC_5. Fluctuations (phase transitions) in the weight percentage heavy organics precipitations were observed as the binary solvents were mixed with varying ratios. The phase transitions that were observed occurred as a result of the instability and incompatibility of the crude oil mixture as the thermodynamic equilibrium is destabilized.

According to Escobedo et al., heavy organic deposition is as a result of multi-phenomena effect which includes solid-liquid phase transition, liquid-solid phase transition (colloidal formations and growth of colloidal particles) and the solid-liquid phase transition (eventual collapse of the resulting colloids due to limitations on the size of the Brownian particles suspended in the media) [9].

In the pure (100%) normal alkane solvents (as in 1:0 and 0:1 ratios), it was observed that heavy organic precipitation decreases with higher molecular single *n*-alkane solvents. This is in line with Branco et al., Mansoori et al., and Frank et al. [10-12]. However, the trend of precipitation as the volume of corresponding precipitant mixture is altered; there is a complete difference from those of the single n-alkane precipitating solvents [13]. Data from this study indicated three-stage phase transitions (fluctuations) of heavy organics precipitation. At pure *n*-alkane solvent (**C_n**), some of the heavy organics are insoluble in the *n*-alkane diluted oil using a single solvent; hence, they appear in the solid phase. As the *n*-alkane solvent mixture (**C_{n+x}**) were added, part of the precipitated solid heavy organics redissolved in the liquid phase leading to a reduction in the value of the precipitate. At the first minimum point, **C_n/C_{n+x}** dissolution of some precipitated components stop; the reduction in the precipitate as **C_{n+x}** was added may be explained by the solubility of some resins or other heavy organics insoluble in pure **C_n** but soluble in **C_{n+x}**. Moreso, some species that co-precipitated with asphaltene may redissolve. Precipitate formation begins to increase as the ratio of **C_n/C_{n+x}** decreases further (as more **C_{n+x}** are added). This continues to the maximum points of varying ratios of **C_n: C_{n+x}** observed in which colloidal formation and growth of colloidal particles probably occurs leading to agglomeration and precipitation. This brought about the increase in the quantity of precipitate up to maximum points as shown in **Figure 1**. The solid-liquid phase transition showed the collapse of the resulting colloids according to due to limitations on the size of the Brownian particles suspended in the crude oil medium. The collapse begins as the volume of **C_{n+x}** exceeds **C_n** volumes and continues to the varying ratios of **C_n : C_{n+x}** where maximum points were observed [8].

Tables 1 to 6 showed minimal precipitations for the crude oil at binary mixture ratio of **1:2 for nC_5: nC_6**; ratio of **3:1 for nC_5: nC_7**; ratios of **3:1, 5:7 and 1:3 for nC_5: nC_8**; ratio of **1:3 for nC_6: nC_7**; ratio of **3:1 for nC_6: nC_8** and ratios of **5:7 and 1:5 for nC_7: nC_8** which gives the lowest and best binary mixtures that is suitable for heavy organics (fractions) precipitation.

Table 1 Heavy Organics precipitate using varying ratios of binary mixture of *n*-pentane (nC_5) and *n*-hexane (nC_6) at 30 ml/g oil.

Test S/No	nC_5: nC_6 Solvent ratios (v/v)	wt. % HO precipitated
1	1:0	1.88
2	11:1	1.16
3	5:1	1.20
4	3:1	1.90
5	2:1	1.31
6	7:5	1.31
7	1:1	1.26
8	5:7	1.17
9	1:2	**1.02
10	1:3	1.74
11	1:5	1.14
12	1:11	2.42
13	0:1	1.19

* nC_5: nC_6 represent binary solvent mixture of nC_5 and nC_6
** indicates the lowest and best binary solvent mixture for heavy organic precipitation

Table 2 Heavy Organics precipitate using varying ratios of binary mixture of *n*-pentane (nC_5) and *n*-heptane (nC_7) at 30 ml/g oil.

Test S/No	*nC_5: nC_7 Solvent ratios (v/v)	wt. % HO precipitate
1	1:0	1.88
2	11:1	0.83
3	5:1	0.24
4	3:1	**0.15
5	2:1	0.35
6	7:5	0.54
7	1:1	0.26
8	5:7	0.44
9	1:2	0.37
10	1:3	0.61
11	1:5	0.39
12	1:11	0.63
13	0:1	0.93

* nC_5: nC_7 represent binary solvent mixture of nC_5 and nC_7
** indicates the lowest and best binary solvent mixture for heavy organic precipitation

Table 3 Heavy Organics precipitate using varying ratios of binary mixture of *n*-pentane (nC_5) and *n*-octane (nC_8) at 30 ml/g oil.

Test S/No	*nC_5: nC_8 Solvent ratios (v/v)	wt. % HO precipitate
1	1:0	1.88
2	11:1	1.28
3	5:1	0.23
4	3:1	**0.16
5	2:1	0.19
6	7:5	0.47
7	1:1	0.30
8	5:7	**0.16
9	1:2	0.35
10	1:3	**0.16
11	1:5	0.31
12	1:11	0.25
13	0:1	0.71

* nC_5: nC_8 represent binary solvent mixture of nC_5 and nC_8
** indicates the lowest and best binary solvent mixture for heavy organic precipitation

Table 4 Heavy Organics precipitate using varying ratios of binary mixture of *n*-hexane (nC_6) and *n*-heptane (nC_7) at 30 ml/g oil.

Test S/No	*nC_6: nC_7 Solvent ratios (v/v)	wt. % HO precipitated
1	1:0	1.19
2	11:1	1.02
3	5:1	0.91
4	3:1	0.94
5	2:1	0.96
6	7:5	0.98
7	1:1	0.93
8	5:7	0.88
9	1:2	0.90
10	1:3	**0.85
11	1:5	0.89
12	1:11	0.95
13	0:1	0.93

* nC_6: nC_7 represent binary solvent mixture of nC_6 and nC_7
** indicates the lowest and best binary solvent mixture for heavy organic precipitation

Table 5 Heavy Organics precipitate using varying ratios of binary mixture of *n*-hexane (nC_6) and *n*-octane (nC_8) at 30 ml/g oil.

Test S/No	*nC_6: nC_8 Solvent ratios (v/v)	wt. % HO precipitated
1	1:0	1.19
2	11:1	0.68
3	5:1	0.72
4	3:1	**0.60
5	2:1	0.73
6	7:5	0.66
7	1:1	0.65
8	5:7	0.73
9	1:2	0.70
10	1:3	0.66
11	1:5	0.64
12	1:11	0.84
13	0:1	0.71

* nC_6: nC_8 represent binary solvent mixture of nC_6 and nC_8
** indicates the lowest and best binary solvent mixture for heavy organic precipitation

Table 6 Heavy Organics precipitate using varying ratios of binary mixture of *n*-heptane (nC_7) and *n*-octane (nC_8) at 30 ml/g oil.

Test S/No	*nC_7: nC_8 Solvent ratios (v/v)	wt. % HO precipitate
1	1:0	0.93
2	11:1	0.69
3	5:1	0.58
4	3:1	0.62
5	2:1	0.70
6	7:5	0.60
7	1:1	0.56
8	5:7	**0.54
9	1:2	0.56
10	1:3	0.64
11	1:5	**0.54
12	1:11	0.75
13	0:1	0.71

* nC_7: nC_8 represent binary solvent mixture of nC_7 and nC_8
** indicates the lowest and best binary solvent mixture for heavy organic precipitation

Conclusion

The investigation showed that at volume ratios of 3:1 of nC_5: nC_7; 3:1, 5:7 and 1:3 of nC_5: nC_8; the weight % heavy organics precipitated (0.15 and 0.16 wt. % HO respectively) in the binary mixtures of the precipitating solvents indicated that it is the most appropriate for the minimization of heavy organics precipitation of Afiesere oil-field crude. With this understanding, therefore, applying same to the crude oil investigated, being transported and/or stored, will keep the heavy organics in solution.

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