Original Research Article

Influence of Heavy Organics Composition on Wax Properties and Flow Behavior of Waxy Crude Oils

.

ABSTRACT

Paraffinic crude oils are desirable because of their high content of saturated hydrocarbons but may present handling challenges due to crystallization of high molecular weight paraffin at low temperatures. The prediction of wax properties and behavior of waxy crude oil is important in order to adopt appropriate mitigative measures to forestall flow assurance problems associated with wax crystallization and deposition. Accurate predictive models are limited mainly by the sheer complexity of crude oil composition. SARA analysis has been used as a simple tool to predict and interpret crude oil properties and behavior but has been found inadequate in predicting wax instability. In this paper, we report on the use of SARA analysis and paraffin distribution data to interpret the wax properties and flow behavior of Niger-Delta crude oils. The crude oil properties determined include wax content, asphatene and resin content by gravimetry, pour point, wax appearance temperature by cross-polarized microscopy and paraffin carbon number distribution of whole oil and wax precipitate by GC-FID. Asphaltene and resin content were found to influence the oil pour point, while saturates content, paraffin carbon number of crystallizing waxes and wax content control its low-temperature flow properties.

Keywords: [Waxy crude oil; pour point; asphaltenes; paraffin; wax appearance temperature]

1. INTRODUCTION

Wax formation and deposition is a flow assurance problem associated with the production and transportation of paraffinic crude oils especially in offshore environments. Such oils are characteristically rich in saturated aliphatic hydrocarbons which crystallize as the high temperature and pressure conditions in the reservoir, which are necessary to keep them in solution, are relieved during production [1, 2]. High molecular weight alkanes (> C-16) precipitate in a regular crystal structure from oil when the temperature of the oil falls below its wax appearance temperature (WAT), increasing the oil viscosity thereby decreasing ease of pumpability. Deposition of waxes in internal surfaces of production tubings and pipelines restricts flow and jeopardizes the safety and profitability of oil production. If the temperature of the oil drops to its pour point, under static conditions, a solid gel is formed resulting in difficulty in restarting production [3]. Knowledge of the composition and wax properties of a reservoir is of interest to industry operators as it informs the best handling practice for the produced fluid. However crude oil is a highly complex mixture and oil from different wells are unique in composition and properties [4].

For simplicity, the components of crude oil may be separated into one of four solubility/polarity molecular group-types: saturates, aromatics, resins and asphaltenes- SARA, which is useful for understanding oil properties and behaviour such as asphaltene instability, emulsion stabilization and compatibility of commingled streams [5 - 8]. However Mmata et al [9] have demonstrated that SARA alone cannot be used as a predictive tool for wax instability because crude oil with high saturates content may exhibit no tendency for wax instability. Baha et al [10] have also arrived at a similar conclusion. The lack of supporting chromatographic data on crude oil paraffin composition in Mmata's work [9] contributed to the difficulty in correlating some of the compositional parameters of the Niger-Delta crude oils such as wax content and saturates content with wax properties, and properly accounting for a number of observations such as negligible wax content of high saturates oil.

Heavy normal paraffins (>C-24) increase the tendency for waxes to crystallize from crude oil and can induce the crystallization of an otherwise soluble alkane of lower carbon number [11, 12]. Conversely, a wide paraffin carbon number distribution reduces wax crystallization potential and oil pour point due to co-crystallization of alkanes of different chain lengths and steric hinderance to crystal growth by associations of shorter alkanes. [13 – 15].

A quantitative correlation (based on increase in fractal dimension of wax crystals) between wax crystal morphology and several compositional parameters of waxy oil indicated that resin and asphaltene content were the most important compositional parameters that influence increase in fractal dimension and consequently flow improvement of waxy crude oil treated with pour point depressants [16]. In this study, the heavy organics composition of some Niger-Delta waxy crude oils is investigated by also considering the paraffin composition of crystallized waxes in relation to the oil in order to gain a better understanding of the influence of heavy organics on wax properties and low-temperature flow properties of crude oil.

2. EXPERIMENTAL

Waxy crude oil from seven wells located in four different oilfields in the Niger Delta were collected and labeled A – G. Prior to pour point analysis the field sample was placed in a water-bath at 60^{o}C after which it was stored in the laboratory for 24hours.The oils were confirmed to contain no water by Dean-Stark distillation

2.1 Crude oil Characterization

2.1.1 Specific gravity

Specific gravity (60^{o}F) and API gravity of the crude oil samples were determined according to (ASTM D 1298-12b).

2.1.2 Kinematic Viscosity

Kinematic viscosity was determined at 40^{o}C &100^{o}C according to ASTM D455-12, using a Stanhope-Seta KV-8 Viscometer bath.

2.1.3 Wax Content

UOP 46-64 method for the determination of wax content reported in Mmata et al [9] was adopted with slight modification by eliminating the clarification step using fuller's earth.

2.1.4 Asphaltene Content

A modification of ASTM D6560 was adopted for the determination of asphaltene content (heptane insolubles) of crude oil. Crude oil samples were dissolved in heptane in a ratio of 1:30 and heated under reflux for 60mins. After cooling, the mixture was vacuum-filtered through 0.45μm Millipore® filter paper.

2.1.5 Pour Point

Pour point was determined by ASTM D5853-17a (Procedure A) using a Seta Pour Point refrigerator. The crude oil was heated to 60^{o}C and the pour point test jar containing the oil was placed in the cooling jacket of pour point refrigerator. Every 3^{o}C decrease in temperature, the test jar is gently extracted from the cooling jacket without disturbing the oil to check for flow. The process is repeated until pour point is reached.

2.1.6 Wax Appearance Temperature (WAT)

The wax appearance temperature was determined by cross-polarized microscopy (CPM), according to ASTM D5772, using an Olympus BX51 cross-polarized microscope equipped with a nitrogen-cooled Linkam sample stage. Linksys32 program controlled the process, heating the sample at a rate of 5^{o}C per minute to 60^{o}C. This temperature was maintained for 1minute, then the sample was cooled at a rate of 1^{o}C per minute and images captured every 30seconds.

2.2. SARA Analysis

A known weight of crude oil was refluxed with heptane and filtered to remove asphaltene precipitate. The filtrate (maltenes) was transferred to a silica gel column. Saturates, aromatics and resins were eluted in order of increasing polarities with petroleum benzine, toluene and a 3:1 dichloromethane: methanol solution respectively.

2.3 Gas Chromatography Analysis

Paraffin carbon number distribution was determined by gas chromatography (GC) (ASTM D3328) using an Agilent 7890A gas chromatograph equipped with a flame ionization detector (FID). 1 micro-liter of crude oil sample was injected at 250^{o}C and 18.54psi. The column was 50metres long, 0.5micrometers thick with an internal diameter of 0.2mm. Helium was used as carrier gas at a rate of 15cm/sec. The maximum column temperature was 325°C.

The crude oil wax was precipitated using the modified UOP 46-64 method. The wax was dried and then dissolved in dichloromethane (DCM). The wax-DCM solution was injected in the chromatograph and analyzed under the same experimental conditions as the whole crude oil

2.4. Viscometric Evaluation

The relationship between shear rate, shear stress, viscosity of the crude oil was determined within a temperature range of 10 – 50°C using a coaxial cylinder viscometer.

3. RESULTS AND DISCUSSION

3.1 Crude Oil Characterization

The physico-chemical properties of crude oil samples are presented in Table 1. The API gravity shows that the samples are light paraffinic crude oil rich in light end hydrocarbons. The crude oil samples have medium to high wax content and pour point ranging from 9 to 27°C. Table 2. shows the SARA composition of crude oils A – G. The high saturates content explains their low specific gravity (high API gravity) but does not correlate with API gravity on a sample basis. For instance crude oil with highest saturates content has the lowest API gravity. This is as a result of the heavy asphaltenes and resins contained in the crude oil. For the same reason, as expected, the lower API gravity oils, generally also have higher kinematic viscosities. The kinematic viscosity describes the fluid's resistance to flow under gravity.

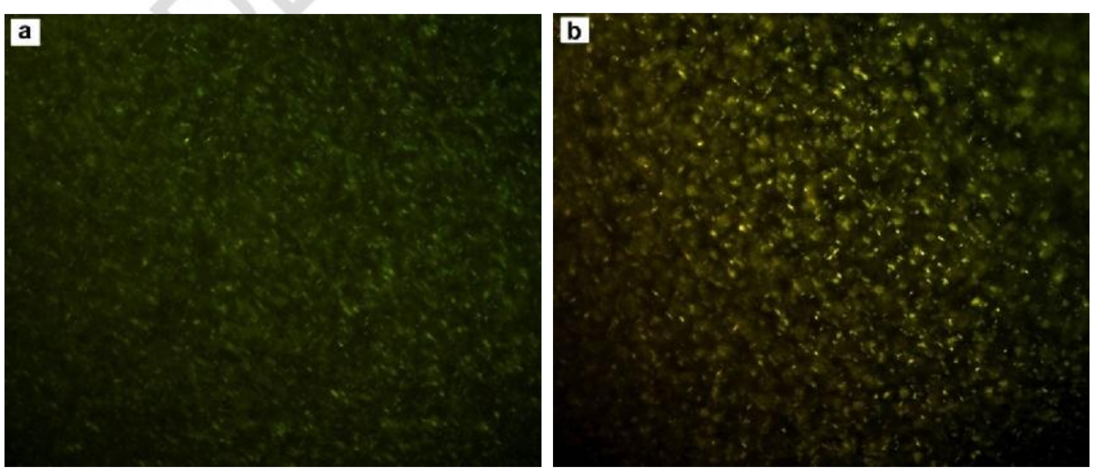
Micrographs of the crude oils are shown in Fig.1.The crude oils exhibit distinct wax morphologies which may be related to the paraffin carbon number distribution and asphaltene and resin content. The wax appearance temperature is determined visually as the incipient wax crystals become visible as bright spots under the cross-polarized microscope.

Table 1.Physico-chemical properties of crude oil samples

	A	B	C	D	E	F	G
Specific gravity(60/60^{o}F)	0.851	0.840	0.828	0.87	0.85	0.818	0.859
API gravity	34.7	36.9	39.3	30.6	34.9	41.5	33.3
Kinematic viscosity cSt(40^{o}C)	3.69	3.06	2.36	5.69	3.26	1.64	3.12
Kinematic viscosity cSt (100^{o}C)	1.29	1.1	1.19	1.98	1.28	0.87	1.39
Wax content (%)	26.5	12.6	11.2	12.3	17.4	8.2	14.6
Wax Appearance Temperature (^{o}C)	36.5	24.1	28.3	32.1	34.7	23.6	36.2
Pour point (^{o}C)	27	9	21	15	24	18	24

Table 2. SARA composition of crude oil samples

% Composition	A	B	C	D	E	F	G
Saturates	79.3	67.7	64.3	80.5	76	66	76.3
Aromatics	17.5	28.5	31.5	16.1	21	30.7	20.8
Resins	2.0	2.0	3.0	2.0	2.3	1.7	1.7
Asphaltenes	0.09	0.27	0.07	0.3	0.11	0.04	0.18



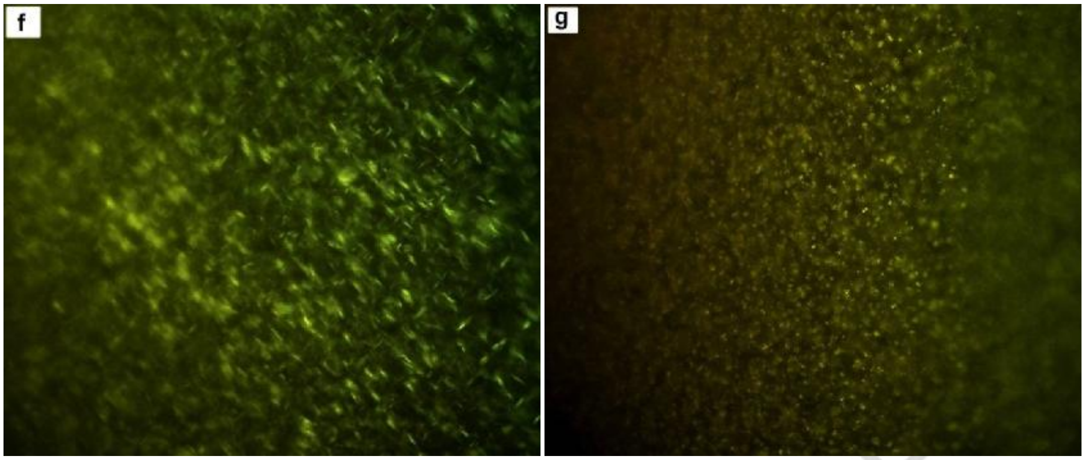


Fig.1. Polarized optical micrographs of crude oil A, B, F and G; A at 16.8°C (a), B at 18.7°C (b), F at 11.8°C (f) and G at 18.5°C (g)

3.3 Paraffin Carbon Number Distribution

Gas chromatograms for the crude oil sample and wax precipitate are shown in Fig 2. The average carbon number distribution of crude oils and wax fraction (Table 3) indicate that the crude oils are rich in light end paraffins (< C -10). The low average n-paraffin carbon number of crude oil F corresponds to its low wax content, indicating that the oil is relatively richer in non-crystallizable low molecular weight alkanes which also provide solvency for the higher molecular weight crystallizable alkanes. Chromatograms of the wax deposit also show an abundance of high molecular weight C -24 to C-32 n-paraffins (Fig. 2). In theory, C-16+ paraffins will be expected to crystallize from the oil, but in practice the degree of crystallization of C-16 to C-20 normal alkanes (in some wax deposits in which they do crystallize) is small. Relative to C-21+ carbon numbers they are generally negligible and their peaks unresolved. It suggests that the main n-paraffin components of wax deposits are the higher carbon number C-21+ fractions. Therefore these are the crude oil fractions of major interest in our discussion.

The carbon number distribution of C-21+ normal paraffins in the crude oils, shown in Fig. 3, may be contrasted with a similar distribution for their corresponding wax deposits from the oil shown in Fig. 4. Expectedly the modal n-paraffin carbon number of each crude oil sample shifts to a higher carbon number in its wax deposit because the higher molecular weight n-alkanes preferentially crystallize from oil as oil temperature decreases. More importantly, for a given carbon number, the degree of crystallization across oil samples is not proportionate to its concentration in the oil such that, for example, although crude oil B has a higher content of C-27 normal paraffin than crude oil C, wax deposit of crude oil C has a higher content of C-27 normal paraffin than crude oil B. Clearly some other compositional factor is responsible for this observation. As demonstrated by Senra et al (2008), this could be as a result of interaction between adjacent n-paraffin carbon numbers via induced co-crystallization or inhibition of crystallization by lower carbon numbers. The case of sample B and C are only illustrative. Several similar trends can be observed in the distributions such as sample D with highest concentration of C-22 to C-34 carbon numbers in crude oil but not in its wax deposit.

Taking the illustration further, wax deposit of sample C has a higher content of C-26 to C-33 n-paraffins than wax deposit of sample B in contrast to their corresponding distribution in the crude oil where crude oil B has higher concentration across all paraffin carbon numbers. The consistency of this trend suggests that beyond the paraffin carbon number interactions, the higher asphaltene content of crude oil B is responsible for inhibition of wax crystallization. This correlates perfectly with the much lower pour point of crude oil B (9^oC) compared to C (21^oC) even though crude oil B has higher saturates content and wax content. Again a comparison of the distributions of sample D and G amongst others buttresses the point. Apparently the asphaltenes have a more pronounced effect on pour point than WAT and is mainly responsible for the poor correlation often observed between wax and saturates content of waxy crude oils and their wax properties.

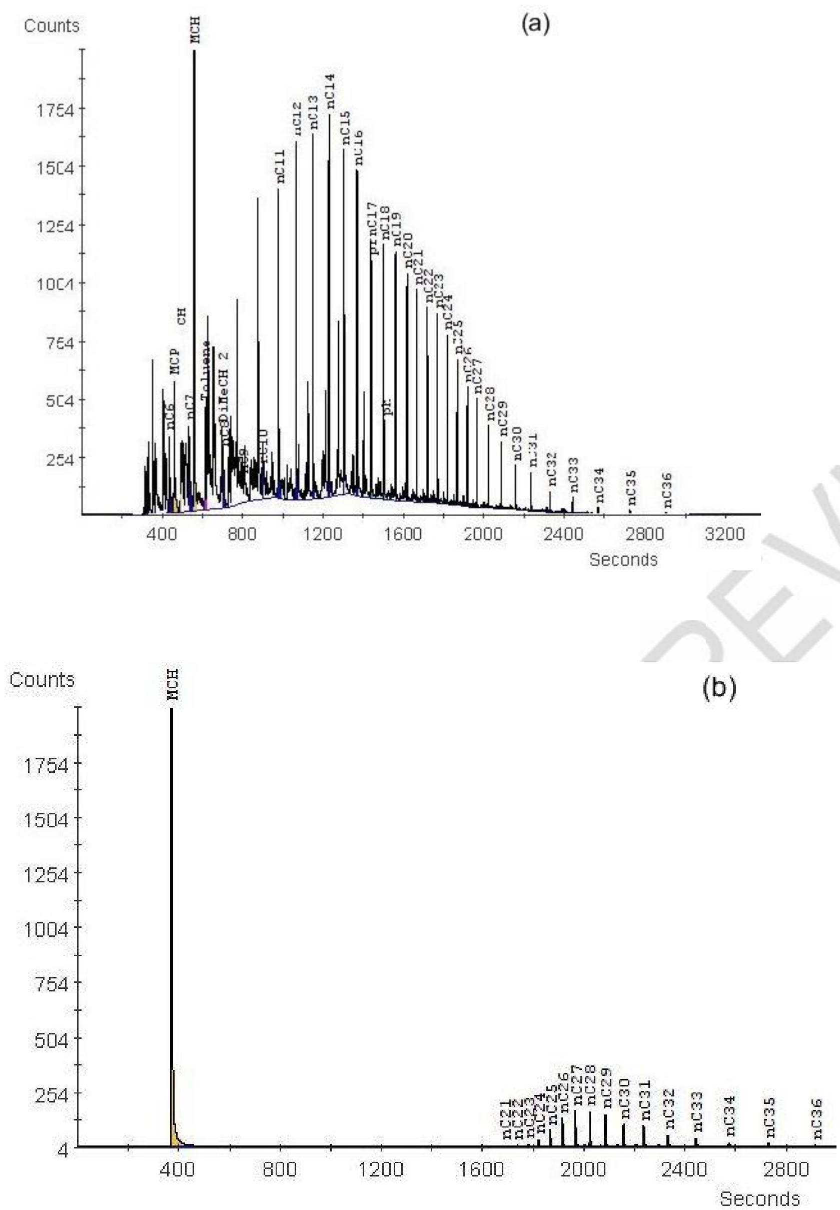


Fig. 2. GC-FID chromatogram of crude oil F (a) and wax precipitate of sample F (b)

Table 3. Average n-paraffin carbon number (CN) of whole crude oil and wax precipitate

	A	B	C	D	E	F	G
Average n-paraffin CN (whole oil)	9.1	9.9	8.4	8.6	8.7	6.9	9.2

Average n-paraffin CN (wax precipitate)	25.4	26	26.6	25.9	24.1	25.8	26.1

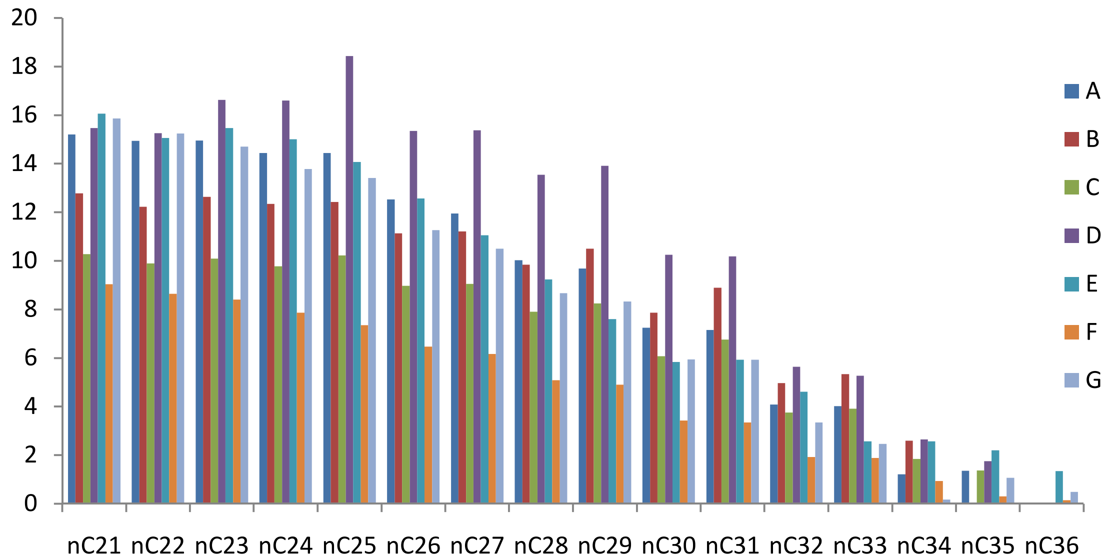


Fig. 3. Carbon number distribution of C-21+ n-paraffins in crude oil

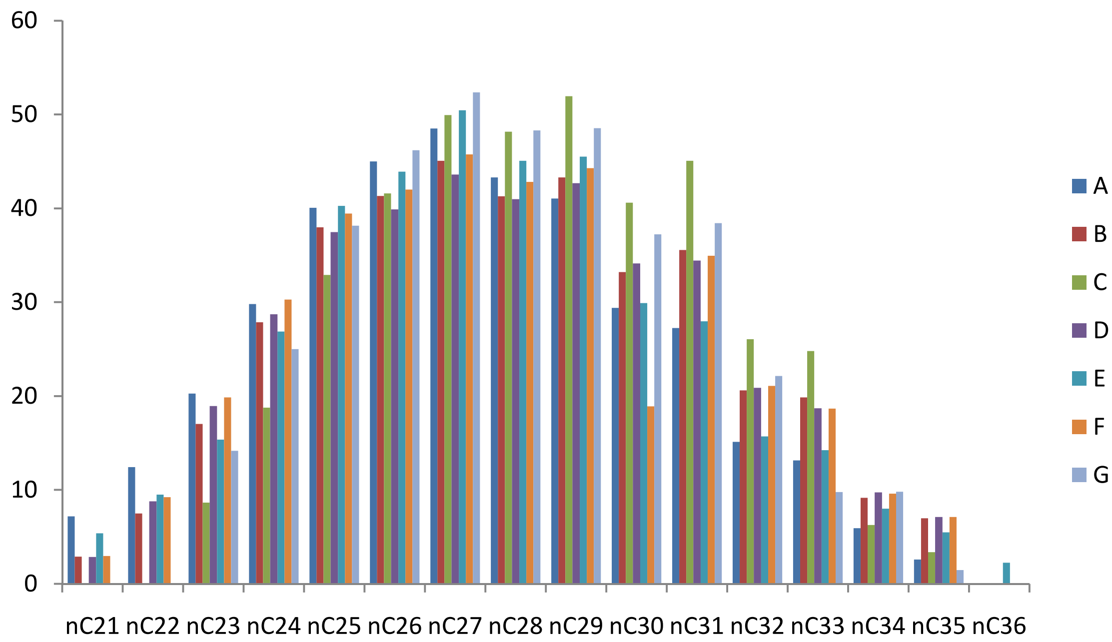


Fig. 4. Carbon number distribution of n-paraffins in wax precipitate

3.4 Viscometry

The relationship between shear rate and shear stress of the crude oils below and above the wax appearance temperature (WAT) is show in Figure 5. As the oil cools to temperatures below its WAT, waxes crystallize in the oil changing its flow behavior and increasing its resistance to shear. It is possible that the amount of crystallized wax in the crude oils at the reference temperature (15^{o}C) may vary slightly since their WAT are different. However it must be noted that since amount of precipitation per time is largely dependent on compositional parameters once physical conditions are identical, an evaluation of the shear rate-shear stress relationship provides a reasonable assessment of the influence of compositional parameters on flow behavior.

The shear stress response of crude oil D to changes in shear rate may be used to obtain a perspective of the influence of compositional parameters on the flow behavior of the crude oils. Crude oil D with the highest saturates content has a shear stress response that is approximately midway between samples A, G and C and samples E, F and B, where A and

G have comparable (and slightly lower) saturates content but higher wax content than D and crude oil E, F and B have much lower saturates content (Table 1). This is due to the higher concentration of asphatenes in crude oil D which are inhibitive to wax crystallization. This is counter-balanced by increase in crystallization potential of the crude oil with increasing content of high molecular weight alkanes. These are the two major factors at play in crude oil D. (Fig 3).

Above the oil WAT, the waxes are in solution, it is observed that the shear stress of the crude oils decreases and is controlled by the resin and asphaltene content (Fig 6). Greater change in shear stress with temperature indicates higher waxiness. The flow behavior of crude oil C below and above WAT is related to the higher abundance of C-28+ waxes and the higher resin content respectively. The shear stress response of the crude oils is influenced by saturates contents, asphaltene content, molecular weight of crystallizing waxes, resin content and wax content.

The viscosity of the crude oil samples decreases with increase in shear rate. The slope of the curve is initially steep but virtually levels out at higher shear rate (Fig 7 & 8). Shear rate of 50/s is optimal for oil flow below WAT. The high viscosity is due to wax crystals in the oil. Above the WAT, the viscosity of the oils decreases in order of their waxiness. At a temperature near the experimental WAT, the viscosity of the crude oils decrease no further with increase in temperature (at constant shear rate) as the precipitated waxes re-dissolve in the oil. This point should approximately correspond to the wax disappearance temperature (WDT)

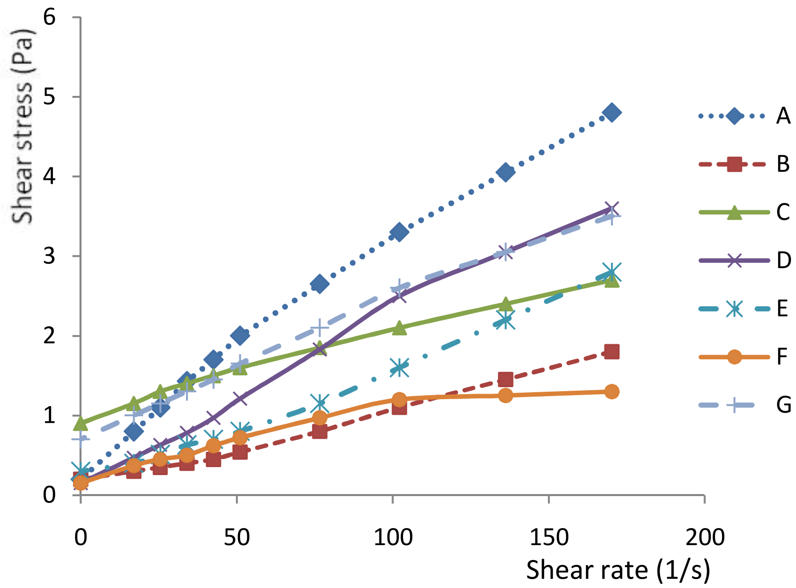


Fig. 5. Shear rate-shear stress relationship of crude oil at 15°C (below WAT)

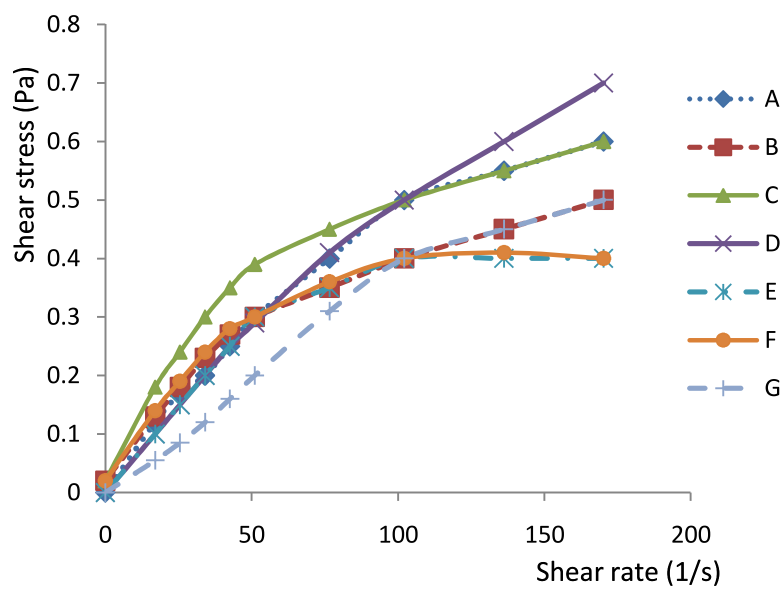


Fig.6. Shear rate-shear stress relationship of crude oil at 45°C (above WAT)

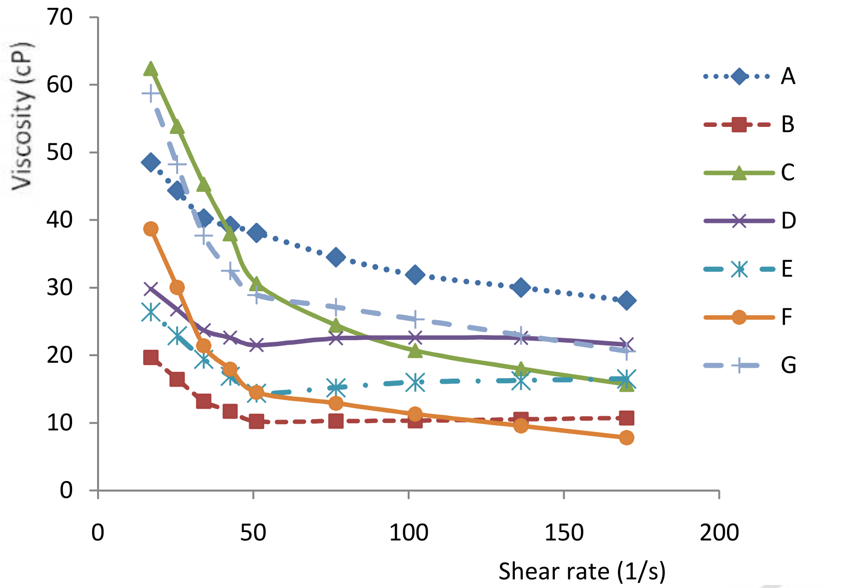


Fig. 7. Effect of shear rate on crude oil viscosity at 15°C (below WAT)

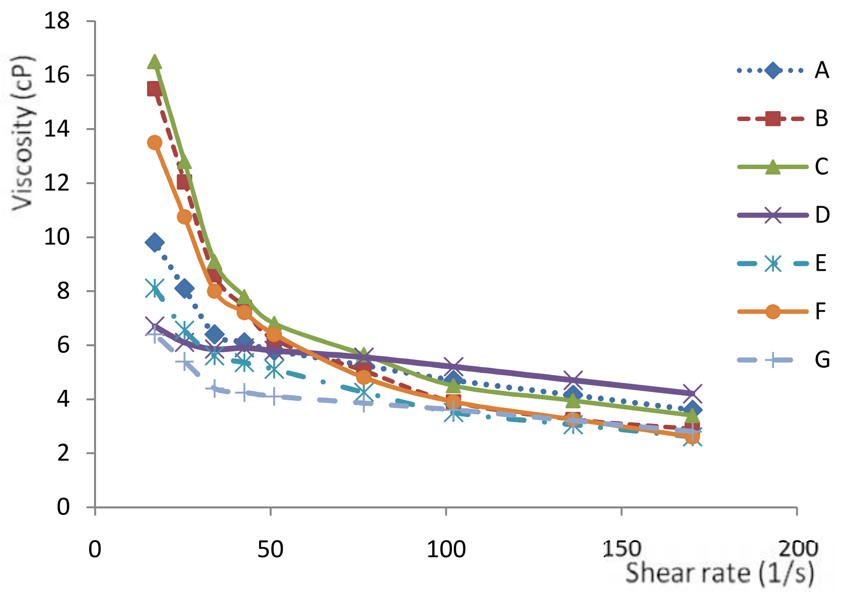


Fig. 8. Effect of shear rate on crude oil viscosity at 45°C (above WAT)

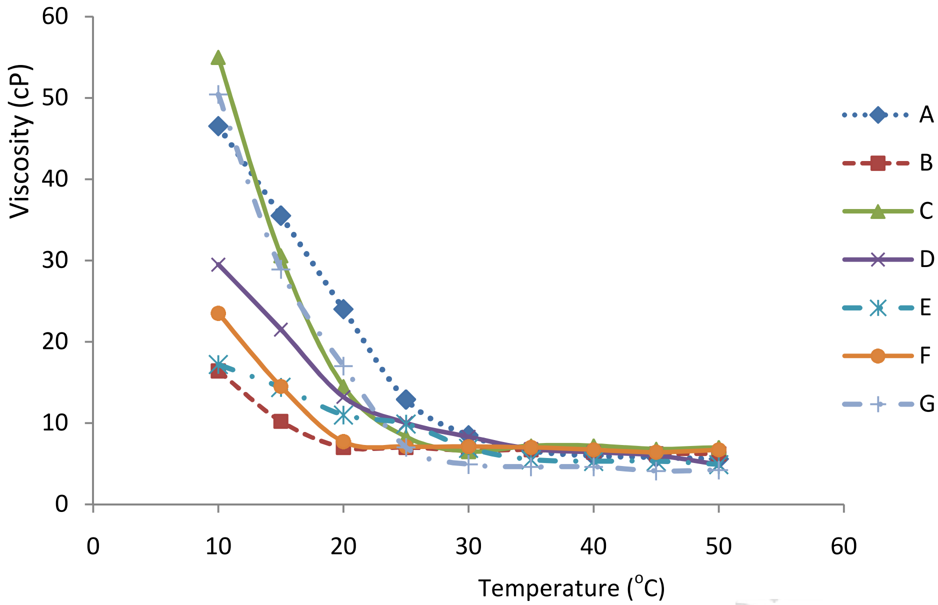


Fig. 9. Plot of viscosity versus temperature at constant shear rate (51/s)

4. CONCLUSION

For low asphaltene waxy crude oils, asphaltenes cause depression in crude oil pour point because the asphaltenes act as natural pour point depressants/wax inhibitors/wax crystal modifiers. Inhibition of wax crystallization by asphaltenes and resins results in poor correlation between saturates content and wax properties because the degree of crystallization of high molecular weight alkane numbers will not correspond to their concentration in the oil. Therefore waxiness cannot easily be inferred based on SARA composition alone. Wax deposits from crude oil are richer in C-21+ n-alkanes, the content of lower crystallizable alkane numbers is small. Below oil WAT, the flow properties of crude oil are controlled by its paraffin composition parameters such as saturates content, wax content and carbon number of crystallized waxes. Above the WAT, the flow properties are influenced mainly by the asphaltene and resin content. SARA analysis can be applied qualitatively in conjunction with oil paraffin distribution to predict the relative waxiness and flow behavior of waxy crude oil and their potential for wax problems in the oilfield.

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