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Characterisation of Malaysian Waxy Crude Oils

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Abstract

The physicochemical characteristics of the crude oil and its flow behaviour is an essential and is a significant part of the flow assurance study. One of the critical issues in flow assurance management is the restrictions to the fluid flow ability caused by the formation of deposits in well tubing and crude oil pipeline systems. In this paper, investigation results on the behaviour of waxy crudes in Malaysian oil basins are presented. Wax Appearance Temperature (WAT), Total Acid Number (TAN), pour point, wax content, water by distillation, density, API gravity, kinematic viscosity, SARA content, heavy metals, carbon number distribution and hydrocarbons recovery of three waxy crude oil samples from different field locations named as PN01, PT03 and SP01 were carried out. Results show that crude oils SP01, PN01 and PT03 have wax content between 20.50 to 37.10% and WAT in the range of 43.40 to 69.90°C. The presence of heavy metals in the analysed crude oils were found to be relatively low in concentration. The crude oils PT03 and PN01 have higher mole percent of carbon distribution between C20 and C40 compared to crude oil SP01. Crude oil PT03 and PN01 also recorded higher content of wax which results in higher WAT compared to crude oil SP01. By studying the crude oil characteristics from different oilfield locations, better understanding on the characteristics of Malaysian waxy crude oils is achieved.

Keywords: chemical composition; physical properties; cold flow properties; acidity; trace elements analysis.

1. Introduction

The economics of crude oil production depends on effective management of the flow assurance. Flow assurance mainly focuses on ensuring uninterrupted flow of hydrocarbon from the reservoir up to the point of sale. Produced fluids which consist of a combination of gas, oil and water together with solid particulates, may have the potential to cause restrictions on the fluid followability. These restrictions to flow may be caused by the deposition of, wax or asphaltenes, formation of hydrates, scales and high viscosity emulsions, the presence of sand, slugging and any combinations of these factors [1].

In Malaysia, one of the prominent problems concerning flow assurance is solid deposition in the crude oil pipelines and on the surface of equipment. For example, wax deposition can occur when there are changes in the physicochemical equilibrium conditions due to the reduction of the temperature of the crude oil to below the WAT causing crystallisation of wax which eventually starts to accumulate and form deposit on the wall of the pipeline [2]. The deposit layer can cause a significant reduction in the cross-section of the pipe resulting in reduction of the flow rate, which eventually may choke the pipelines leading towards production shutdown.

A number of preventive and curative methods are currently being applied in the oilfield which includes mechanical, thermal and chemical methods. However, each preventive and curative methods has its own disadvantages and resultant increase in the operating cost [3].

Moreover, the production problems and developed solutions may vary from reservoir to reservoir due to the differences in wax characteristics and contents. Hence, it is very important to understand the presence and detail characteristics of the waxy crude oils to prescribe the most optimal and cost effective preventive and curative methods to overcome the detrimental flow related problems.

2. Experimental

Three Malaysian crude oils labelled as PN01, PT03 and SP01 were studied in this paper. The selected crude oils presently have wax precipitation and deposition problems during production and transportation. The crude oil samples appeared as non-homogenous waxy samples at room temperature and therefore were homogenised by means of heating in the oven at 80°C for 3 hours. Throughout the heating process, the samples were stirred at every one hour interval to ensure complete dissolution and homogeneity. The samples were then transferred into smaller size containers while the temperature was still high.

Laboratory analysis on the crude oil samples encompasses analysis on the cold flow properties, acidity, crude oil physical properties, compositional analysis and trace elements analysis. The tests were conducted as per ASTM, UOP and/or in-house methods. The details of the tests conducted for every segment of the laboratory analysis are listed in Table 1 below.

Table 1. Laboratory analysis for the crude oils

Description	Method
Cold Flow Properties	
Wax appearance temperature	Cross Polarised Microscopy – In house
Pour Point	ASTM D5853
Wax content	UOP 46
Acidity	
Total Acid Number (TAN)	ASTM D 664
Physical Properties	
Density@80°C	ASTM D70
Kinematic viscosity@80°C	ASTM D445
API Gravity	ASTM D1298
Chemical Composition	
SARA Test	In house
High Temperature Gas Chromatography (HTGC)	ASTM D7169
Trace Elements	
Inductively Coupled Plasma (ICP)	APHA 3120B

3. Results and discussions

3.1. Cold flow properties

Crude oils are complex mixtures of hydrocarbons that may consist of paraffinic hydrocarbon which has limited solubility in the crude oil and if cooled sufficiently will come out of solution as wax causing detrimental effects such as solid deposition in the crude oil pipelines and on the surface of equipment.

The cold flow properties for this study was analysed using results obtained for wax appearance temperature, pour point and wax content. Figure 1 below illustrates the results of the tests carried out to understand the cold flow properties of the three crude oil samples i.e. PN01, PT03 and SP01

Wax Appearance Temperature is similar to cloud point for transparent liquid that indicates the temperature where crystal starts to form when the temperature is reduced to below its WAT. As the temperature is reduced further, pour point can be detected where the liquid completely stops flowing. As observed from the table above, PN01 and PT03 crudes have similar pour points of around 51°C whilst SP01 has a lower pour point of 36°C. The higher pour points for PN01 and PT03 are probably due to the high wax content in both crudes as can be seen in the figure above. The WAT temperatures for crude oil PN01 and SP01 as expected, are higher than their pour points. However, for crude oil PT03, the temperature recorded for WAT is slightly lower than its pour point. To understand this anomaly, the water content in all 3 crude oils was analysed.

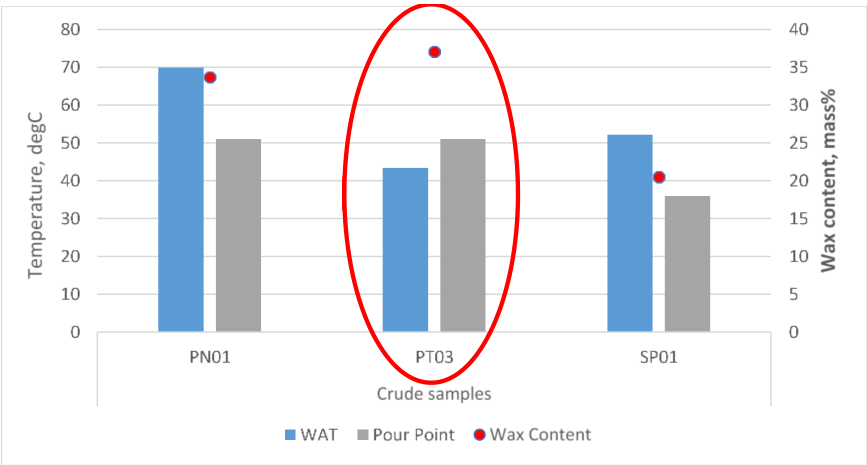

Figure 1. Illustration of the WAT, Pour point and Wax content for PN01, PT03 and SP01

Table 2 below illustrates the water content in the crude oil samples. Comparatively, the PT03 crude oil has the highest volume percent of water. The presence of higher water content in PT03 waxy crude probably has caused higher pour point due to gel formation and viscous wax-oil-gel emulsions [4-5].

Table 2: Water content in the crude oil samples

Physiochemical properties	Crude samples PN01	PT03	SP01
Water content (vol.%)	0.35	1.80	1.00

3.2. Acidity

Acidity is measured by TAN where the amount of potassium hydroxide in milligrams (mg) that is required to neutralize the acids in one gram (g) of oil.

Figure 2 below illustrates the TAN of the three crude oils. Crude oil SP01 recorded the highest TAN indicating highest potential to corrosion problems in related equipment.

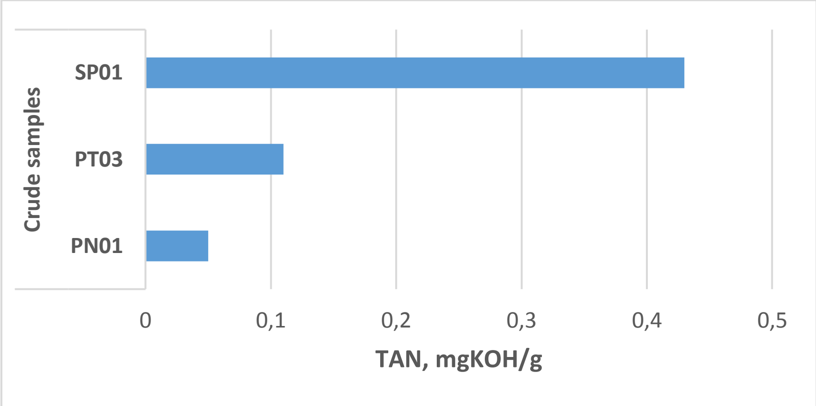

Figure 2. Total acid number (TAN) for the crude oil samples

3.3. Physical properties

Physical properties of the three crude oils were measured by density and kinematic viscosity. Density and kinematic viscosity are important properties because of their relevance to the flow assurance of the crude oils. A change in density and kinematic viscosity will influence the pipeline output and hence affect the timeline for product receive and arrangement for the tankage system.

Figure 3 below illustrates the density and kinematic viscosity data for the three crude oils. The trending of kinematic viscosity and density are similar i.e. when density of the crude oil is high, the kinematic viscosity is also high. The crude oil SP01 has the lowest kinematic viscosity; this probably can be linked to the fact that it has the lowest wax content.

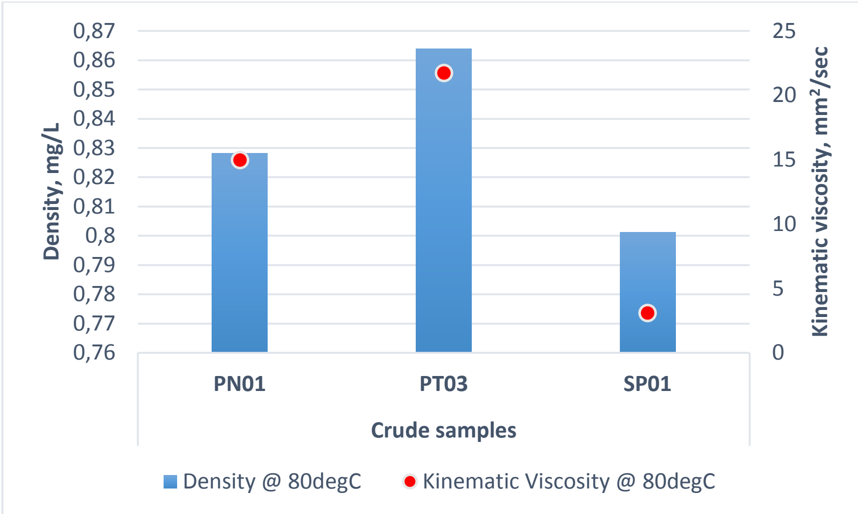

Figure 3. Density and kinematic viscosity at 80°C

3.4. Chemical composition

Chemical composition by SARA analysis and High Temperature Gas Chromatography (HTGC) would reveal important data to understand chemical distribution of the crude oil samples. SARA analysis is a method to characterize crude oils into various chemical groups by preparative column separation by solubility in various solvents of different polarities. In this method, the crude oil is fractionated into four chemical groups i.e. saturates, aromatics, resins and asphaltenes (SARA). Volatile percent and inorganic content in the samples are also measured through SARA analysis.

The detail compositional carbon number distribution analysis was performed by HTGC in accordance to ASTM D7169 method that could separate and analyse the sample up to C120. The weight percent of carbon number distribution is then calculated from area count of each component. The SARA fractions obtained from the samples are tabulated as shown in Table 3 below.

Table 3. SARA analysis for PN01, PT03 and SP01 Crude oils

SARA Composition	Crude samples		
	PN01	PT03	SP01
Saturates	31.53	36.42	29.43
Aromatics	9.46	8.36	1.85
Resins	40.27	35.02	21.04
Asphaltenes	0.01	0.05	0.05
Volatiles	18.67	19.94	47.54
Inorganics	0.07	0.21	0.09
Total Recovery	100.00	100.00	100.00

The saturate content SP01, PN01 and PT03 crude oils are found to be in the range of 29.43-36.42% indicating similar pattern with their wax content. The aromatic and resin content recorded by crude oil SP01 is the lowest, indicating it to be the lightest crude oil among the three crude oils. This observation is supported by the highest volatile content measured for SP01 crude oil. The asphaltenes fraction in all the three crude samples are almost similar i.e. notably low content (less than 1.0%) as shown in the table above. The inorganics content is found to be highest in PT03 crude in line with its highest density and kinematic viscosity measured for PT03 crude oil. Figure 4 below illustrates the carbon number distribution for the three crude oil samples.

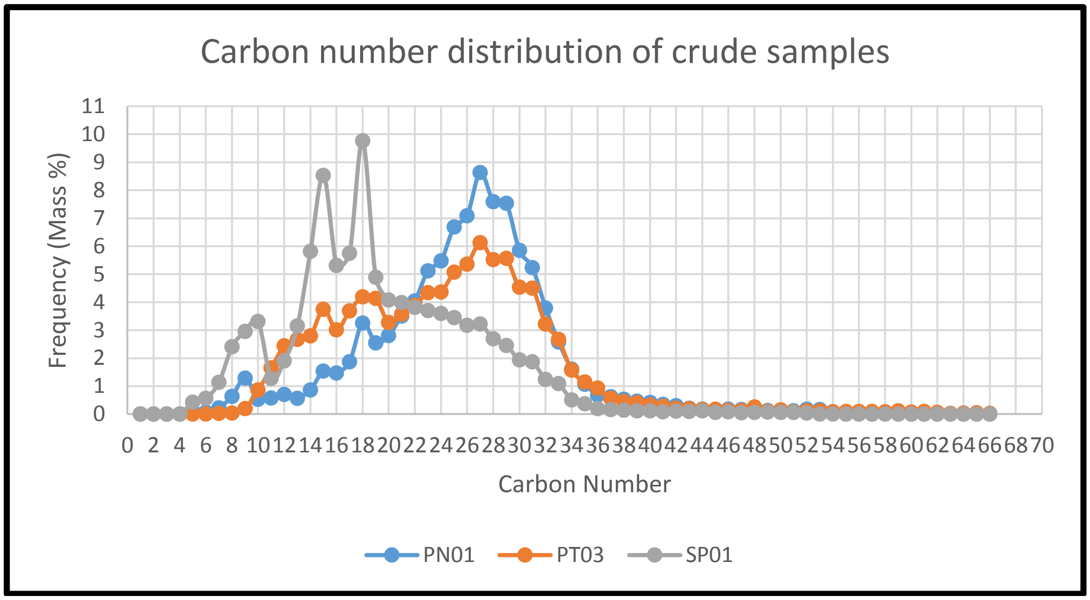

Figure 4. Carbon Number Distribution for PN01, PT03 and SP01

Overall, the carbon distribution for the 3 crude oils are detected to be in between C2 to C66. It can be clearly seen that SP01 crude is the lightest crude oil corresponded by the highest low carbon number (<C18) in the HTGC chromatogram in line with the SARA analysis result.

Based on the chromatogram shown in Figure 4, SP01 has the lowest mode which is carbon number 18 whilst PN01 and PT03 share the same mode which is carbon number 27. The modes indicate that SP01 has a majority of its components having lower carbon number as compared to PT03 and PN01. The mean of the carbon number of the crudes are 35.33, 46.19 and 34.83 for crudes PN01, PT03 and SP01 respectively. It is noted that the mode value for SP01 crude is lower than its mean value which implies that its carbon number distribution behaves as a positive skewed distribution. On the other hand, both PN01 and PT03 crudes have a negative skewed distribution as their mode values are greater than their mean values.

Another important statistical parameter of the carbon number distribution of these crudes oils are the measure of spread of the carbon number from the mean carbon number. This can be quantified by calculating the standard deviation of the carbon number distribution. From Figure 4, the standard deviation of carbon number for PN01, PT03 and SP01 are 35.33, 46.19 and 34.83 respectively. These data shows that PT03 crude has the widest carbon number distribution spread compared to PN01 and SP01 crudes. This may explain that the behaviour of the wax appearance temperature of the crudes as the probability of each molecule to find molecules with the same chain length is higher if the carbon number distribution is concentrated at a smaller range, i.e. lower standard deviation. In short, the wax appearance temperature of PT03 crude is the lowest among the three is probably because it has the highest standard deviation of carbon number distribution. In addition to that, since the standard deviation of PN01 and SP01 are similar but the carbon number mode value of PN01 is higher than for

SP01, the wax appearance temperature for SP01 is less than PN01. The wax appearance temperature for PN01, PT03 and SP01 are 69.9°C, 43.4°C and 52.2°C respectively.

3.5. Heavy metal content

Trace amounts of heavy metal components naturally exist in crude oils due to their presence in rock formations or salt water deposits in which the oils are drawn or introduced during the processing stage [6]. The types of metal present in crude samples can indicate the geological formation, source of rock type and depositional environment where the samples were obtained. Inductively Coupled Plasma/Optical Emission Spectrometry (ICP/OES) was used for the determination of metals in the 3 crude oil samples.

Table 4. Heavy metal content for PN01, PT03 and SP01 Crude Oils

Metals by Inductively Coupled Plasma	Units	PN01	PT03	SP01
Chromium, Cr	ppm	<1	3.48	1.01
Copper, Cu	ppm	<1	<1	2.03
Cadmium, Cd	ppm	<1	281.99	0.55
Iron, Fe	ppm	<1	114.84	1.10
Manganese, Mn	ppm	<1	1.31	0.01
Magnesium, Mg	ppm	<1	8.09	0.45
Phosphorus, P	ppm	<1	<1	2.09
Lead, Pb	ppm	<1	<1	2.36
Silicon, Si	ppm	<1	2.39	4.98
Tin, Sn	ppm	<1	<1	1.16
Vanadium, V	ppm	<1	<1	1.66
Zinc, Zn	ppm	1.01	2.51	0.87
Titanium, Ti	ppm	<1	<1	ND
Molybdenum, Mo	ppm	<1	<1	1.42
Nickel, Ni	ppm	<1	15.01	1.25
Calcium, Ca	ppm	2.53	196.87	2.19
Boron, B	ppm	<1	<1	1.93
Aluminium, Al	ppm	<1	<1	1.42
Barium, Ba	ppm	1.82	7.11	1.36

The results obtained from the ICP analysis would provide an overview on the metals present and its corresponding amount in the crude oil samples. Table 4 shows the overall summary of the metal contents in the PN01, PT03 and SP01 crude samples. Comparatively, PT03 crude oil sample measured to have the highest metal content, i.e. highest Cr, Cd, Fe, Mn, Mg, Zn, Ni, Ca and Ba concentration among the samples analysed. The presence of certain metal such as iron in the crude oil may affect the selectivity and activity of the catalyst in the cracking of the crude oil if it is not eliminated before the refining process. SP01 crude oil also recorded quite high amount of some of the trace metals such as Cu, P, Pb and Si, however, the detected amount is notably lower than some elements detected in the PT03 crude oil. PN01 crude oil was recorded to have the lowest amount of trace metals.

Nickel content is found to be the highest in PT03 crude compared to the other two crudes. A relatively huge amount of calcium was found to be in PT03 crude as compared to the content of calcium in the other 2 crude samples. Although calcium (Ca) is not harmful from a corrosion stand point, it can form inorganic scales which are not readily and easily removed. In addition, significantly larger amounts of Barium (Ba) and Magnesium (Mg) was also found in PT03 crude.

4. Conclusion

Characterisation of crude oils is essential and plays a vital role in order to understand the natural behaviour of the crude oil that may be associated with the flow assurance related issues. By doing this, suitable approach can be identified in order to resolve the issues effecttively. It is significant to attain reliable details pertaining to the characteristic of the wax by carrying out a combination of analytical testing as to provide a better picture on the chemical and physical behaviour of the wax. In this paper, the characteristics of three Malaysian waxy crudes, which are, PN01, PT03 and SP01 crudes and their properties were studied in detail.

In terms of crude physicochemical properties, data has shown consistent agreement with each other in describing the waxy crude behaviour. However it can be observed that the WAT is not directly related to the wax content of the crude but in agreement in terms of its carbon number distribution. Generally, the pour point of crudes is possibly affected due to its wax content and viscosity. However, from this study, it is seen that the direct relationship which correlates the wax content and pour point of the crudes is not achieved. This occurrence might be due high water content present in the crude that may contribute to the gelling effect of the emulsified water which leads to crude oil gelation [4]. In terms of their metal content, all the tested crudes display trace amount of Pb, Cd, Cr, Mn, Zn, and Cu as compared to the recommended levels of these parameters by World Health Organisation in the environment.

In short, the coherence of the data obtained from various analytical techniques aids in providing essential information pertaining to the characteristics of these tested crudes which could be very useful in narrowing down the focus on the synthesis and development of new chemical formulations as the prevention steps to solve the wax deposition issues.

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