The Effect of Aging on Critical Carbon Number (CCN) during Wax Deposition Analysis

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***Abstract*—The process of aging is a critical carbon number (CCN) exists in counter diffusion phenomenon. In the wax deposition phenomenon, the wax molecules with carbon numbers higher than the critical carbon number (CCN) will diffuse into the gel matrices and vice versa in aging process during experiments. The petroleum industry has major problem which is wax deposition that causes the hindrance in subsea pipelines. The experiment of aging of wax deposition was carried out with time and temperature by using cold finger device. Furthermore, the analysis of carbon number distribution was performed by gas chromatography-mass spectrometry (GC-MS) carefully. In this analysis, when the time increases from 2 to 24 hours, the higher carbon number and wax contents in deposition was increases. The aging of wax deposition caused the increasing in the hardness of deposit. In addition, the higher temperature provides effective outcome on the wax content and little outcome on critical carbon numbers (CCN). The bulk oil temperature was used to determine the hardness of the deposit. The CCN of wax deposit is 18.**

***Keywords*—Aging, CCN, GC-MS, time**

I. Introduction

Wax deposition is amongst the critical issues of flow assurance faced by the production and transportation pipelines in deepwater oil and gas industry. The pipeline acts as an intermediate form of transportation between the reservoir fields to oil rig platform and then to onshore upstream refinery plants. In a worst case, the wax deposition caused the pipeline gets plugged and blockage. The plugged pipes effect the decreases of crude oil production and creates the considerable economics losses to the crude oil production industry. In order to prevent the major loss of crude oil, the wax deposit on pipeline was removed. The mechanical treatment such as strong pumping power and frequent pigging is the most typical method to encounter wax deposited.

Typically, crude oils moves out of the reservoir at 70 to 150 °C and 55-103 MPa into subsea pipelines [2]. Crude oil is a blend of hydrocarbons of changing carbon numbers. When the pipe wall temperature lowers than the wax appearance temperature (WAT), the mixture may isolate into a solid-liquid wax phase where wax precipitation is form. The radial concentration gradient was formed when n-paraffin particles precipitated on the pipe wall. These causes by the radial temperature slope from the mass oil to the pipe wall. The n-paraffin molecules were driving more to precipitate on the pipe wall by concentration gradient and the wax deposition was formed [1].

Various investigations have been done for as long as decades on wax deposition mechanism by several researchers [4]. Diverse techniques have been recommended by various analyst and found to play a critical part in wax deposition. It is found that, the molecular diffusion and shear dispersion mechanism is the essential main impetus of wax deposition among the mechanisms that have been proposed.

Shear dispersion happens when wax already precipitated near the wall moves to a location that has a lower momentum in the pipe wall and deposits. This mechanism is appeared to have no impact to deposition without heat flux despite the bulk fluid temperature being under cloud point conditions. Despite this, the application of drag force on the solid waxy crystals from the fluid contributes to the expulsion of wax and aging of wax deposits which is known as shear stripping impact. Thus, flow regime inside the subsea pipelines also plays a significant role in wax deposition. Currently, laminar flow and turbulent flow are two main most fully understood flows that play an influential role on wax deposition.

The resident time of the crude oil to lose heat to encompassing colder pipe walls are longer due to the laminar flow of the bulk fluids allows. This allows the wax particles to stick onto the pipe walls and cluster together easily. On the other hand, the turbulent flow has tendency to reduce the wax deposition from happening as it disturbs the adhering and developing of wax deposition. However, for the most part wax crystals in this flow regime have a tendency to be hard in nature and capable of depositing on pipeline walls.

The deposit layer hardening with time is called as aging phenomenon. The n-paraffin acts as a porous medium in which wax particles extend to dispersed through due to radial variation in temperature. The substantial n-paraffin elements dispersed from bulk oil inside the deposit lamina. The light n-paraffin elements dispersed out of the deposit lamina to the bulk oil. The wax content of the deposit lamina hardens with time [3][5]. The critical carbon number (CCN) is a minimal number of carbon particles in a hydrocarbon (n-alkane) molecule. The waxy crude oil is a blend of hydrocarbon with a numerous carbon number dispersion. When a hot crude oil, turning out from an oil reservoir at a temperature higher than the cloud point, merges with a cold subsea pipe wall, it immediately precipitated and forms a gel layer on the wall. The trapped oil in the beginning gel deposit is associated with the mass oil through the gel pores that open up at the gel interface. The trapped oil gets removed of certain heavier hydrocarbons when differentiated to the mass oil, because of the formation of the solid phase. The minimal carbon number of these heavier hydrocarbons is called CCN [2].

The distinction in the convergence of these heavier hydrocarbons makes the flux of these heavier hydrocarbons particles from the mass oil to the trapped oil. The formation of solid stage likewise leads the trapped oil rich in the hydrocarbons below the CCN. Identically, the distinction in the convergence of these lighter hydrocarbons leads to a flux of the lighter particles from the trapped oil to the mass oil. This counter diffusion process leads to the hardening of wax deposition. The temperature increases, the critical carbon number (CCN) increases [2]. During the aging process, the highest n-paraffin elements dispersed outside of the deposit was described as the critical carbon number (CCN) [1].

The CCN relies on upon the structure of the crude oils, as well as the working conditions, for example, wall temperature. When the wall temperature increase, the dissolvability of the paraffin molecules also rises that causes a rises in CCN. A crude oil framework with greater estimation of the CCN resulted in an aged deposit having a greater estimation of the normal carbon number and, therefore, a greater trouble in eliminating the deposit. The CCN must be assessed in order to choose the suitable method to eliminate the deposit in the pipelines. Hence, indicator of the CCN of the wax deposit is exceptionally fundamental [2].

WAT is which the wax crystals start to form in certain temperature and precipitate constantly from the solution. The composition, temperature and pressure are the major parameters that effect the wax crystallization from crude oil. A crude oil with higher composition of light end hydrocarbons tends to have lower WAT. The presence of light ends acting as a solvent to stabilize the higher end of the hydrocarbons in the crude oil. The higher WAT may result to wax precipitation at elevated temperatures.

Cloud point represents the solubility limit of crude oil where solid waxes crystals first precipitate. It is also known as WAT. On other hand, PPT is the temperature at the lowest point which crude oil will flow or pour. It is also greatly affected by oil flow properties. It results to dramatic changes in the viscosity and flow properties of crystallization of paraffin crystals. It can be modified using chemical inhibition method which lowers its pour point.

Crude oil at high temperature acts as a Newtonian fluid showing viscosity-temperature dependence. As the crude oil temperature drops lower than the wax appearance temperature, WAT, the precipitation of the wax crystals will suddenly rapidly increase the viscosity entering into the non-Newtonian fluid region. The yield stress of a wax-solvent mixture is believed to be a part of wax composition, and thermal and shear histories. The untreated crude oil is found to behave similarly to pseudo plastic fluid. Where with increasing shear rate, the viscosity tends to decrease. This behaviour is termed as shear-thinning.

II. METHODOLOGY

A. Materials

During the experiments, the waxy crude oil was supplied by PETRONAS Refinery Plant in Kerteh, Terengganu, Malaysia. The chemical and physical properties of crude oil was shown in Table. 1 below. Besides that, 0.1558 g of n-octadecane (0.2 mass %) was mixed in 100 ml of cyclohexane to prepare standard solution. The standard solution were used in GC-MS to analyze the carbon number distribution and wax content in wax deposition samples.

Table. 1: Chemical and physical properties of crude oil

Chemical properties	Percentage (%)
Asphaltene	12.13
Aromatic	30.55
Resin	8.76
Saturated	48.29
Physical properties	**Value**
Viscosity at 40 °C (mPa.s)	5.15
Density (g/cm³)	0.8509
SG	0.8509
°API	34.93
WAT (°C)	32
Pour Point (°C)	3
Wax content at 20 °C (wt %)	20.58

B. Experimental apparatus

A cold finger is a device of laboratory apparatus that is used to generate a bounded cold surface. It is called as finger due to the shape of the device. The device usually consists of a chamber that a coolant fluid can enter and leave. The function of cold finger is to simulate the temperate oil that connected to the cold pipe wall. The cold finger were made from stainless steel. The Fig. 1(a) and 1(b) below show the example of cold finger apparatus during experiments.

Fig. 1(a): Cold finger before experiment

Fig. 1(b): Cold finger after experiment

In addition, there are chiller, heating water bath and stirrer power box to run the experiment. The cold finger were placed inside a heating water bath. The heating water bath was used to control the crude oil temperature. A stirrer was attached at the side of cold finger to make the flow fields influences both the shear stress and the rate of heat transfer at the cold finger surface. The nominal operating speed of the stirrer was set at 400 rpm. Fig. 2 show the cold finger apparatus set up.

Fig. 2: Cold finger apparatus set up

C. Experimental procedure and method

The oil specimen was kept in steel vessel at 50 ºC in heating water bath before the experiments. The volume of crude oil was set as 150 ml in all experiments. The cold finger were kept up at coveted temperature. Then, cold finger was inserted into the temperate oils when the time and coveted temperature were gained. Then, the cold finger were taken out from the stainless-steel after the experiments carefully. The deposit at the cold finger surface was scraped for farther weighing and analysing. Deposit tests were acquired at deposit time of 2, 13, and 24 h. The experiment was done in temperature of 5, 10 and 15 °C).

After that, the GC-MS were used to analyses the wax content and carbon numbers dispersion in deposit. The wax was indicated to the n-paraffin. All the carbon number dispersion is n-paraffin carbon number distribution.

III. RESULTS AND DISCUSSION

A. The effects of time on wax deposition

The deposited wax was analyzed by GC-MS to get the wax content and carbon number distribution. Fig. 3 shows the carbon number distribution of crude oil and wax content (wt %). Wax refers to the n-paraffin, so all the carbon number distributions in this experiment was n-paraffin carbon number distribution. The wax content in analysis refers to sum of C18 + n-paraffin in deposit.

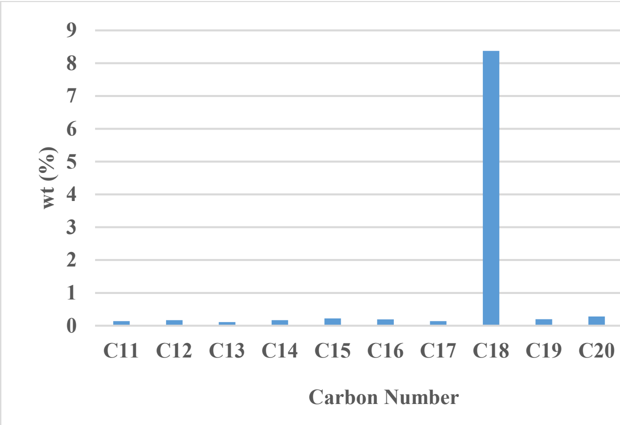
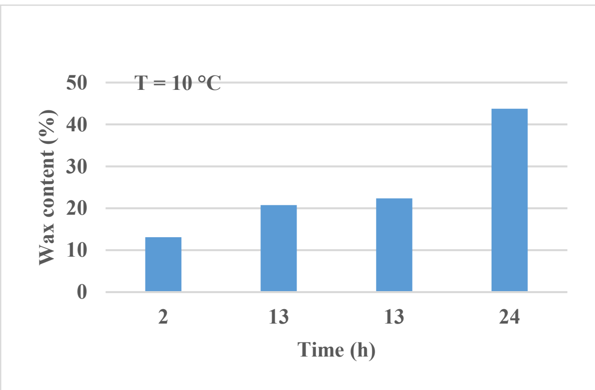


Fig. 3: Carbon number distribution of crude oil

It can be seen that wax content and the higher carbon number components in deposit increase as the deposit time increases from Fig. 4 that shows the changing of deposit versus time. The wax content and the higher carbon numbers component in deposit increase slightly when time varies from 3 h to 13 h and the deposit rates increase sharply when time vary from 13 h to 24 h. during the experiment, the wax molecules with carbon number higher than 18 diffuse into the deposit, while the wax molecules with carbon number lower than 18 diffuse out from the deposit. So, the CCN is 18 under the given temperature.

As the experimental time increases, the phenomenon called as counter-diffusion occurs. The efficiency of pigging mainly depends on the deposit hardness, for which the CCN can be used as a criteria, as a higher CCN yields a mechanically harder wax with a higher melting point, as well as a lower solubility in typical wax solvents [3][5].



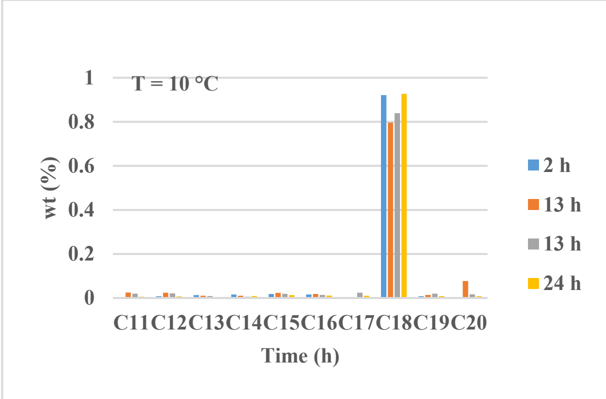


Fig. 4: Variation of wax content and carbon number distribution in deposit with time

B. The effects of temperature range

The deposit samples at different temperature range were analyzed by GC-MS to studying the effect of temperature on aging of wax deposition. Based on the Fig. 5, the amount of lower carbon number components in deposit decreases and the amount of higher carbon number components in deposit increases as the deposit time increases at higher temperature range.

The result compared in Fig. 4 and Fig. 5 show that the variation of wax content in deposit for higher temperature range is lower than that for lower temperature range. The amount of higher carbon numbers component in deposit increases with the increase in temperature range. This is due to the radial concentration gradient and the actual cold finger surface temperature increase as the temperature range increases under the same temperature differential.

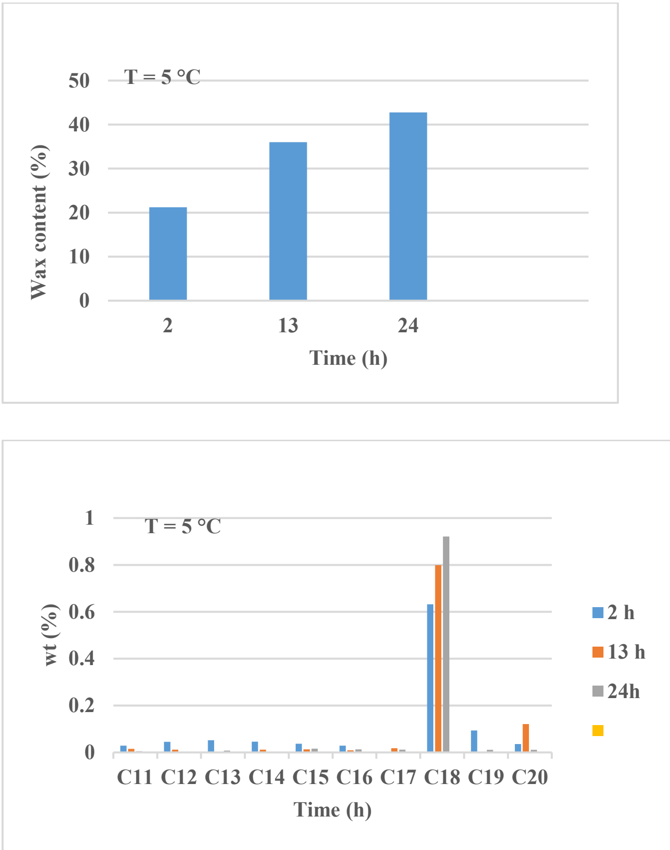


Fig. 5: Variation of wax content and carbon number distribution in deposit with time

IV. CONCLUSION

Based on the result obtain, there exists CCN during aging of wax deposition for crude oil. The wax molecules with lower carbon number than CCN diffuse out from the deposit, while wax molecules with higher carbon number than CCN will diffuse in deposit. So, the time increases, the hardness of deposit increases. In addition, the temperature has active effect on the aging of the wax deposition. The lower the temperature, the hardness the wax deposited. The temperature has only a little effect on the CCN for that change in CCN does not exceed one carbon number under different temperature conditions.

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