The Effect of CO₂ on Wax Appearance Temperature of Crude Oils

Arya Hosseinpoura,*, Azuraien Bt Japper-Jaafarb, Suzana Yusupa

aChemical Engineering Department, Universiti Teknologi PETRONAS, 32610, Perak Darul Ridzuan, Malaysia
bMechanical Engineering Department, Universiti Teknologi PETRONAS, 32610, Perak Darul Ridzuan, Malaysia

Abstract

Wax deposition makes up one of the main problems in the petroleum industry. Different types of techniques and treatments have been used to inhibit wax deposition. In this work, crude oils from Malaysian oil fields and Sudanese oil field are studied to determine their wax formation tendency for flow assurance purposes. In addition, effect of CO₂ injection on the wax appearance temperature (WAT) for these crude oils is studied. In this paper, the high pressure micro differential scanning calorimetry (HPµDSC) has been employed in order to assess the WAT of the crude oils. Results showed that all these crude oils have a WAT ranging from 26.46 to 53.67ºC. This suggests a likelihood of wax production in the reservoir and transportation pipelines. Experimental results showed that the injection of CO₂ reduced the WAT of the crude oils to about 8.53ºC below its original value.

Keywords: Wax appearance temperature; Carbon dioxide; Differential scanning calorimetry; Flow improver

1. Introduction

The petroleum industry is still dogged by a major problem involving the deposition of paraffin wax which occurs on the inner walls of production and transportation pipelines. Accumulated deposition of the material on the inner wall of pipe lines may lead to increase pumping power, a flow rate reduction or in the worst case scenario, a total blockage of pipe line. All these can cause a loss of production and capital investment. Wax appearance temperature
(WAT) is often utilized in assessing the likelihood of a crude oil producing wax with respect to pressure and temperature reduction. WAT, in other words, refers to the temperature at which the first wax crystal occurs [1]. The major parameters affecting wax crystallization from crude oils are composition, temperature and pressure of the system. Wax deposition is one of the major problems faced by Malaysian oil and gas industry. Penara, Angsi and Dulang fields are among Malaysian fields which are located roughly in a water depth of 60 m to 70 m [2-4]. While the surface temperature is at 34 °C, the average seabed temperature for these fields is about 25 °C at depth of 61m [3, 5, 6]. According to the technical reports from crude oil operators in these fields, wax was produced during transportation in relation to the characteristics of these crude oils, the seabed and surface temperatures and their production histories. In Malaysia, there are new and undeveloped CO2-rich natural gas fields. On one hand, the production and purification of natural gas from these fields will require better separation process that can cope with CO2 content that can reach to 70% [2, 7-11]. Supercritical gases have been used to remove polar extracts from distillate and crude oils considering as a remarkable and possibly low-cost method of getting a flow improver which cause reduction in WAT of the crude oils. Carbon dioxide, propylene and ethylene are regarded as these gases [12, 13]. The main difference between CO2 and other gases is its capability of extraction heavier components up to C30. In addition, CO2 has other characteristics such as promoting swelling, reduction in oil viscosity and increasing oil density, etc. [14]. On the other hand, the large amount of CO2 produced offer potential for the enhanced oil recovery purposes in nearby waxy crude oil fields. It is known that CO2 can acts as a solvent to be used as a flow improver of crude oil. By implementing CO2 gas injection in the oil reservoirs, this technique not only can increase drive mechanism and production rate of the wells but also reduce CO2 release to the atmosphere [13].

Since temperature was the main parameter that controls the deposition of wax, the focus of this work is to measure the WAT for a series of Malaysian crude oils. Moreover, influence of CO2 injection on the WAT is studied and the effect of CO2 as a natural flow improver on WAT is investigated.

2. Experimental

2.1 Materials

Five Malaysian waxy crude oils (A-E) along with Sudanese crude oil (F) from Sudan are used in this study. Carbon dioxide with purity of 99.95% is supplied by MOX and used without any further purification.

2.2 Experimental apparatus and method

In this paper, in order to assess the WAT, wax disappearance temperature (WDT) and wax precipitation or solubility curve of the crude oil samples, we used the high pressure micro differential scanning calorimetry (HPµDSC) from Seteram Instrumentation Company. The differential scanning calorimetry (DSC) technique has been employed extensively in examining wax crystallization as it is fast, reliable and simple. The HPµDSC was calibrated using naphthalene. The calibration results were quite consistent with the standard data (80 °C). Hastelloy C was used to make the HPµDSC batch cells (1 ml). This allows an analysis of solid or liquid samples up to 400 bar and temperatures ranging between 45 to 120 °C. In terms of uncertainty, the pressure and temperature measurements were ±0.05 bar and ±0.02 °C, respectively.

Experiment measurements are divided in three parts. Firstly, measurement of the WAT and WDT of six crude oil samples are conducted. Secondly, the effect of temperature on the wax precipitation curves of the crude oils is investigated. Lastly, the effect of the CO2 injection at the different pressures of 16, 26, 36 and 46 bar on the WAT of crude oils is studied.

First and before initiating the measurements, the samples are heated up to 70 °C for 20 minutes in an oven and are shaken rigorously to make sure the wax crystals are all dissolved. When the oil is transferred to the hastelloy batch cell, the mix is then weighted by means of Mettler Toledo AX205. The cell is afterwards put inside the HPµDSC. When mixed well, it is heated up to 70 °C and then cooled down to 0 °C at a rate of 2 °C per minute. The
calorimeter’s temperature is set by thermostatic control of circulating liquid (water) which is heated or cooled via piloting from the CS 32 controller. For the investigation on the effect of CO$_2$ on the WAT, the same procedure is used for preparation of samples except the cell is pressurized to a selected pressure value by injecting CO$_2$ gas. The heating and cooling procedures are the same as previously mentioned. Experiments are repeated at least 3 times and standard deviations and error bars are included in the results presentation to indicate data repeatability.

The DSC technique was used to examine the wax precipitation (i.e. at different temperatures) [15-18]. As noted by Alcazar-Vara et al. [16] and considering that the precipitated wax amount in the total wax content is relative to the percentage of the accumulated heat released in the total heat released (i.e. crystallization enthalpy), thus, the amount of precipitated wax at different temperatures can be determined through dividing the accumulated heat released by the heat of crystallization.

### 3. Results and discussions

#### 3.1 WAT measurement of the crude oils

The measured WAT and WDT of crude oils along with their standard deviation are presented in Table 1. The WAT, during cooling and WDT, during heating were measured using the thermograms of samples recorded on a thermal analyzer operating in the liquid-water sub-ambient mode of the HPµDSC. As the exothermal peak is consistent with crystallization, therefore, the solid wax particles experience precipitation in the course of the cooling process. The WAT is defined as a particular temperature at which the first crystal forms in Figure 1, where y-axis corresponds to the difference of heat flux between a cell containing the sample and a reference cell. As the solvating power of the oil matrix declines in the course of the cooling process, it results in the precipitation of solid particles of wax. The Malaysian and the Sudanese crude oil samples reported in this paper have a WAT ranging from 26.46 to 53.67 ºC. During the heating process, the endothermal peak is consistent with the dissolution of all wax crystals and the WDT is considered the temperature at which the precipitated wax has been dissolved into the oil matrix. This temperature corresponds to the endothermal peak on the DSC curve (Figure 2). The crude oil samples reported in this paper have a WDT ranging from 31.43 to 55.81ºC.

As can be seen in Table 1, the WDT is 1.98 to 4.97 ºC higher than the WAT. In their report, Rønningen et al. [19] indicate that WDT is 5 to 28 ºC higher than WAT for North Sea crude oils. This difference between WAT and WDT could be accounted for by overheating and undercooling which cause non-equilibrium during fast temperature scanning (10 ºC /min.). In order to avoid this from happening, Hansen et al. [20] suggested that the scanning be done at a very low temperature. Moreover, the difference between WAT and WDT could also be explained by the manner in which the processing baseline has been drawn.

As shown in Table 1, all the crude oils having WAT values higher than 25 ºC. Depending on the depth of these fields and their geographical location, the average seabed temperature considered for these fields is approximately 25 ºC at a depth of 61m and the surface temperature of 34 ºC which are quite below or almost the same as the WAT of the Malaysian crude oil samples. The lowest reported ambient temperature has been 25-27 ºC for the Sudanese’s oil field [21]. The results suggest that these crude oils are likely to produce wax in transportation pipelines, especially those with higher WATs.

Therefore, it is essential to use a wax inhibitor to prevent pipeline plugging and works by Halim et al. [22] and Jin et al. [23] for the Malaysian waxy crude oil shows that using wax inhibitors and single-pipe insulation coating are inevitable because of their high WAT and average seabed temperature (25 ºC).
Table 1: Wax appearance and disappearance temperature of the crudes

<table>
<thead>
<tr>
<th>Crude oil</th>
<th>WAT(°C)</th>
<th>WDT(°C)</th>
<th>Standard Deviation WAT(°C)</th>
<th>Standard Deviation WDT(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>26.46</td>
<td>31.43</td>
<td>0.19</td>
<td>0.58</td>
</tr>
<tr>
<td>B</td>
<td>36.66</td>
<td>39.30</td>
<td>0.38</td>
<td>0.19</td>
</tr>
<tr>
<td>C</td>
<td>38.21</td>
<td>41.52</td>
<td>0.33</td>
<td>0.19</td>
</tr>
<tr>
<td>D</td>
<td>43.42</td>
<td>45.40</td>
<td>0.38</td>
<td>0.33</td>
</tr>
<tr>
<td>E</td>
<td>53.67</td>
<td>56.37</td>
<td>1.80</td>
<td>0.00</td>
</tr>
<tr>
<td>F</td>
<td>52.51</td>
<td>55.81</td>
<td>0.76</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Figure 1: DSC thermogram of the wax crystallisation (WAT) of the crude oil (B) at cooling rate of 2°C/min

Figure 2: DSC thermogram of the wax dissolution (WDT) of the crude oil (B) at heating rate of 2°C/min
3.2 The effect of temperature on the wax precipitation

Many factors could impact the paraffin crystallization process including paraffin components, compositions and their structures, pressure, presence of impurities, temperature, kinetics, and rate of cooling. Thus, by developing a better understanding of the parameters that impact wax precipitation, it would be possible to gain a better knowledge about the wax crystallization process in the petroleum industry. The wax precipitation rate is greatly influenced by temperature. Paraffin waxes are semi-crystalline in nature and have tendency to crystallize/precipitate from crude oils at and below the equilibrium solid-liquid temperature which considers the thermodynamic cloud point or WAT [24]. Therefore, to gain such knowledge about the paraffin crystallization process at temperatures below WAT, we obtained solubility curves by means of the DSC data (Figure 3).

As can be seen in Figure 3, the impact of temperature is more significant for crude oils with higher WAT as they have higher hydrocarbon chains [25]. The results are highly consistent with the WAT of the crude oil samples, as the amount of the wax precipitation solid is higher at temperatures lower than WAT. This is due to the temperature reduction slows down the molecular motion of the molecules in the crude oil and causes not to move freely because of less energy. This can bring the wax molecules closer and cause to align together; and finally leads to adhere together to a critical and stable size. The formation process and the cluster of wax molecules are called nuclei and nucleation respectively. The stability of the nuclei depends on the temperature which should be lower than the melting point of the wax. However, raising the temperature increase the thermal motion and cause disruption in the nuclei structure. After formation of the nuclei and while the temperature remains low, more wax molecules precipitate and continue to adhere together on the nucleation site. This refers to as the growth process [24]. Thus, as an important factor, it is essential to have a knowledge of the WAT of crude oils in order to ensure a safe inhibition of wax precipitation and deposition for flow assurance [22, 23].

![Figure 3: Wax precipitation curve of the crude oils at different temperatures without CO2 injections](image-url)
3.3 **The effect of the CO$_2$ presence on the WAT of crude oils**

Results of the WAT measurement along with its standard error bar in the presence of CO$_2$ at the pressures of 16, 26, 36 and 46 bars are shown in Figure 4. This Figure demonstrates that as the pressure of CO$_2$ is increasing, the WAT of the crude oils is decreasing. This might be attributed to the increase of CO$_2$ content in the crude oils and CO$_2$ molecules extracting heavier components and acting as light ends [13, 14]. It is known that light ends of crude oil act as solvents in reducing WAT because of much its capability to hold waxes in the crude oil [13]. This is due to their solubility in oil which leads to wax dissolution and inhibit long hydrocarbon components to precipitate at low temperatures. Therefore, in this case, CO$_2$ acts as a flow improver of these crude oils. Moreover, the solubility of light ends increases as the pressure increases and this cause further decrease of the WAT as observed in this work [13]. Therefore, experimental results showed the applicability of the CO$_2$ as a flow improver for these crude oils and lowering WAT values of crude oils with low percentage of light ends (dead oils). The reductions of WAT for Malaysian crudes along with Sudan crude oil in the presence of CO$_2$ at the different pressures are ranging from 3.88 to 8.53 °C. This reduction is very good enough to reduce the risk of wax formation of these crude oils in the reservoir in case of CO$_2$ injection and then transportation pipelines [26]. In addition, CO$_2$ injection offers good potential for the enhanced oil recovery purposes in nearby waxy crude oil fields and by implementing CO$_2$ gas injection in the oil reservoirs, this technique not only can increase drive mechanism and production rate of the wells but also reduce CO$_2$ release to the atmosphere [13].

![Figure 4: WAT of the crude oils versus different CO$_2$ injection](image)

4. **Conclusions**

In this work, WAT for 5 different Malaysian crude oils with 1 Sudanese crude oil in the presence of CO$_2$ have been measured. Based on the experimental results, all the crude oil samples have a WAT ranging from 26.46 to 53.67 °C. This suggests that these samples are likely to produce wax in the reservoir and transportation pipelines, especially, those with higher WATs. Therefore, it is essential to use a wax inhibitor to prevent pipeline plugging. The results indicate that the amount of the wax precipitation solid is higher at temperatures lower than WAT. Thus, as an important factor, it is essential to have a knowledge of the WAT of crude oils in order to ensure a safe inhibition of wax precipitation and deposition for flow assurance. Furthermore, the results also suggest that following the injection of CO$_2$, the WAT of the crude oils decreased to approximately 8.53 °C (i.e. below its original value) which could be most likely explained by the CO$_2$ molecules that function as light ends.
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Nomenclature

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<tr>
<td>HP</td>
<td>High Pressure</td>
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<tr>
<td>WAT</td>
<td>Wax Appearance Temperature</td>
</tr>
<tr>
<td>WDT</td>
<td>Wax Disappearance Temperature</td>
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</table>

References


