A new method for the determination of wax precipitation from non-diluted crude oils by fractional precipitation

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Abstract

Wax precipitation is one of the most important flow assurance problems. Unfortunately, experimental data are very scarce to confirm existing models for prediction of such precipitation problem. This work reports a new experimental method. Multistage fractional wax precipitation was carried out by decreasing the temperature of crude oil. No solvent dilution was used, so the effect of solvent on temperature wax precipitation was avoided. The reproducibility of the method was tested with comparable results. The precipitation curve and the wax appearance temperature were obtained for two crude oils with different chemical nature using the reported method.

Keywords: fractional precipitation, waxes, wax appearance temperature, pour point.

1. Introduction

Paraffinic waxes present in petroleum mixtures can precipitate when temperature decreases during oil production, transport through pipelines or storage. The presence of such solid waxes increases fluid viscosity and its accumulation on the walls reduces the flowline section, causing the blockage of filters, valves and even pipelines, increasing pumping costs, and reducing or even stopping oil production or transport [1]-[7]. Great savings in operational costs can be achieved by correctly predicting this solid precipitation problem. The two main variables usually considered in wax precipitation studies are wax appearance temperature (WAT) and the amount of wax precipitated as a function of operating conditions (wax precipitation curve, WPC) [8]. These magnitudes may anticipate potential wax deposition and suggest the convenience to rely on oilfield chemicals or alternative technologies to mitigate the problem

Detailed crude oil composition can not be properly determined due to the high number of compounds present in the mixture. It is commonly accepted to group the different compounds present in crude oils in different families according to their chemical structure (paraffins, naphthenes and aromatics, PNA) or polarity (saturates, aromatics, resins and asphaltenes, SARA) [9]. Light components of the crude oil keep the heavier ones in solution, but the solubility of such different species in the mixture depends on pressure, temperature and composition of the crude oil. Waxes may precipitate due to a temperature decrease because their solubility is so low that a solid phase can appear even if the content in long chain hydrocarbons is not superior to 2%. Such waxes are usually considered to be heavy hydrocarbons (C_{20}-C_{60}) mainly formed by linear n-alkanes, and represent the major risks to produce wax deposition problems. Two different types of waxes are usually present in crude oils: macro and microcrystalline. Macrocrystalline waxes are mainly n-alkanes with chain length within

C_{20}-C_{50}. Microcrystalline or amorphous waxes present a high proportion of isoparaffins and naphthenes within the range C_{30}-C_{60} [8].

In order to study wax deposition, the determination of the amount of wax precipitated as a function of temperature is required. Different methods based on solvent dilution have been reported in the literature. One of the most commonly used was proposed by Burger et al. [10] in which the crude oil is dissolved in a solvent mixture (ether/acetone), cooled at 253K and filtered afterwards at this temperature. This method is widely accepted to represent the total amount of wax able to precipitate in a crude oil. Musser et al. [11] reported the characterization of waxes precipitated by this method from different crude oils. Elsharkawy et al. [8] reported a modification of Burger's method, including previous crude oil dissolution in pentane. Nermen et al. [12] carried out a separation of waxes by fractional crystallization at low temperature using different solvents. They studied the most important variables affecting the crystallization process (temperature, solvent composition, dilution solvent ratio and washing solvent ratio) and the results were focused on obtaining the most appropriate conditions for the fractional precipitation of some crude oils. Handoo et al. [13] reported a fractionation method using a mixture of solvents (methyl isobutyl ketone and toluene), recovering and recrystallizing the soluble fraction at lower temperature.

The use of solvents in these precipitation methods presents a series of limitations. The presence of solvents has a great influence on the paraffin precipitating temperature because of the dilution effect, and therefore the WAT can not be properly determined. Thanh et al. [5] also showed that these methods are not able to separate microcrystalline waxes from non-hydrocarbons (resins and asphaltenes). These authors have reported a method in which the previous separation of pentane insoluble products modifies the chemical composition of the crude, and may also affect the phase equilibria. Likewise, in most of these methods the amount of waxes precipitated at a single temperature is determined, but it is not possible to study the amount of wax precipitated against temperature. This is a very important limitation in the available experimental information that has made several authors to propose procedures for the determination of crude oil precipitation curves based on alternative techniques such as DSC [14], NMR [15] and FT-IR [16], but its comparison with experimental data can not be carried out straightforward.

In this work, a new method of multistage fractional crystallization has been developed. This method is based on the same principles as those previously described, but it introduces some differences in the experimental procedure. The precipitation process is carried out by decreasing crude oil temperature in small steps (about 5K) without any previous dilution, thus avoiding the solvent effect on the precipitation temperature. The filtration is carried out with a small overpressure instead of the classical vacuum filtration to avoid undercooling of the crude oil and the cake during filtration and washing of the precipitated wax. The reported technique and a modification of Burger’s method [10] was applied to two different crude oils obtaining the WAT, the complete precipitation curve and the amount of solid precipitated at 253K. Obtained results showed differences related with the different chemical structure of the selected crude oils.

2. Experimental Section

2.1. Materials. Two different crude oils were selected to carry out the different experiments. Crude oil 1 was a naphtenic crude oil from West Africa and crude oil 2 was a paraffinic crude oil from the North Sea provided by REPSOL-YPF. The chemicals, suppliers and purities used in the experiments were the following: ethylenglicol-water mixture (IADA, 50/50%), nitrogen (Air Liquide, 99.999%), dichloromethane (Scharlab, 99.9%) acetone (Scharlab, 99.8%), n-pentane (Scharlab, reagent grade), and n-hexane (Scharlab, reagent grade).

2.2. Wax Precipitation. Wax precipitation was carried out using a similar procedure to that proposed by Burger et al. [10]. Crude oil is dissolved in n-pentane and stirred during 30 minutes. Acetone (acetone/n-pentane ratio 3:1) is added to the mixture and cooled down to 253K for 24 hours. The solid phase present in the oil is separated by filtration in a Buchner funnel using a glass microfibre Whatman filter Nº 934. The solid phase is re-dissolved in n-hexane in order to remove asphaltenes. After solvent removal the final product is weighted.

2.3. Fractional precipitation. The filtration procedure is shown in Figure 1. 50 g of crude oil (stream 1) are cooled in a cryostat at a slightly higher temperature than its wax appearance temperature (WAT) for 24 hours. The crude oil is then filtered by means of the technique described above using a glass microfibre Whatman filter Nº 934 during at least 2 hours. The solid phase (stream 3) is collected for further recovery of the precipitated waxes while liquid phase (stream 4) is used for next precipitation. The filtration area is washed with dichloromethane to recover the remaining crude oil and after that, solvent is removed by vacuum evaporation at 338-343K, and the obtained crude oil is mixed with the liquid phase (stream 4) obtained in the filtration process.

The solid phase (stream 3) is washed with acetone to reduce the soaked crude oil. This washing process is carried out at room temperature in a Buchner funnel using vacuum. Acetone is removed by vacuum evaporation and the remaining crude oil is added (stream 9) to the next precipitation experiment fluid.

The remaining solids (stream 6) are recovered by washing the filter with dichloromethane, and after solvent removal by heating at 323-333K, the final free-solvent product (stream 8) is weighted and stored for further characterization.

The mixture (stream 10) formed by the rest of liquid crude oil is used for the next precipitation step at a lower temperature. This procedure can be repeated 4 or 5 times by decreasing system temperature about 3-5K in each step. This process allows to obtain the amount of solid precipitated at each temperature and therefore to obtain the complete precipitation curve and the WAT of a crude oil.

The main part of the experimental system for fractional precipitation is the filter, which is temperature-controlled. Temperature is controlled by recirculating a mixture of ethylenglicol-water from a thermostatic bath in the range of 243K to 323K. The top of the filter is covered and connected to a dry nitrogen stream in order to carry out filtration under a slight over pressure. Figure 2 shows a scheme of this installation.

A limitation of this new experimental procedure is that at very low temperatures the filtration process can not be applied due to the increase of the viscosity of the crude oils. For that reason, it was not possible to reach the temperature of 253K for the selected crude oils. Such limitation does not affect the procedure of wax precipitation at 253K similar to that described by Burger due to the dilution of the sample. However, the results obtained by the fractional precipitation procedure reported in this work are more realistic as it allows reproducing wax precipitation along a temperature profile similar to that in pipelines where flow assurance problems can appear.

3. Results and discussion

All the results for the crude oil characterization are summarized in Table 1. Wax content at 253K and the fractional precipitation curve were obtained by the methods described above for crude oil 1 and 2. The WAT of each crude oil was extrapolated by fitting the precipitation curve to the temperature value where the precipitated solid is 0%. The pour point was also experimentally determined [17] for the selected crude oils. In order to check the reproducibility of the fractional precipitation method reported two sets of experiments were carried out using crude oil 1 (results were denoted as crude oil 1 and crude oil 1´).

3.1. Wax content. Wax content at 253K is assumed to represent the total amount of wax and it was determined following a modification of the method used by Burger [10] as mentioned before. It can be seen from Table 1 that the amount of solid precipitated at 253K is lower for crude oil 1 (9.56%) than that obtained for crude oil 2 (15.15%), in agreement with the paraffinic nature of this one.

3.2. Fractional precipitation. Fractional precipitation was carried out for the selected crude oils using the system shown in Figure 1. The results, listed in Table 1, show an increase in solid precipitated with temperature decreasing, as it was expected.

The precipitation curves provide estimation for the WAT of the crude oils extrapolating the curves to 0% of precipitated solid. The calculated values are also listed in Table 1. Figure 3 shows wax content at 253K, the results for the fractional precipitation experiments and the calculated WAT for crude oil 1. Wax content at 253K (9.56%) and the fractional precipitation value at 268K (10.60%) are very close for this crude oil. This result is in agreement with the high slope value of the precipitation curve which leads to the paraffins precipitation of this crude oil in a narrow range of temperatures (283-268K). This could be explained in terms of a relatively narrow distribution of paraffins with few long chain paraffins.

The amount of solid obtained by fractional precipitation can not be directly compared to the wax content obtained at 253K because of the impossibility to reach a temperature of 253K in the fractional precipitation method and also because of the effect of the solvent in the wax content method.

The reproducibility of the reported method was checked by repeating the precipitation curve of crude oil 1. These results are also listed in Table 1 and plotted in Figure 3. No remarkable differences or systematic deviations were observed and a good agreement was obtained in both experiments. The absolute average deviation calculated was lower than 0.6% in all cases.

Figure 4 shows the wax content at 253K, the fractional precipitation experimental results and the calculated WAT for crude oil 2. As it is shown in Figure 4 wax content at 253K is clearly superior to that obtained at the lowest temperature (268K) in the fractional precipitation experiment. This corresponds to a low slope of the precipitation curve which makes paraffins precipitate in a wide range of temperature (293-253K), indicating a wider distribution of paraffins for crude oil 2.

When the results obtained in the experiments carried out at similar temperatures for both crude oils are compared a higher amount of precipitated solids were obtained for crude oil 1 (for instance at 268K, the precipitated solids were 10.56% and 5.44% for crude oil 1 and 2, respectively). However, the range of temperature in which paraffins can precipitate is clearly larger for crude oil 2 (293-253K) than that in crude oil 1 (283-268K) in agreement with the higher WAT and total wax content values obtained for crude oil 2. These results can be explained by a wider distribution of paraffins in crude oil 2 than that presented in crude oil 1. For that reason, at the highest temperatures the amount of precipitated solids can be higher for crude oil 2 than that for crude oil 1 as it is shown by the obtained results.

Pour point of the crude oils reported in Table 1 was experimentally determined [17]. The pour point is a physical measurement related with crude oil flow and the amount of solid precipitated at that temperature should be similar for any crude. In this work, the amount of solid precipitated at the pour point was calculated for both crude oils by linear extrapolation of the experimental values obtained by fractional precipitation. It is necessary to remark that for crude oil 2 this procedure represents an extrapolation to a temperature value of about 15 K below the experimental temperature range. A value of 7.43% and 7.61% was obtained for crude oil 1 and 2, respectively. These similar results (about 7.5%) confirm the meaning of the pour point. However, such values are higher than typical values reported in literature (about 2% of precipitated solid) [18], [19] which could be related to the oil trapped in the precipitated paraffinic structure. Figure 5 shows the line representing the 7.5% of solid precipitated, the precipitation curves, the pour point and the extrapolated WAT for the selected crude oils.

4. Conclusions

The increase in the amount of solids precipitated when decreasing temperature for different crude oils can be reproduced by the experimental procedure presented in this work.

The reported method allows the determination of the wax precipitation curve and the estimation of the WAT of crude oils with different chemical composition avoiding the effect of the solvent dilution. Furthermore, the reproducibility test shows a good agreement between the results obtained in different experiments.

The fractional precipitation method presented in this work can be successfully applied to crude oils with different distributions of paraffins obtaining consistent results.

The amount of solids obtained at the pour point temperature is higher than the wax contents proposed in literature due to the crude oil trapped in the precipitated paraffinic structure. Therefore, it is necessary to develop a method to calculate the trapped oil and correct the obtained values. Several methods based on the characterization of the precipitated samples by means of NMR or DSC techniques are being considered.

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