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Evaluating the performance of wax deposition inhibitors under flowing conditions

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Abstract
This work introduces a designed apparatus for the evaluation of wax deposition inhibitors' performance under flowing conditions. This apparatus works by measuring the differential pressure between the inlet and the outlet of a flow tube as the temperature decreases at a constant cooling rate. This requires a smaller amount of sample and takes less time than conventional flowing methods that involve the measurement of wax deposit thickness. Thus, the temperature at which the differential pressure starts to increase indicates the formation of precipitates and wax gelation. The evaluation of the wax appearance temperature (WAT) of some inhibitors by image analysis and calorimetry, suggests that they are not effective since they do not decrease the WAT regarding the blank test. However, the same inhibitors decrease the temperature at which the differential pressure starts to increase, which indicates that they indeed are able to influence the sample fluidity and deposition. Moreover, high-pressure microscopy (HPM) confirms the effect of the inhibitors on the wax precipitates particles' size and their tendency to agglomerate in the blank test. Therefore, the results obtained using the designed apparatus show that the inhibitors can cause a lower adherence of precipitated wax on the pipe wall surface thereby improving the flow assurance.

Keywords
Wax deposition; wax deposition inhibitors; differential pressure

Introduction
The deposition of wax precipitates on the inner pipe walls at low temperatures is a crucial issue that affects the flow assurance in oil production. When the temperature of the pipelines is below the wax appearance temperature (WAT), the wax precipitation can cause several problems: increase in surface roughness, pressure loss, reduction of the pipework and flow blockage [1]. Therefore, the use of wax deposition inhibitors is a known cost-effective treatment to prevent these problems. An effective inhibitor must interact with wax to modify its structure and its ability to adhere tightly to surfaces. Furthermore, it can affect the amount of precipitated wax [2]. The use of wax inhibitors allows for obtaining wax deposits weaker and easier to remove by shear forces in the flow field, and thus, the transportation of the wax is more effective [3].
The WAT is the temperature detected at which the wax separates from the solution at cooling. This is one of the most studied parameters to evaluate both the tendency of a sample to form wax deposits and the performance of wax inhibitors. The determination of the WAT is usually carried out by differential scanning calorimetry (DSC) and other methods such as image analysis [4]. However, the conventional measurement of the WAT may not be a suitable method since it does not occur under mimicked pipeline flowing (dynamic) conditions. On the other hand, the methods performed under flowing conditions usually involve the measurement of the wax deposit thickness. This takes a lot of experimental time to obtain only one thickness measure. Moreover, these methods require the use of high flow rates in tubes with an internal diameter of considerable size, which in turn require a large amount of sample [5]. Thus, the purpose of this work is to introduce a designed apparatus to evaluate wax precipitation/deposition and wax inhibitors' performance under flowing conditions but requiring a shorter experimental time and a smaller amount of sample. The operation of this apparatus is based on the measurement of the differential pressure during cooling and deposition of the wax and its suitability was tested using a wax model solution in toluene.

Methodology
Samples
The sample used in this work was a commercial paraffin wax, containing a mixture of n-alkanes with chain length ranging from C_{19} to C_{38}, in toluene (5% w/w). The inhibitors used were EVA33, EVA19, Inhib1, Inhib2 and Inhib3 at a concentration of 400 ppm. Polyethylene vinyl acetate (EVA) is a linear chain composed of polyethylene copolymerized with vinyl acetate. EVA33 and EVA19 contains 33% and 19% of vinyl acetate polymer, respectively. The inhibitors 1, 2 and 3 are

commercial available products that contain different mixtures of protected compounds (1-5%) in a hydrocarbon mixture rich in aromatics.

WAT determination by RGB imagine analysis and calorimetry

RGB image analysis is a real-time technique that uses a webcam as a sensor to convert the intensity of the light. An increase in the average RGB signal (brightness) is observed when precipitation begins due to the scattering of light. The calorimetric measure was based on the heat that is released when the wax precipitates and the temperature increases. More information about the method is described elsewhere [4]. Samples of 5% w/w wax in toluene, without and with 400 ppm of inhibitor, was cooled from 40 to 5°C at -1°C.min^{-1} analyzed by both techniques.

Wax deposition under flowing conditions

The designed flow apparatus consist of a pump, an accumulator and a reactor containing the test section in Fig. (1).

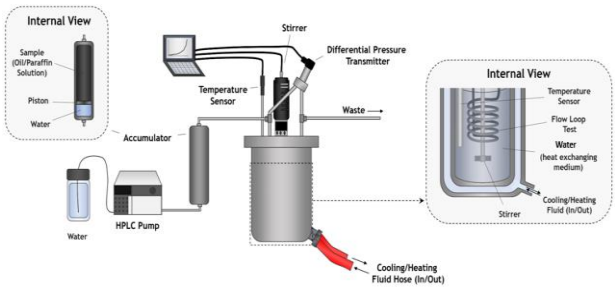

Figure 1: System and internal view of the vessel containing the test tube

The accumulator contain a movable piston that separates the pumped water from the sample containing the wax. As the piston moves upwards, the sample leaves from the top of the accumulator to enter the test section which is a 3-m stainless steel tube with 0.1 cm in internal diameter. The test section is placed inside a reactor containing a fluid to control the temperature and the cooling rate. As the sample flows through the test tube, a differential pressure transmitter (Zurich, 0-1000 mbar) is used to observe the changes in differential pressure between the inlet and outlet of the tube. Additionally, a computer monitor the temperature vs. time and the differential pressure vs. time in real-time. The samples used in this work were a 5% w/w wax in toluene, with and without 400 ppm of inhibitor. These samples were evaluated from 40 to 5°C at -1°C.min^{-1} under a flow rate of 1 mL.min^{-1}.

To later observe if there were wax precipitates inside the tube at the time that the differential pressure started to increase, a cell was inserted after the test tube. The cell, shown in Fig. (2), has a window that allows internal visualization, through which the sample that came out of the flow tube passed through. The cell was set to 40°C and it was cooled at a constant cooling rate by a thermostatic bath to 5°C at 0.6°C.min^{-1}. For these experiments, the temperature of the tube was set to decrease at the same cooling rate. The flow rate was maintained at 1mL/min. It was chosen the inhibitor EVA33 at 400 ppm for this experiment. The moment at which wax precipitated was monitored by RGB image analysis.

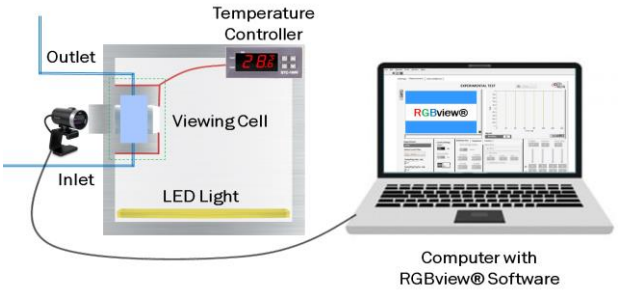

Figure 2: Viewing cell connected after the deposition test tube

Wax precipitates observed by a high-pressure microscope

Samples of 5% w/w wax in toluene, with and without 400 ppm of EVA33, was cooled from 40 to 5°C at -1°C.min^{-1} in a viewing cell coupled to a high-pressure microscope (HPM), as shown in Fig. (3). The software of the HPM collected images of the sample in every 1-min. The experiments occurred in static conditions, in which the samples were added to the cell and maintained in its interior while the temperature decreased. .

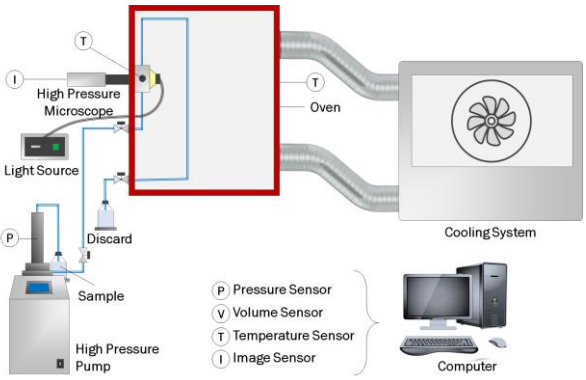

Figure 3: Viewing cell connected to a HPM

Results and Discussion

Table 1 presents the WAT values determined by image analysis and calorimetry for the wax inhibitors used in this work. The results show that none of the inhibitors decreased the average WAT values regarding the blank test and that they actually increase it a little. This suggest that these inhibitors might not be effective, however, this type of evaluation does not consider the impact that the inhibitors have in how these precipitates are formed, impacting the fluidity, which is the main concern for flow assurance. Thus, a proper evaluation to observe the effect on the wax deposition must be carried out under flowing conditions.

Table 1: WAT values by image analysis and calorimetry without and with 400 ppm of various wax inhibitors

	WAT (°C)	
	Imagine analysis	Calorimetry
Blank	18.8 ± 0.3	18.9 ± 0.1
EVA33	19.3 ± 0.1	19.2 ± 0.1
EVA19	19.6 ± 0.1	19.7 ± 0.2
Inhib1	19.5 ± 0.1	19.6 ± 0.1
Inhib2	19.1 ± 0.1	19.3 ± 0.1
Inhib3	19.7 ± 0.8	19.2 ± 0.1

Thus, the performance of the same inhibitors was evaluated using the designed apparatus introduced in this work and the results are shown in Fig. (4).

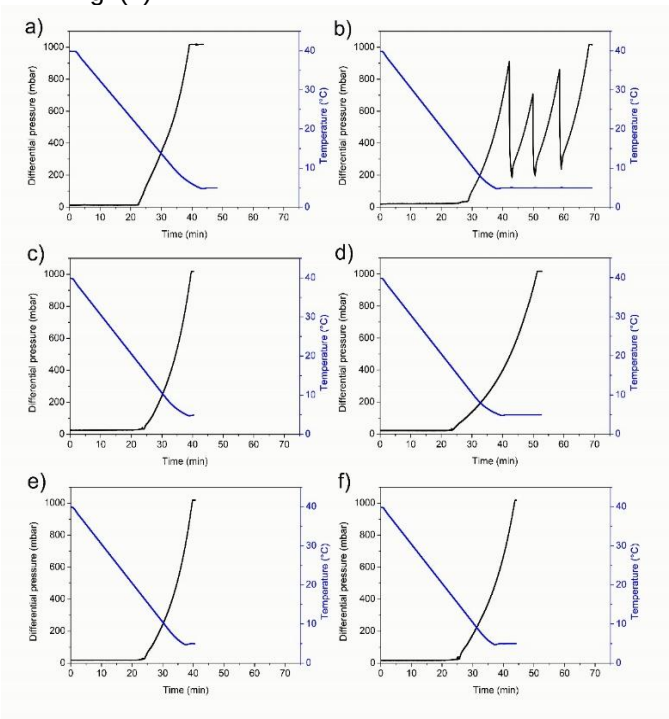

Fig. 4: Differential pressure and temperature versus time of a 5% w/w wax solution in toluene using 400 ppm of wax inhibitors a) Blank b) EVA33 c) EVA19 d) Inhib1 e) Inhib2 f) Inhib3

The temperature values at which the differential pressure started to increase were determined based on the average baseline value of the differential pressure. They are shown in Tab. (2). The increase in the differential pressure indicates that the flow condition inside the tube has changed, which represents precipitation. The wax precipitation leads to gradual pipe restrictions due to the deposition at the wall, increased fluid viscosity and formation of wax gel.

Table 2: Temperature of differential pressure increased without and with 400 ppm of wax inhibitors EVA33, EVA19, Inhib1, Inhib2 and Inhib3

	T (Dif. P) (°C)
Blank	17.6 ± 1.5
EVA33	13.2 ± 1.6
EVA19	16.5 ± 0.4
Inhib1	16.4 ± 0.5
Inhib2	16.5 ± 0.2
Inhib3	14.4 ± 0.5

It was observed that all inhibitors tested presented a lower the temperature, related to the blank experiment, at which the differential pressure started to increase. Contrary to what WAT suggested, the inhibition was effective. The inhibitor EVA33 was considered the best because it lowered the temperature the most and improved the fluidity the best since it took longer until the tube was blocked (that happened when the differential pressure reached the maximum value for the sensor used in this work).

For a better understanding of the different results obtained from the WAT determination and the differential pressure, a viewing cell was coupled to the end of the flow tube. Figure (5) shows the results of the experiment using this viewing cell.

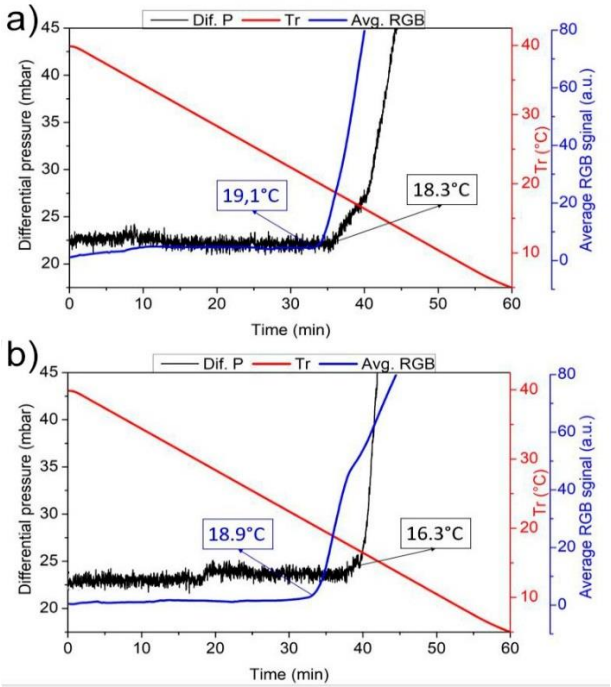

Fig. 5: Differential pressure, temperature and average RGB signal versus time of a 5% w/w wax solution in toluene using 400 ppm of wax inhibitors a) Blank b) EVA33

The viewing cell allows for corroborating that the addition of 400 ppm of EVA33 did not lower the temperature at which the wax precipitates started to appear. However, the inhibitor lowered the temperature at which the wax precipitates started to cause deposition, increasing the differential pressure. This indicates that the inhibitor has no effect on the WAT, but it may have an effect on the particles size and adhesion properties of the

precipitated wax. Thus, a HPM was used to evaluate this phenomenon.
Figure (6) displays the images captured by the microscope at 5°C as well as the particles mean area as the samples were cooled from 40 to 5°C.

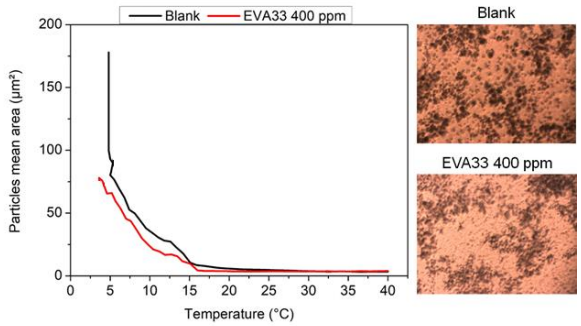

Figure 6: Imagens captured by HPM at 5°C and particles mean area vs. temperature of a 5% w/w wax solution in toluene using 400 ppm of wax inhibitors a) Blank b) EVA33

It is notable that the wax particles are bigger and more agglomerated when the inhibitor was not used. Moreover, the addition of 400 ppm of wax inhibitor EVA33 reduced the size of the wax particles and decreased the particles mean area.

Conclusions

The results of this work show that the determination of the WAT in either batch or flowing conditions is not suitable to evaluate the performance of wax deposition inhibitors. Therefore, the designed flow apparatus introduced here is an alternative to evaluate the inhibitors performance by observing the variation of the differential pressure at cooling without involving the measuring of the wax deposit thickness. Thus, the experimental time takes minutes instead of hours and a smaller amount of sample is required. The best performance of the EVA33 inhibitor was thereby determined using this designed flow apparatus. Moreover, the HMP analysis confirms that the EVA33 improves the flow assurance by allowing the formation of smaller and less agglomerated wax particles.

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