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CHARACTERIZATION AND EVALUATION OF WAXY CRUDE OIL FLOW

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Abstract - Part of the oil found in the Brazilian subsoil has a high wax content, which makes its flow process difficult at low temperatures because of the increase in the viscosity of the fluid. This paper studied the flow behavior of waxy crude oil under variation in the temperature of the external environment of the flow, the volumetric flow rate of the oil and the emulsified water content of the oil. The results were compared with those obtained for a non-waxy crude oil that had similar rheological properties at temperatures above the wax appearance temperature (WAT). The proposed tests were based on the experimental design technique, and the behavior of the fluids was evaluated based on the pressure variation generated by the flow.
Keywords: Waxy crude oil; Pressure variation; Crystallization.

INTRODUCTION

Paraffinization is one of the main problems in oil production and causes considerable losses to the oil industry. The wax precipitation phenomenon associated with paraffin deposition can result in unscheduled production shutdowns and promote operational risk conditions. Moreover, it can cause production losses and irreparable damage to equipment (Pauly *et al*., 2004).

In the Bahian Recôncavo region, the produced crude oil exhibits a density of approximately 30° API, almost no sulfur and high concentrations of dissolved waxes. Although these properties are great for the manufacture of lubricant oils and yield high added value, the presence of wax adds many complications to production, transportation and storage by hindering the flow in pipes (Thomas, 2004; Novaes, 2009).

Paraffins are both linear (n-paraffins) and branched (iso-paraffins) chain alkanes, and they have low reactivity with most compounds. Their chains can have a high carbon number, which implies a higher wax appearance temperature. The low-molecular-weight paraffins are the main components of natural gas, and the medium- and high-molecular-weight ones are found in crude oil (Farayola *et al*., 2010; Gao, 2008; Jamaluddin *et al*., 2001).

Paraffins are in equilibrium with other crude oil components, and any change in pressure, temperature and even composition can affect the equilibrium, thereby influencing the formation of precipitate. According to Santos (1994), the greater the crude oil wax content, the greater the precipitation rate and, therefore, the amount of precipitated wax. The light oil components keep the waxes soluble. The high pressure of the reservoirs maintains the light compounds solubilized in the crude oil, which favors the solubili-

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zation of waxes in the fluid (Tinsley; Prud'Homme, 2010). This condition ensures low viscosity and Newtonian behavior of the crude oil (Azevedo, 2003).

Temperature also influences the solubility of waxes in crude oil. When approximately 5% of the waxes crystallize because of oil cooling, a crystal lattice appears and traps some of the oil inside; this process is called "gelling" and hinders the fluid flow. Thus, the crude oil flow rate also interferes with wax solubility. The lower the oil flow rate, the longer it stays inside the piping, which favors heat exchange with the external environment (Vieira, 2008).

Once production starts, the oil flows through the pipelines, losing heat to the external environment, with consequent temperature decreases and reduced soluble light oil fractions. Such production conditions cause the oil viscosity to increase, which leads to production problems due to the precipitation of waxes (Venkatesan *et al*., 2005; Gao, 2008).

According to Vieira (2008), the first paraffin crystals start to form at a specific temperature, which is called the wax appearance temperature (WAT) and varies depending on the origin of the crude oil. Crystallization occurs in three steps:

- Nucleation – formation of small particles of crystallized material from which the first paraffin crystals will grow.
- Growth – mass transport of the solution towards the nuclei formed during the nucleation stage.
- Agglomeration – when the growing crystals are joined together, thereby yielding larger crystals.

With the nuclei already formed, there is incorporation of new paraffin molecules at the growth sites, and additional molecules of other species are grouped at these sites and become part of the structure. The nuclei form an ordered lamellar-structure arrangement.

After crystallization starts in a medium that contains water as an emulsion, the crystal lattice formation phenomenon occurs in a different manner. When the emulsion is of the water-in-oil type, the oil is waxy and the fluid temperature is below the WAT, the precipitated waxes are deposited onto the surface of the water drops, thereby contributing to the growth of the formed precipitate (Oliveira *et al*., 2010). When a large crystal lattice is in the vicinity of the water drops, a structure is formed; this structure percolates the drops into the lattice and captures them. According to Visitin (2008), this structure also provides mechanical resistance to the flow, thereby resulting in an increase in the viscosity and pour point of the oil.

The present study aims to evaluate and compare the flow of two types of crude oil, waxy and non-waxy, by measuring the pressure variation of the system under the influence of the flow rate, temperature and content of emulsified water.

MATERIALS AND METHODS

Crude Oil

The characteristics that influenced the choice of oils used in this study were obtained from the rheological behavior of the samples. Although the available oils had different wax contents, WATs and compositions, for a comparative study of the influence of the content of emulsified water, temperature and oil flow rate in the context of loss of flow, it was necessary for the oils to be rheologically similar such that any differences originated exclusively from phenomena that characterize the increase in fluid viscosity and its implications for the flow.

After a series of comparative tests to search for a non-waxy oil with rheological behavior similar to that of the waxy oil above the WAT, a non-waxy oil was defined as the reference for comparison in the study.

The WAT of each oil was determined through differential scanning microcalorimetry, μDSC. The analysis was made using a DSC-VII microcalorimeter, Setaram, with a 500 μL stainless steel pressure cell and the data acquisition and analysis was made through the Setsoft 2000 software. The procedure realized in the tests consists of heating the sample to 80 °C during one hour and a sample of known weight is placed in the cell and then in the equipment. The analysis is made by cooling the sample from 80 °C to 0 °C at a rate of 0.8 °C/min. Microcalorimetry measures any release or absorption of heat by the sample while it cools. The evaluated temperature range consisted in the cooling of the oils from 80 °C to 0 °C. The only possible exothermic event in this temperature range is the release of heat related to the crystallization of waxy species present in the sample. The greater the crystallization peak area, the greater the amount of wax present in the sample, and the higher the temperature at which crystallization occurs, the greater the length of the carbon chain of the crystallized paraffins. Figure 1 shows the microcalorimetry curve of the waxy oil, which has a WAT of 310.5 K.

Figure 2 shows the microcalorimetry curve of the low-paraffin oil. This sample exhibits two points at which the line tangent to the crystallization curve crosses the abscissa, thereby generating a WAT at 316.4 K and a second crystallization event at 290.7 K. This effect occurs because the long-chain n-alkanes,

when precipitating, tend to co-crystallize along the nearby paraffin chains, thereby forming the valleys that characterize the second crystallization event (Senra *et al*., 2008).

The microcalorimetry curves provide additional information besides the WAT of the studied oil. The increased flow of latent heat during the crystallization of the waxy crude oil paraffins (approximately 8 mW) compared with the non-waxy crude oil (approximately 1 mW for the WAT and 2 mW for the second crystallization event) results in a much larger area, which indicates a large mass of crystallized paraffin.

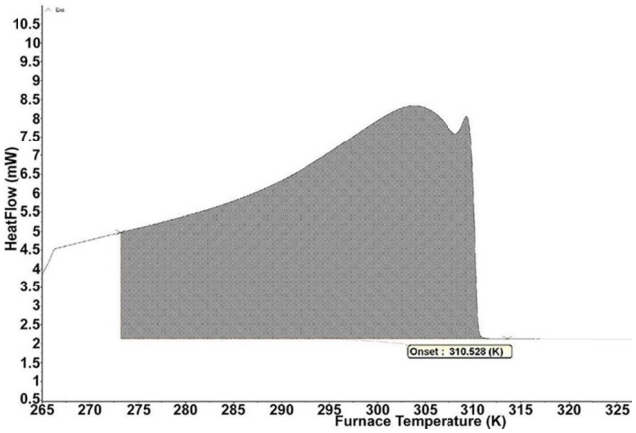

Figure 1: Microcalorimetry curve for the waxy crude oil.

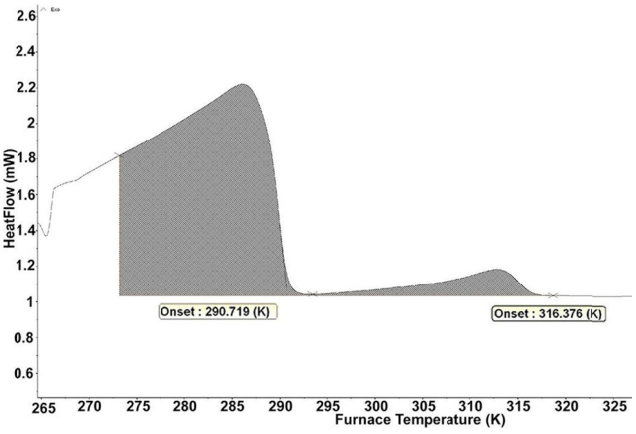

Figure 2: Microcalorimetry curve for the reference crude oil.

The rheological behavior of the crude oils was determined by using the Rheostress 600 equipment from ThermoHaake and started from parameters similar to those used in microscopy. The analysis consisted of collecting one thousand viscosity points along a linear cooling ramp from 353 K to 288 K at a rate of 0.5 K/min and under a shear rate of 100 s^{-1}. The rheological behavior results are found in Figure 3, which presents a comparative rheogram of the two oils.

It can be observed from Figure 3 that both of the oils, with less than 1% of emulsified water content, exhibit Newtonian behavior and very similar dynamic viscosity values during the cooling before reaching the WAT of the waxy crude oil. From the beginning of the paraffin crystallization, the waxy crude oil behavior started to be non-Newtonian and exhibited a marked increase in viscosity during cooling. The non-waxy crude oil started to exhibit such behavior only after the temperature of its second crystallization event.

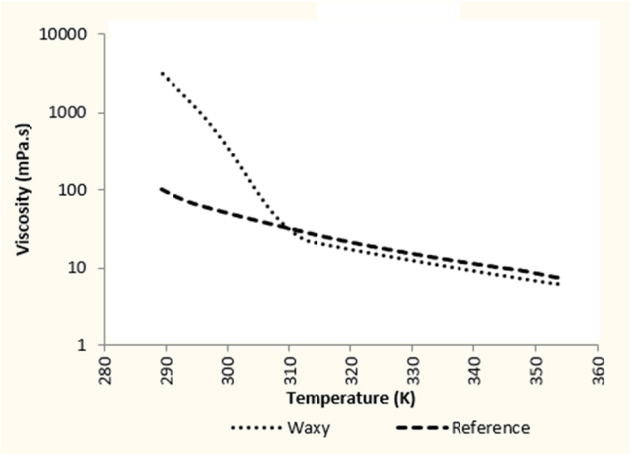

Figure 3: Rheogram that compares the two crude oils.

In addition to similar rheological behavior, the oils must also exhibit stable emulsions because of the high shear caused by the flow test. In stability tests in which the emulsion was subjected to 24 hours of heating at 333.15 K, both oils exhibited good stability for water-in-oil emulsions.

Operational System

The experimental unit used in the tests includes the PSL Systemtechnik WAX LOOP 208, model P2-C50, with a cryostat bath and the WL_Control control and data acquisition software package.

The equipment is a flow simulator in which the sample is pumped at controlled temperature and flow rate. The pressure variation of the oil was obtained from a differential measurement, which was continuously recorded using a test-time diagram. The equipment consisted of a sample storage vessel, a disposal vessel, sample pre-heating and post-heating systems, a dosing pump, a thermal bath, a control and data collection interface and a test tube.

The test tube used in the trials was made of stainless steel and was 3 mm in diameter and 2 m in length. The temperature of the oil in the storage ves-

sel was controlled using a heating plate placed under the vessel, whereas the temperature of the oil passing through the piping was controlled using a system connected to a heating bath. The oil flow rate was controlled using a dosing pump, whereas the inlet and outlet pressures of the line were measured using point gauges.

Initially, 1 liter of sample with known water content is heated to 60 ° C in a reservoir vessel to guarantee the solubility of all the paraffins in the oil. Then, the oil is circulated by the pass system until its temperature is stabilized. The next stage is initiated when the sample flows passing through the test tube, keeping its stabilized temperature due to the thermal bath unit at the desired flow rate.

During the test, the oil in the tank is maintained at 60 °C, so that the fluid inlet temperature is fixed at 55 °C. After cooling along the test tube, the sample is reheated to solubilize the precipitated paraffin and then returns to the reservoir vessel.

The temperature and pressure values at the input and output of the test tube were recorded, through spot meters, every 10 seconds. The pressure difference between the inlet and the outlet of the test tube, over time, was obtained for each test.

Due to the limitation of 10 bar for the process pressure, the tests were conducted at an input pressure of 9 bar, in order to preserve the system integrity. This limitation results in differential pressure values with an 8 bar limit, and, for this reason, the tests relating to the paraffinic oil were conducted up to 8 bar, when the limit was reached. For any specific operation condition where this value had not been reached, the tests were conducted for up to 6h of flow. The tests carried out with the non-paraffin oil were accomplished within 2 hours of operation, due to a small pressure loss.

Figure 4 shows the equipment schematic diagram.

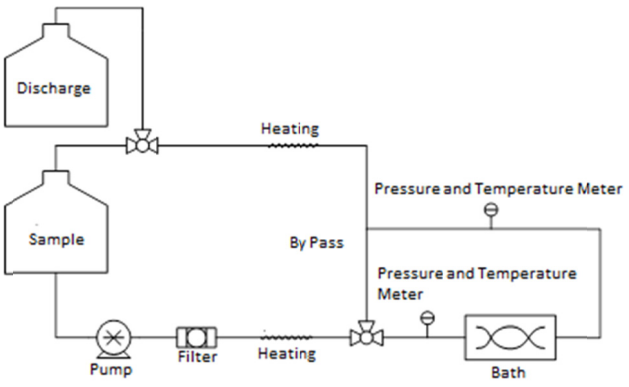

Figure 4: Schematic diagram of the experimental unit.

Experimental Design

Three variables were defined for the tests: the content of emulsified water in the crude oil (A), the bath temperature (T) and the flow rate (Q). These variables influenced the flow of waxy crude oil, which was quantified in terms of the pressure change (ΔP). Two levels were defined for each variable (the extremes of the range to be analyzed), and their values are listed in Table 1.

Table 1: Extreme values of the variables that influence the flow.

Independent variable	Lowest value (-)	Highest value (+)
A (%)	5	35
T (K)	293.15	298.15
Q (mL/min)	150	200

For the tests, a full factorial design was applied for three variables (2^3), with three replicates at the center point, as described in Table 2.

Table 2: Tests conducted according to the 2^3 design.

Tests	A	T	Q
	X1	X2	X3
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+
9	0	0	0
10	0	0	0
11	0	0	0

The factors involved in choosing the values used for each level are described below.

Laboratory tests indicated 5.12% of emulsified water in the waxy crude oil and 0.3% in the non-waxy crude oil, these analyzes were made using the potentiometric titration with Karl-Fischer reagent with the potentiometric titrator model Titrando 852, Metrohm, with the titration unit model Dosino 800. The experimental design created required the level values to be the same for both oils. It was found that hydrating the non-waxy crude oil from 0.3% to 5% was more appropriate because this process preserves the rheological properties of the sample. In contrast, dehydration of the waxy crude oil from 5.12% to 0.3%, conducted under heating, resulted in volatilization of light components, which transformed solvents into paraffins, thereby changing the oil's rheological behavior. Therefore, the minimum level was set to 5%.

The highest levels of the variable "water cut" were set to be 35% because, when this level was greater than 40%, the viscosity increased, which yielded difficulties in pumping the sample.

The influence of the temperature on the crystallization of paraffins dissolved in crude oil, and consequently its viscosity, is of paramount importance to this work. Preliminary tests demonstrated that, below 291.15 K, the waxy crude oil used as a sample did not flow properly because of its high viscosity. For this reason, 293.15 K was set as the lowest temperature level used in this study.

The highest temperature level was defined based on the need to expose the waxy crude oil to conditions in which crystallization of solubilized paraffins occurs, i.e., at temperatures close to its WAT. Therefore, the highest level was set to 298.15 K.

The residence time in the test tube is also a factor that influences the crude oil flow. The greater the residence time, the greater the heat exchange with the external environment, which results in a wider variation of fluid viscosity. Based on this information, it was assumed that 150 mL/min would be adequate for the minimum flow rate level.

The maximum flow rate level was set to 200 mL/min, which is close to its maximum operating condition, 275 mL/min.

Experimental Methodology

One liter of the sample with a determined water cut was initially heated to 333.15 K in a storage vessel such that the solubility of all paraffins in the oil was ensured. At the same time, the oil was circulated through the system's bypass until its temperature was stabilized. At the end of this step, the sample flowed through the cooling system.

During the test, the oil that fed the unit was cooled to 328.15 K. After the cooling that occurred throughout the test tube, the oil returned to the beginning of the process to be reheated to make the precipitated wax soluble.

The temperature and pressure values at the inlet and outlet of the test tube were recorded during the tests every 10 seconds. The pressure difference between the inlet and outlet of the test tube measured over time was the response obtained for each test. In most of the tests, the maximum pressure variation was achieved in less than two hours of operation. The results indicated that the best strategy to compose the experimental design was acquisition of pressure change data at a fixed time. The shortest time at which the maximum pressure was attained was used as the time to measure the differential pressure value for all tests.

RESULTS AND DISCUSSION

Waxy Crude Oil

The tests were conducted according to the distribution in Table 2 and the pressure differential occurred due to the wax precipitation. The pressure difference was calculated from the pressure variation between two manometers, the first one located at the beginning of the flow and the second one at the end of the flow; these manometers present 99 percent accuracy. In most cases, the maximum pressure variation of the system occurred at different times. Because the goal of the research is to study the pressure variation based on the influence of the variables (the emulsified water in the crude oil (A), temperature (T) and flow rate (Q)), the differential pressure values considered as test responses were those attributed to the lowest operating time that reached the maximum pressure variation of the system. The worst flow condition was achieved in test 1, with a temperature of 293.15 K, flow rate of 150 mL/min and water cut of 5%; in this test a pressure difference of 8.03 bar was achieved in 36 minutes. Thus, the reference operating time was 36 minutes. The pressure variation responses are found in Table 3.

Table 3: Pressure differential of the samples prepared with waxy crude oil.

Tests	Temperature (K)	Flow rate (mL/min)	Water cut (%)	Pressure differential (bar)
1	293.15	150	5	8.03
2	298.15	150	5	1.07
3	293.15	200	5	4.92
4	298.15	200	5	0.71
5	293.15	150	35	5.67
6	298.15	150	35	3.06
7	293.15	200	35	3.77

The data in Table 3 were processed with the aid of parametric statistics. The empirical models presented in Figures 6 and 7 were evaluated for significance through analysis of variance based on the Pareto diagram shown in Figure 5.

It can be observed from Figure 5 that the variables that significantly influenced the flow process were the temperature, oil flow rate, the interaction between the temperature and oil flow rate and the interaction between the temperature and water cut. The significance of the interactions between the two variables leads to the conclusion that it is not possible to analyze the behavior of the system based on only one variable while keeping the other variables fixed. The experimental data were properly fitted to a linear plane model with a regression coefficient (R^2)

of 0.98, which implies that the model is appropriate for describing the behavior of the studied system.

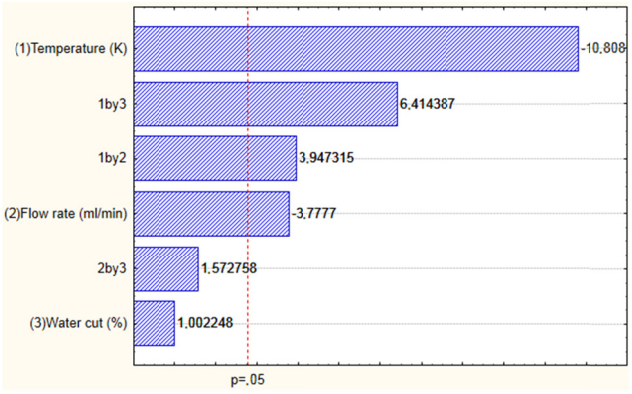

Figure 5: Pareto diagram of the waxy crude oil flow results.

Figure 6 shows the behavior of the ambient temperature and flow rate as a function of the system pressure variation. It can be observed that the lowest pressure drop occurred at the highest level of ambient temperature for all flow rates in the considered range. The highest pressure drop occurred at the lowest ambient temperature and lowest flow rates. The pressure drop was independent of the flow rate only when a higher ambient temperature was imposed.

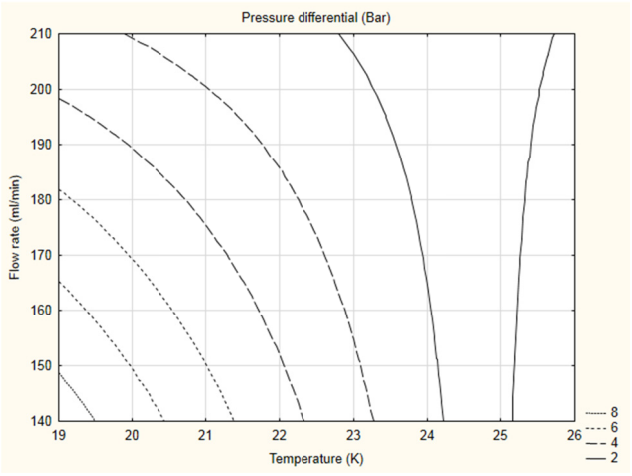

Figure 6: Response surface - flow rate and temperature.

The lowest ambient temperature level (20 °C) imposed an average temperature of the waxy crude oil that was below its WAT (37.4 °C). Thus, crystallization of large amounts of waxes occurred, thereby increasing the viscosity of the oil, as can be observed from Figure 3. The residence time of the oil in the test tube directly influenced its temperature because it lost heat to the environment in which the tube was immersed over a longer time period. Therefore, the lower the oil flow rate in the system, the greater its residence time in the test tube. This implied a lower average temperature of the oil, which increased the amount of crystallized wax and consequently the oil viscosity. Near the highest ambient temperature level (25 °C), the flow rate did not interfere with the system pressure because the outlet temperature of the sample remained above the WAT.

For the studied parameter ranges, the water cut did not have a significant effect on the pressure drop. However, its interaction with temperature was important. Figure 7 shows that the highest temperature and lowest water cut conspired to reduce the pressure drop. This effect occurred because the effect of the wax on the increase in viscosity was much greater than the effect of the emulsified water. This interference was so strong that the larger the amount of oil in the oil/water ratio of the sample, the greater the amount of crystallized paraffin and the greater the pressure drop of the system. This result suggests that the "gelling" of the paraffin in the presence of water led to a more flexible structure than when water was absent. The water droplets increased the flexibility of the precipitate, thereby making its flow easier and leading to decreased pressure gain due to "gelling".

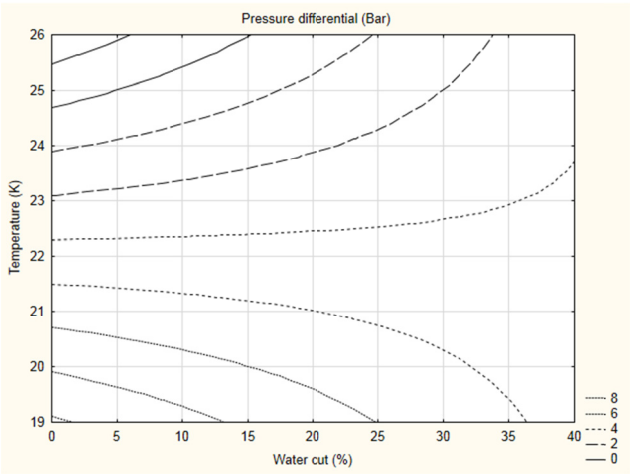

Figure 7: Response surface - water cut and temperature.

At the highest temperature levels, the greater the amount of water mixed with the crude oil, the greater the pressure differential of the system. This phenomenon occurred because the water droplets tended to split and become increasingly smaller under the action of shear stresses caused by the flow. The smaller the size of these drops, the lower their flexibility and divisibility, which caused the fluid flow to have a piston shape.

Reference Crude Oil

The non-waxy crude oil was evaluated according to the same methodology applied for the waxy crude

oil. Table 4 presents the pressure differential values used in the statistical analysis.

Table 4: Pressure differential of the samples prepared with non-waxy crude oil.

Tests	Temperature (K)	Flow rate (mL/min)	Water cut (%)	Pressure differential (bar)
1	293.15	150	5	0.49
2	298.15	150	5	0.37
3	293.15	200	5	0.57
4	298.15	200	5	0.58
5	293.15	150	35	1.48
6	298.15	150	35	1.42
7	293.15	200	35	1.93
8	298.15	200	35	2.02
9	295.65	175	20	1.00
10	295.65	175	20	1.01
11	295.65	175	20	0.95

The data in Table 4 were fitted with a linear model; the significance values for the variables are shown in the Pareto diagram in Figure 8. Figures 9 and 10 show the effects of the operational variables used in this evaluation, with a coefficient of determination (R^2) of 98.96%. This result indicates that the linear model properly represented the physical system under study.

According to Figure 8, the variables that significantly influenced the pressure variation in the non-waxy crude oil flow were the flow rate, water cut, and interaction between the flow rate and water cut. In contrast, the temperature and its interactions were not significant.

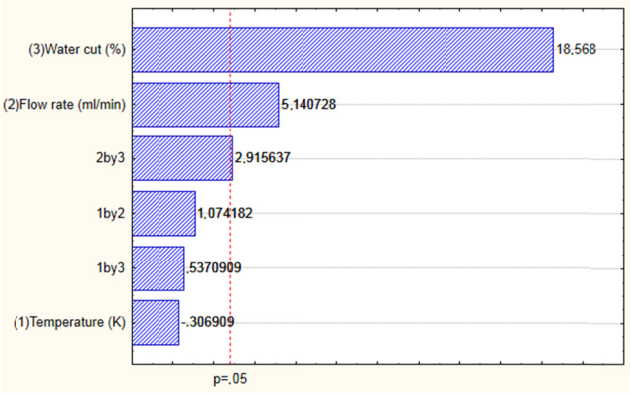

Figure 8: Pareto diagram of the non-waxy crude oil flow results.

Figure 9 shows the influence of the water cut and flow rate on the pressure variation of the flow. It can be observed that the pressure variation was less when the water cut was lower, regardless of the flow rate level. However, the pressure variation was greater when the water cut was higher, as was the flow rate. The water influenced the non-waxy crude oil in the same manner that it influenced the waxy oil, that is, it exhibited a flow similar to that of small solids flowing with a liquid, thus increasing the viscosity of the continuous phase. Because no wax precipitation occurred, this phenomenon appeared to be the most significant phenomenon of those that interfered with the oil viscosity.

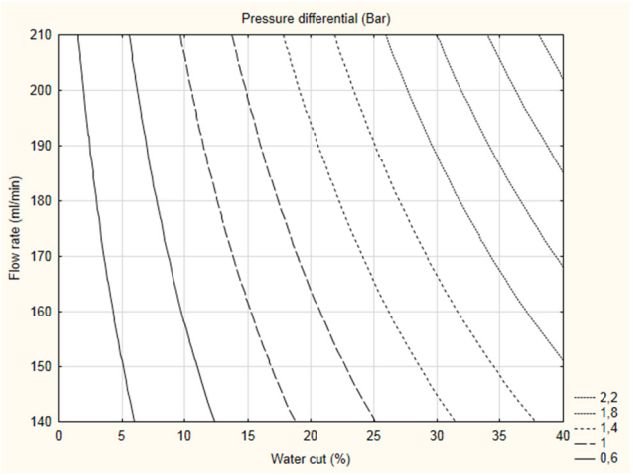

Figure 9: Response surface – water cut and flow rate.

It is noteworthy that, with the presence of water droplets in the flow, the increase in flow rate did not imply wax deposition but rather increased the shear imposed on these droplets and consequently increased the pressure variation. For this reason, the flow rate exhibited behavior that was opposite to that observed for the waxy crude oil. Whereas in the waxy crude oil a decrease in the flow rate increased the pressure variation, in the non-waxy crude oil the increase in the flow rate increased the pressure gain.

Figure 8 shows that the variation of the ambient temperature was not significant, and this fact is also shown in Figure 10. Because the studied temperature range was very small, from 20 °C to 25 °C, the influence of the temperature on the increase in oil viscosity was very small, which justifies its non-significance. The temperature levels set for the tests were well above the temperature of the second crystallization event of the non-waxy crude oil (17.6 °C) observed in Figure 2.

The microcalorimetry curves indicate that at temperatures above the second crystallization event, there was little paraffin crystallization, and most of the paraffin remained soluble, as indicated by the small area observed in Figure 2. In the tests analyzed here, because the inlet temperature was 55 °C, the average temperature of the system remained well above the second crystallization event; thus, this variable was not significant in the defined level range.

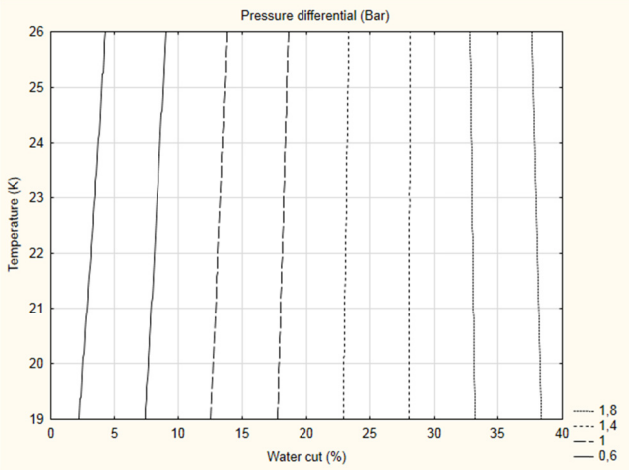

Figure 10: Response surface - water cut and temperature.

Memory Effect

As can be seen in Table 2, trials 9, 10 and 11 occurred in triplicate in the planning in order to investigate phenomena such as a memory effect.

Figures 11 and 12 show the tests performed in triplicate with samples of both oils. It is evident that, at the middle point of 36 minutes, comparing the pressure, the differential values are similar, giving credibility to the test and its repeatability.

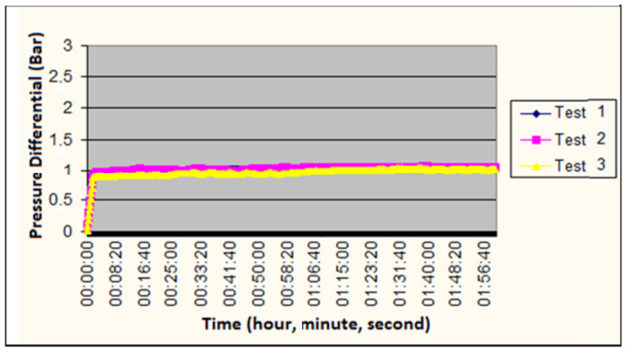

Figure 11: Triplicate test with non-waxy crude oil.

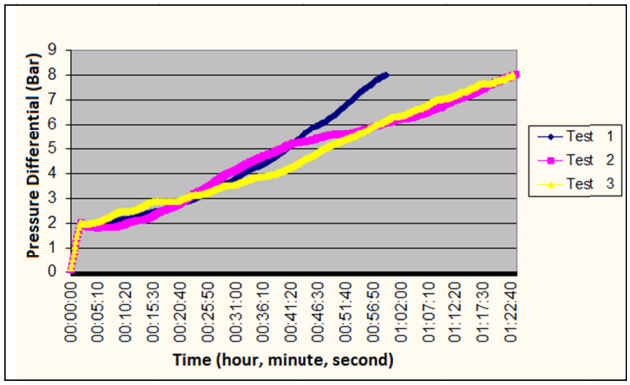

Figure 12: Triplicate test with waxy oil.

CONCLUSIONS

Although the rheological properties of both oils were very similar at temperatures above the WAT, as evidenced by Figure 3, the flow behavior of the non-waxy crude oil was completely different from that of the waxy crude oil at lower temperatures. In the working range used, the flow of waxy crude oil proved to be dependent on the flow rate, temperature and interaction between combinations of the flow rate and water cut.

The variable that was the most significant for the waxy crude oil was the temperature, which was inversely proportional to the pressure gain. Because of the large amount of wax that was present in the crude oil, once the WAT was achieved by lowering the temperature, a large amount of paraffin crystallized and contributed to increasing the pressure change in the system. The flow rate was also significant and was inversely proportional to the pressure gain. This effect occurred because low flow rates caused a longer residence time for the oil in the line, thereby causing further heat loss and consequently decreased temperature. The presence of emulsified water in the flow, with wax precipitation, induced gel formation through the interaction of water droplets with the wax precipitate. This interaction made the precipitate more flexible, thereby facilitating its flow. In the absence of precipitate, the water droplets tended to split because of the shear imposed by the flow and behaved like a solid dispersed in the oil, thereby increasing its viscosity.

The non-waxy crude oil was influenced by the water cut, flow rate and combination of these two effects. Because of the small amounts of wax present in the non-waxy crude oil, the variable that was the most significant was the water cut, which was proportional to the pressure gain. The greater the amount of emulsified water, the greater the system viscosity because the behavior of the water droplets was similar to that of a solid. The flow rate was significant and, unlike the waxy crude oil, its influence was proportional to the pressure gain. The greater the flow rate, the greater the shear and, consequently, the increase in associated pressure variation.

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