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TÍTULO DO TRABALHO:

INFLUENCE OF COOLING ON PARAFFINIC CRUDE OIL BY MICROSCOPY

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Abstract

Petroleum is a complex mixture of hydrocarbons of varying nature and small fractions of nitrogen, oxygen, sulfur and metals compounds. At reservoirs (8,000 to 15,000 psi and 70 to 150 °C) is encountered as Newtonian behavior whereas at low temperatures pseudoplastic behavior is commonly found. A large portion of the Brazilian oil production comes from offshore fields, from the pre-salt layer. These oils have high levels of waxes, which has a high precipitation potential, due to the low sea temperatures (about 4 to 5°C). In temperatures below the wax appearance temperature the wax crystallization takes place with subsequent deposition. This can lead to a strong waxy crystal-interlocking network, which causes pipeline clogs and dramatically affects the rheological fluid behavior. Crystallization kinetics and crystal morphology can be highly affected by some recognized factors, such as cooling rate, carbonic chain nature (branched or linear and average length), resins and asphaltenes content, and shear rate. Gelation and deposition problems, leading to increases in yield stress and losses in production, are probably connected to waxes morphology. This work aims to characterize the structure and morphology of wax crystals present in four pre-salt Brazilian crude oils, under different shear conditions and temperatures using polarized light and bright field optical microscopy. For this, the thermal history of the samples was removed, i.e. the oil was heated until the total wax was solubilized, eliminating the preexisting growth nuclei. In order to characterize the wax precipitation on the dependence of temperature decrease, a continuous cooling protocol was performed. The cooling step was carried out quiescently and in presence of shear for 80°C to 5°C. The samples micrographs were taken using the microscope Axiovert 40 MAT (Carl Zeiss).

Introduction

At room temperature, petroleum can be gas, liquid and/or solid, it is therefore considered a gases and solids dispersing in a liquid phase (FARAH, 2012). These three phases can be very different depending on the crude oil, i.e. oils from different reservoir or even from the same reservoir as different production times shows different compositions. Some have asphaltene characteristics, others predominate resins, in others the paraffinic characteristic, etc. Paraffinic oils have a predominance of alkanes with carbonic chains around 15 to 75 carbons. These molecules can present linear chains (n-paraffin), or branched chains (iso-paraffin). This class of compounds has a high precipitation potential, due to the low sea temperatures (about 4 to 5 °C) (AZEVEDO and TEIXEIRA, 2003; LOPES *et al.*, 1997). According to Létoffe *et al*. (1995), wax appearance temperature (WAT) of a sample increase as the number of carbon chain and the percentage of wax increase. This means that crude oils with high content of waxes and/or composed mostly of longer carbon chains have higher WAT values than oils with shorter chains and/or low wax content.

Waxes crystallize under basically orthorhombic or hexagonal shapes. The orthorhombic form is needle-shaped and it is found in crudes with high waxy content. Crystallization kinetics and crystal morphology can be highly affected by some recognized factors, such as cooling rate (CAZAUX *et al.*, 1998); carbonic chain nature (branched or linear and average length), (PASO *et al.*, 2005); resins and asphaltenes content (ALCAZAR-STICK and BUENROSTRO-GONZALEZ, 2011; VENKATESAN *et al*., 2005), and shear rate (WESSEL and BALL, 1992). Hence is relevant some physicochemical

characterization of crude oil and a rigorous control on experimental conditions in order to address a proper comparison between microscopic images.

The polarized light (PL) optical microscopy is the main technique for wax crystals examination. According Létoffé *et al*. (1995) it allows verifying the anisotropic optical behavior of crystalline materials, named birefringence. When the light beam passes through crystalline structures, as wax crystals, the polarized light plane is altered generating a visible image pattern. On the other hand, isotropic structures, which do not exhibit the same level of organization, are not able to modify the light plane. Apart from PL microscopy, the bright field (BF) regards another important technique for wax crystals visualization. The procedure is very simple and none artifacts are employed at optical path.

Gelation and deposition problems, leading to increases in yield stress and losses in production, are probably connected to waxes morphology. Therefore, this work aims to characterize the structure and morphology of wax crystals present in four pre-salt Brazilian crude oils, under different shear and temperature conditions, using bright field and polarized light optical microscopy.

Methodology

Five petroleum were used, four paraffinic (P1, P2, P3 and P4) and one non-paraffinic (NP) used as wax absence reference, all provided by Petrobras.

The thermal history (TH) removal of 100 mL of oil was carried out by heating the samples for 2h at 80°C in a circulating oven model 400-3ND (Ethik Technology). This condition was sufficient to dissolve all wax present in the crude oil and to prevent that the wax crystal formation was not influenced by pre-existing nuclei (LI and ZHANG, 2003; PEDERSEN and RØNNINGSEN, 2000).

Density measurements were taken on SVM 3000 viscometer (Anton Paar), following ASTM-D7042 at 20°C. The WAT measurements were performed using Nano DSC differential scanning calorimeter (TA Instruments). Firstly, the samples were heated from room temperature to 80°C, at 2°C/min. Secondly, they were hold for 15 min at 80°C, following by a cooling step from 80°C to 4°C, at 0.5°C/min. Finally, they were kept for 15 min at 4°C and submitted to a heating step from 4°C to 25°C at 2°C/min. Kerosene was used as the reference. The determination of saturated, aromatic and polar fractions were obtained by liquid chromatography separation in a silica gel column 60 (2.5 g silica, 0.063-0.200 mm) from Merck. The column was heated for 10 hours at 120°C for activation. Fractions were eluted with 10 mL n-hexane for saturated, 10 mL of n-hexane/dichloromethane (8:2) for aromatic and dichloromethane/methanol (9:1) for polar fractions. Residual solvents were submitted to a rotary evaporation. The wax content for four paraffinic oil were determined followed the standard method UOP 46-85.

Continuous cooling protocol was performed to characterize the wax precipitation, morphology and wax crystals length in dependence of temperature. The samples (after TH removal step) were transferred to a jacketed Becker coupled to a circulation bath (Haake Phoenix II-C25P - Thermo Scientific). Then, the cooling step were carried out quiescently or in presence of shear (mechanical agitation 250 rpm on RW20 Digital-Ika) for 80°C to 5°C. The cooling rate was 0.5°C/min.

Aliquots of crude oil were observed on optical microscope AxioVert 40 MAT (Carl Zeiss), using two microscopy techniques: PL and BF, in order to characterize the morphology and measure the length of wax crystals. **Figure 1** shows the procedure.

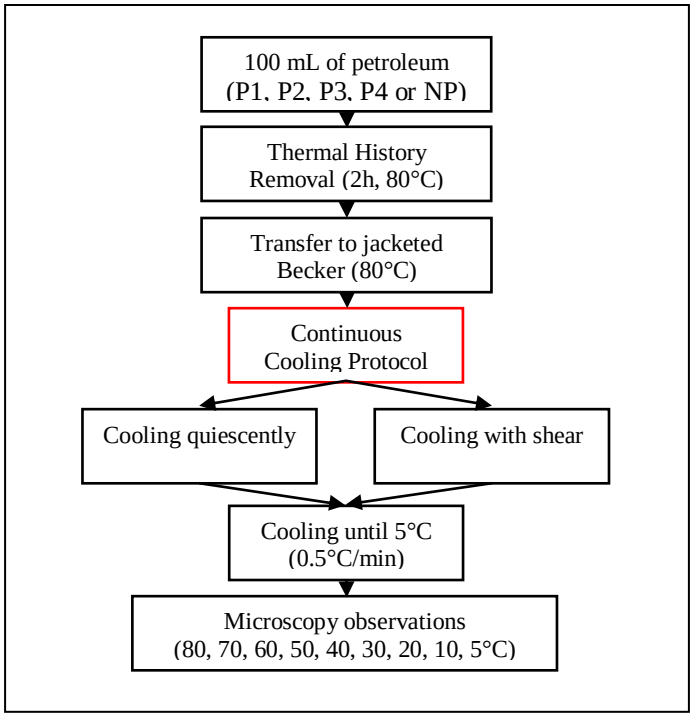

Figure 1: Flowchart for continuous cooling protocol.

Results and Discussion

The physicochemical characterization of five oils analyzed are presented in **Table 1**.

Table 1: Physicochemical characterizations.

Oil	ρ	**WAT** (°C)		**Oil Composition** (wt %)			**Wax content**
	(g/cm³)	1° event	2° event	Saturated	Aromatic	Polar	(wt %)
P1	0.88	46.6	25.7	60.7	26.7	12.5	3.7 ± 0.3
P2	0.91	42.1	23.5	55.1	31.8	13.1	5.7 ± 0.4
P3	0.89	46.8	25.0	52.6	35.8	11.6	5.0 ± 0.1
P4	0.91	53.1	29.4	56.2	34.3	9.5	3.6 ± 0.2
NP	0.93	37.9	19.2	57.6	28.9	13.4	*

* *Undetermined*

All crude oils have relatively similar values of density. **P2**, **P4** and **NP** are classified as heavy oil according to the °API scale (FARAH, 2012). WAT is defined as the onset temperature, which is measured by the intersection point of the baseline and the tangent line of inflection of the exothermic peak (OLIVEIRA *et al.*, 2012). In crude oils, due the complex chemical systems, these values are generally between 25 and 50°C (KANÉ *et al.*, 2003). It depends on the waxes concentration, molecular weight and chemical structure of the hydrocarbon matrix (KOK *et al.*, 1996). It was observed that **P4** were characterized by bigger WAT values when compared the WAT values of other crude oils (**Table 1**). These results were an evidence that the **P4** is composed by more long waxy chains than the others (BAI and ZHANG, 2013). The NP sample shows very small peaks, i.e. paltry variation at the baseline, because of its non-paraffinic characteristic. As can be seen at **Table 1**, all crude oils were characterized by similar saturated, aromatic and polar compounds values. Moreover, the wax content from paraffinic crude oils was between 3.6 and 5.7 wt %.

Figure 2 shows the BF micrographs of **P1**-**P4** and **NP** at 5°C, after quiescent cooling. It was observed the presence of tortuous crystals at paraffinic crudes and absence of crystal in **NP**. The **NP** sample was not characterized by precipitated material in this condition, confirming the result obtained at WAT measurement, since no intense crystallization peak was observed for this sample (**Table 1**).

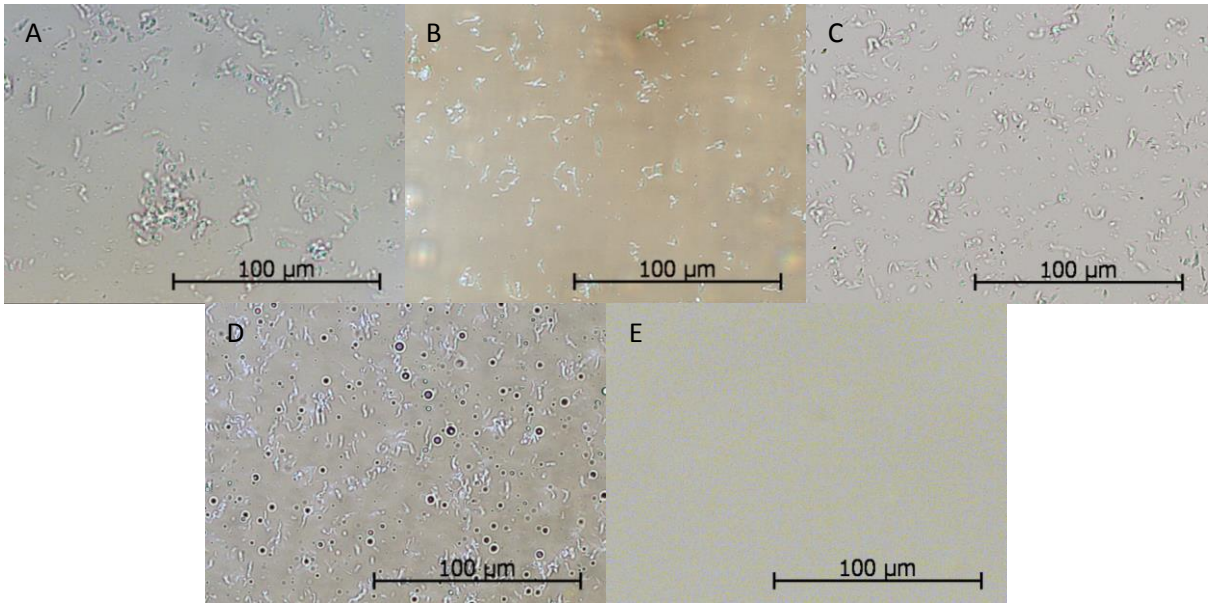

Figure 2: BF micrographs for a) P1, b) P2, c) P3, d) P4 and e) NP at 5°C.

The wax crystals presented in waxy crude oils are elongated. According to Kané *et al*. (2003), waxes precipitated in crude oil tend to crystallize in an orthorhombic structure, which are characterized by an elongated needle-like structure. Evidently, the crystals of **Figure 2** are not linear (needle-like). This sinuosity and tortuosity is probably due to the presence of impurities during nucleation and crystals growth processes (PASO *et al.* 2005). The average lengths at 5°C, of samples **P1**-**P4** are 16.2 µm, 14.9 µm, 15.4 µm and 10.3 µm. The **P4** has the smallest crystals, being on average 35% smaller than the others are. Venkatesan *et al*. (2005) analyzed the aspect ratio, which is the ratio between the length and the width of a crystal. Based on aspect ratio value, it is possible to verify how the structure is elongated. The values of average aspect ratio, at 5°C, of samples **P1**, **P2** and **P3** are 5.5, 6.2 and 5.0 respectively, legitimizing the elongated characteristic. **P4** sample has a 4.0 aspect ratio value, which indicates that the crystals are not elongated like the other samples.

Another characteristic of wax crystals that can be seen (**Figure 3)** is a roughened crystals surface. The roughness, as well as the tortuosity of wax crystals, can be attributed to a heterogeneous nucleation and the presence of asphaltenes, resins, different wax chain lengths or the presence of iso and cycle alkanes (RØNNINGSEN *et al.* 1991; SPEIGHT, 1999).

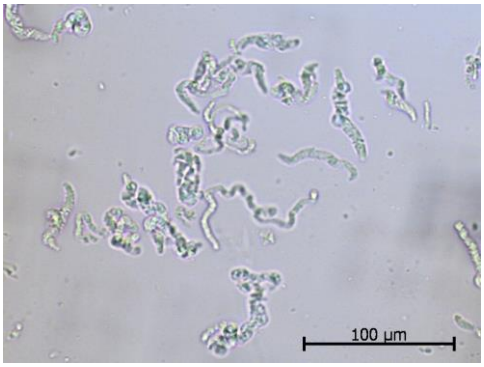

Figure 3: BF micrograph in detail of **P1** at 25°C.

Figure 4 show PL micrographs of **P3** obtained in different temperatures (30, 20, 10 and 5°C) during quiescent cooling which could happen before a restart of pipelines, when the crude oil is cooled under shutdown conditions. It was observed that the concentration and size of wax crystals is a function of a temperature, i.e., the both parameters increase with decreasing of temperature. Since the solubility of high molecular weight waxes decreases sharply with decreasing of temperature, hence they precipitate out and crystallize. The waxy crude oils **P1**, **P2** and **P4** were characterized by the same behavior of **P3** during quiescent cooling.

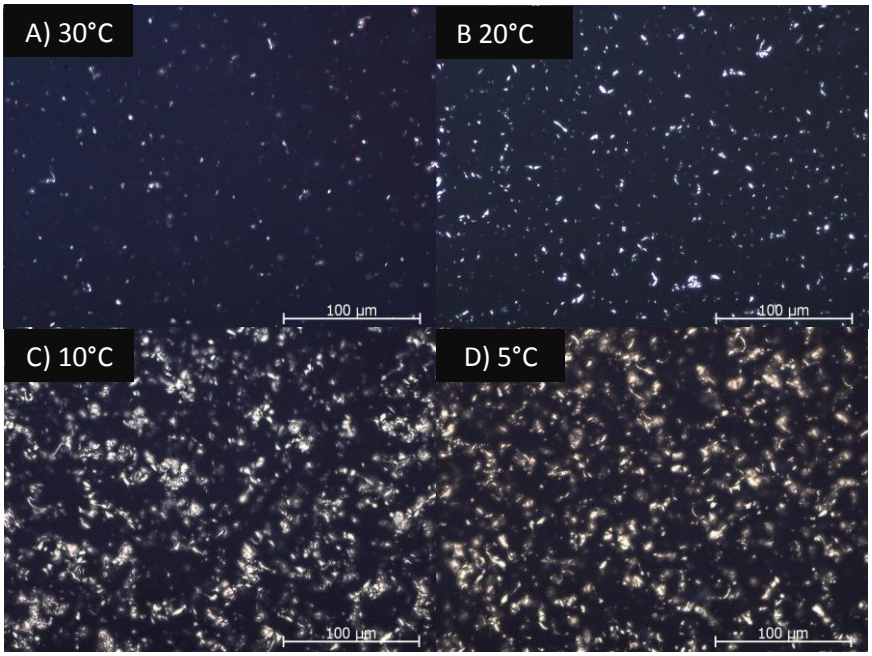

Figure 4: PL micrographs of **P3** obtained in different temperatures (30, 20, 10 and 5°C) during quiescent cooling.

The micrograph of **P3** obtained at 10 and 5° C (**Figure 4C** and **4D**) was characterized by higher wax crystals entanglement degree when compared with 30 and 20°C (**Figures 4A**, and **4B**). This result indicates that in low temperatures is more probably to have problems of flow assurance due to pipeline blockage occasioned by wax crystal depositions and to the formation of a high-strength gel, characterized by yield stress (BARBATO *et al.*, 2014; BAI and ZHANG, 2013; CHANG *et al.*, 2000).

To verify the influence of shear on waxy crystal growth, it was compared the PL micrographs of tests carried out at the same temperature (5°C), on quiescent and shear cooling conditions of waxy crude oils **P1**-**P4** (**Figure 5**).

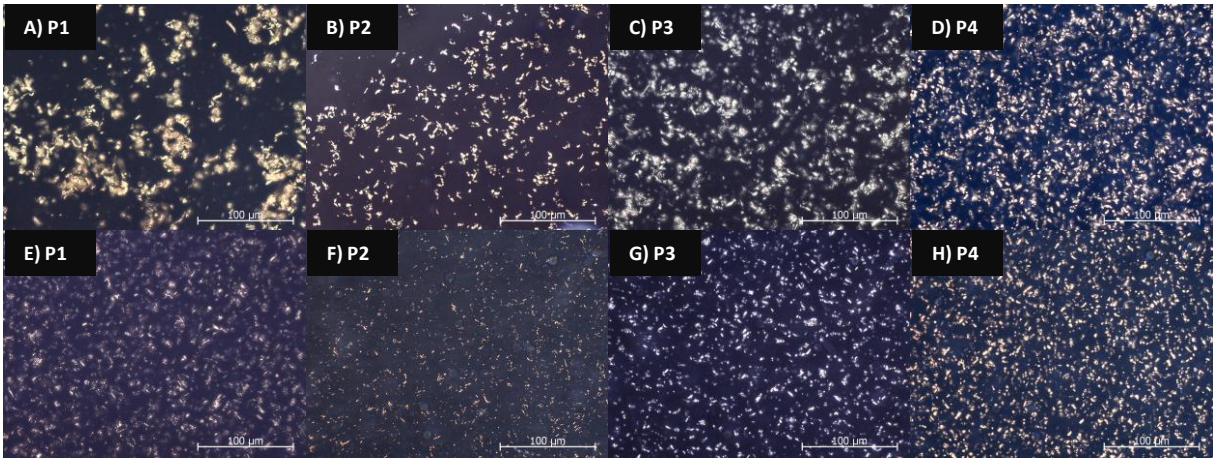

Figure 5: PL micrographs of test performed at 5°C on quiescent (A-D) and shear (E-H) conditions of waxy crude oils **P1**-**P4**.

It was verified that experiments performed with quiescent condition (**Figures 5A-5D**), were characterized by large particles and cluster when compared with the shear condition experiments (**Figures 5E-5H**). Under quiescent conditions, the waxy crystals were characterized by extended and continuous particles (LEE *et al.* 2008; VENKATESAN *et al.* 2005; KANÉ *et al.* 2003). The formation of extended and continuous particles allowed a colloidal network that embodies the oil itself. Probably, the gel would have a high shear modulus, in order to the side-by-side interactions between particles. Under shear condition, the lateral growth of the individual crystals is constricted. However, extended particles are no observed and consequently these particles lost their interconnectivity.

Table 2 shows the average crystals length to **P1**-**P4** at 30 and 5°C, for quiescent (Q) and shear (S) conditions.

Table 2: Length crystals average.

	P1		**P2**		**P3**		**P4**	
	Q	**S**	**Q**	**S**	**Q**	**S**	**Q**	**S**
30 °C	12.0	8.3	6.2	5.3	10.2	10,0	8,2	8,0
5 °C	16.2	12.8	14.9	8.9	15.4	11.3	10.4	9.1

As expected when the temperature decreases from 30°C to 5°C the length increases, and the crystal size is lower in shear conditions than in quiescent condition. For quiescent conditions is possible to note the length increases at low temperatures (10 and 5°C), i.e., the crystal keep increasing, however, for shear conditions the crystals length become stationary. This behavior could be attributed to a possible crystals breakage by the shear, which prevents the crystals from becoming large.

Conclusions

The wax crystals present in the oil have an elongated structure, but they are not linear. They show a roughness surface, possibly due to the presence of crystallization interferers (asphaltenes, resins, organic solids, etc.). The gradual temperature decrease favors the increase of the crystals length, as well as the increase in the quantity and size of the agglomerates. Under shear conditions, crystals of shorter lengths were observed and in less quantity than under undisturbed conditions.

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