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Waxes precipitation in a recombined oil with CO2 by using a high-pressure Solid Detection System

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Abstract

Wax precipitation is a considerable challenge for the oil industry, especially in subsea lines where low temperatures can induce the crystallization of wax particulates. Therefore, flocculation of other particulates and even the complete blockage of the lines can take place affecting the production. In this work, the precipitation and agglomeration of waxes in a system composed by a condensed oil and carbon dioxide (CO_2) is analyzed through the coupling of a PVT cell with a Solid Detection System (SDS) operating at different temperatures and pressures.

Keywords

Waxes; CO_2; Solid Detection System;

Introduction

The precipitation and deposition of waxes in production lines can lead to a significant reduction in the oil production, as well as to a high operational cost to reverse the situation [1,2]. The waxes, below a certain temperature (Wax Appearance Temperature - WAT), begin to precipitate and deposit on the pipeline walls [3]. Thus, the prediction of composition, temperature, and pressure where these particulates occur becomes relevant for the oil industry [4]. The phase behavior of oil systems can be assessed through distinct methodologies. PVT systems using visual, spectroscopic or volumetric methods allows the detection of bubble point, dew point, and solid-liquid phase transitions [5,6]. However, depending on the camera characteristics and the systems studied, the visibility may be affected, and phase detection accuracy can be reduced.

In this scenario, high-pressure microscopy analysis methods were developed to help the visibility of phase transitions in dark systems [7]. The solids detection system (SDS) uses a microscopic cell to analyze oil micrographs at high pressure. The SDS can be composed of LEDs or even infrared lasers that provide measurements of sample transmittance indicating when solids appear [8].

This study aims to investigate the behavior of waxes under different conditions of temperature and pressure in a oil recombined with CO_2 (40% molar) at reservoir conditions. A solid detection system (SDS) coupled to a PVT cell was used to generate the high-pressure data.

Methodology

Materials

The oil used in this work was named O1 and Tab. 1 presents its main properties. The recombined oil was prepared using a mixture of oil and CO_2 (40% molar) under reservoir pressure conditions (568 bar). Carbon dioxide was supplied by White Martins Praxair Inc., with purity ≥99.9%.

Table 1. Main characteristics of oil used in the work.

Oil	J1
API gravity (º)	32.17
Saturates (*wt.*%)	53.8
Aromatics (*wt.*%)	10.7
Resins (*wt.*%)	34.7
Asphaltenes (*wt.*%)	0.8

Experimental Setup

The experiments conducted in this study were carried out in a PVT system (Figure 1) coupled to a Solids Detection System – SDS (Figure 2). The PVT and the SDS units are developed to operate up to 1000 bar and 200 °C. The PVT system

(Sanchez Technologies) is composed of a stainless-steel variable volume view cell with a maximum volume of 400 ml. Pressure, volume, and temperature of the system were monitored and programmed through a supervisory system (Falcon). The agitation system was composed by magnets stirring. The cell presents a sapphire window with an attached camera that allows a complete view of the system and the capture pictures during the experiment.

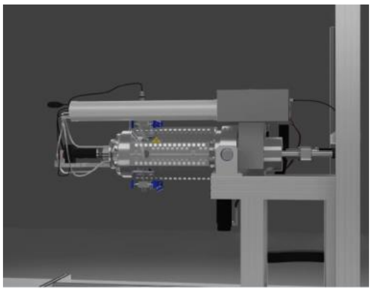

Figure 1. External view of PVT system.

The Solids Detection System – SDS (Sanchez Technologies) is composed by a stainless-steel cell with variable volume (maximum of 40 ml). The system is composed by a microscopic cell and a high-definition camera with magnification that allow the visualization and measurements of solid formation and deposition. In addition, the SDS allows the sample of precipitated particulates through a sintered filter with a PTFE membrane (0.45μm) placed in the lines.

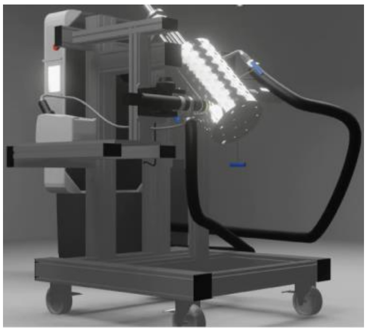

Figure 2. SDS system.

The two units can be coupled enabling the investigation of phase transitions in the PVT unit and the formation of solids like waxes through the SDS. In this work, the physical parameters (area, perimeter, width) of the particulates were not investigated.

Experimental Procedure

A known volume of oil was inserted into the cell, and the volume was completely reduced to remove the air. Afterwards, the lines were purged to remove residual oil. A desired amount of CO_2 was inserted into the system using a syringe pump (Sanchez Technologies). The last step of recombination is given by adjusting the pressure of the system under constant agitation.

The Falcon supervisory was then configured with isothermal depressurization stages. After some tests, the study was conducted at cell decompression rate of 30 ml/h, and stabilization time between each depressurization stage of 20 minutes. All tests started from a pressure of 600 bar and the data (pressure, temperature, volume) were recorded through images captured in the unit. As mentioned, the SDS system was connected to the PVT through a flow line coupled at the bottom, where the sample was transferred to avoid gas separation between the components. The SDS cell was then pressurized to the same pressure as the PVT cell. At each depressurization step, after the phase stabilization time, an aliquot of 30 ml was transferred from the PVT cell to the SDS. This step was monitored with a high-pressure microscope, at 0.58x magnification, recording the images every 5 seconds. Finally, the sample was transferred back to the PVT cell, under agitation, and a new depressurization step was then performed. At the end of the experiment, the images and numerical data were analyzed.

Results and Discussion

The results indicated that turbidity was presented in the PVT cell sapphire window with the recombined oil at 40% molar CO_2 for the tests conducted at low temperatures, even at the reservoir pressure condition,

Figure 3-A presents the initial image of the recombined oil experiment at 597 bar with high opacity, but without particulate definition. In Fig. 3-B, corresponding to 367 bar, it can observed a slight reduction in turbidity, where the red arrow draws attention to a slight definition of the piston edge at the bottom and, still discreetly, some particulates indicated by the yellow arrows.

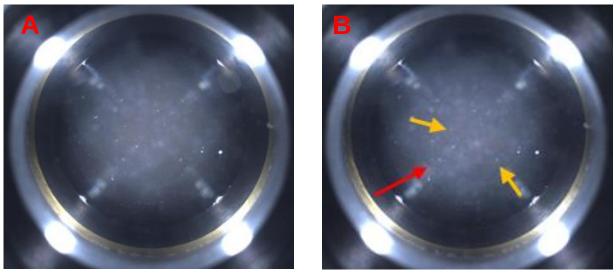

Figure 3. PVT cell images of petroleum and CO_2 (40% molar) at 20 °C.

However, it was not possible to provide a good definition of the material that would be causing such turbidity only through the PVT camera. The precipitation of particles could be induced by temperature variations and by contact with the high amount of carbon dioxide in the present system. Also, a small amount of waxes could already by precipitated in the system prior the contact with CO_2 and the manipulation of process variables would highlight the phenomena [9]. Another point to be mentioned is related to the kinetic of the particulate precipitation, which depending on the oil characteristics, the complete homogenization of the waxes and asphaltenes can takes long period. In this way, enters as a mechanism for the detection and identification of solid phases present at the microscopic level. Figure 4 shows images of the SDS system under the same conditions of temperature and pressure shown in Figure 3.

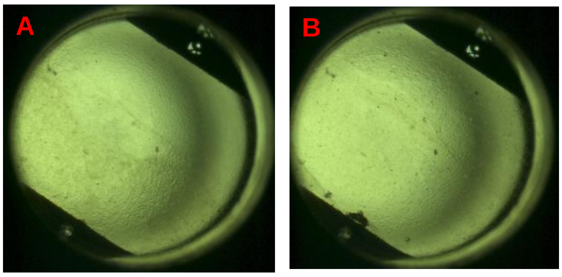

Figure 4. SDS micrograph of petroleum and CO_2 (40% molar) at 20 °C.

From the image obtained by the SDS system, it is possible to observe/confirm that the turbidity observed was related to the presence of precipitated waxes in the recombined oil with CO_2. Furthermore, during the flow at constant temperature and pressure, it was possible to identify the presence of bubbles in the system along with the particulates, as shown in Fig.5. The bubbles have a well-defined boundary and can be evaluated in terms of size distribution using the analysis software (Elix).

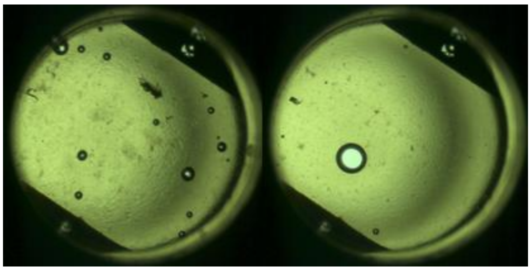

Figure 5. SDS micrographs of petroleum and CO_2 (40% molar) detect the presence of bubbles during the flow through the units.

To evaluate wax formation/precipitation as the temperature changes, the system was cooled at constant pressure from 60 to 20 °C and then reheated to 60 °C. Figure 6 presents this temperature cycle.
It can be observed that the SDS could identify the formation of solids and bubbles in pressurized dark fluids. The SDS images demonstrated an increase in the amount of wax particles from the temperature of 23 °C to the minimum temperature applied. In addition, it was possible to verify an increase in the size of the agglomerates, which start smaller at 23 °C and became larger as the temperature decreases. Upon reheating the system, the waxes were solubilized again in the sample.

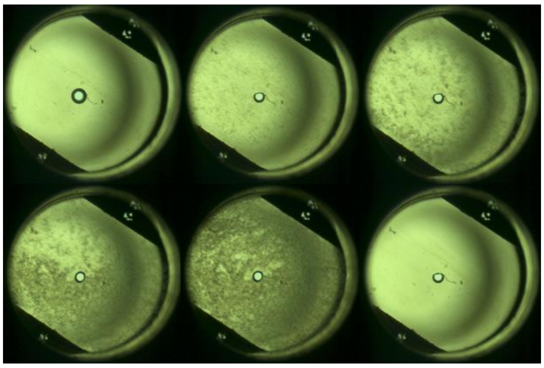

Figure 6. SDS micrographs for the study of cooling and heating the high-pressure system. From the left to the right: 60 °C, 23 °C, 22 °C, 21 °C, 20 °C, 60 °C.

Conclusions

The Solids Detection System (SDS) was able to identify the presence of solids and bubbles in pressurized dark fluids. The detection of solids was possible under different conditions of temperature and pressure. In addition, the acquired micrographs allow the qualitative study of the particulates. The present investigation demonstrates the possibility and reliability of the SDS acting together with a PVT cell unit to study distinct phase transitions and phenomena at high pressure.

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Responsibility Notice

The authors are the only responsible for the paper content.

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