CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oil

Crude oil A, one of the two oils used in this investigation, contains a high concentration of asphaltenes. Another crude oil, Oil W, is light oil due to a low asphaltene content and low viscosity. The SARA composition and physical properties of Oil A are listed in Tables 3.1. The asphaltene content and physical properties in Oil A and Oil W are shown in Table 3.2.

Table 3.1 SARA composition of Oil A

Solubility Class	%wt in Oil A
Saturates	51.77
Aromatics	21.48
Resins	10.48
Heptane-Asphaltenes	10.56
Unrecovered fraction	5.71

Table 3.2 Physical properties of Oil A and Oil W

Properties	Oil A	Oil W
Heptane-Asphaltenes (%wt)	10.8 ± 0.5	0.69 ± 0.04
Density at 20°C (kg/m^3)	869.2 ± 0.2	854.8 ± 0.1
Viscosity at 20°C (mPa*s)	26.3 ± 0.1	7.7 ± 0.1
Viscosity at 60 °C (mPa*s)	6.78 ± 0.07	2.83 ± 0.01
Instantaneous Onset vol%	40%	35% at 20°C 25% at 60°C

3.1.2 n-Heptane Precipitant

N-Heptane was used to destabilize asphaltenes from the crude oil. Table 3.3 shows the properties and source of the n-Heptane used in this study.

Table 3.3 Physical properties at experimental condition (60°C) and source of precipitant

Precipitant	Density (g/ml)	Molar Volume (mL/mol)	Solubility Parameter ($MPa^{0.5}$)	Viscosity (mPa*s)	Purity	Source
n-Heptane	0.6494	154.3	15.2	0.272	99.4%	Fisher

3.1.3 Toluene

Toluene was used to clean the system and measure the diameter of capillary. Diameter measurement was done at 20°C. Table 3.4 shows the viscosity at the experimental conditions and source of toluene.

Table 3.4 Viscosity at experimental conditions and source of toluene

Solution	Viscosity at 20 °C (mPa*s)	Purity	Source
Toluene	0.585	99.9%	Fisher

3.2 Equipment:

3.2.1 Optical Microscope Setup

An optical microscope (Nikon Eclipse E600) has been used to detect the precipitation of asphaltene from crude oil-precipitant mixtures. The microscope setup provides a 500x total magnification. A monochrome Sony CCD video camera was connected with the microscope and linked to a Sony Camera Adaptor CMA-D2. The analog signal from the camera was converted to digital signal by a WinTV USB

NTSC Model 40201 and digital images were captured at a resolution of 640 x 480 pixels.

3.2.2 Ultracentrifuge

A Sorvall Legend X1R centrifuge was used for preparing crude oils.

3.2.3 Stainless Steel Capillary Tubes

The stainless steel capillary tubes that were used for deposition experiments were purchased precut from Upchurch Scientific with part number U-101.

3.2.4 Syringe Pumps

Teledyne ISCO Model 500D syringe pumps were connected to the cylinders as shown in Figure 3.1. Water was pumped from the syringe pump into the cylinder to push the barrier inside the cylinder forward and the solution flowed into the system.

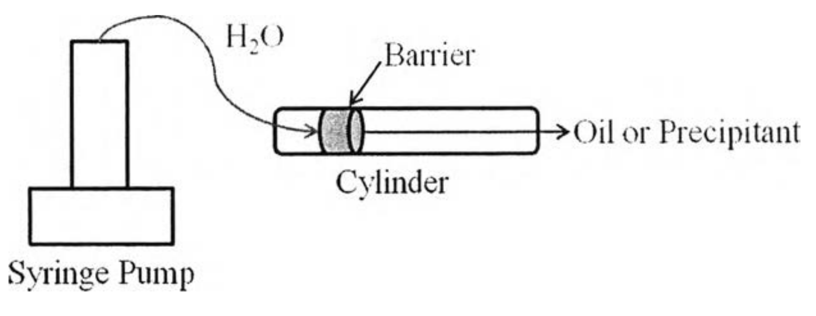

Figure 3.1 Schematic showing how solution was fed into the system using a syringe pump.

3.2.5 Water Bath

A Cole-Parmer Polystat Heated Circulating Bath was used for controlling the environmental temperature, with an accuracy of ± 0.1°C.

3.2.6 Pressure Transducers

There are two pressure transducers in this apparatus. One of them is installed to measure the pressure drop of the mixing section, a Sensotec Z/741-08ZD with a range of 100 psid, 0.25% accuracy. The other transducer measures the pressure drop in the capillary section, the equipment is a Sensotec A-5/882-15 with a range of 10 psid, 0.5% accuracy.

3.2.7 10 μm Stainless Steel Frit

The mixing section was designed to improve the mixing between the crude oil and heptane. Two identical frits from Upchurch Scientific part number A-105-02 were used: the first one is located inside of a mixing tee, and it will help to promote the mixture; the second one works as a pre-filter and it is located in connecting tee.

3.3 Methodology

3.3.1 Pre-treatment of Crude Oil

In order to remove solid particles and water from crude oil samples obtained from the field, samples were centrifuged at 14,000 g for 3 hours by a Sorvall Legend X1R centrifuge. Then, the particle-free crude oil was transferred from the top of the container (around 80% was collected) and kept in 250 mL reusable bottles with polypropylene plug-seal cap. The head space of the bottles was filled by nitrogen.

3.3.2 Preparing the Cylinders of the Syringe Pump

Crude oil and precipitant (n-heptane) were carefully loaded into the sample cylinders to prevent air bubble.

3.3.3 Onset Condition Experiment by Microscopy

Before asphaltene deposition experiments were performed, the instantaneous onset volume was determined in order to be able to choose the appropriate precipitant concentration to study. In order to perform an onset condition experiment, the apparatus was connected without the pressure transducer. The experiment is started by first flowing only pure crude oil through the system. Samples were taken from the effluent using a micropipette and then dropped on a microscope slide. The micrographs obtained, at 500x total magnification, are base case, where pure crude oil is being observed. To obtain the micrographs of the actual mixtures of crude oil and precipitant, the desired flow rate of oil and precipitant were set in order to reach the vol% desired. The effluent was collected and the micrographs were taken. The process was repeated by changing the flow rates until the onset point was reached.

3.3.4 Deposition Experiment

In order to perform a deposition experiment, the system was first connected without the outlet of ΔP_{mix} and ΔP_{cap} to the pressure transducer in order to bleed the air out of the system. The precipitant line was prefilled with liquid and an air pocket was connected before the end of the line in one side of mixing tee, the purpose of this will be described next. The crude oil was prefilled into the system allowing it to move into the precipitant line but the air pocket prevents the mixing of the oil and precipitant. During the process of prefilling, oil will be maintained in the precipitant line by adjusting the flow rate of oil and precipitant before the Back Pressure Regulator (BPR) opened. Further, the positive and negative pressure drop outlets were connected respectively to the pressure transducer once the air has been forced out of the system. Finally, the desired flow rate of oil and precipitant were set. The system was placed in the water bath at 60°C in order to avoid the deposition of waxes. The data signal from the pressure transducer was collected by the program NI Datalogger. The actual pressure drop of the capillary section measured during the experiment (ΔP_{cap}) has been shifted by deducting the value of $\Delta P_{cap,o}$ (which is the mean value of the pressure drop measured in the same section before ΔP_{cap} starts to increase). The value of $\Delta P_{cap,o}$ is the measured pressure drop of the oil:precipitant mixture travelling through the capillary without any detectable increase in the pressure drop due to deposition. The start time of the experiment is defined as when the heptane first enters the capillary after pushing the air bubble and oil out of the connecting line. The time when heptane first enters the system (t_o) is discounted from the overall elapsed time of the experiment (t). After experimentation was performed, the deposits were visualized with scanning electron microscopy (SEM) on a FEI Quanta 200 3D instrument operating in low vacuum mode (0.53 torr).

3.3.5 Flowing Precipitated Asphaltene Solution Through a Capillary

A precipitated asphaltene solution was prepared by mixing crude oil and heptane at 40 vol% C7 in an Erlenmeyer flask. The goal of this experiment is to observe whether precipitated asphaltenes with different size particles can deposit in the capillary at different aging times. The solution was aged for 23, 73 and 95 hours. Then, the solution was pumped through a capillary (0.01" ID and 1' length) at 0.6 mL/min using a peristaltic pump (Masterflex #7523-20) and the pressure across the capillary was measured by a differential pressure transducer as shown in Figure 3.3. All the experiments were conducted at room temperature.

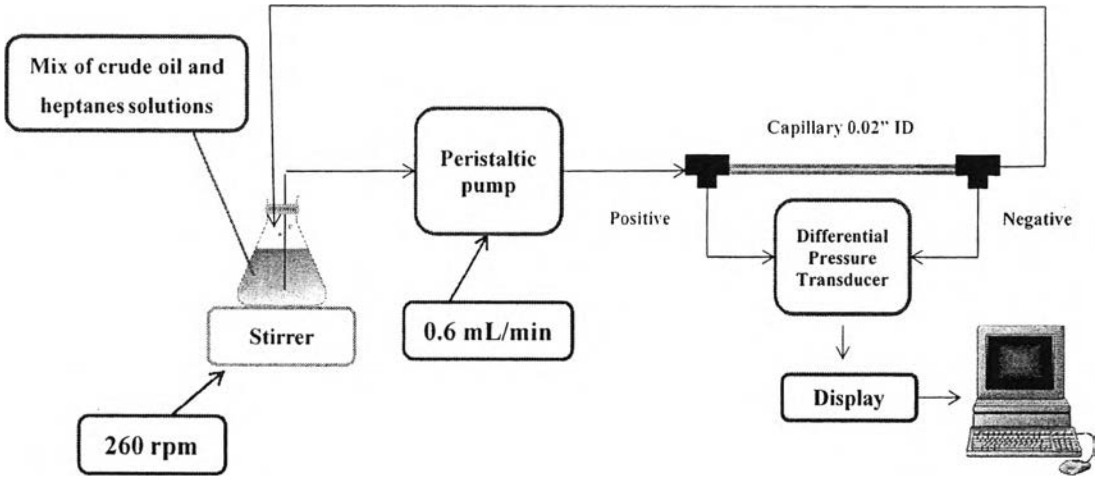

Figure 3.2 Experimental schematic for flowing precipitated particles through a capillary.