CHAPTER III
EXPERIMENTAL METHODS

3.1 Materials

The K-1 crude oil from Alaska used in this study was provided by ConocoPhillips. Tables 3.1 and 3.2 provide the density and composition of the crude oil respectively. Toluene and heptane were obtained from Fisher Scientific International.

Table 3.1 Density of K-1 crude oil at different temperatures

Temperature (^{0}C)	23	45	60
Density (g/ml)	0.9248	0.9111	0.9011

Table 3.2 Composition of K-1 crude oil from SARA analysis

Saturates	41.0%
Aromatics	28.5%
Resins	13.4%
Asphaltenes	15.9%
Total	98.8%
Loss (during experiment)	1.2%

3.2 Crude Oil Treatment and Asphaltene Onset Determination

3.2.1 Sampling

The crude oil from ConocoPhillips was received in a 5 gallon drum. Heavier components of crude oil tend to settle down in the drum and the precipitated fraction of asphaltenes present in crude, if any, may not be distributed uniformly. It is important to ensure that the samples are homogeneous and have the same composition from one run to another. In order to achieve this uniformity, the crude oil drum was heated to 500C in a water bath for four hours and shaken vigorously every 20 minutes. After this cycle of heating and mixing, crude oil was drawn and stored in one liter glass bottles for use in future experiments. When samples were taken, the bottles were vigorously shaken to ensure uniformity in composition.

3.2.2 Determination of Asphaltene Precipitation Onset by Refractive Index Measurement

For mixtures with no significant volume change after mixing, the refractive index function of the mixture, $f(n) = ((n^2 - 1)/(n^2 + 2))$, is equal to the sum of the refractive index functions of each individual component times its volume fraction (φ_i):

$$f(n) = \sum_i \varphi_i f_i(n) \tag{3.1}$$

$$\left(\frac{n^2-1}{n^2+2}\right) = \sum_i \varphi_i \left(\frac{n^2-1}{n^2+2}\right)_i \tag{3.2}$$

where n is the refractive index of the substance.

The onset of asphaltene precipitation was detected from the deviation of the refractive index behavior from the linearity, as discussed in the work of Wattana *et al.* (2003), in section 2.3.

A known volume of crude oil was placed in a flask together with a magnetic stirrer and was vigorously agitated on a stirring plate. Very vigorous agitation of the sample is required in order to prevent the premature precipitation of asphaltenes due to localized high concentration of the precipitant in the mixture. The opening of the flask was covered with aluminum foil to minimize evaporation. The crude oil was then titrated with the precipitant (e.g. heptane) using a syringe pump. The titrations were performed at room temperature and care was taken to minimize the evaporation of solution mixtures during the course of titration by covering the opening of the flask by aluminum foil. Similar titrations were conducted with different amounts of precipitant, corresponding to precipitant volume fractions ranging from 0.1 to 0.9. During the course of titration, samples were taken for mixtures with different crude/precipitant ratios and the refractive index of each mixture was measured using a Schmidt and Haensch DUR-HT refractometer. The temperature of the samples and sample chamber were kept constant at 25^0C using a controlled temperature bath.

3.2.3 Verification of Asphaltene Precipitation Onset

In order to ascertain the precipitant volume fraction at which the asphaltenes actually precipitate from crude oil, the samples were observed under the optical microscope under 100x magnification.

3.3 Apparatus for Asphaltene Deposition

3.3.1 Design

The setup consists of two high pressure pumps, one for the precipitant and one for a mixture of crude oil and precipitant below the asphaltene precipitation onset point. The fluids are pumped and meet at a common point before entering the capillary, which is maintained at a constant temperature.

The experimental setup is shown in Figure 3.1. The pumps used are Core Research Model FDS-210 positive displacement pumps. The capillary tube used is seamless, annealed soft temper stainless steel type 316 tubing with OD 0.0625", ID 0.020" and length 50 ft (from Small Parts, Inc.). Differential pressure transducers from Honeywell Sensotec, Model Z and Model A-5 with ranges of 10,

25, 100 and 500 PSID respectively are used. The accuracy of the pressure transducers was established by comparing them to Ashcroft Model PT Digital Pressure Indicator, with an error of 0.1%. Single channel signal conditioner indicator from Honeywell Sensotec (Model GM) is used for signal processing. USB-6009 14-bit, 48 kS/s Multifunction Data Acquisition system from National Instruments and LabVIEW software are used for data acquisition and logging.

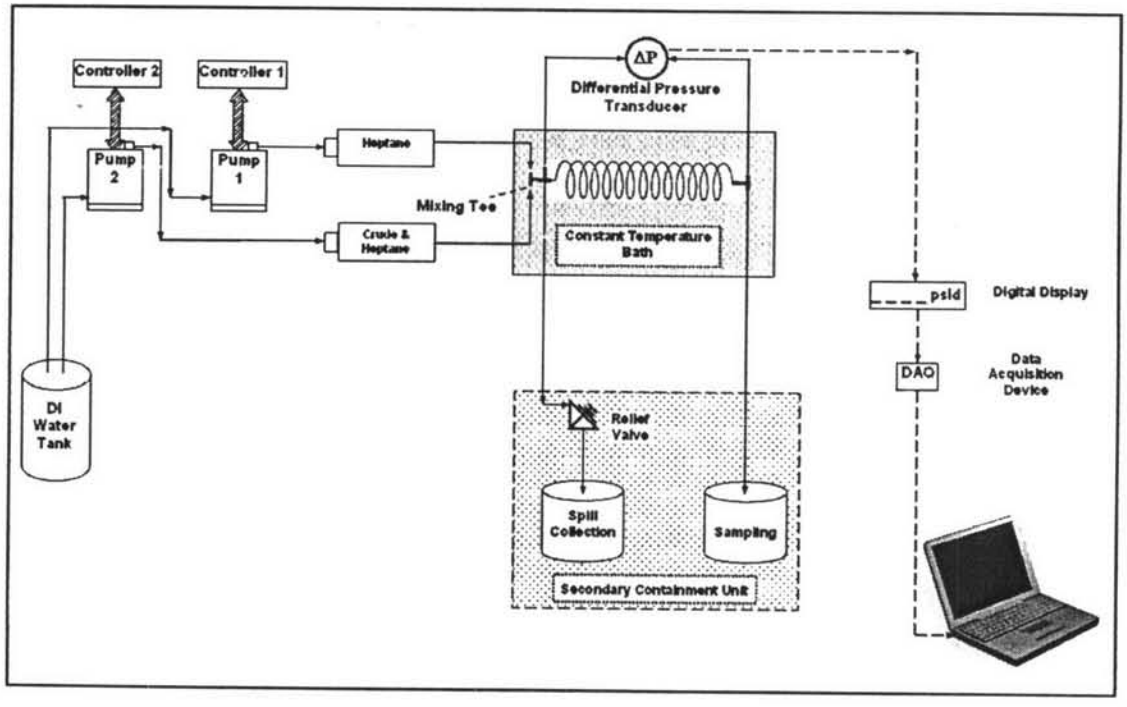

Figure 3.1 Schematic of experimental setup for investigating asphaltene deposition.

3.3.2 Testing the Accuracy of Equipment

In order to determine the accuracy of the equipment, test fluids were run through the system at different flow rates and the pressure drop across the capillary was measured using the data acquisition system. The pressure drop values were compared to theoretical values to verify the accuracy of the designed system.

3.4 Asphaltene Deposition Experiments

Experiments were conducted by simultaneously running the K-1 crude oil and heptane through the capillary, with heptane concentrations above the onset point of asphaltene precipitation. The experiments were carried out a 22^0C. Flow rates for the experiments varied between 4.5 and 5.0 ml/hour. The heptane volume fraction in the mixture varied from 0.55 to 0.60. The capillary was open to atmosphere on the downstream side. The duration of the experiments varied from 10 to 32 hours. The pressure drop across the capillary was measured to observe asphaltene deposition on its inner wall and the pressure drop data was acquired using the LabVIEW software. The change in the radius of the capillary was calculated using the pressure drop data and the specified values of flow rate, capillary length, and fluid viscosity.