CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oil and Bitumen

Bow River Crude Oil (BR) was used to perform the experiments for validating the asphaltene deposition apparatus. The density at 25°C of BR is 910.9 kg/m^3. Athabasca Diluted Bitumen (ADB) was used to perform the experiments for uncovering the asphaltene deposition phenomenon. The density at 25°C of ADB is 912.6 kg/m^3. The viscosity of ADB at 25°C is 0.14 Pa·s. All crude oil were provided by the sponsors of the University of Michigan Industrial Affiliates Program.

Table 3.1 Composition in Athabasca diluted bitumen

Component Name	% Range
Bitumen (naturally occuring)	75 - 80
Pentane/Hexane Diluent	20 - 25
Pentane isomers	10 - 30
2-Methylpentane	1 - 5
n-Hexane	1 - 5
Cyclopentane	1 - 5
Butane, 2,3-dimethyl-	1 - 5
Pentane, 3-methyl-	1 - 5
Butane, 2,2-dimethyl-	1 - 5
Benzene	0.1 - 1.0

3.1.2 Solvent of Asphaltenes

HPLC grade toluene and 99.8% chloroform with 0.75% ethanol as preservative were used as an asphaltene solvent. Toluene was used to clean all the glassware after finish the experiments. Instead, chloroform was used to washing out

all the deposit in the packed-bad column and to clean the column after finishing the experiments. The density of toluene at 25°C is 865 kg/m^3 and the density of chloroform is 1480 kg/m^3.

3.1.3 Precipitant of Asphaltenes

HPLC grade n-heptane was used as a precipitant to destabilize the asphaltenes in crude oil in all the experiments. The density at room temperature (20°C) is 679.6 kg/m^3 and viscosity at 60°C is 0.276 mPa·s.

3.2 Equipment

3.2.1 Syringe Pump

IKA 500D syringe pump was used in a preparation of a small volume of crude oil-heptane solution for exploring the stability of crude oil at a given heptane concentration. The heptane was added into crude oil at a constant flow rate.

3.2.2 Stir Plate

IKA WERKE, RO10 stir plates were used to homogenize the crude oil-heptane solution in a vial during the detection time experiment. Corning PC-353 stirrer was used to homogenize in a preparation of crude oil-heptane solution reservoir and also used during the asphaltene deposition experiment.

3.2.3 Analytical Balance

Mettler Toledo NewClassic MF MS3002S electronic analytical balance was used to weigh the centrifuge tube containing crude oil for pretreating crude oil. It was also used to measure the mass of flasks and crude oil-heptane solution reservoir during the preparation of the solution. The maximum mass that can measure with this analytical balance is 3200 g. Mettler Toledo XS204 electrical analytical balance was used to measure the mass of 1.5 mL microcentrifuge tube before and after adding a crude oil-heptane solution for quantifying the asphaltene content in that solution by centrifugation technique. It was also used to measure the mass of crude oil-heptane solution during the sample preparation for detection time experiments.

Moreover, it was used to measure the mass of collected material from asphaltene deposition experiment. The limitation of this analytical balance is 220 g with a deviation of 0.1 mg.

3.2.4 Optical Microscope

Nikon Eclipse E600 optical microscope was used to detect the asphaltene aggregates in crude oil at a given heptane concentration. The smallest detectable size for this optical microscope is 0.5 micrometer. It was connected to Nikon DS-Fi2 camera head and linked to Nikon DS-U3 digital camera control unit. It was then connected to a computer to capture images by NIS-Elements program.

3.2.5 Cover Glass

The cover glass with the size of 25x25 mm and 18x18 mm from Fisherfinest were used as a microscope slides to put the crude oil-heptane solution sample in between them. It was then transferred to the optical microscope to detect the asphaltene precipitation time.

3.2.6 Vial

1 dram clear 15x45 vial with PTFE lined cap from Scientific Specialities was used to keep the crude oil-heptane solution for detection time experiment. 8 dram clear 25x95 vial with PTFE lined cap from Glass Vials was used to contain the collected material from deposition experiment.

3.2.7 Centrifuge

Sorvall Legend X1R centrifuge with FIBERLite F15-8x50cy rotor from Thermo Scientific was used in a pretreatment of BR and ADB. Moreover, it was used to centrifuge the crude oil-heptane solution reservoir in a case where large asphaltene particles in the solution are detected under an optical microscope. The maximum rotational speed is 14000 rpm. The operation temperature was kept constant at 20°C. Eppendorf 541R microcentrifuge was used to separate the asphaltenes from crude oil-heptane solution in a measurement of asphaltene content in solution using 1.5 mL microcentrifuge tube. The maximum rotational speed is also 14000 rpm.

3.2.8 Incubator and Oven

Fisher Scientific 637D incubator was used to evaporate trapped heptane in the asphaltenes. Thermo Fisher Scientific Linberg/Blue M vacuum oven equipped with DryFast Model 2047 vacuum pump was used to evaporate chloroform from the collected material.

3.2.9 Sonicator

Branson 5510 sonicator was used to re-disperse the asphaltene cake in heptane in order to wash out the trapped maltenes after the supernatant was removed from a 1.5 mL microcentrifuge tube.

3.2.10 Peristaltic Pump

Cole-Parmer Masterflex L/S 07522-20 Digital Pump Drive and EASY-LOAD 77800-603 Pump Heads was used to pump the crude oil-heptane solution through the tubing from the crude oil-heptane solution reservoir into the packed-bed column at different flow rate for each experiment. Moreover, Cole-Parmer Masterflex L/S #7518-10 Peristaltic Pump was used to prepare crude oil-heptane solution reservoir by adding heptane into crude oil. The flow rate used to add heptane is 3 mL/minute for BR-heptane solution and 6 mL/min for ADB-heptane solution.

3.2.11 Recycling Column

Recycling glass column with PTFE seal from Ace Glass with 900 mm in length and 10 mm in inner diameter was used to be a column of packed-bed.

3.2.12 Stainless Steel Sphere

4-mm in diameter stainless steel spheres type 316 from Alfa Aesar and 3-mm in diameter stainless steel spheres type 316 from Goodfellow Cambridge were used to pack in a recycling glass column. The composition of stainless steel is 67.5 wt% of Fe, 17 wt% of Cr, 13 wt% of Ni, and 12.5 wt% of Mo.

3.2.13 Tubing and Connector

Teflon tubing with an inner diameter of 1.5 mm from Ace Glass and Viton tubing L/S 13 from Masterflex were used to connect the packed-bed column with the valve and peristaltic pump. The connectors for connected every part together are connector with 1/16 inch from Masterflex, U-146 Stainless steel capillary tube with 1/16 inch inner diameter, and U-145 Stainless steel capillary tube with 1/16 inch inner diameter. Both capillary tube were supplied by IDEX Health&Science.

3.2.14 Valve

3-Way valve (T) single key from Omnifit was used to connect with the tubing at the inlet and outlet of the packed-bed column for measuring the flow rate of the crude oil-heptane solution.

3.3 Software

3.3.1 Microsoft Excel

3.3.2 NIS-element Imaging Software Version 4.13.00

3.4 Methodology

3.4.1 Crude Oil and Diluted Bitumen Pretreatment

The crude oil and diluted bitumen were firstly homogenized by vigorously shaking the tank for several times. The homogenized crude oil and diluted bitumen were put in 50 mL centrifuge tube then were centrifuged at 14000 rpm for 3 hours to remove all the solid particles, water, and other impurities out of the crude oil and diluted bitumen. Afterward, the supernatant which is the pretreated crude oil and diluted bitumen were kept in the amber bottle then purged with nitrogen gas before sealing the lid to minimize the effect of oxidation.

3.4.2 Asphaltene Deposition Apparatus Set Up

The stainless steel spheres of 4 mm in diameter were systematically placed in a glass column as illustrated in Figure 3.1. A layer of 4-mm stainless steel sphere contains 4 spheres. Then 3-mm stainless steel sphere was put between two layers of 4-mm spheres to prevent a significant channelling of the flow. The total 4-mm spheres in a packed-bed are 292 and the total 3-mm spheres are 72. The packed-bed column was then connected with tubing to crude oil-heptane solution reservoir and peristaltic pump as presented in Figure 3.2.

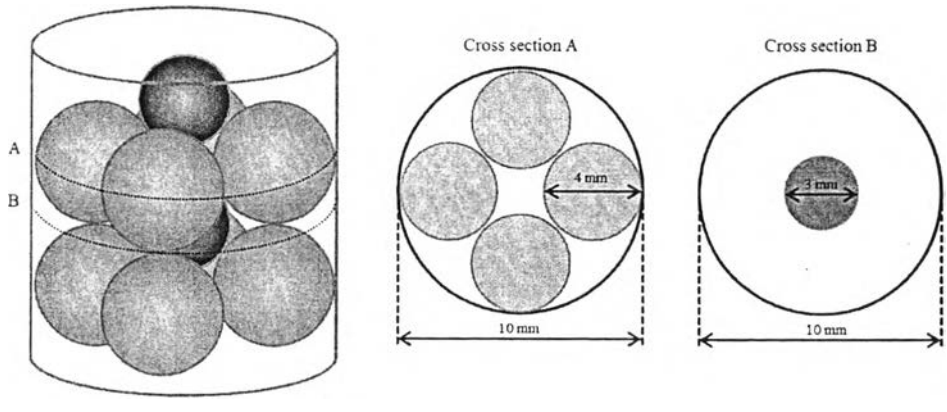

Figure 3.1 Illustration of packing stainless steel spheres in a packed-bed column.

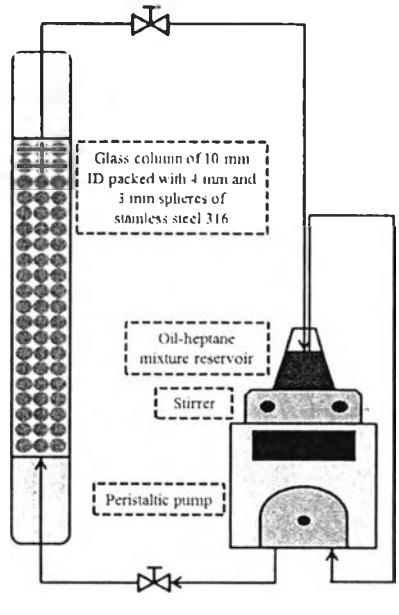

Figure 3.2 Schematic of packed-bed of large sphere flow-loop apparatus.

3.4.3 Crude Oil-Heptane Reservoir Preparation

The measurement of asphaltene detection time at different heptane concentrations were conducted in order to choose the heptane concentration for preparing crude oil-heptane solution reservoir. This measurement is so called detection time experiment. The 3 mL solution of crude oil and heptane at different concentrations were prepared by slowly adding heptane into crude oil. The sample solution was stirred on a stir plate all the time. A small droplet of sample solution was taken and put on a cover glass then placed under an optical microscope to detect the asphaltene particle from time to time until the asphaltene particle was found in the sample solution. The detection time was plotted as a function of heptane concentration. A desired heptane concentration was then chosen from that plot.

Moreover, the amount of unstable asphaltenes at a chosen heptane concentration can be quantified using centrifugation technique. The cut-off size of this technique is about 200 nm. The 110 mL of crude oil-heptane solution at a desired concentration was prepared. The sample solution was kept stirred on a stir plate all the time to confirm the homogenization of the solution. Afterward, a sample was taken at different times by transferred into 1.5 mL centrifuge tubes. Those microcentrifuge tubes were then centrifuged at 14000 rpm for 10 minutes. The supernatant was drained out of the tube then the asphaltene cake was washed with heptane for several times using sonicator to re-disperse the cake in heptane. The asphaltene cake was air dried and placed in an incubator for 48 hours. The final mass of asphaltene cake was then weighed.

Finally, heptane was slowly added to crude oil until a desired concentration was reached. The crude oil-heptane solution will be centrifuged if large asphaltene particles are detected under an optical microscope. The size of asphaltene particles in the bulk solution were kept relatively constant below 500 nm in all experiments. The mass of solution in a reservoir was designed to have a maximum unstable asphaltenes depletion of only 20% during the experiment.

3.4.4 Investigation of Asphaltene Deposition

This experiment is called deposition experiment. It starts with the crude oil-heptane solution at a desired heptane concentration was flowed upward

through the packed-bed column from a reservoir by using peristaltic pump. The flow rate was measured periodically and was kept constant throughout the experiment. The crude oil-heptane solution reservoir was changed every certain period of time to keep the unstable asphaltenes concentration and asphaltene particle size constant. After running an experiment for a desired deposition time, the excess amount of crude oil-heptane solution was reversely flowed out of the packed-bed column using very low flow rate to prevent the deposited asphaltenes from slipping off the surface. After that chloroform was used to flow through the packed-bed column to dissolve the deposited material out then the chloroform-deposit solution was collected in a vial. Chloroform was finally evaporated out until the mass became constant in a vacuum oven at 70°C. The remaining material in a vial is called collected material.

3.4.5 Deposited Asphaltenes Quantification

The collected material was mixed with heptane in a volume ratio of 1:25 in order to precipitate all the asphaltenes in the collected material out. The solution was transferred into 1.5 mL microcentrifuge tube then they were centrifuged at 14000 rpm for 10 minutes. The supernatant was poured out. The asphaltene cake was washed by heptane for several times using sonication technique then dried in a fume hood for 24 hours. The asphaltenes cake was then place in an incubator for 2 days and was finally measured the mass.