

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Crude Oils and Bitumen

Crude oil from Gulf of Mexico (GM) and Bow River (BR) were used in soluble asphaltene experiments. Alaskan crude oil (N2) and Western Canadian bitumen (WC) were used to assess the dissolved oxygen effect. The Western Canadian bitumen (WC) from field operation was provided by University of Calgary, which was supplied by Shell Canada Ltd. It had been treated to remove water and solids and the residual water content was less than 1 wt%. The SARA composition of GM, AM, N2 crude oil and WC bitumen are shown in Table 3.1 and some physical properties are shown in Table 3.2. Crude oils and bitumen were provided by affiliate oil companies.

**Table 3.1** SARA composition of GM, N2 crude oil and WC bitumen

Composition (wt%)		GM	N2	WC
Saturates		37.80	55.10	17.10
Aromatics		46.76	23.60	44.00
Resins		9.18	17.30	19.40
Asphaltenes	C5	-	-	19.40
	C7	6.26	2.40	17.30
Loss		-	1.60	1.70

**Table 3.2** Physical properties of crude oils and bitumen used

Physical properties	GM	N2	WC
Density (kg/m <sup>3</sup> at 20°C)	868.8	873.7	1153.5
Viscosity (mPa·s)	15.69	13.87	-

### 3.1.2 Chemicals and Gas

Toluene and n-heptane were used to dissolve and destabilize asphaltenes, respectively. Both of them were all HPLC grade and obtained from Fisher Scientific. Physical properties and specifications of toluene and n-heptane are shown in Table 3.3.

Nitrogen was used to degas bitumen and n-heptane and create the nitrogen environment. The compressed nitrogen was pre-purify grade and obtained from Purity Plus.

**Table 3.3** Physical properties and specifications of toluene and n-heptane used in this research

<b>Physical Properties</b>	<b>Toluene</b>	<b>n-Heptane</b>
Specific gravity	0.866	0.683
Viscosity (mPa·s) at 20°C	0.6	0.4
Purity	HPLC	HPLC
Assay	99.8% min by GC	96% min by GC

## 3.2 **Equipment**

### 3.2.1 Centrifuge

Sorvall Legend X1R Centrifuge was used to remove impurities (e.g. solids and water) from crude oil. The centrifuge tubes used were made of Teflon and its volume is 250 mL, depends on the volume of crude oils. Eppendorf 541R microcentrifuge, which is the smaller, was used to settle down the precipitated asphaltenes. The centrifuge tubes were made of polypropylene and its volume is 1.5 mL. The smaller centrifuge was used to quantify the mass of precipitated asphaltenes reported in this research. All experiments were conducted at room temperature.

### 3.2.2 Microscope

A Nikon Eclipse E600 Optical Microscope was used to detect asphaltene particles. It was equipped with 50× objective lens and 10× eyepiece. The

microscope was connected to a Nikon DS-Fi2 charge-coupled device (CCD) camera, which was connected to a computer. NIS Element imaging software version 4.13.00 was used to capture images. All experiments were conducted at room temperature.

### 3.2.3 Sonicator

Even though the asphaltenes can dissolve in toluene, it is essential to add some energy to break the asphaltenes and make them dissolved. In this research, energy was added by sonicator. A QSonica Q700 probe sonicator was used to dissolve asphaltenes in toluene. The amplitude of sonic wave was kept the same for all model oils. A Branson 5510 bath sonicator was used in the washing step of asphaltene cakes, to remove trace amounts of maltenes trapped in the cakes.

### 3.2.4 Small-angle X-ray Scattering (SAXS)

Bruker Nanostar SAXS equipment at the University of Michigan was used to perform scattering measurements. The X-ray generator was set at 40 kV and 35 mA with 0.5 sec per frame and 900 sec per sample. All experiments were conducted at room temperature.

### 3.2.5 Scale Calibration

Scale Calibration was used to prepare the solution and weigh the amounts of precipitated asphaltene. In this research, a fisher scientific electronic analytical balance (Series XA) was used.

### 3.2.6 Syringe Pump

Syringe pump was used to slowly add n-heptane to the solution, to ensure the good homogeneity and precise content. A 500D IKA syringe pump was used.

### 3.2.7 Incubators

A Lindberg Blue vacuum oven equipped with DryFast Model 2047 vacuum pump and Fisher Scientific Model 637D incubator was used.

### 3.2.8 Inflatable Glove Chamber

All the experiments in nitrogen environment were performed in inflatable glove chamber. The glove bag was made of polyethylene and connected to a nitrogen cylinder and a vacuum pump.

### 3.2.9 Stirrer

A WERKE plate stirrer from IKA was used to stir all the samples to ensure proper homogeneity during all experiments.

## 3.3 Software

### 3.3.1 NIS Element Imaging Software Version 4.13.00

### 3.3.2 Small-angle X-ray Scattering System (SAXS)

## 3.4 Methodology

### 3.4.1 Pretreatment of Crude Oils

All the crude oil was pretreated by homogenizing and centrifuging at 14000 rpm for 3 hours to remove water droplets and solid impurities. The pretreated oil was kept in amber bottles to prevent possible light oxidation.

### 3.4.2 Asphaltene Extraction

Pretreated GM and BR crude oil was mixed with heptane in a 1:25 volume ratio. The solution was then centrifuged at 4000 rpm for 20 minutes to separate precipitated asphaltenes. The asphaltenes were transferred into a ceramic thimble and were Soxhlet-washed with hot heptane for 24 hours to wash any oil and maltenes trapped in the cake. Then, the washed asphaltenes were dried in an oven at 70°C to evaporate any n-heptane left in the cake. Dried asphaltenes were ground and stored.

### 3.4.3 Model Oil Preparation

A known amount of asphaltenes was added to toluene. The model mixture was sonicated for 1 hour to completely disperse the asphaltenes. In order to ensure the homogeneity, model mixture was monitored under microscope along the sonication process. After sonication, the model oil was kept in a bottle and stirred on a stir plate.

### 3.4.4 Solution Preparation

In order to destabilize the asphaltenes, the desired amount of n-heptane was added to pretreated crude oil, bitumen or model oil using syringe pump.

The n-heptane flow rate was kept at 0.1 mL/min to minimize the offset in concentration and guarantee good mixing of solution. The solutions were kept stirred to ensure homogeneity.

#### 3.4.5 Microscopy Experiment

A droplet of well-stirred destabilized crude oil or model oil is taken using glass pipette tip and placed under the microscope at different times. The pictures of samples at different time were captured by the camera and recorded in a computer. The solution was monitored over time under the microscope until asphaltene particles are detected. The resolution of the microscope used in this research is high enough to detect particle at approximately 0.5  $\mu\text{m}$  in diameter. The detection is the time it takes for particles to be detected. The detection time reported is the average between the time at which the haze of particles appear and the time at which particles are clearly detected. The results of this experiment will be the detection time as a function of n-heptane concentration.

#### 3.4.6 Asphaltene Fractionation

A solution of model oil and n-heptane was prepared using the method described in 3.4.4. The solution was kept well-stirred for 7 days for equilibration. After that, the solution was centrifuged at 14000 rpm for 10 minutes to separate all the precipitated particles. The cake was then separated from the supernatant and dried in oven at 75°C to evaporate any heptane and toluene left. The asphaltenes obtained is the “insoluble asphaltenes”. The supernatant was dried in oven at 70°C for 2 days. The asphaltenes obtained from the supernatant is the “soluble asphaltenes”.

#### 3.4.7 Centrifugation Experiment

1.5 mL of solution between crude oil or model oil and n-heptane was withdrawn and centrifuged at 14000 rpm for 10 minutes. After centrifugation, the supernatant was decanted, and the cake was washed with heptane by cycles of sonication and centrifugation to remove any trapped maltenes or solution. The left cake was then dried in a vacuum oven for 2 days and weighed. The result from this experiment will be obtained as insoluble (or soluble) asphaltene content as a function of time elapsed.

#### 3.4.8 Small-angle X-ray Scattering (SAXS) Experiment

A small amount of model oil and n-heptane solution was placed in a capillary tube using micropipette. The capillary tube was then sealed and placed on a sample holder for SAXS. The scattering was performed on Bruker Nanostar SAXS instrument at University of Michigan. The X-ray generator was set at 40 kV and 35 mA with 0.5 second per frame and 1800 second per sample. The scattering profiles obtained were integrated over same range of 2-theta and Chi, which is 0.1 to 2.8 and 0 to 360 degree, respectively. The results obtained as the scattering intensity (I) at various scattering vector (q).

#### 3.4.9 Establishing Nitrogen Environment

After every ports of the glove chamber were tightly sealed and every necessary thing was put in, the glove chamber was vacuumed to remove air and purged with nitrogen. The cycle was repeated several times to ensure the oxygen free environment.

#### 3.4.10 Degassing of Bitumen, Crude Oil and n-Heptane

To perform experiment on oxygen free basis, all the oils and solvents must be degassed to remove any dissolved oxygen. To degas crude oils and n-heptane, the n-heptane was bubbled with nitrogen and vacuumed simultaneously under nitrogen environment for 2 hours.

To degas the bitumen, the process will be more complicated due to its high viscosity. The bitumen was placed in a water bath at 70°C under vacuuming for 3 days, to reduce its viscosity. Then, it was connected to a nitrogen cylinder and bubbled under vacuuming for 5 days. After that, the water bath was removed and the bitumen was kept bubbling for another 2 days. This procedure was previously performed by Castellanos-Diaz *et al.* (2014) and had been shown to not significantly evaporate the light components from the bitumen.