

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Crude Oil and Asphaltenes

Crude oil or petroleum is a mixture of hydrocarbons containing several components with different physical and chemical properties [Speight, J. G., 2007]. Crude oil is composed of low molecular weight hydrocarbons to high molecular weight hydrocarbons and is often divided into four majors: saturates, aromatics, resins, and asphaltenes (SARA).

Asphaltenes are defined as the components of crude oil that soluble in aromatics such as toluene but insoluble in normal alkanes such as n-heptane [Hammami *et al.*, 2007]. They consist of polycyclic aromatic hydrocarbon, a distribution of heteroatoms (N, S, O) and metals (V, Ni, Fe) [Hammami *et al.*, 2007].

2.2 Asphaltene Precipitation

In crude oil production, asphaltenes can be destabilized by changes in temperature, pressure or composition [Gonzalez *et al.*, 2005; Kraiwattanawong, K. 2007]. The destabilized asphaltene increase production costs and reduce well productivity by blocking the pore throats and plugging pipeline [Nabzar, 2008; Maqbool *et al.*, 2009].

To study asphaltene precipitation in a laboratory, normally n-pentane or n-heptane is added to crude oil at a volume ratio of 40:1 [ASTM D2007]. Figure 2.2.1 shows that the lower carbon number of precipitant used, the higher amount precipitated asphaltenes are observed. However, lower carbon number precipitants have a higher propensity to evaporate, which adds experimental difficulty. In order to perform experiments accurately, heptane is usually used.

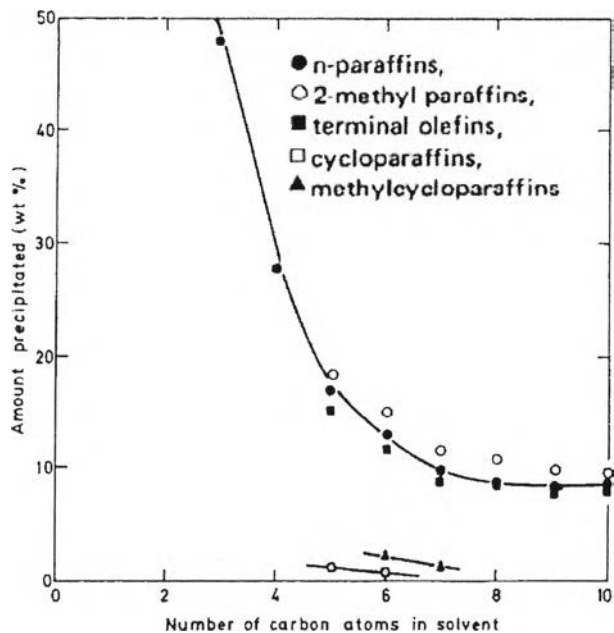


Figure 2.2.1 The amount of precipitated asphaltenes as a function of precipitant [Mitchell, 1972].

Maqbool *et al.* revealed that the time to detect unstable asphaltenes at low precipitation concentrations using optical microscopy ($0.5 \mu\text{m}$ detection size) can be weeks, months, or years. Even when the instability of asphaltene at high precipitations can be immediately detected, the final value of asphaltene solubility can take weeks to measure. This means that asphaltene precipitation does not only depend on precipitant and precipitant concentration but there is also a kinetic playing an important role as shown in Figure 2.2.2 and 2.2.3.

Figure 2.2.2 shows images from the optical microscopic and Figure 2.2.3 demonstrates the amount of precipitated asphaltene as a function of time using a centrifugation technique to separate the precipitated asphaltene from the crude oil-precipitant mixture. It can be observed that the amount of precipitated asphaltene increases as a function of time.

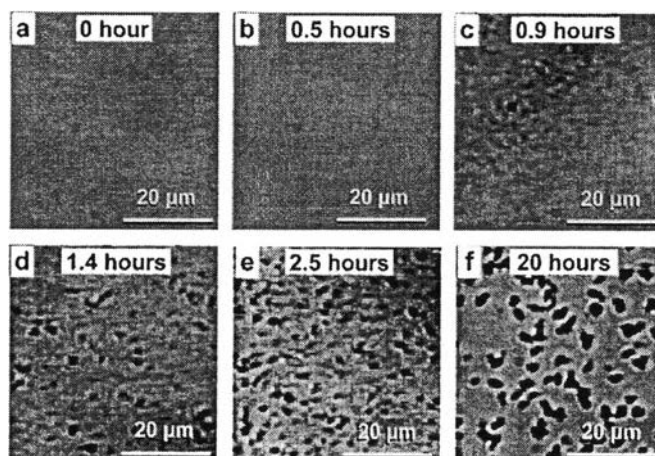


Figure 2.2.2 Micrographs showing asphaltene precipitation for a crude-heptane mixture containing 50 vol. % heptane and 50 vol. % K-1 crude oil as a function of time [Maqbool *et al.*, 2009].

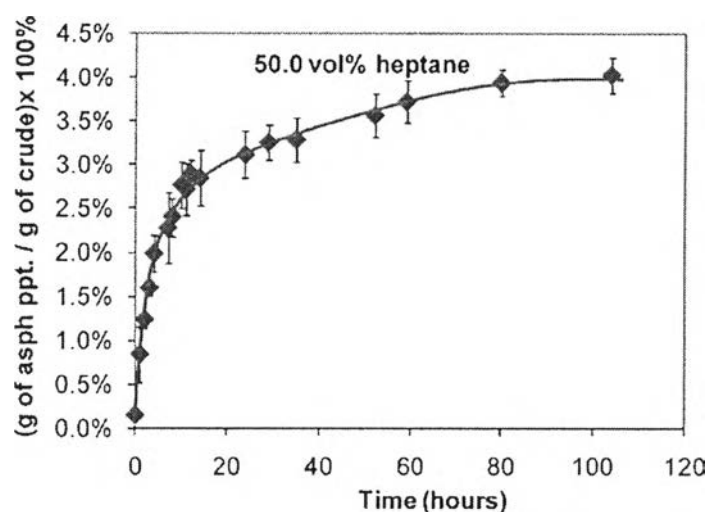


Figure 2.2.3 The amount of precipitated asphaltene as a function of time at 50 vol. % heptane for K-1 crude oil [Maqbool *et al.*, 2009].

Srikiratiwong, 2010's work reveals that the yield of precipitated asphaltenes at high precipitant concentrations decreases with higher carbon number of precipitant while the yield of precipitated asphaltenes at low precipitant concentrations either increased or remained constant with higher carbon number of precipitant, as shown in Figure 2.2.4.

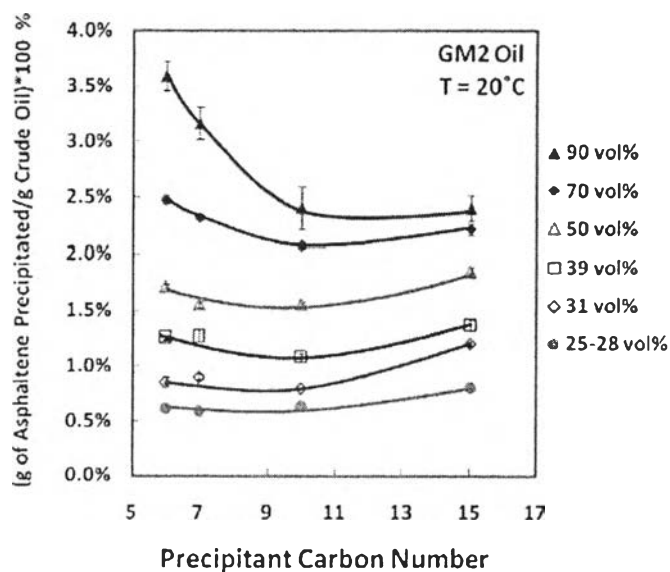


Figure 2.2.4 Yield of precipitated asphaltene at various precipitants and precipitant concentrations as a function of carbon number of precipitant.

Due to the slow detection time, the correlation between detection time, $t_{\text{detection}}$, and the difference between solubility parameter of asphaltene and solution squared, $(\delta_{\text{asphaltene}} - \delta_{\text{solution}})^2$, at 20°C was established from previous work using heptane as a precipitant which is shown in Figure 2.2.5 [Haji Akibari Balou, N., 2013]. This correlation assumes that asphaltene solubility parameter for the same crude oil is constant and the maximum potential barrier, U_{max} , which depends on the overall interaction energy between asphaltenes, is assumed to be inversely proportional to the difference between solubility parameter of asphaltene and solution squared. By applying this correlation, detection time at 20°C can be estimated leading to the decrease in number of the experiments for detecting the instable asphaltenes at low heptane concentrations. However, asphaltene solubility parameter has to be known.

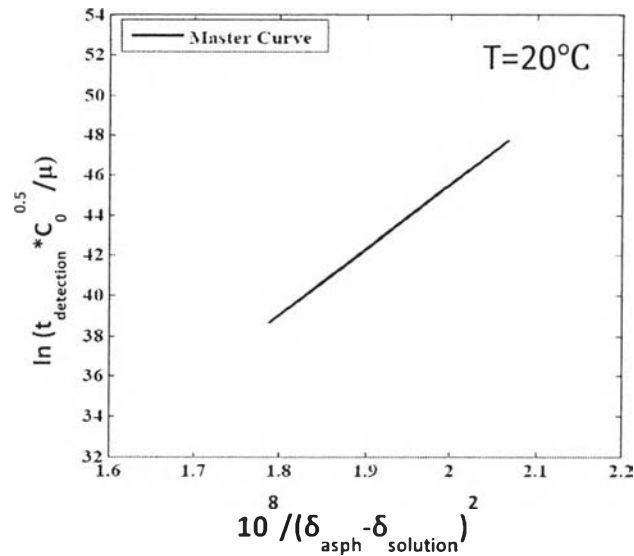


Figure 2.2.5 Master curve for relation between detection time and the difference between solubility parameter of asphaltene and solution squared at 20°C.

An onset time, the time to detect unstable asphaltenes using optical microscopy (0.5 μm detection size), at one heptane concentration has to be performed to obtain the detection time at 20°C. In addition, the refractometer is used to measure the refractive index, RI, of crude oil and heptane and a linear relationship between the RI and solubility parameter for paraffinic and aromatic hydrocarbons is used to determine solubility parameters of crude oil and heptane as shown in equation 2.2.1 [Wang, J. X., and Buckley, J. S., 2001].

$$\delta = 52.042F_{RI} + 2.904 \quad (2.2.1)$$

where δ is solubility parameter and $F_{RI} = \frac{n^2-1}{n^2+2}$; n is the refractive index.

The solubility parameter of a mixture can be estimated by volumetric average of solubility parameters of its components [Haji Akibari Balou, N., 2013]. By knowing detection time and solution solubility parameter, asphaltene solubility parameter can be obtained and detection time at other heptane concentration is then determined.

2.3 Population Balance Model

The aggregation of asphaltene nanoaggregates in crude oil-precipitant systems has been previously modeled using a geometric population balance model, as shown below [Maqbool *et al.*, 2011].

$$\frac{dC_k}{dt} = \frac{1}{2} \sum_{\substack{i+j \rightarrow k \\ i=1 \\ i=k-1}}^{i=k-1} K_{i,j} C_i C_j - C_k \sum_{j=1}^{\infty} K_{k,j} C_j \quad (2.3.1)$$

$$K_{i,j} = \frac{2RT}{3\mu_m} \frac{(d_i + d_j)^2}{d_i d_j} \beta \quad (2.3.2)$$

where C_k is the molar concentration of the k th aggregate (kmol m^{-3}), $K_{i,j}$ is the collision kernel between aggregate sizes i and j ($\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$), d_i, d_j are the diameters (m) of colliding aggregates i and j , μ_m is the viscosity of the medium ($\text{kg m}^{-1} \text{ s}^{-1}$), R is the universal gas constant ($\text{J K}^{-1} \text{ kmol}^{-1}$), T is the absolute temperature (K), β is collision efficiency. Following a geometric scaling factor of two, the number of nanoaggregates in the k th particles size is twice the number in the $k-1$ aggregate. Figure 2.3.1 shows that the model is in a good agreement with the experimental data. The experimental data obtained from centrifugation technique.

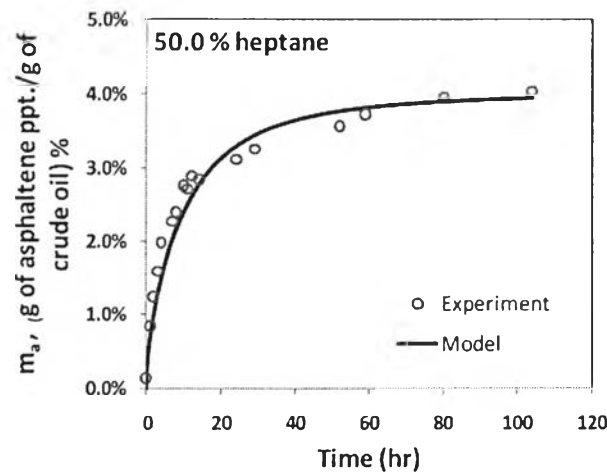


Figure 2.3.1 Experimental and simulated evolution of the separated aggregates using for 50 vol. % heptane [Maqbool *et al.*, 2011].

The definition of collision efficiency is the number of successful adhesions divided by total number of collisions as shown in the equation below.

$$\beta = \frac{\text{Number of successful adhesions}}{\text{Total number of collisions}} \quad (2.3.3)$$

Using population balance model to estimate the particle-particle collision efficiency, β , of asphaltene, it shows that the collision efficiency depends significantly on the precipitant concentration [Maqbool *et al.*, 2011] as shown in Figure 2.3.2 which demonstrates that the collision efficiency of K1 crude oil increases with increasing heptane concentration. One of the explanations for the increase in the collision efficiency at higher heptane concentrations is that the solution becomes a weaker solvent for asphaltenes leading to destabilized asphaltenes tend to collide and aggregate with each other at higher heptane concentrations. This leads to the slow detection time for instable asphaltenes at low precipitant concentrations.

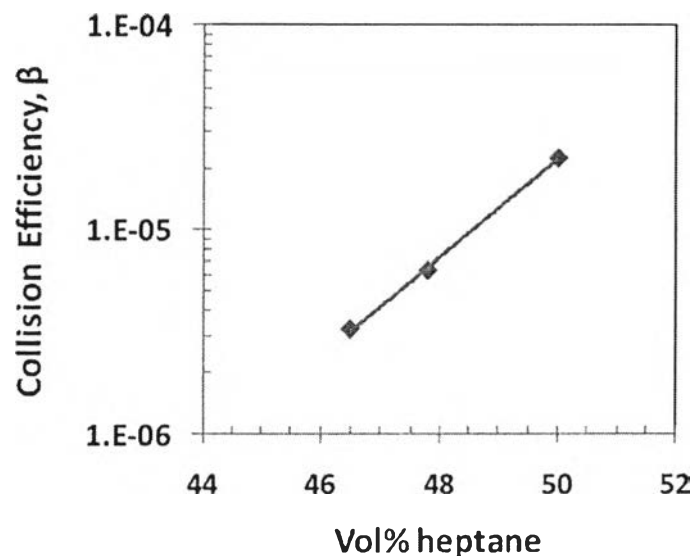


Figure 2.3.2 The collision efficiency of K1 crude oil as a function of heptane concentration from previous work [Maqbool *et al.*, 2011].

2.4 Asphaltene Deposition

A capillary deposition apparatus is used to investigate the stability of asphaltenes in oil-precipitant mixtures because it can detect destabilized asphaltenes faster than a batch aggregation process [Hoepfner *et al.*, 2013]. The principle of capillary deposition apparatus is to flow fluid with desired flow rate and to measure the pressure drop between the inlet and outlet of a capillary [Broseta, 2000]. This pressure drop across the capillary can be calculated with the Hagen-Poiseuille equation:

$$\Delta P = \frac{8\mu Q}{\pi} \frac{L}{R^4} \quad (2.4.1)$$

where R is radius, L is length, μ is viscosity and Q is volumetric flow rate.

From Hoepfener *et al.*'s work in 2013, a capillary deposition apparatus, as shown in Figure 2.4.1, was used to study asphaltene deposition at low degrees of destabilization. Using this apparatus, crude oil and heptane were pumped to the mixing section that had porous frits to make them well-mixed. A CFD simulation was also used to observe that crude oil and heptane mix in the mixing section and as shown in Figure 2.4.2, they are well-mixed. Additionally, the heptane concentration was controlled by changing the flow rates of oil and heptane. After mixing section, the mixture was fed into a capillary and then into a collected container.

As mentioned earlier, adding heptane leads to the destabilization of asphaltenes and the destabilized asphaltenes tend to precipitate and deposit inside a capillary increasing the pressure drop in it. The more asphaltenes that deposit inside the capillary, the higher the pressure drop between the inlet and outlet of a capillary can be detected. In addition, the pressure drop is recorded over time to create a pressure drop profile.

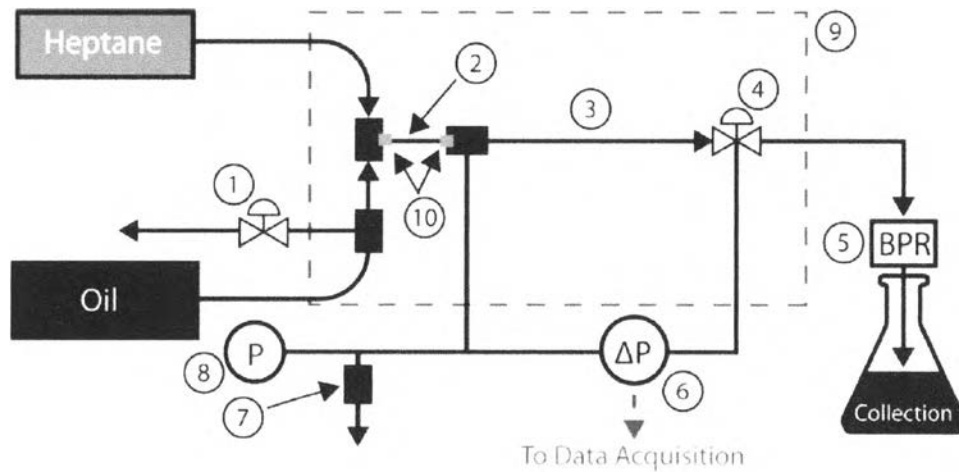


Figure 2.4.1 The capillary deposition apparatus set up [Hoepfner *et al.*, 2013].

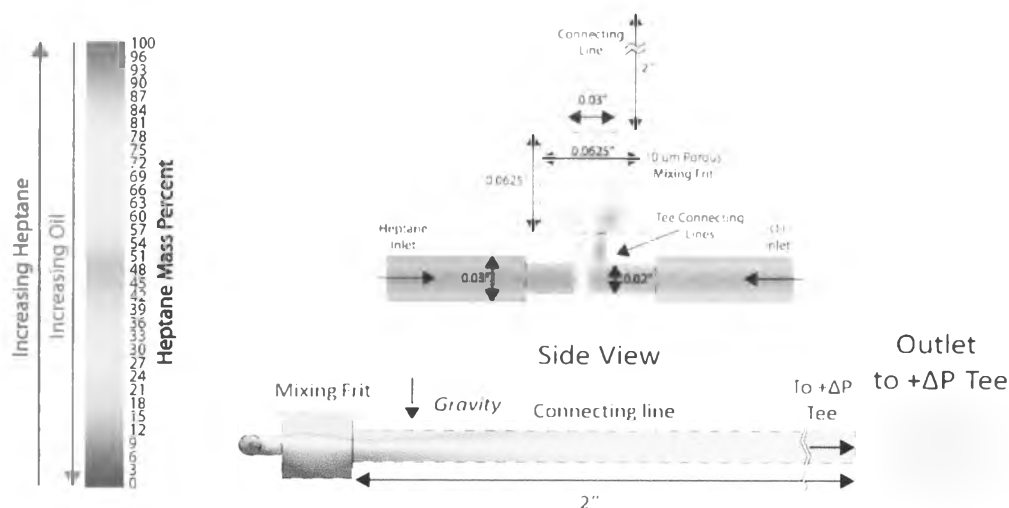


Figure 2.4.2 The CFD simulations of the mixing section indicated that crude oil and heptane are completely mixed before they reach the outlet [Hoepfner, 2011].

Figure 2.4.3 shows the pressure profile with varying heptane concentrations from a capillary flow. It can be observed that the pressure drop in each concentration increased over time indicating that a deposit was formed. Moreover, it can be seen that different heptane concentrations had different profiles and reducing the heptane concentration resulted in a decrease in the rate of pressure drop increase. In addition, the induction time decreases with higher heptane concentration. For example, at 40 vol. % heptane, the asphaltene deposition was formed in about 1 hour while at 30 vol. % heptane, the asphaltenes deposited in approximately 2 hours. The results also

demonstrates that a capillary deposition apparatus can detect the asphaltene deposition even at 20 vol. % heptane after about 12 hours and at 25 vol. % heptane it can detect after about 3 hours.

However, destabilized asphaltene at 25 vol. % heptane can be detected after about 30 days using microscopic technique, which is significantly longer time than the detection time with capillary deposition.

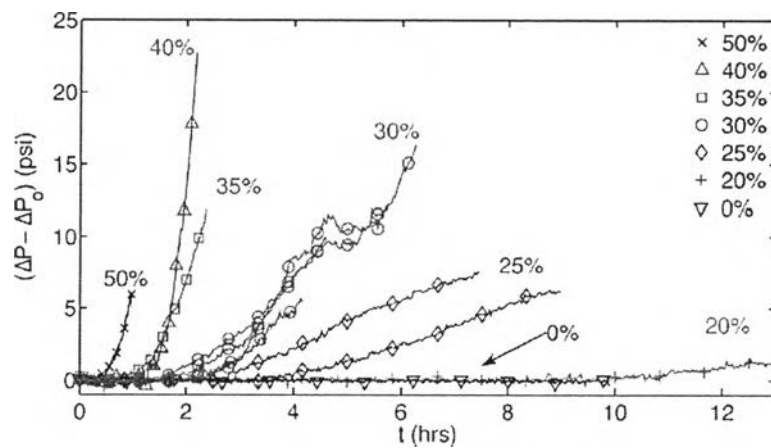


Figure 2.4.3 The pressure drop profile with varying heptane concentrations [Hoepfner *et al.*, 2013].

By normalizing the pressure drop profile using viscosity and the concentration of insoluble asphaltenes in the capillary and shifting the induction time, t_d , as shown in Figure 2.4.4, it reveals that the behavior of asphaltene deposition is identical at different precipitant concentrations. However, the 40 and 50 vol. % heptane experiments deviate from the normalized pressure drop as pressure drop increases significantly and the deviation at 50 vol. % heptane occurred faster than that at 40 vol. % heptane. The reason is that higher heptane concentrations may have a higher propensity to deposit.

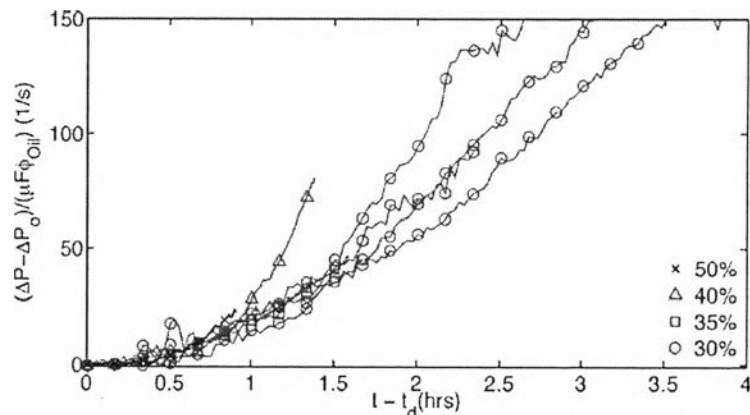


Figure 2.4.4 Normalized deposition pressure drop for heptane in Oil A, scaled by viscosity and the concentration of insoluble asphaltenes in the capillary and time is shifted by the deposition induction time, t_d [Hoepfner *et al.*, 2013].

Additionally, the mixing was investigated using SEM images as shown in Figure 2.4.5. SEM images indicate that the mixing is good because the deposited asphaltene formed around the entire capillary inlet. Moreover, the deposit at the capillary inlet occurred more than that at the capillary outlet indicating that it is a non-uniform deposition. An energy dispersive X-ray spectroscopy (EDX) was used to identify the presence of carbon for the large particle at capillary outlet of run #1 to test whether they are asphaltene. The result reveals that it is a contaminant.

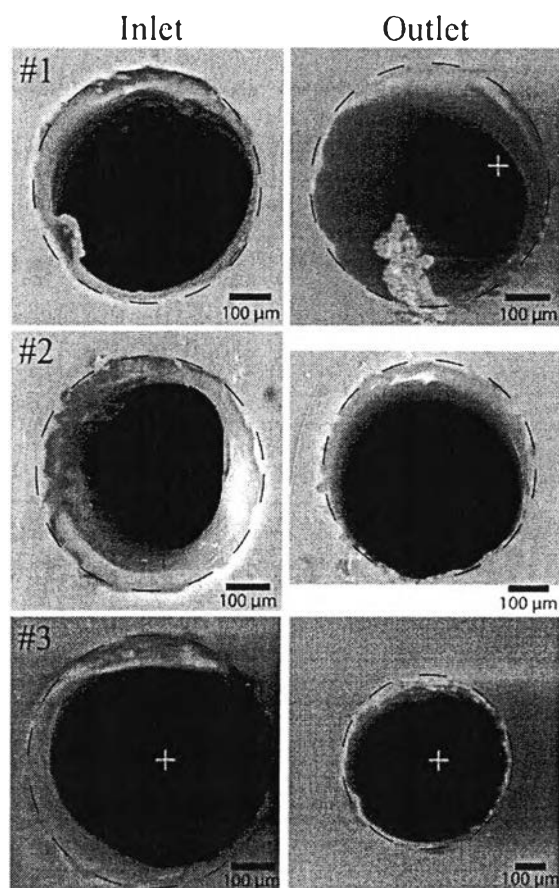


Figure 2.4.5 SEM images from the capillary inlet (left) and outlet (right) with 0.02 inch ID and 5 cm length capillary at 30 vol. % heptane for 3 runs [Hoepfner *et al.*, 2013].