CHAPTER II
LITERATURE REVIEW

2.1 Crude oil

Petroleum crude oil is a complex mixture of hydrocarbons containing variety of molecules with different physical and chemical properties. Crude oil is commonly separated into four major fractions: saturates, aromatics, resins, and asphaltenes (SARA). The schematic of SARA separation is shown in Figure 2.1.
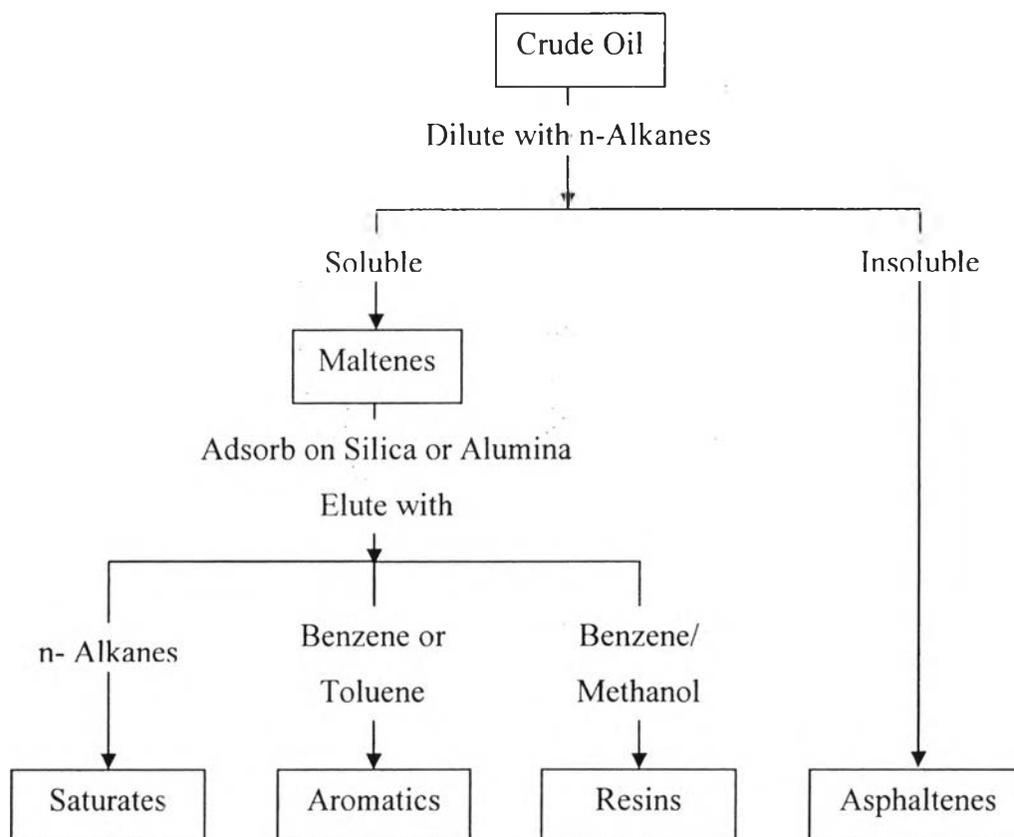
Figure 2.1 Scheme of crude oil separation (SARA) into four components: saturates, aromatics, resins and asphaltenes (Wattana, 2004).

2.2 Asphaltenes

As discussed earlier, asphaltenes are operationally defined as a solubility class of crude oil that is soluble in benzene or toluene but insoluble in liquid normal alkanes, such as n-pentane or n-heptane. They are dark brown to black dry powders with no definite melting point (Mullin, 2007). In addition, the amount precipitated and their properties are dependent on the type of precipitant (n-alkane) used. Due to the conditional definition of asphaltenes, they are named based on the precipitant used, for instance, pentane asphaltenes and heptane asphaltenes are separated from crude oil by using pentane and heptane precipitants respectively. One method that is used to find the fraction of asphaltene in a crude oil is ASTM D2007-80 (1980), where crude oil is diluted by either n-pentane or n-heptane at a volume ratio of 1:40 then filtered to the separate asphaltenes after two days. Speight (1999) precipitated asphaltenes by adding different precipitants (n-alkanes) to the crude oil at volume ratio of 40:1. Experimentally, a greater quantity of asphaltenes was recovered with the lower carbon number n-alkanes, as seen in Figure 2.2.
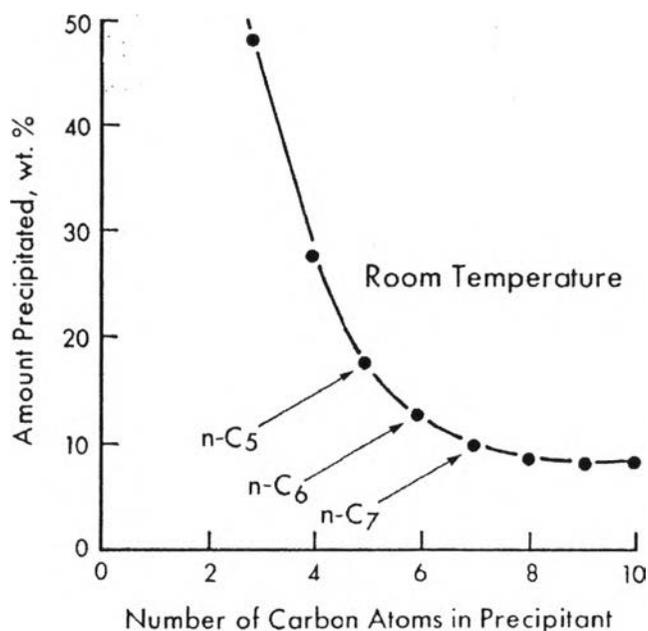
Figure 2.2 Amount precipitated asphaltene as a function of precipitant (Speight, 1999).

The main components of asphaltenes are carbon and hydrogen (C and H) but there are small quantities of heteroatoms such as N, S and O and some metals like Ni, V and Fe. Kaminski *et al.* (2000) separated an asphaltene sample into various components depending on their polarity.

2.3 Asphaltene Precipitation Onset Point

Asphaltenes are stable in crude oils at reservoir conditions, high pressure and high temperature. Changing the pressure, temperature or composition can lead to asphaltene destabilization. For field cases, the most common mechanism for asphaltene precipitation and deposition is pressure depletion induced while the oil moves up the wellbore to the surface (Haskett *et al.*, 1965). As the reservoir pressure is depleted, enhanced oil recovery (EOR) can be performed by injecting a miscible or immiscible solution. Although additional oil is recovered, EOR leads to compositional changes and, can cause asphaltene precipitation in the porous rock in the reservoir (Vafaie-Sefti *et al.*, 2006). Using an n-alkane precipitant in the laboratory can simulate the effect of depressurization that occurs in the reservoir. The minimum volume of n-alkane precipitant that can induce precipitation is defined as the onset point. Maqbool *et al.* (2009) has shown in his work that the asphaltene precipitation process is kinetic and the onset point is time dependent and can take days or months to detect, as shown in Figure 2.3.

2.4 Asphaltene Deposition Experiment

Most of the previous capillary deposition work has largely studied asphaltene deposition at or past the onset point. Broseta *et al.* (2000) used oil-heptane-xylene mixtures as the feed to the capillary and then measured the pressure drop (ΔP) to detect deposition and thus, precipitation. The Hagen-Poiseuille equation can be used to calculate the pressure drop for a certain flow rate (Q):

$$\Delta P = \frac{8\mu Q}{\pi} \frac{L}{R^4} \tag{1}$$
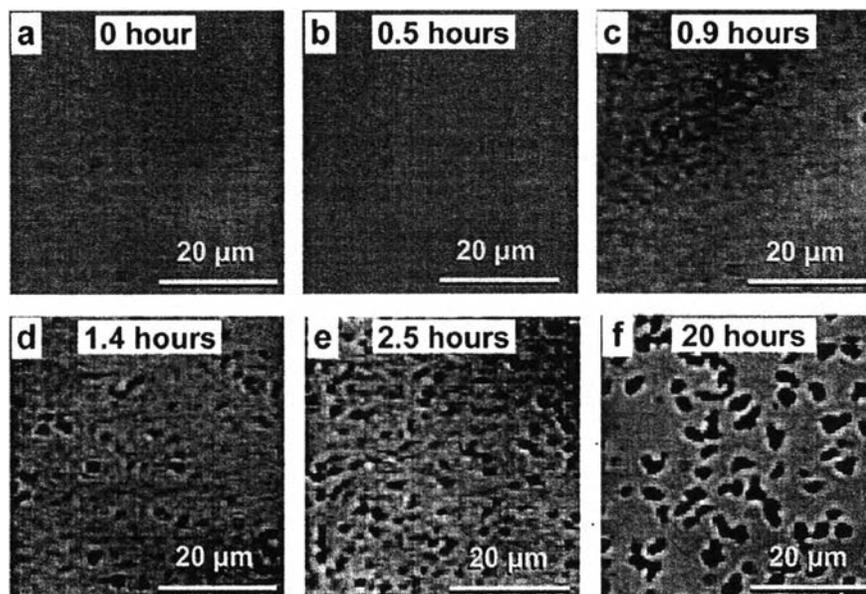
Figure 2.3 Micrographs showing the time dependence of asphaltene precipitation for mixture containing 50 vol% C7 and 50 vol% oil (Maqbool *et al.*, 2009).

where R and L are the radius and length of capillary respectively and μ is the fluid viscosity. The concentration of heptane, the precipitant, was increased until the pressure drop increased, indicating deposit formation. An example result from this work can be seen in Figure 2.4. This technique can detect asphaltene precipitation like other techniques, such as IR light scattering.
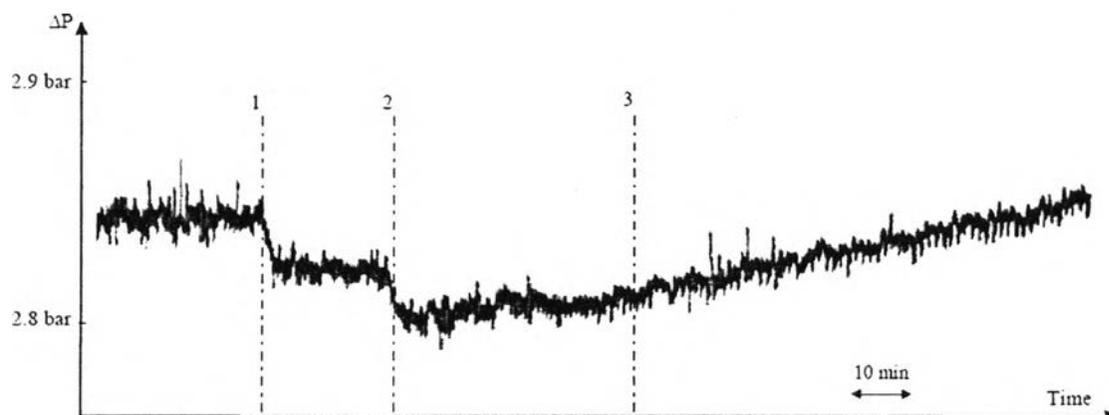
Figure 2.4 Pressure drop evolution from increasing the precipitant concentration at points 1, 2 and 3 respectively. After point 3, the increase in pressure drop signifies the start of a deposition forming (Broseta *et al.,* 2000).

Wang *et al.* (2004) studied the uniformity of asphaltene deposition in capillaries by collecting the deposit. In these experiments, oil-precipitant mixtures were fed into a capillary at a low flow rate of 4.8 mL/hr. To ensure the proper mixing, the solution flowed through a sonicating bath before entering the capillary. The pressure drop was measured in this work also. Nitrogen (N_2) was used to displace the remaining oil in the capillary with a low flow rate and then dry the deposit with a high flow rate. The deposit was dissolved with toluene and THF and weighed after the solvent had evaporated. With the assumption of a uniform deposit, the Hagen-Poiseulle Equation, (1), was used for calculate the deposit thickness in the capillary by approximating Equation 1:

$$\Delta P(t) = \frac{8\mu Q}{\pi} \frac{L}{[R_o - \Delta R(t)]^4} \qquad (2)$$

where R_O and $\Delta R(t)$ are the actual radius of capillary and thickness of deposit at time, t, respectively. The conclusion of this work was that the deposit is uniform when the concentration is close to the onset point. The collected deposit is approximately the same as calculated, and the authors considered the deposit as uniform, as can be seen in Figure 2.5.

(a) Oil S   (b) Oil F
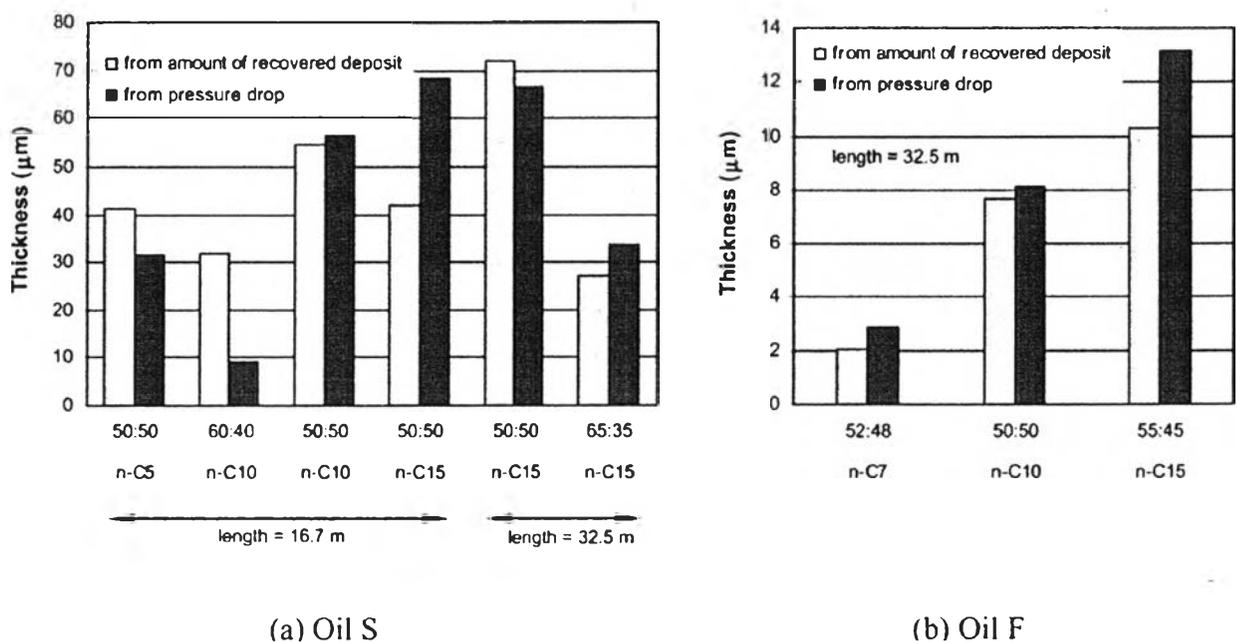
Figure 2.5 Thickness from predicted and collected of two crude oils, Oil S and Oil F (Wang *et al.*, 2004).

Hoepfner (2009) investigated asphaltene deposition below the onset point. The onset point of the oil used was 40vol% heptane and was measured by microscopy of the effluent after mixing oil-heptane. Proper mixing was obtained by flowing the oil:heptanes solution through a mixing tee, which contained a 10 μm porous frit, at a low flow rate 5 mL/hr. This experiment also used the pressure drop measurements to detect the formation of a deposition. Asphaltene deposition at lower concentration than onset precipitant concentrations can be seen in Figure 2.6.
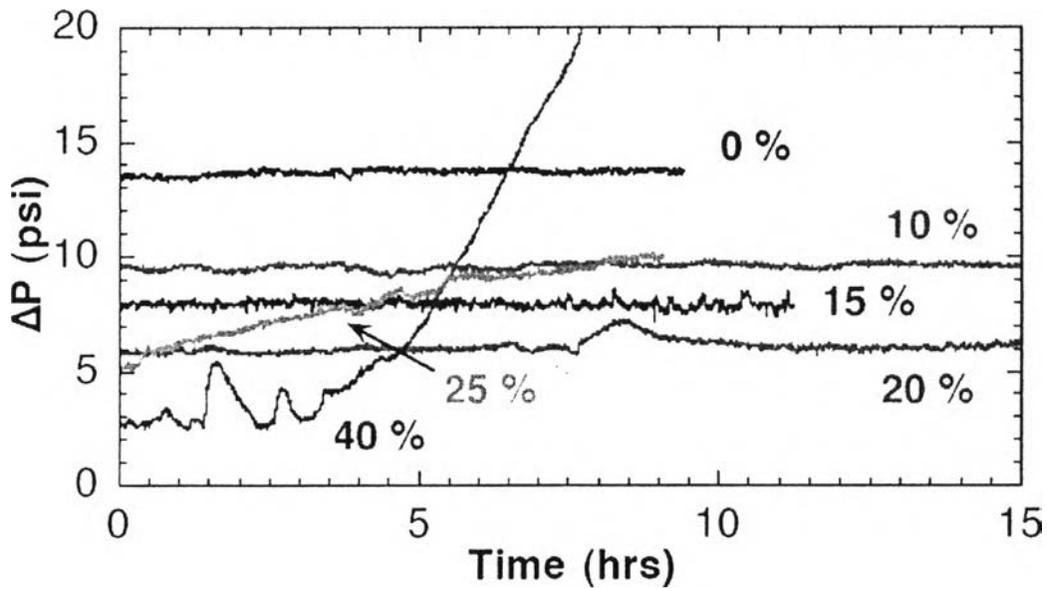
Figure 2.6 Pressure drop profile of different precipitant concentration (Hoepfner, 2009).

Another conclusion from this work was that deposit is non-uniform. For characterizing the non-uniformity, the author considered dividing the capillary into two sections, one with a uniform deposit and one without a deposit. Modifying the Hagen-Poiseulle Equation, (1), and using the collected mass, Hoepfner was able to calculate the length and thickness of the deposit section with the two below equations below:

$$\Delta P = \sum_{i=1}^{segments} \frac{8\mu L_i Q}{\pi R_i^4} \qquad (3)$$

and

$$m_d = L_d \pi \rho_d (R_o^2 - R_d^2) \qquad (4)$$

where ρ is density. For subscriptions, d and o mean deposit and oil.

Reproducibility in previous studies has not been strongly emphasized. For example, Boek *et al.* (2008) studied colloidal asphaltene deposition by adding heptanes to a asphaltene:toluene solution in a glass capillary at low flow rate of 5 or 10 μL/min. A Y connector was used for mixing. The results are shown in Figure 2.7. It can clearly be seen in Figure 2.7 that the results are not reproducible. Reproducibility must be obtained before conclusions can be made. One possible explanation for the inconsistent results is poor mixing.
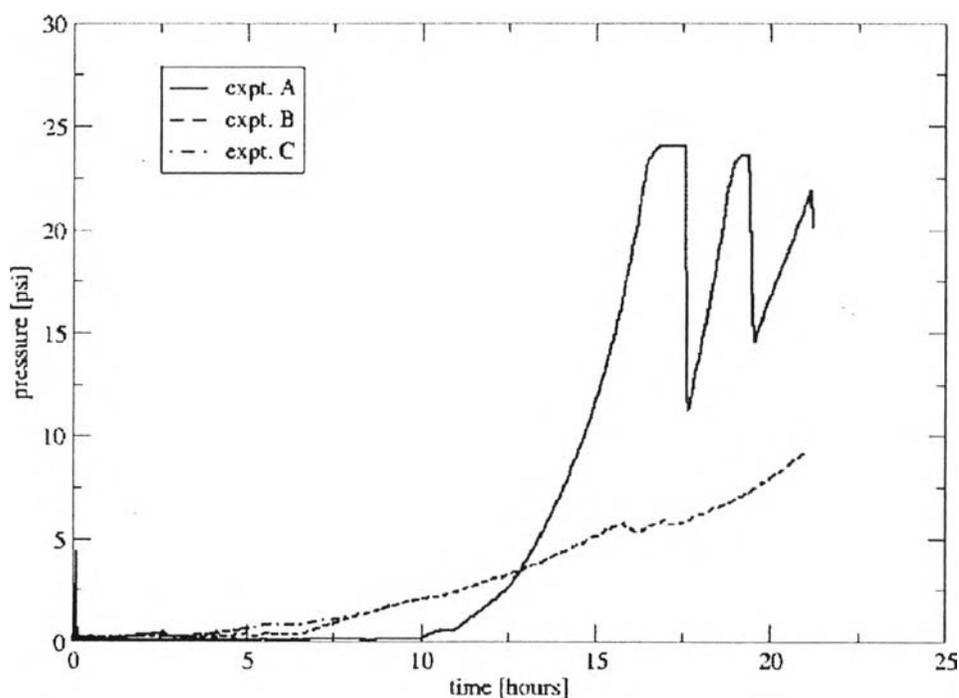
Figure 2.7 Pressure drop profile for three repeat experiments at 5 μL/min (Boek *et al.*, 2008).

Hoepfner (2010) considered the mixing problem in capillary deposition apparatuses. In his later work, Hoepfner added a 2 inch stainless steel capillary with 0.03 inch inner diameter (ID) after the mixing tee. Computational fluid dynamic (CFD) simulations were performed to confirm proper mixing by the outlet of the 2 inch capillary. Figure 2.8 shows the new apparatus from Hoepfner's work.
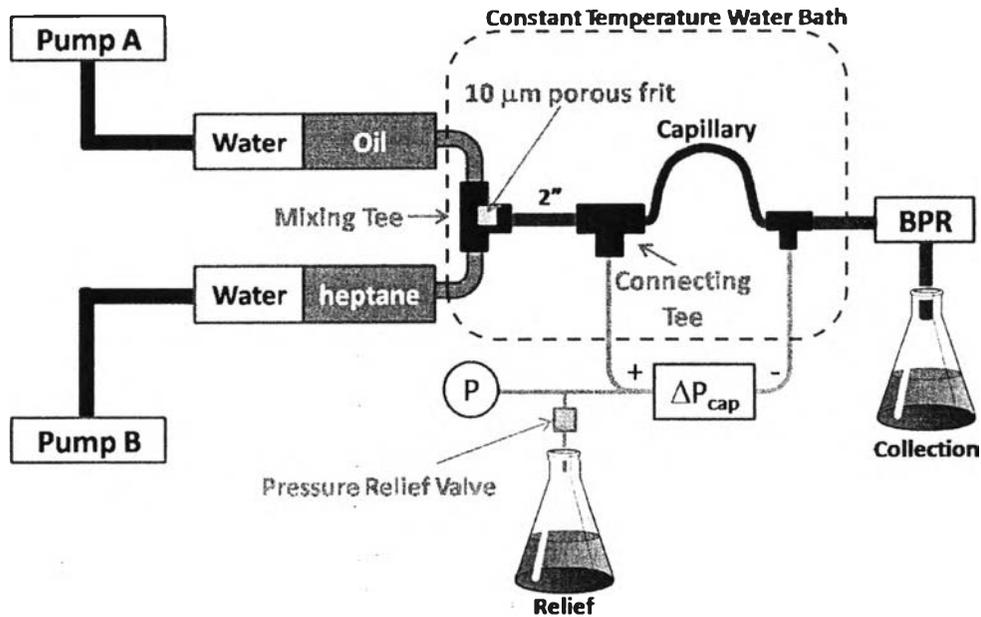
Figure 2.8 Asphaltene deposition apparatus setup (Hoepfner 2010).

2.5 Effects on Asphaltene Deposition

Nabzar *et al.* (2008) mixed an asphaltene:toluene solution with heptane to study the shear effects on asphaltene deposition by using the same capillary and varying the shear rate by adjusting the flow rate. A sample result is shown in Figure 2.9. The conclusion was that asphaltene deposition is sensitive to the shear rate until it reached a critical shear rate, no more shear effect after passing the certain point (120mL/hr for this work).

Jamialahmadi *et al.* (2009) studied flocculated asphaltenes depositing inside a capillary with different surface temperatures. Stock tank oil (STO), oil at room temperature and pressure, was mixed with pentane in a controlled stirred tank until reaching desired concentration then fed to the testing chamber, a capillary with heater section. For this work, the mass deposited was calculated by heat and mass transfer theory with the equation below:

$$m_d = \rho_d \lambda_d \left(\frac{1}{\alpha_t} - \frac{1}{\alpha_0} \right) \tag{5}$$
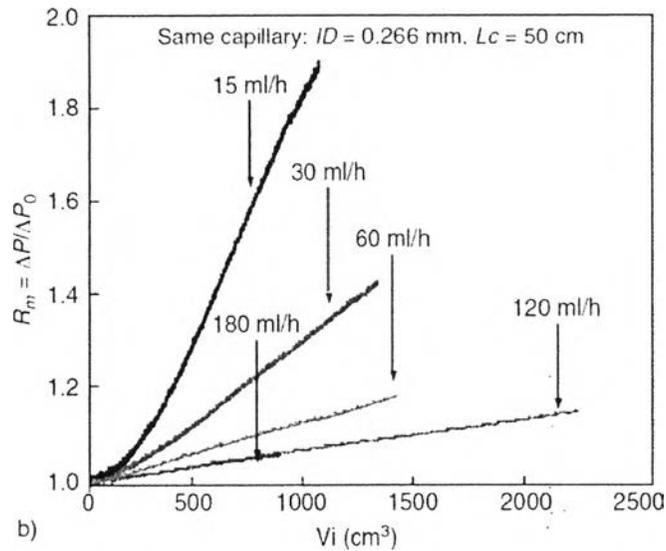
Figure 2.9 Evidence of shear limitation from experiments (Nabzar *et al.*, 2008).

where α and λ are heat transfer coefficient and thermal conductivity respectively. Subscripts, t and o mean time at t and time at initial of experiment respectively. The heat transfer coefficient decreased faster when the difference between bulk and surface temperature was larger. An example can be found in Figure 2.10. The results indicated that the deposition process depends strongly on the surface temperature.
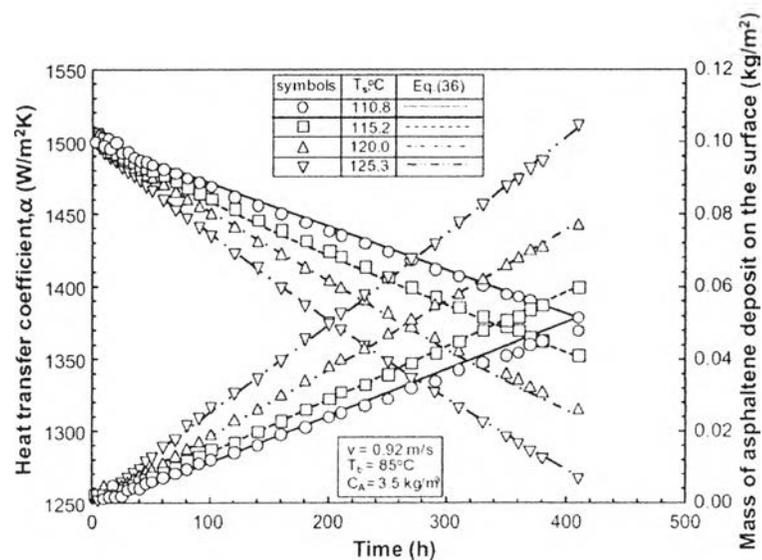
Figure 2.10 Heat transfer coefficient and collected deposit with different surface temperature (Jamialahmadi *et al.*, 2009).