CHAPTER IV
RESULTS AND DISCUSSION

4.1 Asphaltene Deposition Apparatus

The basic characteristics of the packed-bed have been determined. All of the parameters are shown in Table 4.1 which indicate that the deposit will not occur from mechanical entrapment unlike the packed-bed proposed by Hu and Hartman because a large pore size of the packed-bed (Hu et al., 2014). Therefore, there is a large difference between the asphaltene particle size in a solution and the pore size of the packed-bed. The size of asphaltene particle is in an order of magnitude of nanometre but the pore size is in an order of magnitude of millimetre. Hence, the main mechanism of asphaltene deposition in this apparatus is the asphaltene particle adhesion or attachment onto a surface.

Table 4.1 Characteristics of the packed-bed

Bed length	26.04 cm
Inner diameter of column	1 cm
Cross-sectional area of column	0.79 cm^2
Total surface area in column	249 cm^2
Volume average diameter of sphere	3.8 mm
Pore size	1-2 mm
Porosity	0.47
Permeability	~ 3x10^{-8} m^2

4.1.1 Validation of Asphaltene Deposition Apparatus

One of the advantages of the packed-bed flow-loop apparatus is the transparency of the glass column. Therefore, the initial validation of the apparatus is by visual inspection of the packed-bed. The picture of a clean packed-bed is presented in Figure 4.1 (a). Figure 4.1 (b) shows a packed-bed after perform an experiment for 1

minute. There is only trapped liquid in a small angle between glass column and sphere as well as between sphere and sphere because of the surface tension of the crude oil-heptane solution. Moreover, there is no significant deposit formed in the packed bed. However, a significant deposit can be observed in the packed-bed in a 12-hour experiment as demonstrated in Figure 4.1 (c). The deposit formed mostly on stainless steel spheres but a little bit on glass column.
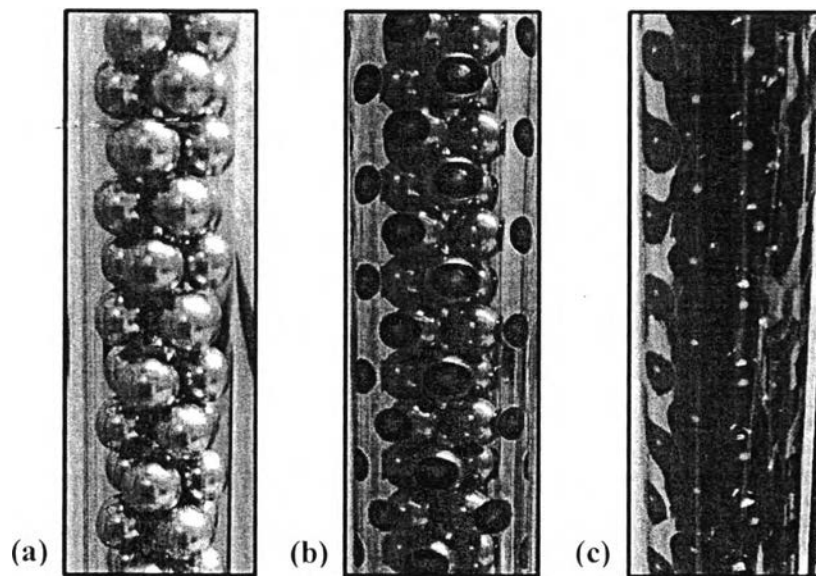

Figure 4.1 Pictures of packed-bed column (a) clean packed-bed column before perform an experiment (b) packed-bed column after perform an experiment for 1 minute (c) packed-bed column after perform an experiment for 12 hours.

The mass of the material collected at the end of the experiment will be called a collected material. A deposition phenomena occurring in a packed-bed during the experiment was proposed to describe the composition in a collected material. Firstly, there is a trapped liquid at small corners of the packed-bed. It can be measured from 1-minute run time experiment. Secondly, the asphaltenes will attach to the surface and form a deposit layer over the surface which increases as an experimental run time increases but still the same amount of trapped liquid at a small corners in a packed-bed. Therefore, the collected material is composed of a trapped liquid and

deposit. Moreover, the mass of a trapped liquid was considered to be constant in all collected materials.
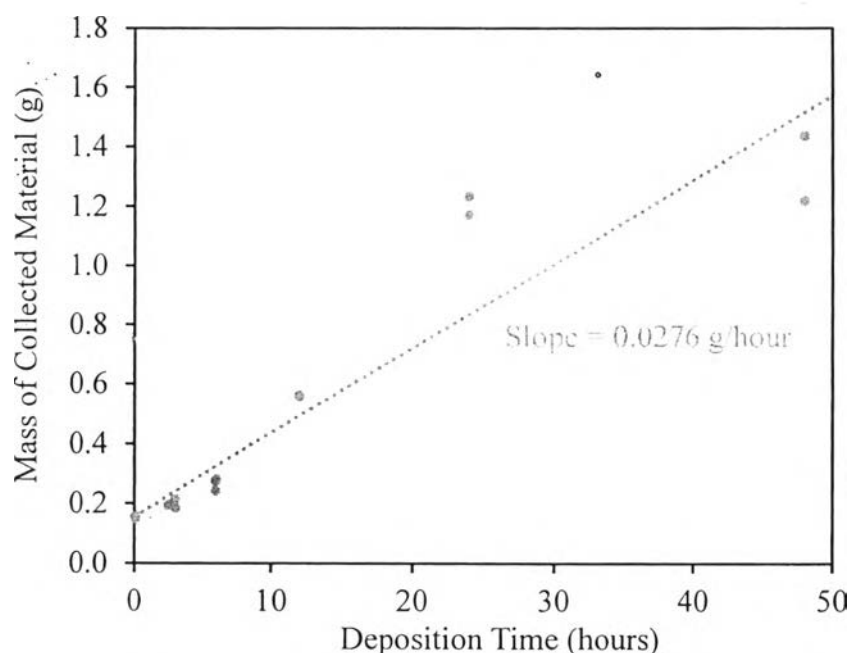

Figure 4.2 Mass of collected material as a function of deposition time for 62 wt% heptane in Bow River crude oil at a flow rate of 0.93 g/min.

The results presented in Figure 4.2 quantitatively validate the asphaltene deposition apparatus. The mass of collected material was in an order of magnitude of one gram with the highest mass of 1.43 g. Hence, the mass of collected material was measurable and sufficient for further characterization. The mass of collected material increases with deposition time. Although these results demonstrated a high reproducibility of the apparatus, a deviation from the slope was recognized at long deposition time. The source of this deviation is a systematic error by some experimental factors in performing this first set of experiments. Consequently, the refined experimental procedure has been established in order to minimize the systematic error for performing new experiments. However, the deposition rate can be obtained from the slope of the plot. Hence, the deposition rate is 0.0276 g/hour or 30.4 g/m^2/day for a specific deposition rate. The deposition rate measured here is

comparable to the asphaltene deposition rate reported in other literatures (Akbarzadeh et al., 2010; Eskin et al., 2012). The capture efficiency is a ratio of asphaltenes deposit on surface in a packed-bed to a total unstable asphaltenes that is flowed through a packed-bed. The capture efficiency for the experiments presented in Figure 4.2 is 3.86%. Moreover, the critical settling down diameter of the asphaltenes was estimated from Stokes equation to analyse the undesired effect of gravitation in asphaltene deposition in the packed-bed. The critical settling down diameter of a particle at a flow rate of 0.93 g/min is 65 micron but the asphaltene particle in the crude oil-heptane solution was kept well below 0.5 micron. So, the effect of gravity on deposition can be neglected.

Once heptane is added to destabilize the asphaltenes, two types of asphaltenes are observed, e.g., stable asphaltenes and unstable asphaltenes (Hoepfner et al., 2013). The amount of unstable asphaltenes that precipitate out varies with heptane concentration which can be measured with centrifugation technique. The amount of unstable asphaltene in a solution of 62 wt% heptane in BR is 0.55 wt% and the amount of stable asphaltenes in this solution is 0.95 wt%.
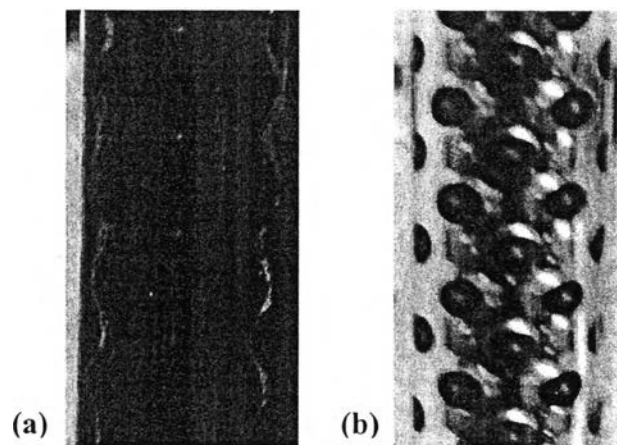

(a)　　　(b)

Figure 4.3 Picture of the packed-bed column after performing the experiment for 24 hours (a) the crude oil-heptane solution with both stable and unstable asphaltenes was used to perform the experiment (b) the crude oil-heptane solution with only stable asphaltenes was used to perform the experiment.

The two-week aged solution of 62 wt% heptane in BR was centrifuged to remove all the unstable asphaltenes. It was then used to perform an experiment in comparing with the experiment using fresh crude oil-heptane solution with both stable and unstable asphaltenes. The picture of the packed-bed at the end of the experiment is shown in Figure 4.3. There is no deposit formed but only the liquid trapped in the packed-bed using crude oil-heptane solution without unstable asphaltenes. On the other hand, a significant amount of deposit formed in the packed-bed from crude oil-heptane solution with unstable asphaltenes. Therefore, only the unstable asphaltenes play a major role in asphaltene deposition.
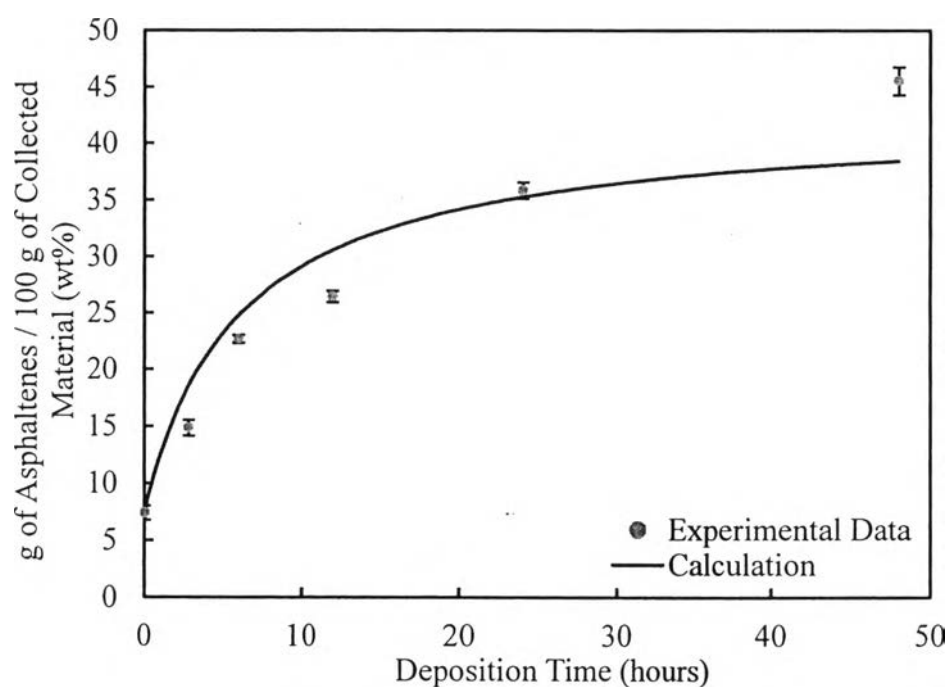

Figure 4.4 Asphaltene content of collected material as a function of deposition time.

The collected material is not composed of pure asphaltenes but some maltenes from crude oil. Therefore, the collected material was further characterized in order to quantify the amount of asphaltenes in the deposit. The amount of asphaltenes in the collected material measured experimentally over time is presented in Figure 4.4. The asphaltene content in the collected material was apparently increasing then levelling off as the experimental run time increases. As the deposition phenomenon

explained earlier, the collected material is composed of a constant fraction of trapped liquid and a deposit. Therefore, the asphaltene content of only the deposit portion in the collected material can be calculated from the mass fraction correlation which is expressed by,

$$AC_{collected\ material} = \theta_{trapped\ liquid} AC_{trapped\ liquid} + \theta_{deposit} AC_{deposit} \qquad (4.1)$$

where AC is asphaltene content and θ is mass fraction.

The asphaltene content of the deposit was used as a fitting parameter in a mass fraction correlation. The calculated asphaltene content of collected material fitted well with the experimental data. Hence, the adjusted asphaltene content of the deposit in the collected material is 42 wt%. This result is a confirmation of the enrichment of asphaltenes in the collected material.

4.1.2 Asphaltene Deposition Apparatus Verification at Various Conditions

The measurement of asphaltene deposition rate in a packed-bed of large stainless steel spheres is similar to the measurement of reaction rate in a packed-bed filled with catalyst. The operational condition is very important in order to obtain the true reaction rate that governs by the reaction of reactants on catalyst surface not the diffusion of reactants toward the catalyst surface. If consider two limiting cases which are diffusion limited and reaction limited, the flow velocity can be adjusted in order to probe the limiting case of the reaction on catalyst surface. The reaction rate will increase with the flow velocity in diffusion limited case. However, it will be independent and remains constant with increasing of flow velocity in a reaction limited case. Likewise, the deposition rate on stainless steel spheres is expected to be governed by the diffusion of asphaltene particles toward the surface or the attachment of asphaltene particles on the surface and, moreover, the similar trend is expected for the deposition rate with flow velocity. Therefore, the verification of the apparatus at different flow velocity is necessary with the purpose of probing the true deposition rate from surface attachment of asphaltenes. The result as present in Figure 4.5 had verified the apparatus for performing the experiments at various flow condition. The deposition rate initially increases then decreases as the superficial velocity of the flow increases.

The highest specific deposition rate was 55.79 g/m²/day at a superficial velocity of 1.89 mm/s. The lowest specific deposition rate was 26.75 g/m²/day at a superficial velocity of 5.80 mm/s. This preliminary result is different from the expectation where the decreasing of deposition rate takes place at high superficial velocity of the flow. Therefore, it could be another effect instead of diffusion and surface attachment that controls the deposition rate in that decreasing regime.
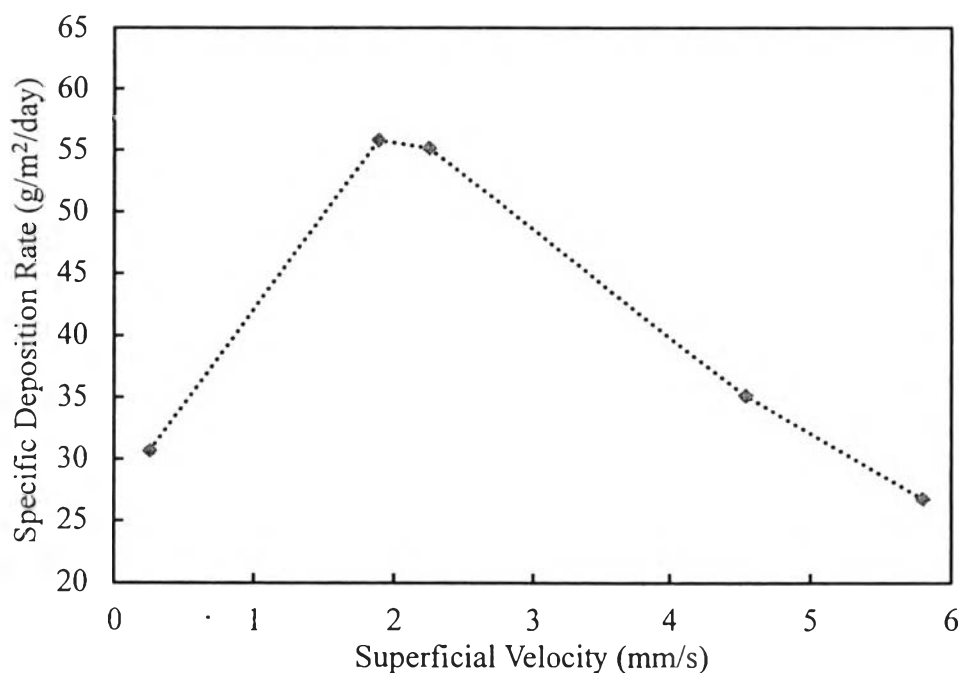

Figure 4.5 The specific deposition rate as a function of superficial velocity of the flow for 62 wt% heptane in Bow River crude oil solution.

4.2 Investigation of Asphaltene Deposition Mechanism

The hypothetical scenario of asphaltene particles in a flow is where they move randomly in a crude oil-heptane solution. They also have the advection in the direction of the flow. Once the asphaltene particles move closer to the surface and then contact the surface, they will attach to the surface. All the asphaltene particles are assumed to attach irreversibly to the surface upon contact. The attachment of asphaltene particles is a result of wall-particle interaction. The asphaltene attachment

on the surface induces the difference in concentration of asphaltenes from surface to the bulk. Therefore, the diffusion of asphaltenes occurs in the direction from the bulk toward the surface. The deposition of asphaltenes could be a competition of two effects, e.g., the diffusion of asphaltenes toward the surface and the attachment from asphaltenes-surface interaction.
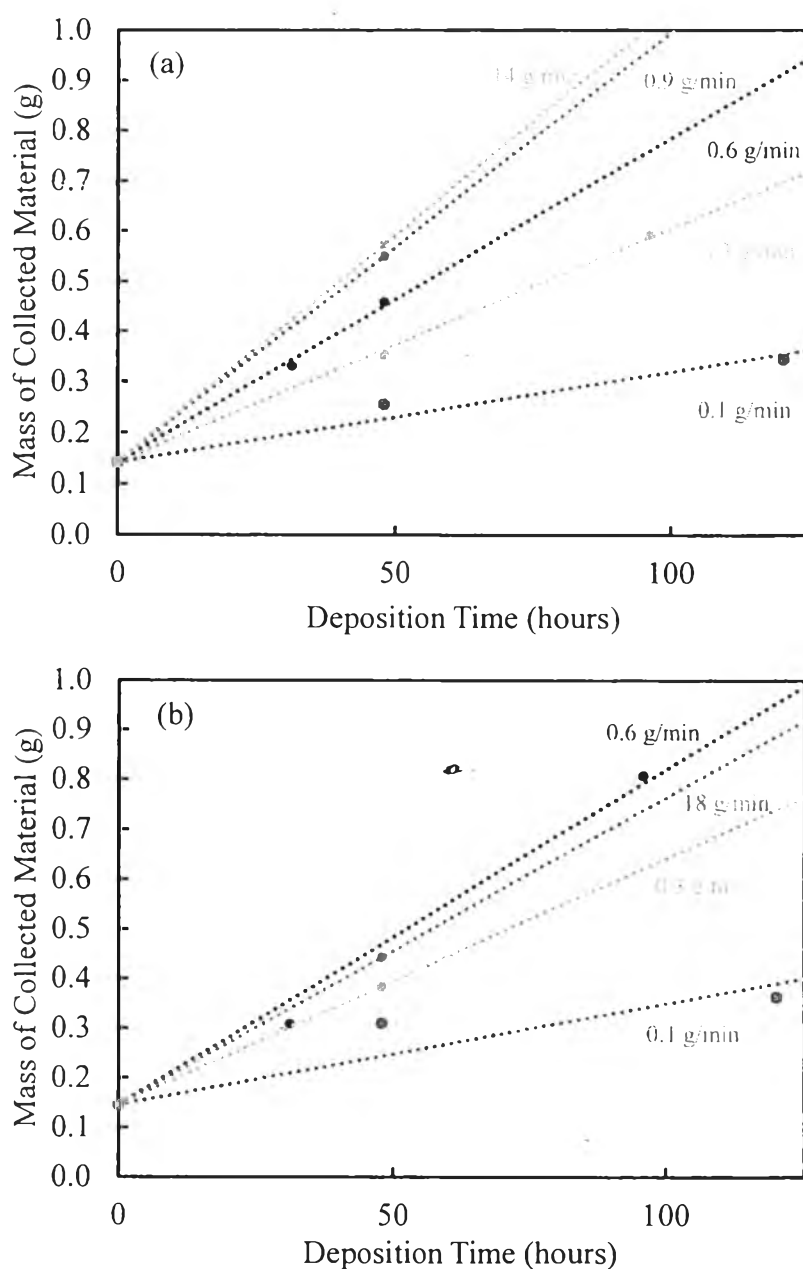

Figure 4.6 The mass of collected material as a function of deposition time for 67 wt% heptane in Athabasca Diluted Bitumen solution (a) apparatus 1 (b) apparatus 2.

The solution of 67 wt% heptane in ADB was used to perform the experiments to uncover the mechanism of asphaltene deposition in the range from low to high superficial velocity in a precisely controlled environment and experimental procedure. This crude oil-heptane solution had a detection time of 12 hours and contained 0.14 wt% of unstable asphaltenes. Figure 4.6 (a) and (b) present the raw data of the mass of collected material as function of deposition time. The deposition rates obtained from both apparatus are comparable at the same flow rate. Moreover, the deposition rate changed with the flow rate of crude oil-heptane solution.
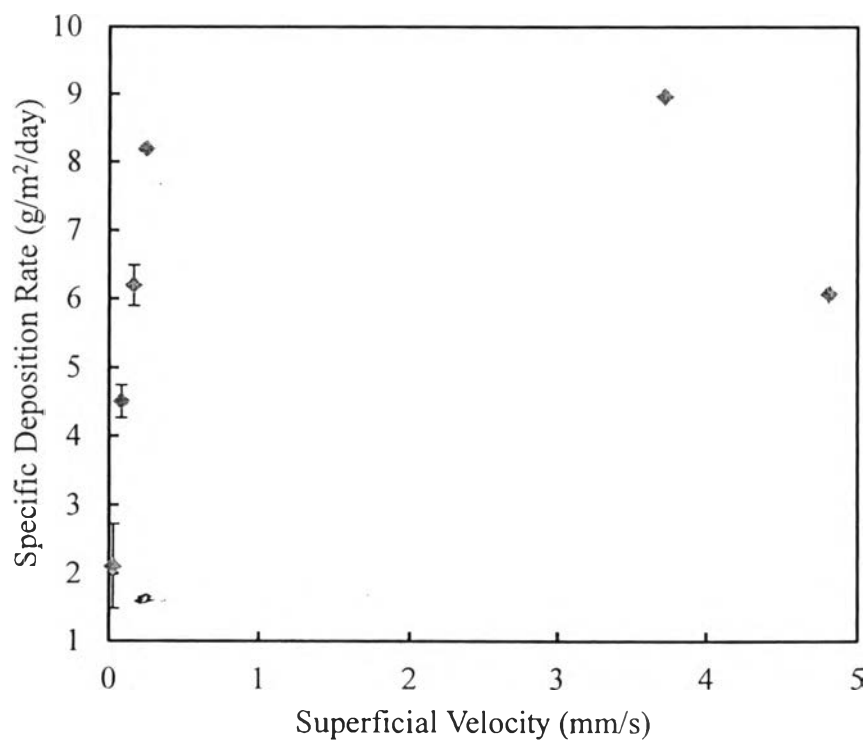

Figure 4.7 The specific deposition rate as a function of superficial velocity for 67 wt% heptane in Athabasca Diluted Bitumen.

The same trend as the preliminary result using BR-heptane solution had been observed again as presented in Figure 4.7 using ABD-heptane solution. The deposition rate was firstly increases then decreases as the superficial velocity of the flow increases. Two recognizable deposition rate regions were observed at low superficial velocity regime and high superficial velocity regime. Hence, the deposition behaviour

of asphaltenes in the flow condition can be primarily summarized that the difference in a composition and origin of the crude oil does not play an important role on deposition behaviour but it significantly depends on the flow velocity.

4.2.1 Mechanism of Asphaltene Deposition at Low Superficial Velocity Regime

The deposition rate was increasing with superficial velocity in this regime. The minimum specific deposition rate measured in this regime was 2.10 g/m²/day at a superficial velocity of 0.03 mm/s while the maximum specific deposition rate was 8.19 g/m²/day at a superficial velocity of 0.25 mm/s. Hence, the mass-transfer of asphaltene particles toward the surface controlled the deposition rate. The dependency of the deposition rate on superficial velocity can be gotten from the slope of the plot between log of specific deposition rate and log of superficial velocity of the flow. So, the dependency of the deposition rate on superficial velocity was a power of 0.5 as shown in Figure 4.8.
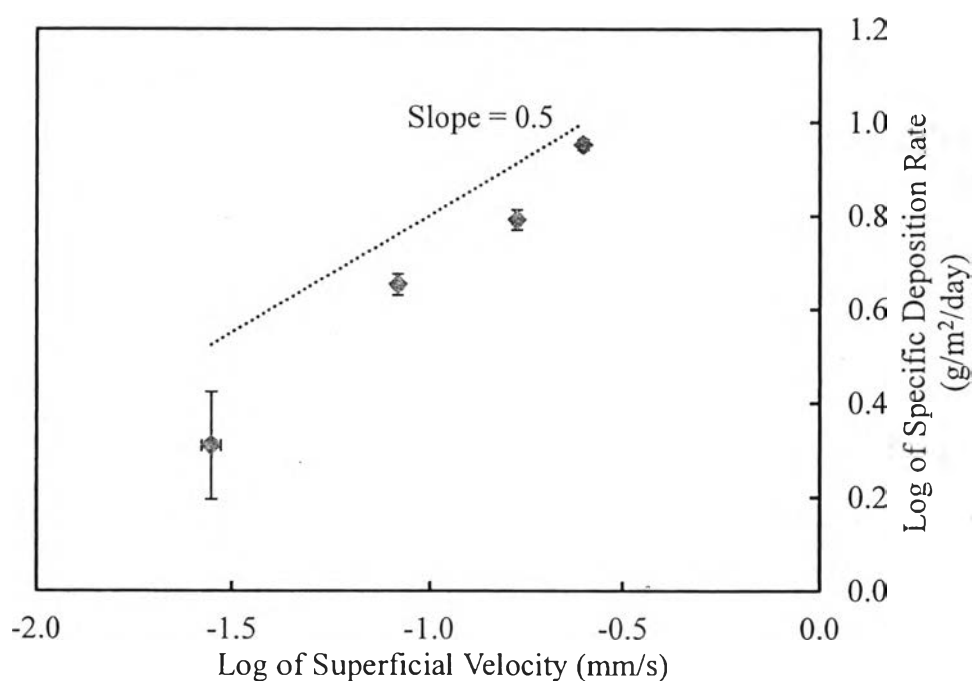

Figure 4.8 Log of specific deposition rate as a function of log of superficial velocity for 67 wt% heptane in Athabasca Diluted Bitumen at low superficial velocity regime.

The dependency of deposition rate of colloidal particles on the superficial velocity for the uniform flow with a simple geometry of surface is a power of 1/3 (Elimelech et al., 1995). The number of dependency observed from the packed-bed was different from the simple geometries in the literature. It is possibly due to the complexity of surface geometry of the packed-bed and flow pattern of fluid in the packed-bed. Hence, the correlation for mass transfer coefficient for packed-bed proposed by Thoenes and Kramers was instead used as a mass-transfer controlled asphaltene deposition model (Thoenes et al., 1957). The diffusion coefficient was used as a fitting parameter in the correlation which is expressed by,

$$Sh = 1.0Re^{\frac{1}{2}}Sc^{\frac{1}{3}}$$
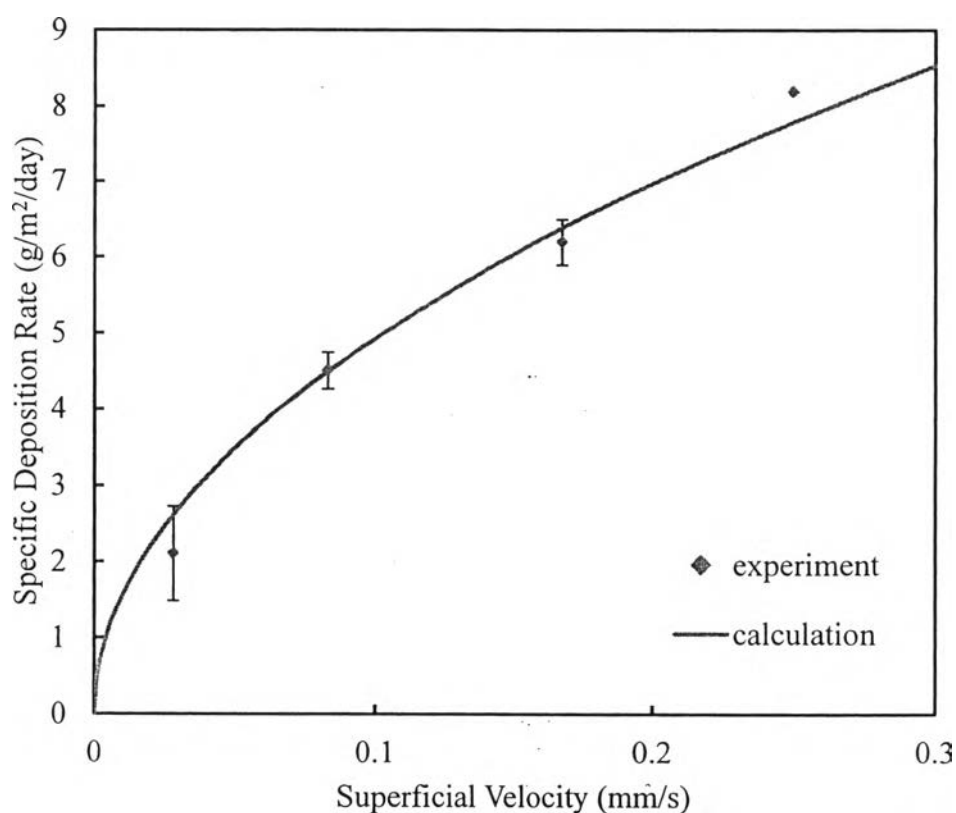(4.2)

Figure 4.9 The experimental specific deposition rate as a function of superficial velocity fitted with the calculation from the correlation of mass transfer coefficient for packed-bed in low superficial velocity regime.

The deposition rate as a function of superficial velocity calculated from the correlation fitted well with the experimental data as present in Figure 4.9. The adjusted diffusion coefficient had a value of 3×10^{-12} m^2/s. The equivalent asphaltene diameter was estimated from Stokes-Einstein equation by using adjusted diffusion coefficient in order to confirm whether the adjusted diffusion coefficient is reasonable. The equivalent diameter of asphaltenes was   which seems reasonable because the size of asphaltenes in crude oil-heptane solution used to perform all the experiments were kept well below 500 nm. Therefore, the diffusion coefficient obtained from the correlation was a realistic value. Moreover, the deposition limited by mass-transfer of asphaltene particles toward the surface in the low superficial velocity regime was further confirmed from these calculations.

4.2.2 Mechanism of Asphaltene Deposition at High Superficial Velocity Regime

The deposition rate in high superficial velocity regime was decreasing with increasing superficial velocity. The minimum specific deposition rate in this regime was 6.07 $g/m^2/day$ at a superficial velocity of 4.81 mm/s while the maximum specific deposition rate was 8.96 $g/m^2/day$ at a superficial velocity of 3.73 mm/s. The dependency of deposition rate in this regime on superficial velocity as shown in Figure 4.10 which is a power of -1.

The deposition behaviour in high superficial velocity regime cannot be explained by the mass-transfer or the surface attachment mechanism. However, this behaviour can possibly be explained by the competition between the effect of asphaltene attachment onto the surface and the effect of shear imposed by the fluid flow on depositing asphaltene particles. The similar trend was observed by Nabzar et al. and Akbarzadeh et al. in a porous media and couette device, respectively (Nabzar et al., 2008; Akbarzadeh et al., 2010). Although the mechanism of shear effect on deposition behaviour has not yet investigated, it could be the shear from flow inhibits the deposit to form at the first place or the deposit normally forms up to a certain thickness then it is sloughed off the surface by the shear of flow.
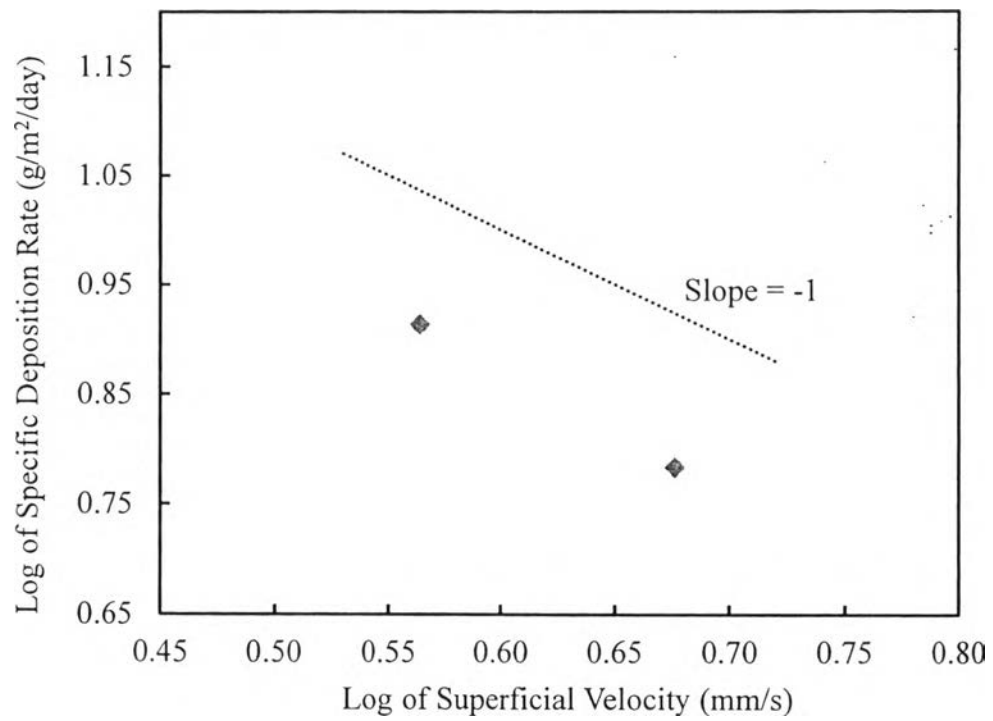
Figure 4.10 Log of specific deposition rate as a function of log of superficial velocity for 67 wt% heptane in Athabasca Diluted Bitumen at high superficial velocity regime.