



CHAPTER IV RESULTS AND DISCUSSION

4.1 Onset Point of Crude Oil Sample

Before running the asphaltene deposition experiment, it is important to determine the onset point in order to be able to choose the appropriate concentration to study. A sample from the effluent, taken by a micropipette, was placed under the microscope to detect precipitated asphaltenes; the point which asphaltene particles can be seen is called onset point. Precipitated asphaltenes can be seen as black particles under the microscope as shown in red circle of Figure 4.1 (d). The onset point for CH and GM3 was measured to be around 40 and 50 vol% C7 respectively. The results can be seen in Figure 4.1.

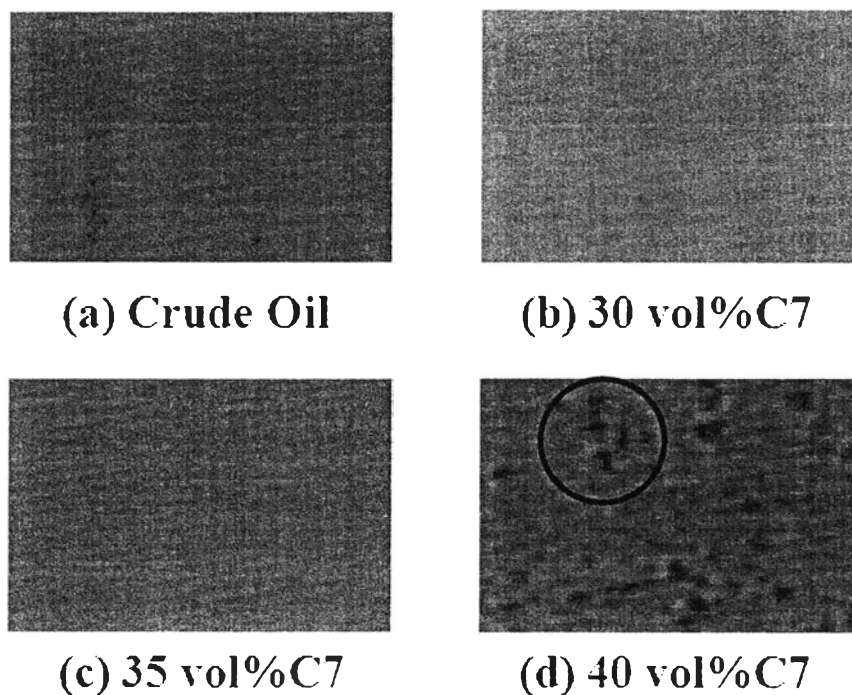


Figure 4.1 Micrographs showing the pictures of CH and precipitant's solution effluent of different concentrations (Onset point of CH is around 40 vol% C7).

Precipitation concentrations less than or equal to 30 vol% C7 were chosen in order to study conditions below the onset point for CH crude oil. For GM3, concentrations less than or equal 45 vol% C7 were used.

4.2 Modification of Apparatus

The primary goal of this work is to validate and standardize the deposition apparatus. As mentioned before, Hoepfner (2010) used CFD simulations to demonstrate that the oil:heptane mixture will be well mixed if a 2-inch stainless steel capillary with a 0.03-inch ID, connecting line, connects the mixing tee to the capillary as shown in the Figure 2.8.

4.2.1 Apparatus Modification 1

To improve the mixing in the system, a 2-inch connecting line was connected after the mixing tee, which contains the mixing frit. The experimental conditions for this work are as follows: 30 vol% C7, a 1-ft capillary with a 0.01-inch ID and 5 mL/hr as the total flow rate. The experiment results from the systems with and without connecting line were compared and shown in Figure 4.2.

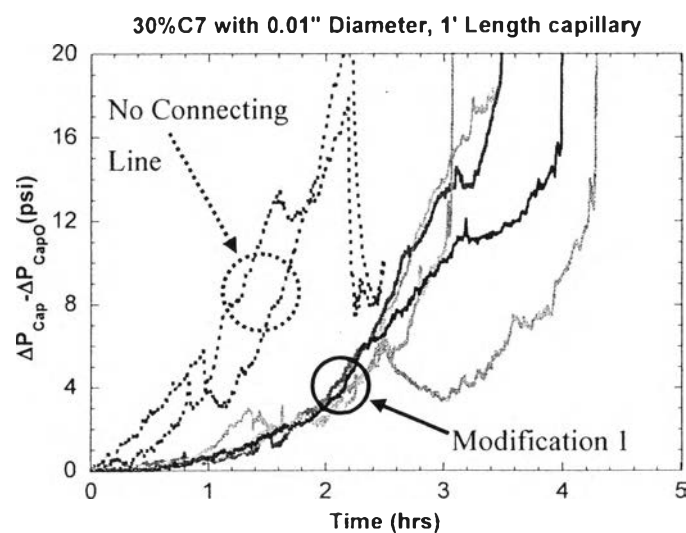


Figure 4.2 Comparison results between Modification 1 (solid line) and apparatus setup without connecting line (dot line).

Figure 4.2 presents the pressure drop (ΔP_{Cap}) shifted by the mean pressure drop of the solution before the deposition starts ($\Delta P_{\text{Cap}0}$). The time, $t=0$, is the time at which heptanes is first introduced into the system. The results from Modification 1 were more consistent than no connecting line setup because the solution was well mixed before flowed into capillary that made asphaltene particle was everywhere in solution. In the case of no connecting line, some asphaltene particles that destabilized from the interface of crude oil and precipitant before the solution was well mixed have a higher chance to adhere directly to the wall because crude oil and precipitant will diffusion to each other that made particles move along as well. Also the poor mixing will cause the pocket of heptanes in some point and cause the asphaltene comes out than it should.

4.2.2 Apparatus Modification 2

To improve the reproducibility, a 10 μm pre-filter was added before the connecting tee as shown in Figure 3.2. The purpose for adding the pre-filter is to prevent any asphaltene particle formed in the mixing section from flowing into the capillary. The results from Modification 2 (Figure 3.1) and the comparison with Modification 1 setup (Hoepfner, 2010 in Figure 2.8) are shown in Figure 4.3.

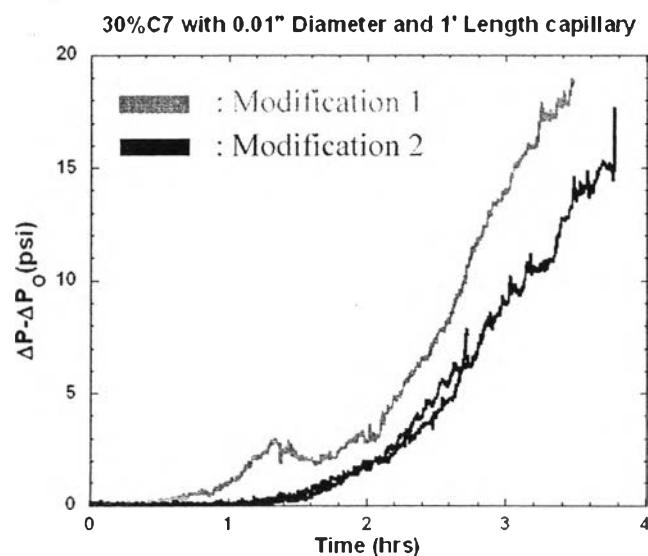


Figure 4.3 Comparison results between Modification 2 and Modification 1 setup.

The pressure drop from the Modification 1 appears to increase faster compared to the results using Modification 2. Two possible reasons for this delay with the pre-filter are that there could be deposition occurring in the connecting tee before the capillary or the pre-filter causes a lag time in the process. However, the pre-filter should not cause a significant difference because the residence time in the mixing system only increased slightly after adding the pre-filter (18.2 seconds compared to 17.5 seconds). The properties of the 10 μm pre-filter can be found in the reference from Hoepfner (2010). The residence time was calculated by Equation 6.

$$\text{Residence time} = \frac{\text{Volume of mixing section}}{\text{Volumetric Flow Rate (Q)}} \quad (6)$$

One major disadvantage of Modification 2 is that we cannot measure the effectiveness of the pre-filter. In order to understand how the pre-filter is operating, we incorporated a second pressure transducer to measure the pressure drop of the mixing section.

4.2.3 Apparatus Modification 3

As mentioned previously, another pressure transducer needs to be installed to further understand the mixing section. The second pressure transducer will be connected between the oil inlet line and the connecting tee. The schematic of this modification is shown in Figure 4.4.

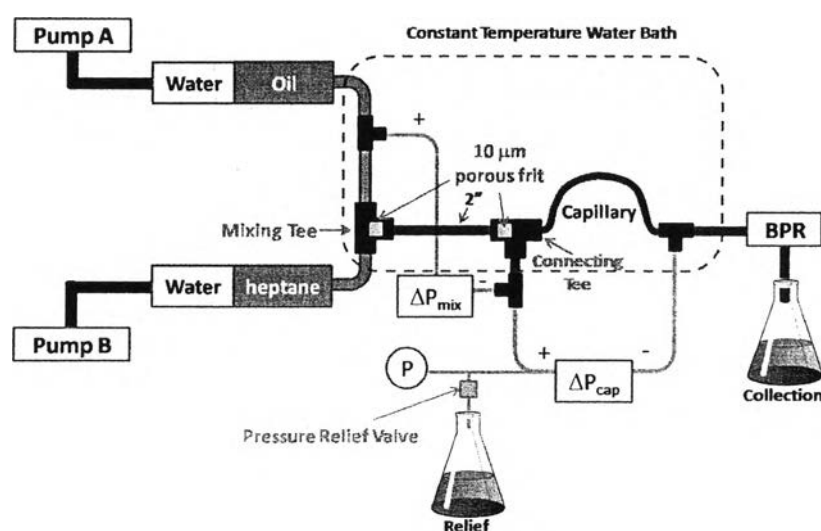


Figure 4.4 Asphaltene deposition apparatus (Modification 3: second pressure transducer was installed).

The experiments were performed at the same conditions as previous Modification 1. The example of results from Modification 3 is shown in Figure 4.5.

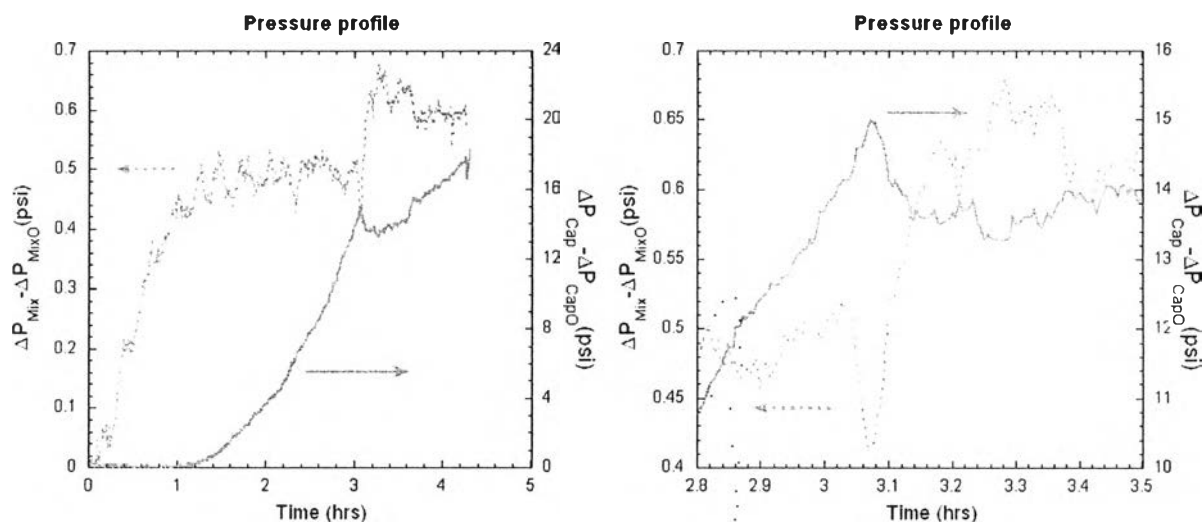


Figure 4.5 Sample of pressure profile from Modification 3. Dash line shows the pressure profile in mixing section while solid line shows in capillary.

The left y-axis in Figure 4.5 presents the pressure drop in mixing section (ΔP_{Mix}) shifted by the mean pressure drop of the solution before the deposition starts in the mixing section (ΔP_{MixO}). The time is shifted by when heptane is first introduced into the system. We can divide the left graph into two periods. In the first few hours, the results from the mixing section and the capillary show those deposits are forming in both sections. After few hours, as shown in Figure 4.5 (Right), the pressures in both sections fluctuated in different direction. A possible reason for this occurrence is that part of the asphaltene deposit formed in the mixing section caused a change in the velocity of the fluid entering the system. This surge is temporary and the system will return to normal operating conditions. The magnitude of the fluctuations is small with respect to the overall pressure drop induced by asphaltene deposition in the capillary.

4.2.4 Comparison Results from Modification 2 and 3 with Modification 1

Figure 4.6 shows a comparison of the results from the Modification 1, Modification 2 and Modification 3. We can conclude that the results, including the pre-filter's setup, appear to generate more reproducible results but this observation

needs to be investigated further to validate this conclusion. Even with the small difference results in Figure 4.6, the reproducibility is significantly improved from Boek *et al.* (2008).

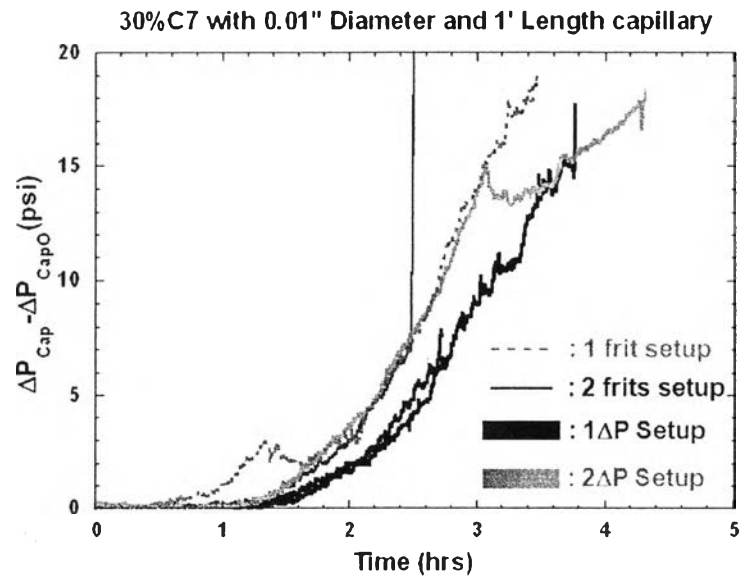


Figure 4.6 Comparison of all the 30 vol% C7 results from every setups.

4.2.5 Effect of Mixing Frit

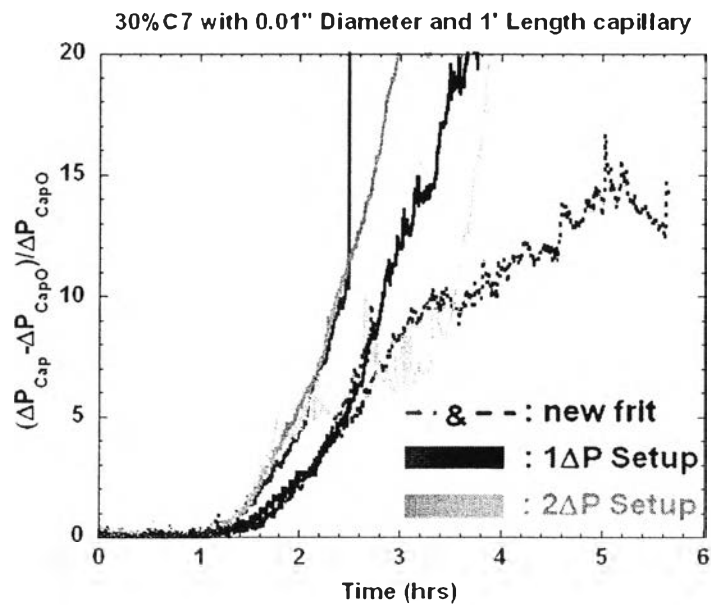


Figure 4.7 Comparison of the results of new and reused mixing frits.

From the results of Modification 2 and 3, we can see that the results separate into two groups. First group is the results that deposits occurs faster and second is the slower one, as shown in Figure 4.7. The experiments that used a new mixing frit, located in the mixing tee, started to deposit slower than the runs with a washed and reused frit which means the frits can't completely clean so future experiments will use a fresh mixing frit each time.

4.3 Precut Capillary

The differences of lag time in previous results, i.e. Figure 4.6 and Figure 4.7, may have been as a result of roughness introduced in the capillary during the cutting process by rotary cutter and hole drilling by microdrill so the precut capillaries, which have smoother surface compared to cut capillaries, should be the key to solve this problem.

To prove this hypothesis, a precut capillary was used to run under same conditions as the cut capillary: 30 vol% C7 with 5 mL/hr flow rate. The results can be seen in Figure 4.8.

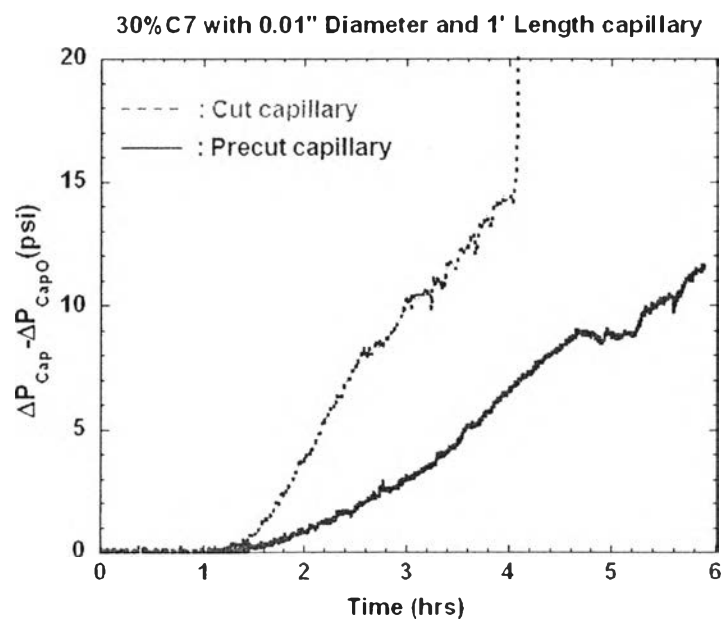


Figure 4.8 Comparison of the results between cut capillary and precut capillary.

The deposition started to occur slower in case of precut capillary which indicate that the roughness of the cut capillary may have aided deposition process. A possible mechanism is that unstable asphaltenes adhere to the rough surfaces more easily than smooth surfaces and the subsequent attachment of other asphaltene particles.

4.4 Asphaltene Deposition in Different Precipitant Concentration

Figure 4.9 shows the results of asphaltene deposition in different precipitant concentrations from onset point and below of CH crude oil that have been done with 1-ft precut capillary.

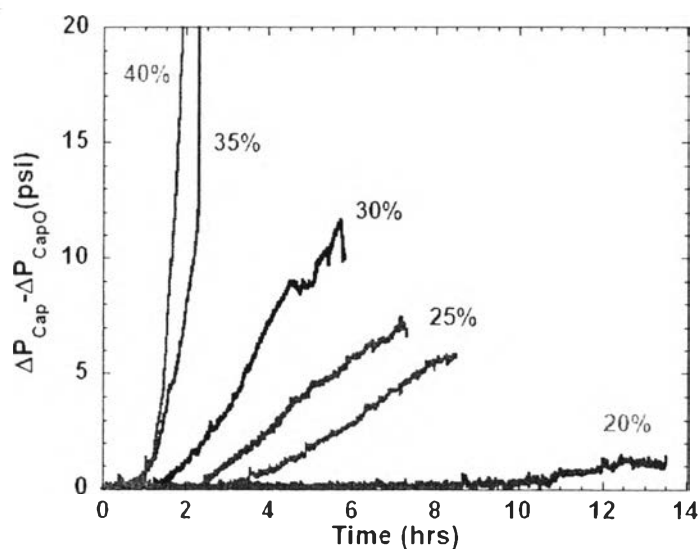


Figure 4.9 Deposition results from 20 vol% to 40 vol% C7 (onset point).

From the results in Figure 4.9, the deposition process occurred faster in the cases when more unstable asphaltenes separate from the crude oil. For 35 vol% C7, the precipitated asphaltenes can't be seen under microscope, smaller than $0.5 \mu\text{m}$, as shown in Figure 4.1 but the deposition trend was almost the same as 40 vol% C7 which means the deposition doesn't need the large particle to start the deposition process and asphaltenes can deposit before they grow to a detectable size. However, asphaltene deposition still occurs although the little amount of precipitant was added.

4.5 Asphaltene Deposition Uniformity and Location

We want to know how deposition form and where it belongs inside capillary so the short and long precut capillary, 2-in and 12-in capillary, were used in this experiment under 30 vol% C7 with 5 mL/hr flow rate. The results were shown in Figure 4.10.

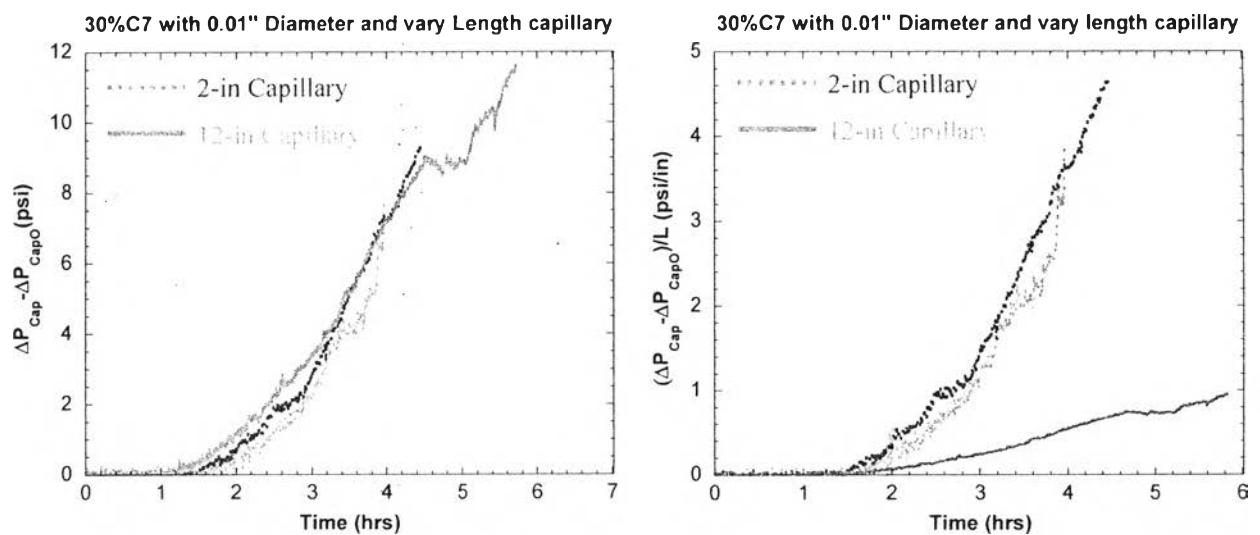


Figure 4.10 Deposition results from 2-in and 12-in capillary.

From Hagen-Poiseulle Equation, (1), length can be cutted in case of uniform deposit. The y-axis from Figure 4.10 (R) shows the pressure drop scaled by length to prove the deposit was uniform or not and we can see that the deposit wasn't uniform at all. In other hand, the results from Figure 4.10 (L) showed the results which almost lies on each other that meant the deposit occurred within the first 2 inches of capillary.

4.6 Extend Study to Second Crude Oil, GM3

From the experiment with CH, Modification 3 was the best apparatus. To fully validate this apparatus, we need to perform experiments with other crude oils as well. A low asphaltene content crude oil, GM3, was used for this experiment. The asphaltene content and viscosity in second oil is less than CH almost 4 times and 2

times respectively. The experiments were done in the Modification 3 (Normal setup for GM3), Modification A and Modification B. Full apparatuses can be seen in Appendix B. Connecting line and second pressure transducer were used in every setup. The results can be seen in Figure 4.11.

Table 4.1 Summary of asphaltene deposition apparatus for GM3 crude oil

Apparatus for GM3	Compare with CH experiment
Normal setup	Same as Modification 3
Modification A	Same as Modification 1
Modification B	Same as Modification 1 but no mixing frit

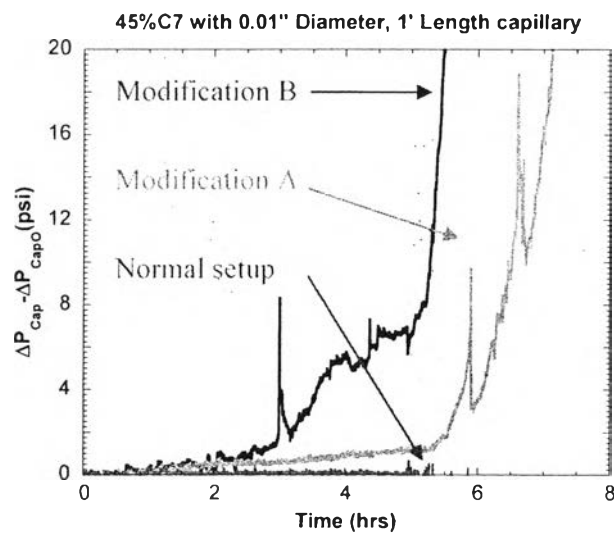


Figure 4.11 Comparison results between normal setup, Modification A and Modification B.

The deposition occurs inside capillary when Modification A and Modification B were applied. The slower mixing, no mixing frit helped mixing both solutions into each other, in Modification B may be the possible reason why deposition was faster than Modification A. In case of Normal setup, pre-filter possibly acted as a sink for asphaltenes to deposit.

To understand more what's happen with GM3, the pressure profile in mixing section needed to study too. The results of these three setups were shown in Figure 4.12.

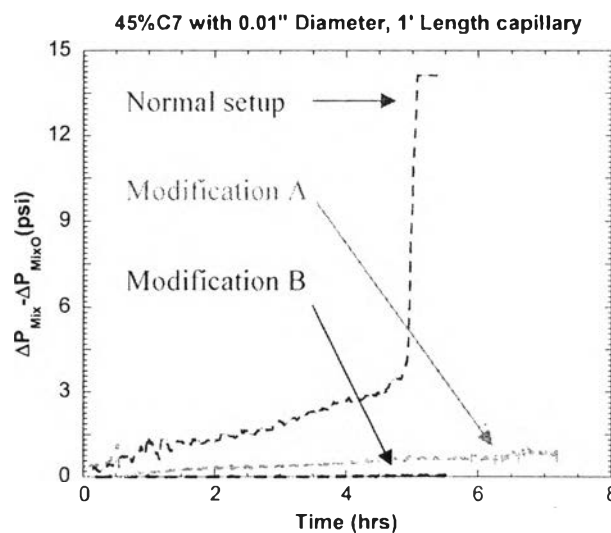


Figure 4.12 Comparison results of mixing section between Normal setup, Modification A and Modification B.

Most of the deposition occurred in the mixing section just only when Normal setup was applied but there was the small deposit or nothing in other setup's experiment as shown in Figure 4.12. We didn't know exactly why it happened like this. All we know was that the pressure drop in the mixing section was from the frits and that having two frits prevents deposition from occur in the capillary. For Modification A and Modification B's results, there was a deposit happen when mixing frit was added. The possible reasons were asphaltene can adhere inside the mixing frit or the mixing frit helped the solutions to have better mixing then asphaltene will destabilize faster.

From Figure 4.11 and 4.12, the appropriated apparatus for GM3 should be Modification A because there was the deposition in both mixing section and capillary same as the results from CH experiment. When crude oil and heptanes contact with each other, the asphaltene particles should come out and start to deposit because of this reason that's why Modification B wasn't good enough.

4.7 Comparison Results from CH and GM3 Crude Oils

Both crude oils were studied below onset point with the same experimental conditions such as temperature and total flow rate. From previous sections, we can see the deposition occurred inside the mixing section, when mixing frit was added. The mixing frit may improved mixing the solution or acted like a sink for asphaltene to deposit inside. In the other hand, the first purpose of pre-filter for CH experiment was prevent the formed asphaltene flowed into capillary but it looked like the best place to form deposition in GM3 experiment as we can seen in Figure 4.11 and 4.12. The reasons for these results may be happen due to the different in viscosity and amount of asphaltene content in crude oil. Oil and heptanes will diffuse into each other better when the lower viscosity crude oil was used. Asphaltene may help other particles stable with each other so the deposition in higher asphaltene content will occur slower. For CH, the deposition inside capillary with Modification 2 occurred slower than Modification 1. Maybe the asphaltene in CH also deposited inside pre-filter as well but less significant compare to GM3.

From these two crude oils, we have to adapt the apparatus in each crude oil for finding the best apparatus.