Supporting information for:

A Fundamental Study of Asphaltene Deposition

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1 Preliminary CFD Mixing Investigation

To investigate the mixing in the capillary deposition apparatus, computational fluid dynamic (CFD) simulations were performed on the mixing tee and connecting line. The goal was to determine if the oil and heptane were fully mixed at the desired bulk composition when the mixture enters the capillary. The simulation was performed in FLUENT v.12.0.16 using the following settings: 3D, laminar, pressure based and species. The grid was generated with GAMBIT v.2.4.6 and consisted of 242,654 tetrahedral cells. The mixing frit was modeled as porous media (porosity = 0.35, random close packed spheres) and no additional structural features of the frit were considered.

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Simulating the frit in this manner will represent the “worst possible case scenario” for system mixing because none of the advantageous structural features of the frit are represented and only the superficial velocity is increased in the frit. The mixing system consists of oil and heptane inlet lines (0.03” ID) connected to the mixing tee (round 0.02” ID thru holes). The frit is cylindrical (1/16” in diameter and 1/16” in length) and located at the outlet of the thru hole. The connecting line is a 5 cm section of 0.03” ID capillary. The true length of the connecting line in experiments is 5 cm, however, the CFD simulation used a 2” length section. The difference between 5 cm and 2” is less than 2% and the difference will not influence the conclusions of the CFD simulation results. The oil and heptane entrance lines were sufficiently long in order to ensure that each line had fully developed hydrodynamics by the entrance of the mixing tee.\textsuperscript{S1}

The diffusivity for heptane in oil was estimated by the Hayduk-Minhas correlation and was calculated to be $4.04 \times 10^{-10}$ m\(^2\)/s.\textsuperscript{S2,S3} Heat capacities and thermal conductivities were not considered because the simulation was performed isothermally at 60°C. Table S1 lists the required material properties used in simulation and Figure S1 shows both the results and dimensions of the mixing system.

Table S1: Input Parameters for CFD Simulation

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density (kg/m(^3))</th>
<th>Viscosity (mPa(^s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>869</td>
<td>8.93</td>
</tr>
<tr>
<td>Heptane</td>
<td>680</td>
<td>0.276</td>
</tr>
</tbody>
</table>

**CFD Simulation Results** The CFD simulation result converged to an acceptable level and the results can be seen in Figures S1 and S2. Three important views of the mixing system are presented. The top view, Figure S1, shows a horizontal cross section of the oil (from the right) and heptane (left) mixing in the frit and connecting line. Heptane is less dense than oil, and thus due to the low flow rate, gravitational flow is significant. The side view (Figure S2 - Left) clearly indicates that the concentration of heptane is higher near the top of the mixing frit and at the solution is not well mixed by the exit of the frit. As can be seen in the outlet cross section (Figure S2 - Right), the oil
and heptane are homogenous by the outlet of the mixing section, in support of good mixing for the deposition experiments.

Figure S1: Top view of the CFD simulations of the mixing system. NOTE: the connecting line extends for 5 cm but not all of the result was shown due to the large aspect ratio.

Figure S2: Side view (left) and outlet view (right) of the CFD simulations of the mixing system. NOTE: the connecting line extends for a full 5 cm but figure was shortened due to the large aspect ratio. By the time the mixture reaches the outlet, it is completely mixed.

2 Deposit Location Pressure Drop Comparisons

To determine the uniformity or the location of the asphaltene deposit axially, independent experiments were performed in a long and short capillary. Four scenarios are possible for the deposit to form inside a capillary:
1. The deposit is uniform along the length of the capillary

2. The deposit is non-uniform and contained entirely in the length of the short capillary

3. The deposit in non-uniform and present in both the initial short section and the long section

4. The deposit is non-uniform and present near the outlet of the long capillary, with no deposition near the inlet in the short section

First, if the deposit is uniform along the length of the capillary, the pressure drop as a function of time scaled by the length will be the same for a long or short capillary. This can be seen by comparing the Hagen-Poiseuille equation for a long and short capillary:

\[ \Delta P_{\text{Long}}(t) = \frac{8\mu L_{\text{Long}}Q}{\pi r_{\text{Long}}^4(t)} \]  

\[ \Delta P_{\text{Short}}(t) = \frac{8\mu L_{\text{Short}}Q}{\pi r_{\text{Short}}^4(t)} \]  

where, \( \Delta P \) is the pressure drop through the capillary, \( \mu \) is the viscosity, \( Q \) is the flow rate and \( r \) is the capillary radius. If the deposit is uniform, the radius will be changing the same between the long and short capillary and uniformly along the length of the capillary:

\[ r^4(t) = r_{\text{Long}}^4(t) = r_{\text{Short}}^4(t) \]  

Solving the pressure drop equations of the long and short capillary for \( r^4(t) \) yields:

\[ \frac{8\mu L_{\text{Long}}Q}{\pi \Delta P_{\text{Long}}(t)} = \frac{8\mu L_{\text{Short}}Q}{\pi \Delta P_{\text{Short}}(t)} \]  

It is clear that once you eliminate the flow rate, viscosity and constants that the following relation exists for a uniform deposit is capillaries of two lengths are compared:

\[ \frac{P_{\text{Long}}(t)}{L_{\text{Long}}} = \frac{P_{\text{Short}}(t)}{L_{\text{Short}}} \]
The second possibility is if the deposit is non-uniform enough that it is entirely contained within the short capillary and preferentially forms near the inlet. To determine the relationship between a long and short capillary, let’s assume that the capillary is split into two sections: the first section contains the entire deposit, “Deposit” and the second contains no deposit “Clean”. Neglecting and pressure drop associated with expansion, the Hagen-Poiseuille can be split into the pressure drop from the two sections.

\[
\Delta P(t) = \frac{8 \mu L_{\text{Deposit}} Q}{\pi r_{\text{Deposit}}^4(t)} + \frac{8 \mu L_{\text{Clean}} Q}{\pi r_{\text{o}}^4(t)} = \frac{8 \mu Q}{\pi} \left( \frac{L_{\text{Deposit}}}{r_{\text{Deposit}}^4(t)} + \frac{L_{\text{Clean}}}{r_{\text{o}}^4(t)} \right) \tag{6}
\]

At the start of the experiment there is no deposit, and an initial pressure drop, \(\Delta P_o\) can be measured:

\[
\Delta P_o(t) = \frac{8 \mu L Q}{\pi r_{\text{o}}^4(t)} \tag{7}
\]

\[L = L_{\text{Deposit}} + L_{\text{Clean}} \tag{8}\]

where \(r_o\) is the initial radius. If we shift both the long and short capillaries by their initial pressure drops:

\[
\Delta P_{\text{Short}}(t) - \Delta P_{o,\text{Short}}(t) = \frac{8 \mu Q L_{\text{Deposit}}}{\pi} \left( \frac{1}{r_{\text{Deposit}}^4(t)} - \frac{1}{r_{\text{o}}^4} \right) \tag{9}
\]

\[
= \frac{8 \mu Q L_{\text{Deposit}}}{\pi} \left( \frac{1}{r_{\text{Deposit}}^4(t)} - \frac{1}{r_{\text{o}}^4} \right) \tag{10}
\]

\[
\Delta P_{\text{Long}}(t) - \Delta P_{o,\text{Long}}(t) = \frac{8 \mu Q L_{\text{Deposit}}}{\pi} \left( \frac{1}{r_{\text{Deposit}}^4(t)} - \frac{1}{r_{\text{o}}^4} \right) \tag{11}
\]

\[
= \frac{8 \mu Q L_{\text{Deposit}}}{\pi} \left( \frac{1}{r_{\text{Deposit}}^4(t)} - \frac{1}{r_{\text{o}}^4} \right) \tag{12}
\]
Both the long and short capillary equations reduce to the same form, and we can thusly conclude that:

\[ \Delta P_{Long}(t) - \Delta P_{o,Long}(t) = \Delta P_{Short}(t) - \Delta P_{o,Short}(t) \]  \hspace{1cm} (13)

The relation above says that if we compare \( \Delta P(t) - \Delta P_{o}(t) \), as is the standard procedure for the pressure drop results, the results from a long and short capillary will be the same if the second case is occurring.

The third scenario is where the deposit forms non-uniformly but the deposit is not entirely contained within the short capillary. In such a case, neither the scaling or shifting derived above for the first and second scenarios will unify the long and short capillary results. The fourth scenario is where the deposit exists near the outlet of the long capillary, in which case, no deposition will be measured in the short capillary.

**References**

