Title: An Automated Microfluidic System for the Investigation of Asphaltenes Deposition and Dissolution in Porous Media

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Section 1. Fabrication Procedure for the AUTO³-µPBR

The fabrication of the microfluidic device followed a standard microelectronic process briefly described below:

I. **Negative Photoresist Patterning:** The negative photoresist SU-8 50 was spin coated onto the first side of the silicon wafer. The coated silicon wafer was then soft baked in an oven at 65 °C for 5 mins and 95 °C for 15 mins in that order. The baked silicon wafer was then exposed to a constant dosage of 220 mJ/cm² UV source through the EVG620 Mask Aligner. A 1-min and 6-min post-exposure bake was applied to the exposed silicon wafer in an oven at 65 °C and 95°C, respectively. The 54-µm thick pattern was developed by immersing the silicon wafer into SU-8 developer for 6 mins.

II. **Deep Reactive Ion Etching (DRIE):** The patterned silicon wafer was etched at a rate of about 2.8 µm/min for 250 min in the Oxford PlasmaPro System 100 Cobra through the BOSCH process. After the completion of the etching process, the residual photoresist was cleaned by Piranha solution.

III. **Positive Photoresist Patterning:** The positive photoresist AZ9260 was spin coated onto the second side of the etched silicon wafer after applying the primer hexamethyldisilazane (HMDS). The coated silicon wafer was then soft baked in an oven at 65 °C for 5 mins and 95 °C for 30 mins in that order. The baked silicon wafer was exposed to a constant dosage of 1600 mJ/cm² UV source through the EVG620 Mask Aligner. The 14.2-µm thick pattern was developed by immersing the silicon wafer into AZ-400K for 8 mins. A hard bake at 110 °C was applied afterward.

IV. **Deep Reactive Ion Etching (DRIE):** The patterned silicon wafer was etched at the rate around 2.8 µm/min for 110 min in the Oxford PlasmaPro System 100 Cobra through the BOSCH process. After the completion of etching process, the residual of photoresist was cleaned by Piranha solution.

V. **Plasma Enhanced Chemical Vapor Deposition (PECVD):** A thin layer of 0.5 µm silicon dioxide was deposited onto the second side of the silicon wafer through plasma-enhanced chemical vapor deposition. (Oxford PlasmaPro System 100 PECVD)

VI. **Anodically Bonding:** A 1.5 mm thick Pyrex glass wafer was anodically bonded to the second side of the silicon wafer in the EVG501 Wafer Bonding System. The devices were then obtained by dicing the stack of wafer in the Disco DAD3220.
Section 2. Design and characterization of AUTO³-µPBR

Figure S.1 (a) Pressure test of the AUTO³-µPBR. The ultimate operating pressure was seen at 15.39 bar, after this the reactor cracked at the inlet of the channels. (b) Photo of the resulting crack from the pressure test.

Figure S.2 (a) Temperature profile of microsystem at set temperature of 423 K. The results are simulated by COMSOL Multiphysics. (b) Temperature profile of different regions of the AUTO³-µPBR.
Figure S.3 (a) Photo of the temperature test setup done for the AUTO$^3$-μPBR. (b) IR imaging was used in testing the homogeneity of the temperature distributions and the stabilization time for a set temperature of 60 °C. The images show a homogenous temperature distribution within our reaction zone.

Figure S.4 IR images of the temperature distribution at different times. The reactor took a total of about 60 seconds to reach the target temperature and about 12 minutes to reach temperature stabilization (<1°C fluctuations).
Figure S.5 (a) Temperature fluctuations from IR images up to 10-hour period. Temperatures show little fluctuations after reaching temperature stabilization time. (b) Temperature graphs for one-hour period. Sharp temperature declines were seen at the 0.2-hour mark due to a slight malfunction of the temperature sensor, swift corrections were implemented and corrected the detachment of the sensor. (c) Close up image of the temperature graph for 10-hour period. Fluctuations were minimal and within acceptable range (<1°C).
Section 3. RTD acquisition procedure

The RTD of the AUTO$^3$-μPBR was obtained using a traditional pulse tracer method. To start, the mean residence time was first experimentally measured for the RTD system without the reactor and chuck by direct connection of tubing with an inner diameter of 0.005” at a constant flow rate of 40 μl/min. The tracer species, acetone was injected using a microinjector (IDEX Health & Science, Oak Harbor, WA, USA) with a sample loop of 1.0 μl. The injection was tracked for a total of 30 minutes, noting that the time starts once the acetone is introduced into the main line, upstream of the region of interest. The absorbance values were directly translated as concentration measurements and were converted into unitless E(t) values by the following:

\[ E(t) = \frac{C(t)μ}{\sum C(t)μ} \]  \hspace{1cm} (S1)

The reactor and chuck were then connected to the region of interest and the mean residence time was measured using the same procedure described above for an empty reactor (EμPBR) and packed bed reactor(μPBR). The mean residence time was calculated for each set of data by the following equation:

\[ τ = \int tE(t) \]  \hspace{1cm} (S2)

It was found that the RTD system, without the reactor connected to it, had a residence time of 10.04 minutes. Once the reactor chuck was connected this time was extended to 12.22 minutes and the inclusion of the packed bed resulted in a residence time of 12.15 minutes. From these measurements it is clear that the time difference between the EμPBR and μPBR reflects the packed bed region and translates to approximately 2.48 μl, which gives us a void fraction for the packed bed of 0.45 and a residence time of 3.72 seconds.

![Figure S.6 Residence time distribution (RTD) measurements of AUTO$^3$-μPBR under three different setups: the system without AUTO$^3$-μPBR, with empty AUTO$^3$-μPBR, and with packed AUTO$^3$-μPBR. The volume of the system was calculated by flow rate and mean residence time. The volume of microsystem, AUTO$^3$-μPBR and packing were calculated to be 87.08 μL, 16.43 μL and 2.48 μL respectively. The resultant porosity is about 44.85%](image)

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Section 4. Experimental setup and process flow diagram

Figure S.7 Process flow diagram of automated fluid delivery system.
Section 5. Influence of system priming to the dissolution

**Figure S.8** Photos of the reaction channel after the system priming step. The priming step cleans out the low occupancy regions and provides a baseline for dissolution.
Section 6. Fluorescence of asphaltenes

Figure S.9 (a) Optical images of asphaltenes in toluene samples at different concentration. (b) Fluorescence emission spectra of asphaltenes samples with different concentration at the incident light of 532 nm. When the concentration is below 80 mg/L, the fluorescence intensity increases as the concentration increase. When the concentration is larger than 80 mg/L, the fluorescence intensity decreases as the concentration increase. At concentration above 640 mg/L, the fluorescence intensity is negligible.
Section 7. Complete data set of occupancy at different regions

Figure S.10 Complete data set of occupancy at different regions on AUTO$^3$-μPBR.
Section 8. Sheet size of asphaltenes at different regions

Figure S.11 (a) An example of histogram of sheet sizes at xylenes palpable region and its corresponding normalized distribution for Depo45. The normalized distribution of sheet size at xylenes palpable region, impalpable region, and before dissolution for (b) Depo25, (c) Depo35, (d) Depo45, (e) Depo 55, and (f) Depo 65.