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In situ Analytical TEM of Asphaltene Formation and Aggregation from Crude Oil

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Asphaltenes are aromatic hydrocarbons found in crude oils or carbonaceous materials. They are characterized by complex chemistry and their presence in crude oils impacts the oil properties. Phase changes, viscosity, and interfacial properties of crude oils are strongly affected by asphaltenes and, perhaps most importantly, they tend to clump together when exposed to changes in temperature and pressure, such as in pipelines pumping oil up out of underground reservoirs [1]. It is this aggregation of the particles that makes asphaltenes such a problem, once they have come together, they aggregate further and further until they begin to depose onto the walls of the pipe. This poses an obvious issue to oil production, not just in the primary pipelines that first transport the oil (the "upstream" sector) but also in the transportation of that oil and finally the refining of the oil (the "midstream" and "downstream" sectors, respectively) [2]. Therefore, preventing flocculation of asphaltene in crude oil is an important goal.

Extensive research has been performed in the last years to study the molecular and colloidal structure of asphaltenes. Many models have been proposed [3], however what is known as the Yen model and later the modified Yen model (also known as the Yen-Mullins model) is one of the longest enduring and most widely adopted models of asphaltene formation [4,5]. This model proposes that there are three stages to asphaltene aggregation, firstly the ~1.5 nm asphaltene molecule on its own; a cluster of arene rings with substituent alkanes around its edge. These asphaltenes then stack up into ~ 2nm nanoaggregates, a long and thin structure with the same alkane offshoots. These nanoaggregates then stick together to form what are known as the clusters of nanoaggregates. The clusters are most likely fractal, and the smallest size of clusters is ~6 nm. Depending of the instability of asphaltenes in the crude oil, larger clusters with dimensions from tens of nanometers to macroscopic scale can form [5].

TEM images of asphaltene have already been obtained and used in asphaltene research to understand the mechanisms of flocculation, aggregation and precipitation [6]. However, the disadvantage is that the sample may be altered during the sample preparation. *In situ* analytical TEM has huge potential to permit direct observations of the oil emulsion system at the nm scale, without the requirement of sample pre-treatments, which may be able to have an affect of the structural and chemical evolution of the sample.

Initial *in situ* TEM experiments of asphaltene formation and aggregation were conducted in a FEI Talos F200X TEM operated at 200 keV using the Protochips Poseidon P210 analytical liquid cell holder. Crude oil with a nominal asphaltene content of 3.7% were mixed with heptane to initiate flocculation of the asphaltenes in the liquid *in situ* cell. Our first results providing novel insights into the mechanisms of asphaltene flocculation, aggregation in oil + heptane emulsion. Figure 1 shows the further development of asphaltene coalescence of an agglomerate after 4 h in the oil + heptane emulsion and after 1 and 3 min under the electron beam. The aggregation process is driven by the initial formation of 10-20 nm

spherical clusters. These clusters agglomerated into larger globular structures. The observed flocculation sequence follows the proposed Yen model. However, the size of the initial clusters is slightly larger compared to the proposed model. The size of the aggregates and also the precipitation rate is likely to be influenced from the electron beam and will be further investigated.

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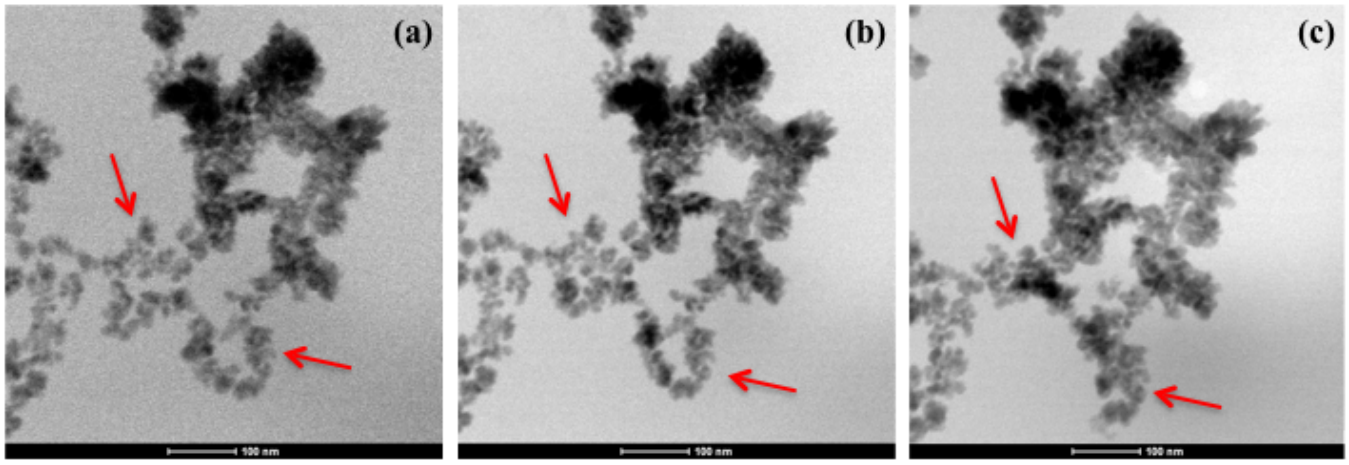

Figure 1. *In situ* STEM-BF images showing the further development of asphaltene coalescence of an agglomerate after 4 h in the oil + heptane emulsion (a) and after 1 min (b) and 3 min (c) under the electron beam. The aggregation process is driven by the agglomeration of 10-20 nm asphaltene clusters (marked by red arrows).

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