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# Characterisation of Asphaltenes Extracted from an Oil Sand and Two Petroleum Vacuum Residues Using HRTEM

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**Abstract**

This paper reports findings from a preliminary study into the stacking characteristics of asphaltenes extracted from an oil sand and two petroleum vacuum residues. The stacking morphology was examined using high resolution transmission electron microscopy (HRTEM). The stacking parameters of the three samples including the average stacking number, the average interlayer spacing and the average layer size were estimated. The results showed that the asphaltenes extracted from the petroleum vacuum residues possessed higher stacking numbers with smaller interlayer spacing as compared to the asphaltene from the oil sand. This indicates that the intermolecular forces of the petroleum vacuum residue asphaltenes are stronger than that of the oil sand. The average layer size across the samples is ca. 0.9 nm, implying the average PAH size of 6~7 fused rings for all samples.


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*Keywrods:* Asphaltenes; HRTEM; Molecular structure; Oil sand; Vacuum residue

## 1. Introduction

Oil sand comprises a significant proportion of the world's oil reserves [1, 2]. The extraction and processing of hydrocarbons from oil sands are very challenging due to the presence of asphaltenes, the most refractory species causing most of the processing problems. Hence investigating and understanding the mechanism of asphaltene aggregation as well as remediation of asphaltene deposits are of great practical significance and economic value. Although there has been remarkable progress in the understanding of several fundamental properties of asphaltenes [3, 4], the molecular structures of asphaltenes are still poorly understood. While extensive studies [5-11] have been carried out on coal-derived asphaltenes and petroleum asphaltenes using high resolution transmission electron microscopy (HRTEM) to study their aggregation characteristics, research efforts on studying oil sand asphaltenes are

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also called for.

In this work, HRTEM was adopted to study the stacking characteristics of asphaltene samples from an oil sand and two petroleum vacuum residues. The TEM images were converted to binary images and subsequently measured manually. A set of stacking parameters including the average stacking number, the average interlayer spacing and the average layer size, were estimated. It was expected that by comparing the stacking characteristics of the asphaltenes from different origins, this work would provide new insights into aggregation mechanism of the asphaltenes.

## 2. Experimental

### *2.1. Materials*

The asphaltene samples were extracted from three sources of different origins: Buton Oil Sand from Indonesia (Buton), a vacuum residue from Liaohe Petroleum Refinery, China (Liaohe), and a vacuum residue from Vene Petroleum Refinery, Venezuela (Vene). The "run of mine" Buton Oil Sand was first crushed and pulverised into fine powders with sizes <200 μm, which was then subjected to solvent extraction using toluene in a Soxhlet extractor to obtain the organic fraction. This organic fraction was further subjected to asphaltene extraction, along with the two vacuum residues provided by China University of Petroleum, Beijing.

The asphaltene fractions were isolated from these three sources in accord to the method prescribed by the ASTM D-3279. Briefly, a sample of the organic fraction of Buton or the vacuum residues was firstly subjected to Soxhlet extraction using *n*-heptane as the solvent for at least 48 hours until no discoloration was observed in the reflux. The extraction was then continued by replacing *n*-heptane with toluene as the solvent for a further period of at least 8 hours till no further discoloration. The final extract was filtered, evaporated to dryness at 40°C using a rotary evaporator and further dried at 100°C under vacuum in an electric oven. The asphaltene samples thus prepared were collected in clean glass vials, sealed and stored in darkness before further characterisation and analysis.

Table 1. Elemental composition of the three asphaltene samples.

| | Liaohe | Vene | Buton |
|---|---|---|---|
| Elemental analysis (wt%) | | | |
| Carbon | 86.32 | 82.85 | 75.06 |
| Hydrogen | 8.30 | 7.93 | 7.86 |
| Nitrogen | 2.19 | 1.82 | 0.83 |
| Sulphur | 0.29 | 5.06 | 8.35 |
| Oxygen (by diff.) | 2.91 | 2.35 | 7.91 |
| H/C atomic ratio | 1.16 | 1.15 | 1.26 |
| Metals (wppm) | | | |
| Sodium | 13.6 | 11.8 | 8.21 |
| Nickel | 6.57 | 4.93 | 1.16 |
| Vanadium | 0.25 | 26 | 1.94 |

### *2.2. Materials characterisation*

The organic elemental compositions of the three asphaltene samples were obtained using a PerkinElmer 2400 Series II CHN elemental analyser following ASTM D-5291. The sulphur contents were measured according to ASTM D-4294 using a Sande KZDL-5000 sulphur analyser. In addition, Na,