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Characterisation of subfractions of asphaltenes extracted from an oil sand using NMR, DEPT and MALDI-TOF

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ABSTRACT

This paper reports the findings of an investigation into molecular structures and properties of an oil sand asphaltene sample and its subfractions. The asphaltene sample extracted from Buton Oil Sand (Indonesia) was fractionated stepwise into four subfractions by precipitation in a binary solvent system made from mixtures of dichloromethane/*n*-heptane with volumetric ratios of 30/70, 20/80 and 10/90, respectively. The average molecular structural parameters, including the average polycyclic aromatic hydrocarbon size, average side chain length and average molecular weight of the oil sand asphaltene sample and its subfractions, were measured and compared, using characterisation data obtained from nuclear magnetic resonance in combination with distortionless enhancement by polarisation transfer. The molecular weight distributions of the asphaltene samples were measured using a matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry. The results indicated that the island molecular architecture was featured in all the asphaltene samples. The average polycyclic aromatic hydrocarbon size was found to be 7 rings for the least soluble subfraction, 6 rings for the other subfractions and the oil sand asphaltenes. The fractionation mechanism was dictated by polarity difference amongst subfractions as a result of relative luxuriance of the aliphatic parts. The use of ^{13}C NMR, DEPT and MALDI-TOF was shown to provide a useful means for characterisation and estimation of molecular structures of the asphaltenes.

1. Introduction

In dealing with heavy petroleum resources, asphaltenes are the most refractory compounds among all the petroleum fractions that often lead to many operational challenges from extraction to refining, exemplified by reservoir damage, well plugging, pipeline blockage, sediment formation in tanks and tankers and, during refining and processing, catalyst deactivation, reactor failure and plant outage (Ancheyta et al., 2010; Mullins et al., 2007). Although there has been a remarkable progress in the continuing effort to understand the fundamental properties of asphaltenes (Mullins, 2010, 2011; Mullins et al., 2012), the level of knowledge about the molecular structures of asphaltenes is still in a nascent stage. In the meantime, oil sand, also known as tar sand or bituminous sand, is an unconventional resource of liquid hydrocarbons that has received less attention. The bitumen extracted from oil sand is very viscous and sticky because of its high content of asphaltenes. While extensive studies have been carried out on petroleum asphaltenes and coal-derived asphaltenes (Andrews et al., 2011; Artok et al., 1999; Begon et al., 2003; Christopher et al., 1996; Clutter et al., 1972; Dickinson, 1980; Fergoug and Bouhadda, 2014; Kaminski et al., 2000; Masuda et al., 1996; Michon et al., 1997; Sanchez-Minero et al., 2013; Sheremata et al., 2004; Snape et al., 1979; Tojima et al., 1998; Trejo et al., 2004, 2007), more effort has been called for in order to understand the chemical structures of asphaltenes in oil sand.

As a complex mixture, the polydispersity of asphaltenes has greatly hampered the progress of its characterisation studies. A great deal of work has been conducted on fractionation of asphaltenes in the past (Andersen et al., 1997; Andreatta et al., 2005; Buch et al., 2003; Buenrostro-Gonzalez et al., 2002; Dickie and Yen, 1967; Groenzin et al., 2003; Jacobs and Filby, 1983; Kaminski et al., 2000; Nalwaya et al., 1999; Ovalles et al., 2012; Petrova et al., 2013; Tojima et al., 1998; Trejo et al., 2004; Wiehe and Liang, 1996; Yang and Eser, 1999). In the literature, binary solvent systems are commonly used to fractionate asphaltenes. Tojima et al. (1998) used a toluene/heptane system to fractionate asphaltenes into heavy and light subfractions. In their findings, the least soluble subfraction defined as heavy asphaltenes, consisted of the most highly condensed polycyclic aromatic hydrocarbons (PAHs) in the asphaltenes. Trejo et al. (2004) used the same

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binary solvent system to fractionate asphaltenes and compared the elemental composition across different fractions. Kaminski et al. (2000) reported fractionation work using a dichloromethane (DCM)/*n*-pentane system, in which the asphaltenes were firstly dissolved in DCM and then precipitated stepwise by adding increasing amounts of *n*-pentane. The precipitates were collected as subfractions by filtration when the DCM-to-*n*-pentane volumetric ratio reaching 30/70, 25/75, 20/80 and 10/90, respectively. Their results showed that the most polar subfraction (30/70) was not as soluble as the least polar subfraction (10/90). In addition, they also reported that unfractionated asphaltene samples appear to behave as a sum of their subfractions.

Many previous reports have discussed the trends amongst subfractions when using similar binary solvent systems, for example aromaticity was found to monotonically increase across subfractions with decreasing solubility and H/C ratio (Buch et al., 2003; Buenrostro-Gonzalez et al., 2002; Jacobs and Filby, 1983; Kaminski et al., 2000; Ovalles et al., 2012; Petrova et al., 2013; Tojima et al., 1998; Trejo et al., 2004; Yang and Eser, 1999). However effort to compare the subfractions in terms of their structural differences and use this approach to further probe the fractionation/precipitation mechanisms are scarce.

Among the spectroscopic techniques applied in characterising complex compounds, nuclear magnetic resonance (NMR) has been shown to have the potential for revealing the chemical nature of asphaltenes. Clutter et al. (1972) developed a technical method and protocol to characterise petroleum fractions with ^{1}H and ^{13}C NMR. They examined “aromaticity” through measuring aromatic carbon as a fraction of the total carbon, and brought forward a series of structural parameters, such as average number of aromatic rings and average number of alkyl substituents of an “average molecule”. Snape and Ladner (1979) compiled a survey of ^{13}C chemical shift in aromatic hydrocarbons in coal-derived materials. Since then a large body of literature on asphaltene molecular parameters using ^{13}C NMR has been reported (Artok et al., 1999; Begon et al., 2003; Buenrostro-Gonzalez et al., 2001; Calemma et al., 1995; Christopher et al., 1996; Dickinson, 1980; Fergoug and Bouhadda, 2014; Gillet et al., 1980; Korb et al., 2013; Masuda et al., 1996; Michon et al., 1997; Myhr et al., 1990; Netzel, 1987; Ostlund et al., 2004; Rafenomanantsoa et al., 1994; Sanchez-Minero et al., 2013; Sheremata et al., 2004; Storm et al., 1994; Trejo et al., 2007; Yoshida et al., 1980). Likewise, since its introduction in 1988, laser desorption ionisation mass spectrometry has been increasingly used in the study of heavy fractions of petroleum (Karas and Hillenkamp, 1988). Because this technique tends to use a laser intensity that is low enough to vaporise the compounds without breaking their covalent bounds, it is considered a “soft” mass spectrometric technique. Since the method is also used to analyse compounds that display low light absorption and therefore require the addition of a laser-absorbing matrix, it is often known as the matrix-assisted laser desorption ionisation (MALDI) mass spectrometry. In practice, for high laser-absorbing samples such as asphaltenes, matrices are found not to be necessary (Acevedo et al., 2005; Apicella et al., 2007; Martínez-Haya et al., 2007; Pantoja et al., 2013; Rizzi et al., 2006; Tanaka et al., 2004).

In the present contribution, asphaltenes extracted from an oil sand sample was fractionated using a binary solvent system. The chemical structures of the asphaltene sample, together with its four subfractions, were studied using ^{13}C NMR in combination with DEPT-135, a method reported in our previous work (Zheng et al., 2017). A set of average structural parameters, such as average polycyclic aromatic hydrocarbon (PAH) size, average side chain length and average molecular weight (AMW), were calculated based on the NMR and DEPT results. MALDI-TOF was also employed to measure the molecular weight distributions (MWDs) of the asphaltene sample and its subfractions, in order to assist the interpretation of the ^{13}C NMR spectra. It was expected that the combined use of the three techniques would provide further insights into the understanding of the structural differences of the subfractions and shed new light on the fractionation mechanisms of the asphaltenes in the binary solvent system.

2. Experimental

2.1. Materials and sample preparation

The asphaltene sample was extracted from Buton Oil Sand from Indonesia. The “run of mine” oil sand was crushed and pulverised into fine powders with sizes < 200 μm. The crushed sample was then subjected to solvent extraction using toluene in a Soxhlet extractor to obtain the organic fraction. The asphaltenes were isolated from the organic fraction in accordance with the method prescribed by the ASTM D-3279. Briefly, a sample of the organic fraction of the oil sand was firstly subjected to Soxhlet extraction using *n*-heptane as the solvent for at least 48 h 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 h 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 sample thus prepared, denoted as *Buton*, was collected in clean glass vials, sealed and stored in darkness before further characterisation and analysis.

The Buton asphaltene was subjected to fractionation following a procedure as illustrated in Fig. 1. Briefly, the asphaltene sample was initially dissolved in DCM and stirred for 2 h. A solvent-to-sample ratio of 80:1 by weight was used, which had proven to be sufficient to fully dissolve the sample in preliminary filtration trials prior to this research. Subsequently, *n*-heptane was slowly added into the solution under stirring to form a binary solvent with a volumetric ratio of DCM/*n*-heptane being 30/70. The mixture was left stirring for further 24 h. The *first fraction* (F1), also known as the *least soluble fraction*, was recovered by filtering the mixture through Waterman GF/B glass microfiber filters, while the filtrate in the DCM/*n*-heptane solvent was evaporated in a rotary evaporator to recover the soluble fraction. For the subsequent fractions, the same separation procedure was repeated except the ratio of the binary solvent was in turn changed to 20/80 and 10/90. The insoluble fractions isolated from 20/80 and 10/90 were denoted as the *second fraction* (F2) and *the third fraction* (F3), respectively. The soluble

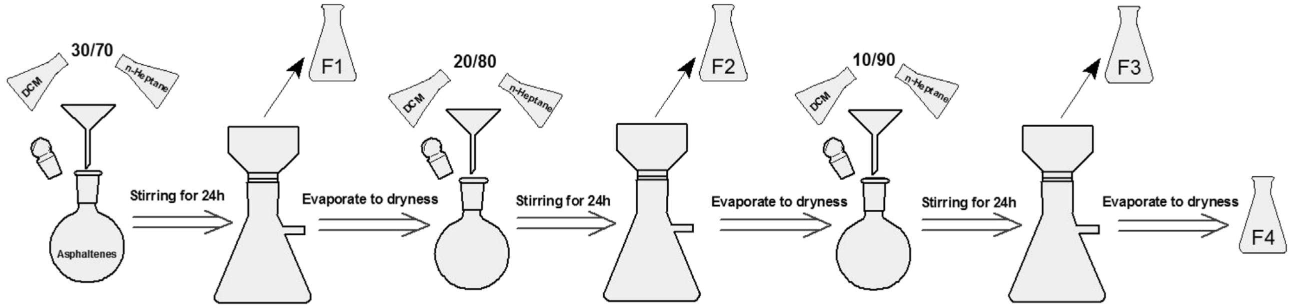

Fig. 1. A schematic illustration of the fractionation procedure.