Effects of experimental conditions on the molecular composition of maltenes and asphaltenes derived from oilsands bitumen: Characterized by negative-ion ESI FT-ICR MS

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A vacuum topped Canadian oilsands bitumen (VTB) was subjected to solvent precipitation and subsequently characterized by elemental analysis, gel permeation chromatograph (GPC), 1H-NMR spectroscopy and negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Effects of experimental conditions such as solvent types (\(n\)-C5, \(n\)-C6, and \(n\)-C7), solvent purity, and solvent washing time on asphaltenes yields, bulk composition, and molecular composition of detectable heteroatom compounds in ESI source were determined. Elemental nitrogen and sulfur were enriched in asphaltenes while elemental oxygen had comparable content in maltenes and asphaltenes. Molecular composition of asphaltenes varies with separation conditions. The N1 and O1 species identified by ESI FT-ICR MS were enriched in maltenes. The O2 species exhibited two different double bond equivalents (DBE) distributions and solubility in normal paraffin solvents, indicating two types of molecular structures. Multi oxygen atom containing compounds mainly detected in asphaltenes. Compound class distributions are similar for maltenes derived from \(n\)-C5, \(n\)-C6, and \(n\)-C7, as well as for asphaltenes. The cyclic paraffin impurities in normal paraffin solvents had a significant influence on asphaltenes yields and heteroatom molecular composition. A portion of neutral N1 species and acidic O2 species adsorbed on asphaltenes could be dissolved by increasing washing time. Cautions should be exercised when interpreting the properties and composition of asphaltenes obtained with different experimental conditions.

1 Introduction

Asphaltene constituents are insoluble in low molecular weight normal paraffins, such as \(n\)-C5 to \(n\)-C7, whereas soluble in benzene [1, 2]. On the other hand, maltenes contain constituents that are soluble in those low molecular weight normal paraffins. Asphaltenes and maltenes are named according to the precipitating solvent involved. Compared with light petroleum fractions, asphaltenes are often considered the most inferior and hardest to refine fraction, which have been named as “the cholesterol of petroleum” [3]. Asphaltenes are problematic to be extracted, transported, processed and can lead to catalyst deactivation, fouling and plugging of tubes and reactor walls [4]. Many studies have been dedicated to asphaltenes, including the physical and chemical properties [5–7], molecular weight [8–13], molecular structure [14–19], and asphaltenes aggregation [20–25]. So far, consensus has been reached that asphaltenes are the heaviest fraction of crude oil, containing most unfavorable components, such as metals and heteroatom-containing compounds [26]. However
systematic information is still lacking in terms of the molecular weight distribution, composition, and structure [12]. The properties and composition of asphaltenes depend on the separation method used and sometimes the specific technique. A series of ASTM methods have been developed for asphaltene preparation, including ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124 [27]. Alboudwarej et al. [7] evaluated four asphaltene precipitation methods and found that asphaltene yields and chemical properties are sensitive to the separation conditions. Studies have been performed to investigate the influence of separation conditions, including using different solvents [1, 28–31], contact time between the precipitating solvents and crude oil [32], ratio of precipitating solvents to crude oil [1, 32], and the temperature during the separation process [1, 33]. Although asphaltene preparations were mentioned frequently in literature, few of them were operated under the same experimental conditions [14, 34]. Comparing results from different methodologies is risky and could lead to controversies even erroneous conclusions [33]. It is difficult to perform asphaltene separations on chemical or structural features [32], and operation parameters (such as temperature, contact time, and precipitating solvents) cannot be related to the separation of distinct chemical types [27].

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been proven to be a powerful tool to characterize molecular composition of asphaltenes [34–40]. However, the challenges for characterizing these ultracomplex materials appear to arise not only from the resolution power and the mass accuracy of the FT-ICR MS, but also from the effectiveness of ionization methods. Rodgers and Marshall have applied various ionization methods to characterize heavy petroleum fractions, including low voltage electron impact ionization (EI), electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), atmospheric pressure photoionization (APPI), atmospheric pressure laser ionization (APLI), field desorption/field ionization (FD/FI), matrix-assisted laser desorption ionization (MALDI), as well as atmospheric pressure laser-induced acoustic desorption chemical ionization (AP/LIAD-CI) [41–43]. The ESI source is often coupled with FT-ICR MS for heavy petroleum fractions characterization due to its convenient use. Klein et al. used ESI FT-ICR MS to compare the compositional difference between crude oil and its n-C7 asphaltenes and found that oxygen-containing compounds and multi-functional groups of heteroatom-containing compounds are concentrated in the asphaltenes [44]. Similar results were reported by Liao et al. [45], who separated Canadian bitumens into malmene and asphaltene fractions, and analyzed the heteroatom species by ESI FT-ICR MS. Although ESI selectively ionizes the polar species which may occupy a small proportion of the whole fraction, the results revealed much information on the composition of asphaltenes.

This paper investigated the influence of experimental conditions such as solvent type, solvent purity, and solvent washing time on asphaltene separation. ESI FT-ICR MS was used for the molecular characterization of VTB, and its maltenes and asphaltenes.

2 Experimental

2.1 Materials

Vacuum topped Canadian oilsands bitumen (VTB, boiling point > 525 °C) was obtained from Syncrude commercial oilsands plant. Analytic-reagent grade (AR-grade, 95% purity) normal pentane (n-C5), normal hexane (n-C6), normal heptane (n-C7) and toluene were purchased from Beijing Chemical Reagent Factory. Another n-C7 (AR-grade, > 98% purity) was obtained from Tianjin Fu Chen Chemical Works. The gas chromatographic grade (GC-grade, 99% purity) n-C6 was purchased from Shanghai Aladdin Reagent Company. Solvents were used without further purification.

2.2 Precipitation of asphaltenes

Asphaltene precipitation was conducted for 6 times under different conditions. In each run, One gram VTB and 70 mL normal-paraffin were loaded to a 250 mL round-bottom flask (Flask 1, another two round-bottom flasks were labeled as Flask 2 and Flask 3) equipped with a heating jacket, an extractor, and an Allihn-type condenser (the separation device see Figure S2 in supporting information). The resulting mixture was heated to reflux for 2 h until no visual undissolved sample observed in the solution. The solution was cooled to ambient temperature and kept standing for another 2 h to ensure the insoluble matters settled down. Filter the prepared sample solution using a filter paper (with a pore diameter of 1–3 μm) under ambient condition. This filtrate represents the first portion of malmene solution. The filter paper with all insoluble materials collected was transferred into the extractor and extracted by 50 mL fresh normal-paraffin loaded in Flask 2 for 4 h (defined as washing time) to remove the remaining soluble material potentially entrained in the filter cake. Sixty millilitor toluene was added to Flask 3 to extract the insoluble materials which remain in the filter at refluxing condition until the reflux turned colorless. Decant the malmene solution from Flask 2 to Flask 1. Maltene and asphaltene fractions were recovered after removing solvents from Flask 1 and Flask 3 respectively by rotary evaporator and vacuum drying. At last, six pairs of maltenes and asphaltene fractions were obtained. Maltenes were labeled as C5-Mal, C6-Mal-AR, C7-Mal-GC (with washing time of 4 h), and C7-Mal-1, C7-Mal-2, C7-Mal-3 (with washing times of 2 h, 4 h, and 6 h, respectively), and the corresponding asphaltenes were labeled as C5-Asp, C6-Asp-AR, C7-Asp- GC, and C7-Asp-1, C7-Asp-2, C7-Asp-3.