



Full Length Article

Optimized asphaltene separation by online coupling of size exclusion chromatography and ultrahigh resolution mass spectrometry

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ABSTRACT

The asphaltene fraction is the heaviest part of a crude oil and is obtained as the fraction which contains compounds that are not soluble in paraffinic solvents such as *n*-heptane. Due to the limited solubility the use of separation methods is strongly reduced to methods that include solvents that dissolve asphaltenes. Here, the direct coupling of size exclusion chromatography with ultrahigh resolution mass spectrometry to investigate the separation of asphaltenes is accomplished. Different mobile phase systems have been investigated using THF and different mixtures of chloroform and toluene to optimize the separation conditions. Due to the separation the complexity of the asphaltene sample can be reduced, therefore mass spectra with increased information depth can be obtained due to the smaller amount of interacting species. Additionally, correlations can be proposed between molecular mass and structural characteristics of highly condensed aromatic molecules: compounds having both aromatic core and long aliphatic chains with higher masses were detected earlier and the smaller ones containing mostly highly aromatic structures and only a low amount of short alkyl chains (with the same DBE values) have stronger retention. Different experimental conditions such as stationary phase and mobile phase of asphaltene separation with size exclusion chromatography are investigated.

1. Introduction

The asphaltene fraction is the heaviest and most polar fraction of crude oil and is defined by their solubility in toluene and insolubility in normal paraffinic solvents (e.g. *n*-heptane) [1]. After the SARA fractionation of a heavy crude oil [2] into the different fractions the asphaltene fraction still remains a mixture of many tens of thousands of different compounds resulting in a heterogeneous mixture varying in both chemical composition and molecular size. The fraction consists of hydrocarbons and high amount of components with heteroatoms (N, O and S) and trace amount of metals (e.g. V, Ni, Fe). Structurally, asphaltene compounds are composed of highly condensed aromatic rings substituted with aliphatic chains [1]. The behavior of asphaltenes is highly influenced by the solvent and in some cases that can result in the formation of aggregates and flocculation, therefore the determination of their properties remains always a challenge [3–5].

Heavy crude oils play an important role in replacing diminishing light oil resources. Therefore, the analysis of these resources having high asphaltene content with high viscosity and high heteroatom content, has drawn significant attention [6]. Asphaltenes can cause blockages during oil production and during processing it can form coke deposits in reactors, additionally it can poison or deactivate catalysts

[6,7]. Therefore, there is a need to gain information on their characteristics, including their molecular weight and structure, which might help to understand these issues.

Several analytical techniques such as NMR or fluorescence measurements can give information about the bulk characteristics of asphaltenes, but these are average features describing only general characteristics [8,9]. While the exploration of their elemental composition is established, there are still doubts regarding the investigations of their molecular architecture. This is related to the evaluation of the molar mass range of asphaltenes which has been debated in the literature [5,10–16].

Mass spectrometry (MS) with high mass accuracy and ultrahigh resolution can provide detailed information of molecular species even in extremely complex samples and has shown to be the method of choice for detailed petroleum analysis [17]. Information like unique elemental composition from accurate masses, component classes based on containing heteroatoms and degree of aromaticity can be obtained easily [8]. Due to the high complexity matrix effects, ion discrimination suppression effects and the sensitivity of the instrument limit the type and amount of detected compounds [8,18,19].

Thus, more detailed information can be obtained with coupling of different analytical methods. The combination of mass spectrometry

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and chromatographic separation is a possible way to reduce the complexity of the sample and therefore increase the obtainable information depth [20,21]. However, asphaltenes are not volatile enough for gas chromatographic analysis [22,23]. Although, asphaltenes have a wide range of polarity, their aromatic feature and the van der Waals intermolecular attractions are more dominant [1]. Therefore, the difficulty of such an aromatic structure is their low solubility in solvents which are commonly used in reversed-phase liquid chromatography such as methanol and water. Finding an appropriate solvent system can be complicated and therefore, strongly limiting the choice of chromatographic methods.

It is discussed that mass range of asphaltenes can differ due to the formation of associates and it is important to choose the right analytical method and conditions for its investigation to avoid the potential formation of associates [3,11]. Taking into account the aforementioned conditions and limitations, size exclusion chromatography (SEC) seems to be a very promising method for the separation of asphaltenes. In SEC, ideally, the molecules in solution are separated according to their hydrodynamic volume [24], so it is a suitable method for investigation of molecular mass distribution [25,26]. For determination of the exact molecular size, polymer standards (e.g. polystyrene, poly(methyl methacrylate), polysaccharides) are usually required, although it is a critical point which can lead to ambiguous information [27–29].

Direct coupling of SEC and MS has been reported to be a very promising technique in determination of molecular mass and to study e.g. polymeric products and aggregates [30–32].

In general, simplification of a crude oil sample increases the data depth [17,33] about the compounds present in the sample and this holds also true for chromatographically separated samples. In this case when coupling SEC with ultrahigh resolution MS the separation results in a smaller number of different species present in each MS scan. The reduced number of ions in the Orbitrap leads to less ion-ion interaction avoiding competition of different ions which allows detection with higher sensitivity.

The direct coupling of liquid chromatography with mass spectrometry always needs to be optimized in regard to what is more important: better chromatographic separation or better mass spectrometric resolution. Faster scanning is required to obtain as much information about the separation as possible without losing any separation information [34]. On the other hand the transient time should be long enough to have sensitive detection [35]. The difficulty of this approach is that an optimum needs to be found between the chromatographic separation and the mass spectrometric scan time.

Recently we have introduced the direct coupling of SEC with MS reporting first results on the separation of asphaltenes with a focus on increased mass spectrometric detection. The major drawback with this first results was that the mixture of benzene/chloroform is not the best combination of chromatographic solvents [6]. Therefore, in this study the focus was placed on improved separation conditions by studying different solvent systems involving tetrahydrofuran (THF), chloroform and toluene which are compared as mobile phases in order to achieve an effective separation and the possibility of better characterization of highly aromatic compounds. In this respect, harmful and carcinogenic solvents such as benzene were aimed to be excluded. Furthermore, different experimental conditions such as SEC columns with different pore sizes were investigated to find the optimized separation conditions.

2. Experimental section

2.1. Sample preparation

Asphaltenes were precipitated from a heavy crude oil with *n*-heptane using a modified IP 143 method [36]. 30 mL of *n*-heptane per g of heavy crude was mixed thoroughly. The mixture was then refluxed for 1 h, and then stored in the dark overnight. It was filtered through a

Whatman filter paper (type 589.3) and the precipitated sample on the top of the filter paper was rinsed with hot *n*-heptane. It was then placed into a Soxhlet apparatus and extracted under reflux with *n*-heptane for additional 2 h. The extraction was finalized by completely dissolve the asphaltenes from the filter paper with fresh toluene (ca. 20 h). The toluene was evaporated under vacuum afterwards.

Chemicals used for sample preparation and for chromatographic separation are HPLC grade and were purchased from Sigma-Aldrich (Germany), except *n*-heptane (HPLC grade, Merck, Germany).

For SEC-MS measurements, the asphaltene sample (2 mg) was dissolved in 1 mL of solvent, THF and chloroform/toluene (70/30 and 30/70 v/v), respectively. For direct injection, further dilution was applied in order to reach the final concentration of 250 µg/mL.

2.2. Size exclusion chromatography

Size exclusion chromatography was performed by injecting 100 µL of sample using an Agilent 1100 HPLC system (Agilent Technologies, Waldbronn, Germany). Five SEC columns were tested at room temperature, a Varian PLgel column (300 × 4.6 mm ID, 3 µm particle size, 10² Å pore size; highly cross linked, porous polystyrene/divinylbenzene material) and four PSS SDV (styrene-divinyl benzene copolymer) analytical columns (300 × 8.0 mm ID, 5 µm particle size) with different pore sizes: 10² Å, 10³ Å, 10⁵ Å and 10⁶ Å, respectively. THF and mixtures of chloroform and toluene (70/30 and 30/70 v/v) were used as mobile phases at a flow rate of 1 and 1.5 mL/min, respectively.

2.3. Mass spectrometry and data analysis

Mass analysis was performed on a research-type LTQ-Orbitrap Elite mass spectrometer (Thermo Fisher, Bremen, Germany) which provides a maximum resolving power of up to 900 000 at *m/z* 400 equipped with a combination of atmospheric pressure photo ionization (APPI) and atmospheric pressure chemical ionization (APCI) source. A Syagen Krypton VUV lamp (Syagen, Tustin, CA, USA) was used with photon emission at 10.0 and 10.6 eV. For online coupling of SEC-MS, the outlet of the UV detector was connected to the ionization source of the mass spectrometer using Peek capillaries and the flow rate was adjusted with the help of a splitter. Thus, the sample was infused with a flow rate of 0.3 mL/min and evaporated in the heated nebulizer at 350 °C. Nitrogen was used as a continuous sheath gas flow and set to 20 (arbitrary unit). Samples were pumped through a transfer capillary (275 °C), the RF level of S-lenses was 60% and the discharge current for APCI needle was set to 4.0 µA. In case of direct infusion of the asphaltene samples, the same parameters were applied.

Data were collected in positive mode with a scan range of *m/z* 200–1000 in full scan mode and processed with the LTQ FT Ultra 2.5.5 (Thermo Fischer Scientific, Bremen, Germany) data acquisition system. The data were recorded using a 768 ms transient resulting in a mass resolution of 240 000 (at *m/z* 400). This set-up allows a fast detection by recording one scan about every second correlating well to the broad separation where all compounds appear in a large and broad peak.

The acquired data were analyzed by Xcalibur 2.2 software (Thermo Fischer Scientific, Bremen, Germany) and Composer V1.5.0 software (Sierra Analytics, USA). The applied parameters and chemical constraints for the peak assignments were the followings: H: 0–1000, C: 0–200, N: 0–3, O: 0–3, S: 0–3, DBE: 0–40 with a maximum mass error of 1.4 ppm. The calculated molecular formulas were classified into different compound classes with a distinction of radical cations (X) and protonated ions (X[H]), as well. Excel (Microsoft Office Professional Plus 2010, Microsoft Excel 2010) and Origin (Origin 8.5.0) software were used for further data evaluation.

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