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Direct Mass Spectrometry of tar sands: A new approach to bitumen identification

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HIGHLIGHTS

- Direct Insertion Probe–Mass Spectrometry analyses bitumen directly from tar sands.
- Method applied on real tar sand samples coming from different geological areas.
- Peculiar DIP–MS mass profiles are used as fingerprint of tar sand composition.
- Information correlated with bitumen properties determined with conventional analyses.
- On-field application for fast screening and rough evaluation of tar sand fields.

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ABSTRACT

The activities related to the evaluation of the organic fraction of tar sands are acquiring more importance from economical and technical points of view due to the increased variety of sample composition and origin. Conventionally, the analyses of bitumen in tar sands are based on preliminary extraction from the inorganic matrix and further characterisation of physical and chemical features by means of different methods.

A new approach to characterise the tar sand is now proposed, based on the direct insertion of tar sand into mass spectrometer chamber without any previous separation or treatment and further vaporisation under vacuum at increasing temperature and analysis of its components. DIP–MS (Direct Insertion Probe–Mass Spectrometry) allows separating the bitumen components from the solid inorganic matrix according to their boiling points up to masses of 700 m/z and directly analysing them in one only step, even if they are characterised by high boiling point, high steric hindrance or low solubility, that usually limit their evaluation by chromatographic methods.

This new application of DIP–MS approach is here described on model materials and on a series of real tar sand samples coming from different geological areas. Differences are evidenced among the tar sands on the basis of the evolution of their mass spectra.

The information so obtained was compared and confirmed with other analytical techniques that are commonly used for crude oil and bitumen characterisation. This approach is proposed for an on-field application for fast screening of real samples in the perspective to acquire information on the most relevant organic species in the bitumen for comparative purposes and rough evaluation of the potentiality of tar sand fields.

1. Introduction

The growth in the economy of any country is connected to a strong increase in the energy demand that now combines with declining of conventional oil reserves. The shortage of oil of known petroleum reserves makes more attractive less attended energy resources, especially considering that their availability ratio to conventional crude oils is 5–1. Processing unconventional or opportunity crudes, i.e. heavy sour crudes, oil sands/bitumen, extra-heavy oil, high-TAN crudes, oil shale, is considered a huge potential resource to fulfil energy requirements and the most viable option at a time of rising oil prices and disproportionate demand for light sweet crudes. Among the unconventional crudes, bitumen from tar sand reservoirs appears an appealing fuel.

The exploitation of tar sand reservoirs has a historical background in Canada, as in other areas as West Africa is just considered a new opportunity. The activities related to the evaluation of the organic fraction of tar sands consequently acquire more importance from economical and technical points of view due to the increased variety of sample composition and origin.

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The utilisation of tar sands as a fuel source depends not only on the amount of organic matter, but also on the nature of its components, from which depend i.e. the easiness to extraction and the amount of valuable materials. In fact, the physical and chemical properties of the bitumen ultimately determine its value because these properties influence the recovery, processing, conversion and utilisation as fossil energy resources. Among the different properties, thermal conductivity and viscosity are important to the in situ recovery process with thermal/chemical techniques to gasify and/or increase bitumen mobility so it can be brought to the wellhead [1], as chemical composition (e.g. saturates or asphaltenes) leads to appropriate refining process [2].

Nowadays, the analyses of bitumen in tar sands are based on preliminary extraction from the inorganic matrix and further characterisation of physical and chemical features by means of different methods, such as viscosity, density, acidity and distillation cuts (Simulated Distillation) by ASTM methods, molecular weights by GPC (Gel Permeation Chromatography) [3,4], aromaticity by NMR (Nuclear Magnetic Resonance) [5], oxygenated groups index by IR (InfraRed) [6].

The application of high resolution mass spectrometers (e.g. Fourier Transform Ion Cyclotron Resonance FT-ICR-MS, Orbitrap instrument) is now applied to the study of crude oils and bitumens, giving rise to a new scientific area: petroleomic [7–10]. High resolution Mass Spectrometry allows creating an accurate and comprehensive map of the species present in the bitumen, but it requires specific conditions from the point of view of the machinery (no-vibration floor, liquid helium supply, stabilised temperature room, etc.) and of the samples (extracted bitumen, very diluted samples, clean conditions) and it needs the support of elaborate softwares for the accurate mass evaluation. These requirements make it unsuitable to preliminary screening of a large number of samples or to the on-field analysis of real tar sand samples.

A new approach to characterise the bitumens from tar sands is proposed, based on DIP–MS (Direct Insertion Probe–Mass Spectrometry) technique that allows the direct insertion of tar sand into mass spectrometer chamber without any previous separation or treatment. Its application is here described on model materials (i.e. crude oils impregnated in/on sand) and on a series of real tar sand samples coming from different geographical areas. The purpose of DIP–MS application to tar sands is to offer a fast and direct evaluation of the bitumen fraction through similarities and differences with other bitumens and not to draw an exhaustive and comprehensive map of all the species that compose the organic matter.

The DIP–MS technique has been applied for the analysis of polar or thermally labile samples (e.g. aromas) for more than 30 years [11,12] and very recently of insoluble or solid organic samples (e.g. asphaltenes) [13], although the direct introduction of compounds at low volatility into the ion source has been already reported [14]. Based on introduction and vaporisation under vacuum at controlled temperature of solid samples directly into the ionisation chamber, DIP–MS allows separating the bitumen components according to their boiling points up to masses of 700 m/z and identifying some classes of chemical compounds in such complex mixtures, giving more information than a simple routine analysis does.

The evidences obtained by DIP–MS analysis of tar sands were compared with a multidisciplinary characterisation of the bitumen obtained by solvent extraction of tars at laboratory scale and completely confirmed.

2. Experimental

2.1. Samples

Silica (Sigma–Aldrich) and natural sand (mainly composed by quartz and clay) were impregnated (5–10 wt%) with crude oils (oil 1 and oil 2 from reservoirs in different geological areas) at room temperature and maintained in contact for 48 h at 30 °C before analysis. They were considered as model materials to simulate real tar sand samples. Tar sands collected from different geological areas (reference tar sand from Athabasca region and samples A–D) were collected as received from reservoirs and analysed without any previous treatment. Bitumen from tar sands (30 g) was extracted with dichloromethane (200 ml) at 45 °C under reflux up to complete clean solution; the solvent was then removed from the extract at 30 °C under vacuum (350 mbar).

2.2. Apparatus

DIP–MS analyses were performed with a Trace DSQ Thermo system equipped with a single quadrupole Mass Spectrometer (MS) detector with electron-impact ionisation and DIP (Direct Insertion Probe) module. The probe temperature program was the following: 120 °C for 10 s; 60 °C/min up to 200 °C; 50 °C/min up to 340 °C; 340 °C for 15 min. The analyses were performed with ionisation voltage of 70 eV, source temperature of 270 °C, mass range between 33 and 1000 m/z, scan rate of 2.14 scan/s, vacuum better than 7×10^{-5} mbar. As this approach is not focused in identification of single compounds, it does not require the application of highly sophisticated and expensive high-resolution mass spectrometers.

The solid is introduced into a quartz cup located into the tip of the probe that enters the vacuum chamber through an inlet. The tip of the probe is directly introduced into the ionisation chamber, close to the ionisation source (the distance is less than 5 mm). The inner diameter of the cup is 1 mm, the length is 7 mm and the sample amount which can be introduced is about 0.2 mg. The tip, heated in a temperature-programmed mode, makes the different components of the sample available for detection, with a procedure similar to the fractional distillation, but in this case re-enforced by the combined effect of vacuum and heat. The heating rate was chosen to avoid a too rapid vaporisation of the sample and the saturation of the signal. Eventually these species are ionised by electronic impact and monitored. A turbomolecular pump system coupled to the mass spectrometer creates a dynamic vacuum (7×10^{-5} mbar) in the ionisation chamber and near the source zone. The very short distance between the ionisation source and the vaporised molecules coming from the tip of the probe, the small amount of molecules undergoing the collision with the electron flux, and the dynamic vacuum prevent the permanence of the molecules near the source zone with consequent molecule collision and recombination, and guarantee the rapid ionisation before thermolitic degradation. A detailed description of the apparatus is reported elsewhere [13].

It is important to note that vacuum dramatically decreases the boiling temperature of the compounds, allowing the vaporisation of high boiling-point species even when not very high temperatures are applied; e.g. the boiling point of benzocoronene is 566 °C at atmospheric pressure and decreases to 303 °C at 10 mbar and 48 °C at 7×10^{-5} mbar. For this reason no direct relation between the vaporisation temperature registered in DIP approach and that applied in the conventional Sim-Dist measure at atmospheric pressure is immediately available.

The results of the DIP–MS analysis are depicted as sum of all mass spectra collected over the course of the whole experiment, or in a selected range of vaporisation temperatures.

2.3. Characterisation of the materials

Crude oils and bitumens extracted with dichloromethane from tar sands were characterised, applying several techniques: GPC (Gel Permeation Chromatography), NMR (Nuclear Magnetic