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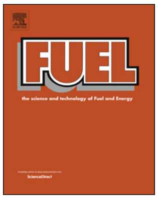

Full Length Article

Molecular profiling of crude oil by using Distillation Precipitation Fractionation Mass Spectrometry (DPF-MS)

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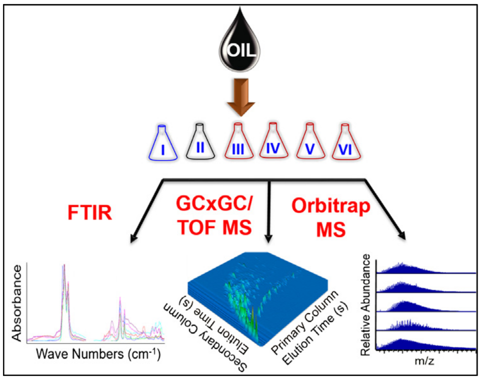
GRAPHICAL ABSTRACT



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ABSTRACT

Molecular profiling of crude oil is a tremendous challenge due to its inherent complexity. An accurate molecular fingerprint of a crude oil may facilitate rational design of crude oil recovery efforts, such as enhanced oil recovery, improve the efficiencies of the refining processes, and enable a better assessment of the value of the crude oil. Herein, a new approach (Distillation Precipitation Fractionation Mass Spectrometry (DPF-MS) method) is introduced for the molecular level characterization of crude oil. This method involves the separation of crude oil into six fractions followed by high-resolution mass spectral analysis optimized for each individual fraction. The separation methods are distillation, precipitation, and fractionation in an auto column followed by solid phase extraction. Initially, the fractions were examined by using Fourier transform infrared spectroscopy to determine the bulk chemical nature of each individual fraction, such as the extent of aromaticity, degree of polarity, etc. Based on this bulk information, model compounds representative of compounds in each fraction were selected and employed to develop the optimal high-resolution mass spectrometric analysis method for each fraction. An especially important aspect of this work was the optimization of the ionization method separately for each fraction by using appropriate model compounds so that most compounds in each fraction are ionized at approximately the same efficiency to generate only one type of stable ions (either molecular ions, protonated molecules or cations formed by hydride abstraction) containing the intact analyte molecule. This allows the DPF-

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MS method to produce reasonably accurate relative abundances for compounds present in each fraction, thereby making the method semi-quantitative. The compositional data thus obtained for the individual fractions were utilized to provide meaningful molecular level information for the crude oil. Inclusion of a mass balance for each fraction allows for data consolidation, which provides an accurate overall analysis of the crude oil, including average molecular weight and weight percentages of different compound classes.

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1. Introduction

The light oil deposits of the world are depleting, which has generated a need to better understand the chemical composition of crude oil of different geographical origins. Specifically, for chemically enhanced oil recovery processes, this information would enable producers to investigate the phase and interfacial interactions between oil, surfactants, and reservoir rock, and thereby help the industry develop smarter, more efficient solutions for the economic recovery of oil [1–3]. Further, the ability to obtain an accurate estimate of the average molecular weight of crude oil would facilitate the optimization of refinery processes [4]. This is especially important for conversion of crude oil via reactions such as alkylation, dimerization, cracking, and hydrotreating, since access to an accurate average molecular weight would enable a better estimation of the amount of reagent required for the conversion [4].

The challenge of analyzing crude oil is that it is a complex mixture, predicted to contain as many or more compounds than the number of genes in the human genome [5]. To study such complex mixtures, powerful high-resolution mass spectrometers, such as Fourier-transform ion cyclotron resonance or orbitrap mass spectrometers, are desirable [6,7]. These high-resolution instruments can be used to determine the elemental compositions of ionized crude oil components, which facilitates categorizing them into different compound classes (such the hydrocarbon class containing only carbon and hydrogen and heteroatom classes containing oxygen, nitrogen and/or sulfur in addition to carbon and hydrogen) or compound types (*e.g.*, saturated and aromatic compounds). While the information provided by these techniques is invaluable, problems associated with the ionization methods employed include inefficient ionization, competition for ionization, and matrix effects, all of which may reduce sensitivity toward or even entirely prevent the detection of some components of crude oil. Indeed, most of these studies have employed atmospheric pressure chemical ionization (APCI) for nonpolar analytes [8], atmospheric pressure photo ionization (APPI) for aromatic analytes [7,9] and electrospray ionization (ESI) for polar analytes [10,11]. Unfortunately, all these methods selectively ionize only some of the crude oil components.

Above problems of competition for ionization and matrix effects are reduced when the mass analysis is preceded by a chromatographic separation [12–14]. Chromatography reduces the complexity of the mixture by separating it into fractions, but it does not necessarily eliminate issues having to do with mixture components with widely differing ionization efficiencies.

In this paper, a new separation and characterization method for crude oil is introduced, entitled Distillation Precipitation Fractionation Mass Spectrometry (DPF-MS). DPF-MS involves separation of the crude oil into several fractions that contain compounds with similar chemical characteristics, followed by molecular level characterization of each fraction by using an optimized mass spectrometric method. The novelty of this method lies in the optimization of the ionization and mass spectrometry method separately for each fraction by using representative model compounds so that all compounds in each fraction are ionized at approximately the same efficiency to yield stable ionized molecules, which makes the DPF-MS method semi-quantitative. Following the weighing and analysis of each fraction, consideration of mass balance facilitated the molecular profiling of the fractionated crude oil.

2. Experimental section

2.1. Sample

Freshly collected crude oil from an active oil well in the Illinois oil basin was provided by the Pioneer Oil Company (Illinois). The crude oil was collected and stored in amber colored glass bottles to prevent oxidation and the container was tightly sealed with a screw cap to minimize loss of volatile compounds. The viscosity and density of the crude oil (at 20 °C) were measured to be 12.28 cP and 0.87 g/cm^3, respectively.

2.2. Chemicals and materials

HPLC grade *n*-hexane (C_6H_{14}), dichloromethane (CH_2Cl_2) and isopropanol (i-C_3H_7OH) were used as eluents in flash chromatography. A normal-phase silica (40 g) auto column was purchased from Teledyne Isco, Inc. A total of 23 model compounds were used in this study. Table S1 in the supporting information gives details of the model compounds used and their purities.

2.3. Separation of crude oil into fractions

Crude oil was separated into six fractions by using different techniques. As a first step, the most volatile compounds in the crude oil were separated by vacuum distillation at room temperature to yield fraction I (distillate) to avoid their loss during fractionation. The remaining residue was separated into asphaltenes (fraction II) and maltenes (all remaining fractions) through precipitation of the asphaltenes by using hexane as reported in the literature [15]. Maltenes were further chromatographically separated into three fractions (C_6H_{14}-eluted fractions III and IV combined, CH_2Cl_2-eluted fraction V, and i-C_3H_7OH-eluted fraction VI) on an auto column (Combi-flash Rf 200 from Teledyne Isco, Inc.) by using hexane (C_6H_{14}), dichloromethane (CH_2Cl_2) and isopropanol (i-C_3H_7OH) as eluents. The C_6H_{14}-eluted fractions were further separated into fractions III and IV by using a solid phase extraction technique reported in the literature [16,17]. Further details of each separation step are provided in the Supporting information (Table S2). All the fractions were weighted gravimetrically to obtain mass balance and recovery.

2.4. Mass spectrometry

2.4.1. GCxGC/TOF mass spectrometry

A LECO Pegasus 4D GCxGC/(EI)TOF instrument equipped with an Agilent 7890B two-dimensional gas chromatograph (Agilent technologies, Santa Clara, CA) and a high-resolution time-of-flight (TOF) mass spectrometer (up to 50,000 resolution) was used for the analysis of the volatile compounds (fraction I) in crude oil. Two columns (Rxi-17sil ms (intermediate polarity), 60 m, and Rxi-1 ms (nonpolar), 4 m) were connected in series by using a modulator that enhances the peak capacity available for the chromatographic system. After separation of the compounds, positive ion mode electron ionization (EI) (70 eV) was used to ionize the compounds upon entrance into the mass spectrometer. The EI mass spectra measured (at high resolution) for unknown compounds were compared to extensive EI mass spectral libraries for identification (NIST libraries). This analysis yielded a list of identified compounds, their gas chromatographic peak areas and two retention times, and