



Comprehensive two-dimensional liquid chromatography of heavy oil

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ABSTRACT

Heavy oil refers to the part of crude oil that is not amenable to further distillation. Processing of these materials to useful products provides added value, but requires advanced technology as well as extensive characterization in order to optimize the yield of the most profitable products. The use of comprehensive two-dimensional liquid chromatography (LC × LC) was investigated for the characterization of de-asphalted short residue, also called maltenes. Initial studies were performed on a polycyclic aromatic hydrocarbon standard, an aromatic extract of hydrowax, and the fractions obtained after solvent fractionation of the maltenes. Cyanopropyl- and octadecyl-silica were used as first-dimension and second-dimension columns, respectively. The analysis of the maltenes and fractions thereof required a change in first-dimension stationary phase to biphenyl as well as an increase in modifier strength to improve recovery. The extensive characterization of maltenes with LC × LC within four hours was demonstrated.

The Program for the Interpretive Optimization of Two-dimensional Resolution (PIOTR) has been applied to aid the method development, but due to the absence of specific peaks in the chromatograms it was challenging to apply to the maltenes or its fractions. Nonetheless, an approach is suggested for resolution optimization in cases such as the present one, in which regions of co-elution are observed, rather than clearly separated peaks.

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1. Introduction

A part of heavy oil is the short residue, also called vacuum residue or vacuum bottoms. This is the solid hydrocarbon that remains at the bottom of a vacuum distillation column after the volatile material has removed at reduced pressure (Fig. 1). Extracting higher value products out of this material requires additional processing using delayed coking technology, such as Exxon's Flexicoker [1] or Shell's Hycon [2]. To optimize the yield of the most profitable products from these processes, the material needs to be thoroughly characterized in order to optimize the conversion process [3]. The characterization of the short residue still has room for improvement, although optimization is definitely a challenge.

Since the molecular composition of short residue is so complex, the material is often separated before analysis into sub-fractions

based on solubility behavior [4,5]. One of the main methods for this is a liquid chromatographic (LC) method known as SARA analysis, in which a hydrocarbon mixture is separated into four fractions: Saturates, Aromatics, Resins, and Asphaltenes [6]. The saturate fraction includes alkanes (paraffins) and cyclic alkanes (naphthenes). The aromatic fraction consists of molecules incorporating at least one aromatic ring. The resin fraction consists of compounds that contain heteroatoms, hence it is often referred to as the polar fraction or the "polars". This is evident by the fractionation process as the resins stick to the stationary phase until (back)flushing with a relatively polar solvent, such as dichloromethane (DCM). Asphaltenes are defined by their solubility range. They are soluble in toluene, but precipitate upon addition of excess *n*-heptane or *n*-pentane [7]. One has to be aware that SARA fractions are never completely excised from one another [8]. This remains inevitable when employing solvent fractionation. Understanding the composition of a specific SARA fraction can provide valuable insights, whilst retaining much of the sample dimensionality [9], and provide feedback for further processing of the short residues into profitable products.

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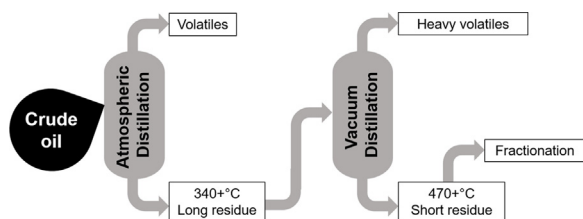


Fig. 1. Schematic of a petroleum refinery, adapted from Speight et al. [6].

For the analysis of heavy oils many techniques have been applied, including Fourier-transform ion-cyclotron-resonance mass spectrometry (FT-ICR MS) [10–12], high-temperature comprehensive two-dimensional gas chromatography (HT-GC \times GC) [13,14] and comprehensive two-dimensional supercritical-fluid chromatography (SFC \times SFC) [15,16]. Dutriez et al. [17] analyzed resin fractions using both FT-ICR MS and HT-GC \times GC in order to compare the analytical capabilities of these techniques for heavy oils. However, as the components become heavier and less volatile, their analysis becomes more difficult. Volatility of a sample is an inherent requirement for gas chromatography (GC) and since this property decreases as the molar masses and polarity of oil components increases, GC \times GC becomes more complicated and eventually impossible for materials such as short residue. FT-ICR MS is able to deal better with heavier samples, but struggles with accurate quantification and with the separation of isomeric components. Techniques like supercritical-fluid chromatography (SFC) and LC are better suited for characterizing short residue, since they do not require volatile analytes. Nevertheless, the analysis of heavy components heavier than C_{90} is troublesome for SFC [16].

While one-dimensional liquid chromatography (1D-LC) is most often employed for sample preparation and fractionation of heavy hydrocarbons, comprehensive component analysis is impossible due to broad, unresolved peaks in the chromatogram caused by the molecular complexity of the sample [18,19]. The purpose of this work is to determine if comprehensive two-dimensional liquid chromatography (LC \times LC) could be a possible alternative approach.

LC \times LC is a method in which the first-dimension (1D) chromatographic column is coupled to a second-dimension (2D) chromatographic column through a switching valve or another transferring device in order to subject the entire 1D effluent to 2D separations [20,21]. The effluent from the 1D should be sampled 2–4 times over the $4\text{-}\sigma$ width of the 1D peak to ensure two-dimensional resolution [22,23]. In LC \times LC the peak capacities of the two dimensions can ideally be multiplied, giving rise to an immense increase in separation power [18,23,24]. In order to deal with complex samples that require more peak capacity than an LC method can offer, LC \times LC seems to provide good prospects. Duarte et al. [25] applied LC \times LC on natural organic matter, where 1D-LC could not handle the sample complexity, and showed great improvement in their ability to resolve individual components in the sample. Similarly, Murahashi [26] performed LC \times LC on polycyclic aromatic hydrocarbons (PAHs) in environmental samples and showed that the technique provided valuable additional information. More specifically, Jakobsen et al. [27] applied LC \times LC with pulsed elution of the first dimension to a heavy oil fraction of vacuum gas oil and coker gas oil.

Nevertheless, the advantages of the additional dimension in LC \times LC come at the cost of significantly more complicated method development [21,28–30]. As the two columns are coupled through a modulation device, often consisting of a switching valve and two loops that are filled and emptied consecutively, the optimization of both separations is no longer independent. Similar to 1D-LC, LC \times LC also requires optimization of individual parameters, such as column dimensions, particle size, flow rate, mobile-phase com-

position, temperature, pH, etc. In addition, LC \times LC requires the compatibility of the two dimensions and the way they are connected to be considered, i.e. modulation time and the effects of the 1D effluent on the 2D separation [31]. Recently described software called “Program for Interpretive Optimization of Two-dimensional Resolution” (PIOTR) developed by Pirok et al. [32] was shown to speed up LC \times LC method development, based on only a few experiments, taking into account the retention behavior of the analytes under varying isocratic or gradient mobile-phase conditions.

Vanhoenacker et al. [33] achieved a separation of a petroleum short residue by multiple-heart-cut two-dimensional liquid chromatography (2D-LC), using a combination of normal-phase LC (NPLC) and reversed-phase LC (RPLC). Although they were specifically interested in the quantification of PAHs to deal with regulations, their work suggested that comprehensive two-dimensional separation of short residues could provide a more complete overview of sample composition. In fact, Vanhoenacker et al. [34] investigated LC \times LC of the aromatic fraction of mineral oil after liquid-liquid extraction using *n*-hexane and nitromethane. Although this method provided more comprehensive information on the sample, the mineral-oil fraction studied was probably still light enough to enable analysis by the previously mentioned methods, i.e. FT-ICR/MS and HT-GC \times GC, which are more mature and already used routinely. To the authors’ knowledge the application of LC \times LC to short residue fractions has not been reported previously.

In this work, an LC \times LC method has been developed to separate the saturate, aromatic and resin fractions of de-asphalted short residue in order to provide feedback for oil processing. To streamline method development and to test the efficacy of the available software, PIOTR [32] was applied in the current work.

2. Material and methods

2.1. Instrumental

The main instrument used in this study was an Agilent 1290 Infinity II 2D-LC Solution (Agilent, Germany). The system included two binary pumps (G7120 A) with V35 Jet Weaver mixers (G4220-60006), a multisampler (G71678), two thermostatted column compartments (G71168) equipped with a 2-pos/6-port valve (5067-4137) and 2-pos/8-port valve (5067-4214) fitted with two 40- μ L loops, and a diode-array detector (DAD; G7117B) fitted with a Max-Light Cell (G4212-60008). After the DAD a Thermo Scientific Dionex Corona Veo RS charged-aerosol detector (CAD) was attached, through a T-piece with a pressure release (G4212-68001), which communicated with the system through a transformer box (G13908).

An Agilent stable-bond cyanopropyl column (CN; 100 \times 2.1 mm, 3.5 μ m), or a Phenomenex Kinetex pentafluorophenyl column (F5; 100 \times 3.0 mm, 2.6 μ m), or a Phenomenex Kinetex biphenyl column (BiPh; 100 \times 3.0 mm, 2.6 μ m) was used in the first dimension. An Agilent Zorbax RRHD Eclipse PAH column (C_{18} ; 50 \times 3.0 mm, 1.8 μ m) was used in the second dimension.

The system was controlled by Agilent OpenLAB CDS Chemstation Edition A02.02 software. Data were collected using Agilent OpenLAB CDS ChemStation Edition for LC & LC/MS Systems, Version C.01.07 [27] with Agilent 1290 Infinity 2D-LC Software, Version A.01.02[025]. Data was processed using MatLAB R2015a version 8.5.0.197613 (Mathworks, Woodshole, MA, USA).

2.2. Chemicals

2-Propanol (IPA, gradient grade), acetonitrile (ACN, Reag. Ph Eur gradient grade), dichloromethane (DCM, for liquid chromato-

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