



Analysis of the molecular weight distribution of vacuum residues and their molecular distillation fractions by laser desorption ionization mass spectrometry



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HIGHLIGHTS

- Use of LDI mass spectrometry to study petroleum is known to present challenges.
- Vacuum residues and their fractions were studied using LDI mass spectrometry.
- Under careful conditions, reliable average molecular weights were determined.
- The data was used to statistically classify the samples.
- The results can be correlated with physical properties, such as density.

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ABSTRACT

Average molecular weight analysis of vacuum residues using laser desorption ionization (LDI) can be a difficult task due to the significant influence of the experimental parameters and gas-phase reactions. In this paper, laser desorption/ionization time-of-flight mass spectrometry in reflectron mode (LDI TOF MS) was used to analyze vacuum residues and their molecular distillations (MD) fractions obtained at distillation cuts of 510–603 °C, 510–645 °C and 510–687 °C. Those samples associated with the lowest distillation temperature presented the narrowest molecular weight distributions and lowest average molecular weight (Mw) indicating lower complexity. American Petroleum Institute gravity, or API gravity (API°), is a measure of the weight of liquid petroleum compared to water, as expected a correlation between Mw and API° was determined, where lower API° correlated with higher molecular weight. When using higher laser energies mass spectra were acquired with a spacing of 24 Da between the peaks, indicating the production of carbon clusters or “fullerenes”. This suggests that asphaltenes could be the precursors of the clusters that extend over 2500 Da in reflectron mode. Under appropriate experimental conditions, it was possible to produce repeatable molecular distribution for all the samples. Likewise, mass spectrometric data can be used in Principal Component Analysis (PCA) and Partial Least Square (PLS) analysis to discriminate and to predict density of the samples with low percentage of errors.

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1. Introduction

Vacuum residue (VR) is defined as the fraction of petroleum that does not evaporate under vacuum in a distillation process. It is known that VRs are a mixture of hydrocarbons and compounds with heteroatoms species (S, N and O) and metals. Effective production and utilization of these heavy fractions of petroleum requires better understanding of their chemical composition, including molecular weight distribution and physicochemical

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properties like API° [1]. However, heavy oils are more difficult to characterize because of their complex and heterogeneous nature [2]. In recent, many researchers have described molecular distillation (MD) process in the fractionation and characterization of heavy crude oil [3–6].

The main characteristic of high-boiling-point petroleum fractions is the presence of compounds such as resins and asphaltenes, which comprise the most polar fractions of these products [7]. In terms of the physicochemical properties [7], found an increase in density and viscosity, and a decrease in API° for distillate cuts of atmospheric petroleum residue when the temperature of the MD increase. Fractionation processes reduce the high complexity of heavy crude oil and, combined with mass spectrometry (MS), improve the detection capability by reducing matrix effects and ionization suppression [8].

Average molecular weight, elemental analysis, partial simulated distillation; saturates, aromatics, resins and asphaltenes (SARA) separation method, and ¹³C NMR has been included in a objective function in order to reconstruct vacuum residues by Oliveira et al. [9,10]. Experimental average molecular weights were obtained from a correlation between simulated distillation and specific gravity. However, extrapolation of these methods to large compounds may increase the uncertainty of average molecular weight because it is applied to a database that includes molecules of low boiling points. Because of this, average molecular weight has been considered as having the highest inaccuracy in the measurement of the structure–property correlation in molecular reconstructions models [9,11]. Furthermore, Size Exclusion Chromatography (SEC) has been used in the characterization of heavy hydrocarbons. Nevertheless, as has been discussed by Marshall et al. [12], this method is controversial in the analysis of heavy fractions of crude oils due to aggregation and flocculation of asphaltenes that have been observed in the usual eluting solvent (N-methylpyrrolidinone). Laser desorption ionization (LDI) can be used as an alternative in the analysis of average molecular weight (Mw) because this overcomes the issue of volatility and microliter quantities of sample are sufficient for analysis [13–17]. Such samples are also highly suitable for LDI, due to their highly polycondensed aromatic system which feature strong UV absorption. It is well known, however, that the laser desorption/ionization process is influenced by experimental parameters, such as laser fluence, sample abundance and sample composition [19,20,18]. If the laser energy is too high, it is possible for gas-phase reactions to lead to the generation of carbon clusters [19,21]. It is therefore important to pay particular care to the experimental parameters to avoid artefacts, such as gas phase clustering reactions, which would result in error during the calculation of average molecular weight [22].

Principal component analysis (PCA) has been used successfully with spectrometric data in the evaluation of similarities and differences between crude oils [23,24]. However, chemometric analysis in the prediction of physicochemical properties as density with low resolution mass spectrometric data using partial least squares (PLS) has not been carried out. In this paper, the average molecular weight of Colombian vacuum residues and their molecular distillation fractions (distillates and residues for each distillation cut) was obtained by laser desorption/ionization time-of-flight mass spectrometry (LDI TOF MS). The results suggest that Mw increases with the boiling point and it was observed that samples with high asphaltenic content were more likely to produce carbon clusters at higher laser energies. Samples with higher asphaltene contributions can therefore be more prone to artefacts during average molecular weight determination. Additionally, it was possible correlate the API° of the samples with the average molecular distribution. Furthermore, it was possible to use mass spectrometric data

to differentiate between the samples with PCA and to find a model for density prediction by PLS.

2. Experimental section

2.1. Samples

Three VR samples were supplied by the Colombian Petroleum Institute (ICP) were produced using the standard distillation processes detailed in ASTM 2892 and ASTM 5236-06. A molecular distillation unit KD-6-1S (Chemtech Services, Inc.), was used to fractionate the VRs. Three distillation cuts were obtained: 510–603 °C, 510–645 °C and 510–687 °C, these temperatures correspond to atmospheric equivalent temperatures (AET). The VRs fractionated were obtained from crude oils with different physicochemical properties and were identified by their theoretical names VRR, VRG and VRT (see Table 1). For each MD process, two samples were produced: one condensate and one residue sample, in Table 1 was summarized the naming convention. Vacuum residues and their fractions were characterized by density (API gravity, ASTM 4052) and SARA analysis (ASTM 2007). Table 2 shows the API° values for each sample, and Fig. 1 shows the composition following SARA analysis.

2.2. Mass spectrometry

LDI mass spectra were acquired in positive-ion mode using a TOF mass spectrometer, ultrafleXtreme (Bruker Daltonik GmbH, Bremen, Germany). The instrument uses a pulsed Smartbeam II laser, emitting photons at 355 nm with a repetition rate of 500 Hz, and laser pulse duration of 6 ns. The diameter of laser beam focus was 31 μm, and a laser power setting of 60% corresponded to a energy of 3.8 μJ, while a laser power setting of 95% corresponded to a energy of 8.5 μJ. The spectra were measure using 60%, as this represented a suitable choice for sufficient signal while minimizing fragmentation. Acceleration and linear voltages set up were: target voltage 25 kV, first grid at 87.6% and a delay extraction at 50 ns.

The samples for the LDI measurement were prepared by standard dried-droplet method [25]. Using this method, samples were dissolved in chloroform with a concentration of 1 mg/mL for the distillate samples and 0.2 mg/mL for the VRs and residues. The samples were then prepared by spotting 1 μL of the solution on to a target on a stainless-steel plate and the solvent was allowed to evaporate in air.

2.3. Data analysis

Prior to multivariate analysis, the mass spectrometric data were normalized within each row. Multivariate data analysis was performed with Unscrambler X 10.3 software (CAMO ASA, Norway).

Table 1
Samples theoretical names and their distillation temperature conditions.

Sample	VR	Residue	Name	Distillate	Name
T	VRT	603 °C+	R2T	510–603 °C	C2T
		645 °C+	R4T	510–645 °C	C4T
		687 °C+	R6T	510–687 °C	C6T
R	VRR	603 °C+	R2R	510–603 °C	C2R
		645 °C+	R4R	510–645 °C	C4R
		687 °C+	R6R	510–687 °C	C6R
G	VRG	603 °C+	R2G	510–603 °C	C2G
		645 °C+	R4G	510–645 °C	C4G
		687 °C+	R6G	510–687 °C	C6G

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