



Full Length Article

Determination of crude oil physicochemical properties by high-temperature gas chromatography associated with multivariate calibration

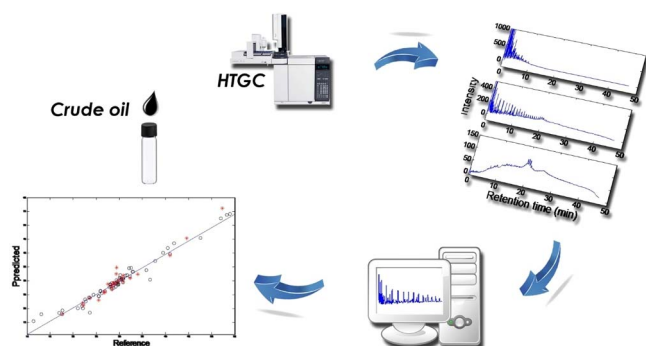


Érica V.A. Rodrigues^a, Samantha R.C. Silva^a, Wanderson Romão^{a,b}, Eustáquio V.R. Castro^a, Paulo R. Filgueiras^{a,*}

^a Center of Competence in Petroleum Chemistry – NCQP, Laboratory of Research and Development of Methodologies for Analysis of Oils – LabPetro, Chemistry Department, Federal University of Espírito Santo, Av. Fernando Ferrari, 514, Vitória, Espírito Santo CEP: 29075-910, Brazil

^b Instituto Federal do Espírito Santo (IFES), Av. Ministro Salgado Filho, Soteco, Vila Velha, ES 29106-010, Brazil

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Crude oil
HTGC
PLS
Multivariate regression

ABSTRACT

Determining the physicochemical properties of petroleum is important for rapid decision-making during the production process. True boiling point (TBP) curve is the most important parameter in the petroleum characterization. However, the TBP can be estimated by high temperature gas chromatography (HTGC). In this paper, the HTGC technique associated with PLS regression was used to estimate API gravity, kinematic viscosity, pour point, carbon residue, saturated and aromatic content in crude oil. We use 98 samples with API gravity ranging from 11.4 to 54.0. Afterwards the developed methods were applied in nine samples from a field of production of the Brazilian coast. PLS model for API gravity, carbon residue, saturates and aromatics contents show root mean square error of prediction (RMSEP) set of 1.7, 0.83 wt%, 6.76 wt% and 4.05 wt% respectively. These models were applied to the nine samples and presented an exact equivalent to the models developed. The models for logarithm of kinematic viscosity and pour point show RMSEP of 0.31 and 12 °C respectively. Furthermore, tests applied in all models for evaluating the presence of systematic and trend errors indicate that there are no significant evidences of the presence of these types of error in the residues, at significance level of 5%.

* Corresponding author.

E-mail address: paulo.filgueiras@ufes.br (P.R. Filgueiras).

1. Introduction

Crude oil is the most used source of energy in the world and it is also the main source of feedstock for various types of industries [1,2]. Determination of many physicochemical properties of crude oil is required for maximum exploitation and to support operational decision-making along the whole production process [1,2]. Among the various properties analysed in the industry, we can highlight: API gravity, kinematic viscosity, content of saturates, content of aromatics, pour point and carbon residue.

API gravity and kinematic viscosity are fundamental properties in the initial production process, as they are the foundation for scaling pipelines, valves, storage tanks, pump, compressors and oil measuring equipment [2,3]. Contents of saturates, aromatics and polar components (resins and asphaltenes) (SAP) are auxiliary parameters used for infer physicochemical properties of crude oil [4]. Pour point is a critical parameter to a proper functioning of the production line. This parameter is related to the content of and the kinematic viscosity [5], because at temperatures close to the pour point, the rheological behaviour of the oil modifies due to increase in the viscosity resulting from the phase change of the *n*-paraffins. This viscosity increase hampers the oil transportation through the pipelines compromising the production process [5,6]. Carbon residue is an auxiliary parameter in crude oil valuation, as it is an indication of asphalt content or the amount of lubricant oils which can be produced in the refining process [1,2,7].

The determination of physicochemical properties enables a better understanding of rheological behaviour and chemical composition of the crude oil. However, most characterization assays are time-consuming and require large amounts of sample [1]. Infrared spectroscopy and nuclear magnetic resonance (NMR) techniques are broadly used as alternatives to conventional methods to estimate physicochemical properties of crude oil [8–17]. Filgueiras et al. [18] used the attenuated total reflection with Fourier transform infrared spectroscopy (ATR-FTIR) associated with multivariate calibration based on support vector regression (SVR) and partial least squares (PLS) regression to estimate API gravity, kinematic viscosity and water content of medium crude oil. In 2016, Duarte et al. [19] used ¹H NMR associated with PLS regression to determine API gravity, carbon residue (CR), wax appearance temperature (WAT) and basic organic nitrogen (BON) of a great variety of crude oil.

Another technique that has gained particular importance in the chemometric approach is gas chromatography, as it is already consolidated by the oil industry in the analysis of crude oils and its derivatives [20,21]. Crude oils are usually analyzed by high temperature gas chromatography (HTGC) according to ASTM D7169-11 [22] to estimate the true boiling point (TBP) curve using the methods described in ASTM D2892 [23] and D5236 [24]. TBP curves are used in the industry as standards to establish the price of crude oils [25,26]. Furthermore, the HTGC method is automatized, requires low amount of samples and enables fast visualization of the chemical profile of the oil. This way, HTGC chromatograms were used by Medina and Guzmán (2012) to predict API gravity and kinematic viscosity of Colombian crude oils associated with principal component analysis (PCA) and PLS regression [27]. This work aims to determine API gravity, kinematic viscosity, pour point, saturates and aromatic contents and carbon residue in crude oils (light to heavy) associating HTGC chromatograms with multivariate calibration.

2. Methodology

2.1. Characterization of samples

In this paper we used 98 different crude oils samples from the Brazilian coast sedimentary basin with API gravity ranging from 54.0 to 11.4. Physicochemical characterization of the oils was performed according to the standard methods. The API gravity was determined by

ISO 12185 [28], the assay consists of the injection of about 1 mL of crude oil into an automatic density meter Anton Paar model DMA 5000, which operates at 50 °C. This temperature is corrected to 60 °F and the result is used to obtain the API gravity using the equation below:

$$API = \frac{141.5}{\text{density}(60\text{ }^{\circ}\text{F})} - 131.5 \quad (1)$$

The kinematic viscosity was determined by the standard ASTM D7042 method [29]. The assay consists of injecting the crude oil sample into an Anton Paar Stabinger SVM 3000 digital viscometer and the measurement is made at 50 °C. Viscosity varies exponentially regarding density, thus the regression models were constructed with the logarithm of kinematic viscosity to obtain a linear relationship [30].

Pour point was determined by ASTM D5853 [31], as described by Sad et al [5]. Carbon residue was determined according to ASTM D4530 (micro) [32], by weighing a quantity of crude oil sample in a glass vessel and heating to 500 °C under a controlled and inert atmosphere of nitrogen. Under these conditions, the sample undergoes coking reaction, the volatile compounds are swept away by nitrogen, and the resulting carbonaceous residue is weighed and represents the mass percentage of carbon residue in the original sample. Saturates, aromatics and polar contents were determined using modified ASTM D2549 [33], as described by Filgueiras et al. [4].

2.2. Obtainment of HTGC chromatograms

The samples were analyzed in a chromatograph from Agilent Technologies, model 6890N with automatic injection system by programmable temperature, equipped with a metallic capillary column internally coated with polydimethylsiloxane (Agilent Technologies; 5 m × 0.53 mm i.d.; 0.09–0.15 μm) and flame ionization detector (FID). The method is based on the standard ASTM D7169-11. All samples were diluted in carbon disulfide (2 wt%) and injected in the column with a ramp of 50 °C–430 °C at a rate of 15 °C·min⁻¹. The carrier gas was helium with a flow rate of 20 mL·min⁻¹. The initial temperature of the column oven was of –20 °C and it was increased at a rate of 10 °C·min⁻¹ up to 430 °C and remained constant for 2 min. The detector's temperature was 435 °C. For the retention times calibration two different standards were used (a mixture of C₅–C₂₈ light *n*-paraffins and a mixture of C₃₀–C₁₂₀ heavy *n*-paraffins), both from Analytical Controls. The chromatograms data was processed by Agilent Technologies' GC ChemStation software.

2.3. Construction of the PLS models

Partial least squares (PLS) regression is the most used calibration method to construct multivariate calibration models in fairly complex data [18]. This method uses the analytical signal and the information of interest enabling a mathematical relation between instrumental response and a determined property of the sample [34]. This can be done in the presence of interfering factors, given that those are also in the calibration set [35]. In order to construct the calibration model, the spectral matrix **X** and the interest variables matrix **y** are simultaneously decomposed in scores and loadings matrices according to the following equations:

$$\mathbf{X} = \mathbf{TP}^T + \mathbf{E} \quad (2)$$

$$\mathbf{y} = \mathbf{Tq}^T + \mathbf{f} \quad (3)$$

Where **T** is the scores matrix, and **P** and **q** are loadings matrices and, **E** and **f** are the associated residues. The linear relation between both blocks can be made by correlating scores for each component using a linear model. The regression vector **b** is determined by the following relation:

$$\mathbf{b} = \mathbf{W}(\mathbf{P}^T\mathbf{W})^{-1}\mathbf{q} \quad (4)$$

Download English Version:

<https://daneshyari.com/en/article/6631680>

Download Persian Version:

<https://daneshyari.com/article/6631680>

[Daneshyari.com](https://daneshyari.com)