Fuel 181 (2016) 660–669

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Determination of some physicochemical properties in Brazilian crude oil by ^{1}H NMR spectroscopy associated to chemometric approach

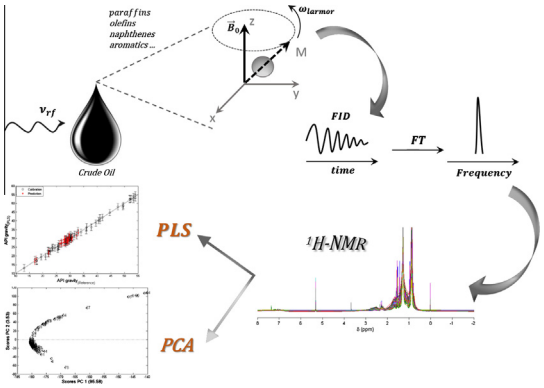
Lucas M. Duarte [a], Paulo R. Filgueiras [b], Samantha R.C. Silva [b], Julio C.M. Dias [c], Lize M.S.L. Oliveira [c], Eustáquio V.R. Castro [b], Marcone A.L. de Oliveira [a,*]

[a] Analytical Chemistry and Chemometrics Group – GQAQ, Departament of Chemistry, Institute of Exact Sciences, Federal University of Juiz de Fora, University City, CEP 36036-330 Juiz de Fora, MG, Brazil
[b] 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, CEP: 29075-910 Vitória, Espírito Santo, Brazil
[c] CENPES/PETROBRAS, CEP 21941-598 Rio de Janeiro, RJ, Brazil

HIGHLIGHTS

- API gravity, carbon residue, wax appearance temperature and basic organic nitrogen in crude oil were determined.
- ^{1}H NMR spectroscopy associated to partial least squares regression to determine such properties were used.
- A previous study involving pattern recognition to better known of sample set was performed.
- Principal component analysis was used as pattern recognition method.
- Accuracy, confidence intervals, systematic and tendency errors were evaluated in each models fitted.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 February 2016
Received in revised form 6 May 2016
Accepted 9 May 2016
Available online 17 May 2016

Keywords:
Crude oil
Physicochemical properties
PCA
PLS
^{1}H NMR

ABSTRACT

An alternative method for establishing crude oil properties, using ^{1}H nuclear magnetic resonance (^{1}H NMR) associated with partial least squares regression is proposed. It can be used for determination of API gravity, carbon residue (CR), wax appearance temperature (WAT) and basic organic nitrogen (BON). At a 95% confidence level, the main results obtained for API gravity, CR, WAT and BON models provide determination coefficients for prediction (R^2_p) and root mean square error for prediction (RMSEP) equal to 0.945, 0.802, 0.857 and 0.789; and 0.8, 0.598% w/w, 3.8 °C, 0.009% w/w, respectively. The residuals of each fitted model were evaluated taking into account systematic and random errors and all results were considered acceptable. The determination of these physicochemical properties in Brazilian crude oil was successfully achieved using a chemometric approach in association with ^{1}H NMR.

1. Introduction

Petroleum, meaning literally "rock oil", is the term used to describe variety of hydrocarbon-rich fluids that have accumulated in subterranean reservoirs. Crude oil varies dramatically in color, odor and flow properties that reflect the diversity of its origin

* Corresponding author.
E-mail address: marcone.oliveira@ufjf.edu.br (M.A.L. de Oliveira).

http://dx.doi.org/10.1016/j.fuel.2016.05.049
0016-2361/

[1]. Chemically, crude oils are formed in most of its constitution by different hydrocarbons families – paraffinic, naphthenic or aromatic compounds – giving them different physicochemical characteristics [2]. The wide range of compounds present in crude oil implies a complex characterization, which is made by checking for over twenty physicochemical parameters such as density, carbon residue, viscosity, refractive index, among others. This culminates in a long time evaluation, many times reaching six months and resulting in higher economic costs.

The API gravity is an arbitrary scale for measuring the density of petroleum and its derivatives and reference methods are given by ASTM D4052 [3] (American Standards for Testing and Materials) and ISO 12185 [4]. On the other hand, the amount of carbon residue (CR) generated by an oil suggests an indication of the relative tendency to oil coke formation and the ASTM D4530 is the official methodology used to determination [5]. Regarding the wax appearance temperature (WAT), such monitoring is of great importance because it assists in preventing blockage of the fluid by precipitation on the walls of pipelines, production plants and transportation pipelines during the oil and gas production. The WAT is an indicator of how well the oil will leak under cold conditions. The WAT can be analyzed in crude oil by cross polarization microscopy, viscosimetry, thermomicroscopy, fluidity point, and differential scanning calorimetry (DSC) [6]. In crude oil is very important to investigate and identify nitrogen compounds such as basic organic nitrogen (BON), which could be related to the efficiency decrease in the catalytic processes and contribute to the instability of the products associated to crude oils during storage step [7]. The BON is officially analyzed by UOP 269 method [8].

In order to save time and cost for the determination of the many physicochemical parameters of oil, in recent years many studies involving spectroscopy associated to chemometrics approach has gained prominence in scientific literature due to its intrinsic advantages such as non-destructive method, compatible efficiency, quickness and low cost compared with conventional methods recommended by ASTM. Aiming the crude oil characterization, quantitative methods developed by multivariate calibration using infrared data [9–12] are the most common found in literature and some of these works are also shown as mid infrared (MIR) [13,14] and near infrared (NIR) [15–17] according to the spectral range used. Another kind of spectroscopy that has been gaining prominence for crude oil analysis is the nuclear magnetic resonance (NMR) due to the qualitative (in molecular level) and quantitative power for investigation of chemistry and physical properties in complex mixtures [18–22]. Molina et al. [23] in 2007 analyzed a wide range of crudes using proton NMR (^{1}H NMR) associated to partial least squares (PLS) in order to estimate cut product yields. Three years later they published other paper with similar methodology, where vaccum residue of Colombia crudes were used to predict saturated, aromatic, resin and asphalthens (SARA) composition and some physicochemical properties [24]. Masili et al. [25] also used ^{1}H NMR/PLS to predict density, UOP characterization factor, total acidity number, sulfur content and true boiling point distillation yields, while Peinder et al. [26] worked with IR, ^{1}H NMR, ^{13}C NMR and three sets of merged spectra to predict the long residue properties. A recent paper applied support vector machine to ^{1}H NMR to predict some distillation temperatures was published and their results were compared to conventional PLS method [27]. In our knowledge there is no previous works to predict BON by ^{1}H NMR associated to multivariate calibration.

Within this context, the present work aims explore ^{1}H NMR data in order to build and validate PLS models for determination of API, CR, WAT and BON in a wide range of Brazilian crude oil from light to heavy oils. Prior to construct the predictive models, a principal component analysis study to the better knowledge of the sample set and outlier identification was performed. The predict values for all models have been shown within 95% confidence interval. For the models validation, besides to take into account the conventional multivariate parameters, the prediction residues by statistical tests to systematic and tendentious errors were evaluated.

1.1. Partial least squares

The pioneering work with PLS has been done in seventies by Herman Wold in Econometrics area. However, using this approach to chemical applications, initiated by Svante Wold and Harald Martens, only came in the late seventies after the first publication of Kowalski and his collaborators [28]. The PLS has its simplest form used in many areas of chemistry and technology, i.e. in the form of two predictive blocks. This is a method for relating two data matrices, $\boldsymbol{X}$ and $\boldsymbol{Y}$, using a linear model that goes beyond traditional regressions, which also modeling $\boldsymbol{X}$ and $\boldsymbol{Y}$ structures; where $\boldsymbol{X}$ contains the variables (instrumental responses) and $\boldsymbol{Y}$ the property of interest to be modeled [29]. In the present work have been used PLS1 and every time that $\boldsymbol{Y}$ is referred to matrix, in fact, $\boldsymbol{Y}$ will be a column matrix (vector), because just one property will be estimated by each model built. The matrix $\boldsymbol{X}$, having $\boldsymbol{n}$ samples and $\boldsymbol{m}$ variables and column matrix $\boldsymbol{Y}$ containing $\boldsymbol{n}$ samples with $\boldsymbol{k}$ properties values, they are simultaneously decomposed into a sum of $\boldsymbol{h}$ latent variables according to the following equation:

$$\boldsymbol{X}_{(nxm)} = \boldsymbol{T}_{(nxh)} \cdot \boldsymbol{P}'_{(hxm)} + \boldsymbol{E}_{(nxm)} = \sum_{h} \boldsymbol{t}_i \cdot \boldsymbol{p}'_i + \boldsymbol{e}_i \quad (1)$$

$$\boldsymbol{Y}_{(nxk)} = \boldsymbol{U}_{(nxh)} \cdot \boldsymbol{Q}'_{(hxk)} + \boldsymbol{F}_{(nxk)} = \sum_{h} \boldsymbol{u}_i \cdot \boldsymbol{q}'_i + \boldsymbol{f}_i \quad (2)$$

where $\boldsymbol{T}$ and $\boldsymbol{U}$, and $\boldsymbol{P}$ and $\boldsymbol{Q}$ refer to the scores and loadings from the matrices $\boldsymbol{X}$ and $\boldsymbol{Y}$ respectively; $\boldsymbol{E}$ and $\boldsymbol{F}$ relate to residues matrices. The product of $\boldsymbol{T}$ by $\boldsymbol{P}$ approaches the spectral data while $\boldsymbol{U}$ by $\boldsymbol{Q}$ the reference values.

The regression vector $\boldsymbol{b}$ can be determined by the following relationship:

$$\boldsymbol{b} = \boldsymbol{W}\left(\boldsymbol{P}'_{(hxm)}\boldsymbol{W}\right)^{-1}\boldsymbol{Q}'_{(hxk)} \quad (3)$$

where $\boldsymbol{W}$ is the matrix of weights of the PLS model. The regression vector $\boldsymbol{b}$ considers the contribution of each variable to the PLS model, i.e., the higher the b value, indicates how much the variable for model calibration is important.

2. Material and methods

2.1. Reference methods

In the present work were considered 106 samples of Brazilian crude oil. Samples from different oil fields – off-shore and on-shore – located in sedimentary basin of Brazilian coast were used. These oils showed different characteristics since the sample set was comprised from light to heavy oils, i.e., with API values covering the range from 54 to 11.4. The analytical tests of physicochemical properties were performed by standard methods. The API gravity was determined according to ISO 12185 standard method [4]. A small, typically less than 1 mL, portion of crude oil sample was introduced into an oscillating sample tube (Anton Paar DMA 4500 digital density meter) using a dry and clean syringe. The change in oscillation frequency caused by the change in the mass of the tube is used to calibrate data and to relate with specific gravity of the sample.

The CR was determined according to ASTM D 4530 (micro) standard method [5]. The CR is the tendency to form carbon deposits