



Determination of naphtha composition by near infrared spectroscopy and multivariate regression to control steam cracker processes

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ABSTRACT

Naphtha is an important feedstock for the petrochemical industry and accurate measurement of its detailed composition is essential for the optimization of pyrolysis processes. In the present work, the suitability of using near infrared (NIR) for the determination of 38 parameters used to characterize naphtha was evaluated: pooled composition (PIONA); specific composition groups (C3 paraffins; C4–C12 n-paraffins; C4–C12 iso-paraffins; C5–C7 + naphthenics; C8–C10 aromatics; C4–C6 olefins) and individual components (toluene, benzene, iso-pentane, cyclopentane, methyl cyclopentane; cyclohexane, xylenes, 1,3 butadiene and isoprene). Besides the usual comparison against reference methods, NIR predictions were also evaluated for their ultimate use in determining the coil outlet temperature (COT) for process control. 28 models for the naphtha parameters presented root mean square error (RMSEP) values lower or close to the reproducibility of the reference method and exhibited satisfactory correlation values (r^2) when compared with r^2_{max} . Among the ten remaining parameters, two (1,3 butadiene and isoprene) presented very low concentrations and it was not possible to obtain a suitable model. Eight parameters had RMSEP values higher than the intralaboratory reproducibility and/or r^2 values lower than expected. Despite this, the complete naphtha composition obtained from NIR prediction was demonstrated to be quite suitable for COT simulation, providing accurate COT values compared to the values estimated from the reference method.

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1. Introduction

In the chemical industry, very important products such as ethylene and propylene are obtained from hydrocarbon cracking in pyrolysis furnaces. Among the hydrocarbon feedstocks, naphtha is one of the main raw materials for the petrochemical industry. Accurate and detailed measurement of the complex naphtha composition is a fundamental requirement for process optimization since the target ethylene yield of the pyrolysis furnace is set based on the current naphtha quality [1–3].

Naphtha is composed of hundreds of C4–C15 hydrocarbon compounds, mostly n-paraffins, isoparaffins and naphthenics, in the distillation range from 20 to 220 °C [4,5]. The concentration of the major constituents varies widely, depending on the origin of petroleum as well as the operating conditions of the refinery [3–5].

Naphtha is used by the petrochemical industry to produce basic raw materials for second generation chemical industries such as the

polymerization industry (eg. polyethylene and polypropylene). Such products can be obtained from pyrolysis furnaces through naphtha stream cracking, i.e. the thermal decomposition of long-chain molecules into short-chain compounds such as ethylene and propylene [3]. In this process, the heat from combustion gas in the furnace convection section is absorbed by naphtha, which is then mixed with water vapor, reaching temperatures as high as 600 °C. This mixture passes through the tubular radiation section, where the temperature is raised until it reaches a pre-established coil outlet temperature (COT) that can vary typically from 810 to 860 °C, under controlled conditions of pressure and residence time [6]. COT is a critical variable and must be accurately tuned to produce the required ethylene to propylene ratio, and also maximize the yield of such products. Since other important process variables are kept constant (e.g. furnace geometry and air inlet to combustion chamber) or at controlled conditions (e.g. feed flow and dilution steam to hydrocarbons ratio), the most important parameter to define COT is the naphtha composition. Based on 38 parameters of naphtha composition, the optimum COT for a given feedstock can be defined using a simulation tool for furnace operating conditions optimization

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(SPYRO®, Technip Benelux B.V./Pyrotex Divison, France). The 38 parameters of naphtha composition required for Spyro simulation are: pooled composition (PIONA); more specific composition groups (C3s paraffins; from C4s to C12s n-paraffins; from C4s to C12s iso-paraffins; from C5s to C7s naphthenics; from C8s to C10s aromatics; from C4s to C6s olefins) and individual components (toluene, benzene, iso-pentane, cyclopentane, methyl cyclopentane; cyclohexane, xylenes, 1,3-butadiene and isoprene). Such parameters are quite important to maximize the furnace pyrolysis efficiency. For example, the olefins content is related to coke formation that leads to a decrease of furnace operational time, iso-paraffins are related to methane and propylene production, and higher content of C5s to C8s n-paraffins is desired for maximum ethylene generation. If the composition of a feedstock being actually processed is not available, the COT may not be set to the optimum value resulting in excess energy consumption or significant losses in terms of high value petrochemical products. It is worth noting that, besides the intrinsic variation of naphtha composition, the feed of the pyrolysis furnaces is also influenced by the use of several internal recycles resulting from the petrochemical processing.

Several analytical methods have been proposed to determine naphtha composition. Most methods are based on chromatographic techniques, such as gas chromatography [7], multidimensional chromatography [8], capillary chromatography [2] and gas chromatography mass spectrometry [9]. The ASTM D-5134 [10] method, based on gas chromatography with flame ionization detector, is commonly used for this application by petrochemical industry laboratories. However, it requires an extended analysis time (usually more than 2 h) to get suitable peak resolution for the hundreds of compounds present in this kind of sample. Since huge amounts of naphtha are continuously processed in pyrolysis furnaces (typically more than 70 tons per hour per furnace) such analysis time is not suitable for adequate process optimization. This drawback has been observed in similar applications and has been overcome by the use of near infrared spectroscopy (NIRS) allowing the fast, precise and accurate analyses required for process control [3,11].

The feasibility of using NIRS to determine quality parameters of naphtha has been demonstrated [4,12,13]. Chung et al [13] used NIRS in the determination of paraffins, iso-paraffins, aromatic and naphthenic content in synthetic naphtha samples. The authors also evaluated the effect of resolution (in the range from 4 to 32 cm^{-1}) for the NIR spectra acquisition in the chemometric model performance, using partial least squares regression (PLS). The results showed the importance of spectral resolution in the construction of PLS models in complex samples such as naphtha, which requires a minimum of 8 cm^{-1} resolution to estimate the sample composition satisfactorily. Lee et al [12] employed PLS-MW (Moving Window PLS) to find the best spectral range to determine the quality parameters in naphtha (total paraffins, n-paraffins, iso-paraffins, naphthenics, aromatics and distillation temperatures) and in gasoline (number of octane and vapor pressure). The results showed that the best spectral region for paraffins, iso-paraffins, n-paraffins and naphthenic was within the range of 4550–4040 cm^{-1} . For aromatic determination the best region was over the 4700–4540 cm^{-1} region. To determine the physical properties of naphtha (distillation temperatures), a narrow spectral range was selected within the 4460–4020 cm^{-1} range. Rebouças et al. [4] proposed an analytical method using NIR spectroscopy with PLS calibration models to predict chemical and physical properties such as relative density, distillation curve and chemical composition (n-paraffins, iso-paraffins, naphthenics and aromatics) in medium naphtha in order to improve the process control of a naphtha fractionation unit for aromatics production.

In the works using NIR spectroscopy for naphtha analysis found in the literature, few parameters were evaluated and only the main grouped composition was estimated (n-paraffins, iso-paraffins, naphthenics and aromatics). In the present work, the suitability of using NIRS for determination of 38 parameters in naphtha samples was evaluated: pooled composition (PIONA); more specific composition groups (C3s paraffins; from C4 to C12s n-paraffins; from C4s to C12s iso-paraffins;

from C5s to C7s naphthenics; from C8s to C10s aromatics; from C4s to C6s olefins) and individual components (toluene, benzene, iso-pentane, cyclopentane, methyl cyclopentane; cyclohexane, xylenes, 1,3-butadiene and isoprene). Such a detailed measurement is required as input to the furnace optimization software (SPYRO®, Technip Benelux B.V./Pyrotex Divison, France) as mentioned before. This is an enormous challenge to NIRS application due to its inherently lower sensitivity compared to chromatography and to the complex sample composition.

In this work, the initial evaluation of the performance of the NIR multivariate models constructed to determine the naphtha composition was performed in the traditional manner, by comparing the results with those obtained from the reference methods. In contrast to previous works, however, the results obtained by the NIR method were also evaluated for their ultimate use in the determination of COT, aiming at the control of the naphtha pyrolysis process.

2. Experimental

2.1. Samples

162 samples of straight run naphtha were collected from the Braskem site (Basic Petrochemicals Unit) located in Bahia, Brazil, in sampling points at the raw materials storage tanks or from the pyrolysis units. In order to have a representative data set of the process variability, samples were collected over a two-month period, between April and June 2010. Samples from the database of the laboratory, collected in August and October 2008 were also included. All samples were collected in stainless steel cylinders directly at the process sampling points and stored in a refrigerator at 4 °C. Prior to analysis, they were left to reach room temperature of 20 ± 2 °C.

2.2. Spectra acquisition

The near infrared transmission spectra were recorded in the 10000–3900 cm^{-1} (1000–2564 nm) region on a MB 160 Series Fourier-Transform NIR Spectrometer (Bomem/Hartmann & Braun, Canada). A CaF_2 sample cell, model SI-4, with 0.5 mm pathlength (International Crystal Labs, NJ, USA) and an InAs detector under nitrogen purge were used. The room temperature was kept at 20 ± 2 °C for spectrum acquisition. Before each analysis a background spectrum of air was recorded with a clean empty cell. All FT-NIR spectra were collected with an average of 32 scans and at a resolution of 4 cm^{-1} .

2.3. Reference analysis

The chemical composition of all samples was determined, according to the ASTM Standard D-5134 [10]. A gas chromatograph equipped with a flame ionization detector (FID), from Agilent Technologies—USA (model 7890A), with 40 m \times 0.10 mm i.d. \times 0.25 μm fused silica methyl silica capillary column (J&W Scientific) was employed.

2.4. Data analysis and software

The sample set was divided into calibration (60%) and prediction (40%) subsets by applying the SPXY (sample set partitioning based on joint x–y distances) algorithm [14]. Detection and elimination of outliers were made using score, residual and leverage plots. After outlier elimination, the number of calibration samples varied between 81 and 97, depending on the parameter. For the external validation sets, the number of samples varied between 60 and 76. All spectral data were mean-centered before modeling procedures.

The models were built using Partial Least Squares Regression (PLSR). This regression method has been described in detail in relevant references [15,16] and, therefore, only a brief explanation is presented here. The data matrix **X** is formed by the NIR spectra of the naphtha samples and the matrix **Y** contains the reference values for the

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