

Application Note AN-PAN-1047

Monitoring water content in refined products inline with NIR spectroscopy

Crude oil consists of at least 500 different components. It is processed by fractionation and refining to create many products including liquefied gas, gasoline, diesel, heating fuel, and lubricants. As per recent projections, the anticipated demand for crude oil is set to rise to 113 million barrels per day by 2025 [1].

This vital resource is used in many applications across various sectors. Crude oil is utilized during the manufacturing of plastics, textiles, dyes, cosmetics, fertilizers, detergents, building materials, and

pharmaceuticals.

This Application Note introduces a method for the «real-time» monitoring of water content in crude oil or refined products in refineries. To ensure safety, reliability, and optimal performance, a single explosion-proof inline process analyzer is recommended, such as the 2060 *The* NIR-Ex Analyzer by Metrohm Process Analytics. This minimizes human intervention, enhances product quality, and boosts profits, especially in the hazardous environment of a refinery.



INTRODUCTION

In a refinery, crude oil is desalted then separated into several intermediate materials via an atmospheric or crude distillation unit (also known as a distillation tower or CDU), depending on its boiling temperature. The quality of fractions from the CDU must be continuously monitored.

To satisfy the high demand for gasoline, the heavier side cuts from the CDU are reformed and resolved to increase the light intermediate materials, thus increasing the gasoline fraction. The overhead distillate fraction naphtha (a mixture of C5 to C10 hydrocarbons) is produced from relatively light components and is supplied to ethylene plants as a raw material (Figure 1).

The CDU must operate efficiently at all times; however, the crude feed is full of impurities which cause corrosion and fouling throughout the refining process. Operating conditions that also influence corrosion and fouling include the temperature of the crude column overhead, crude, and reflux, as well as the water wash and overhead vapor water content.

Water extracts acids and amines present in the crude oil (see AN-PAN-1001 for more information). This

vaporized water condenses as reflux liquid flowing down the column. The resulting heated salts are therefore deposited on the tower trays. These salts accumulate, causing a higher pressure drop, resulting in a loss of distillation column efficiency and profit.

Determining the water content in crude oil, refined petroleum products, fuels, biofuels, lubricants, and other related products is important for maintaining quality control, meeting trade specifications, protecting financial value, and enhancing process optimization. Monitoring this parameter enables the refinery to mitigate corrosion, safety problems, and infrastructure damage which can result from undesired moisture levels.

Generally, the determination of water content in naphtha fractions is performed with a reference method (i.e., Karl Fischer titration also provided by Metrohm) which requires several reagents. A safer, faster way to monitor the water content in CDU overhead fractions is inline with reagent-free near-infrared spectroscopy (NIRS). Spectroscopy offers numerous advantages over many wet-chemical analytical methods.



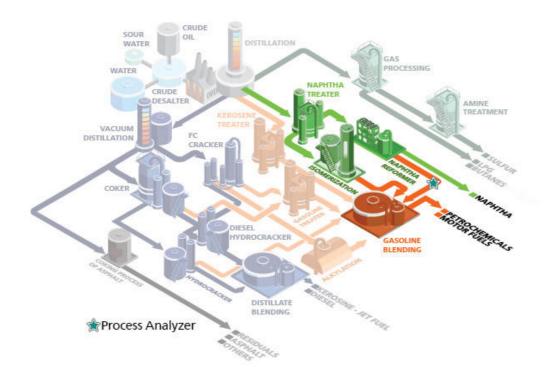


Figure 1. Illustration of the petrochemical refining process with a focus on the naphtha gas stream. The green star notes a suggested NIR measuring point.

Near-infrared spectroscopy is economical and fast, enabling qualitative and quantitative analyses that are noninvasive and nondestructive. A diverse range of parameters can be determined simultaneously in seconds from just one analysis. NIRS is an indispensable analysis technique that can be used along the entire production chain—from incoming materials to processing to the quality control of finished products.

Metrohm Process Analytics manufactures NIRS process analyzers that gather «real-time» spectral data from the process. These are used for comparison to a primary method (e.g., Karl Fischer titration) to create a simple, yet indispensable model to easily monitor QC parameters in near real-time. Gain more control over the refining process with a 2060 *The* NIR-Ex Analyzer configured for applications in ATEX zones (Figure 2). This process analyzer is capable of monitoring up to five sample points per NIR cabinet with the multiplexer option.



Figure 2. The 2060 The NIR-Ex Analyzer from Metrohm Process Analytics is suitable for use in hazardous areas.

APPLICATION

Each sample is measured in a 2 mm pathlength flow cell after the drying phase of naphtha. Wavelength

range used: 1800–2100 nm. An ATEX NIR process analyzer is recommended for explosion-proof areas.

Table 1. Typical concentration range of water content in naphtha fractions.

| Components | Range (%) |
|------------|-----------|
| Water | 0-0.3 |

TYPICAL RANGE

Modeling and comparison to Primary Method:

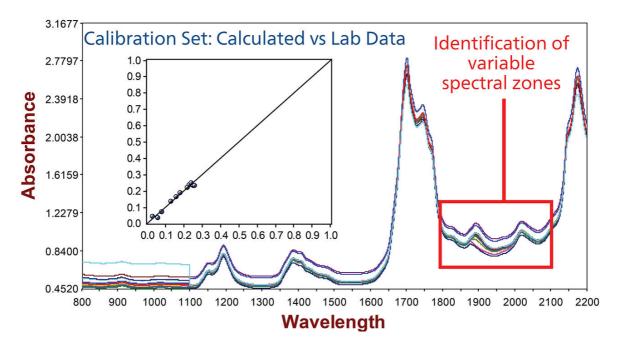


Figure 3. Data correlation between the primary method (Karl Fischer titration) and NIR spectra illustrating how accurate the correlation is between both methods.

REMARKS

A reference method (e.g., Karl Fischer titration) must still exist as a check method. An appropriate range of samples covering the process variability should be analyzed by both methods to build an accurate NIR model. Correlations are made to specific process specifications.



CONCLUSION

Accurately monitoring water content in crude oil and its intermediate products in a refinery is of critical importance. Impurities in the crude oil lead to corrosion and fouling, affecting operational efficiency. The utilization of reagent-free NIRS provides a safer, faster, and noninvasive method for this purpose. Metrohm Process Analytics offers the 2060 *The* NIR-Ex Analyzer which is specifically designed for hazardous

areas. This process analyzer is ideal for monitoring water content and other parameters in various petrochemical products within seconds.

It is still recommended to maintain a reference method like Karl Fischer titration for verification purposes. Analyzing a range of samples with both methods is essential for building an accurate NIR model.

RELATED PROCESS APPLICATION NOTES

AN-PAN-1007 Online analysis of peroxide in the HP-PO process

<u>AN-NIR-025</u> Real-time inline predictions of jet fuel properties by NIRS

AN-NIR-022 Quality Control of Gasoline – Rapid determination of RON, MON, AKI, aromatic content, and density

OTHER RELATED DOCUMENTS

8.000.5325 Water Content Analysis

BENEFITS FOR NIR IN PROCESS

- Optimize product quality and increase profit with faster response time to process variations.
- Greater and faster return on investment.

- No manual sampling needed, thus less exposure of personnel to dangerous chemicals.
- Increase profits by reducing the occurrence of corrosion and fouling (i.e., controlled water content levels).











REFERENCE

1. OPEC: Oil Outlook to 2025. https://www.opec.org/opec_web/en/1091.ht m (accessed 2023-10-16).

CONTACT

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CONFIGURATION



2060 The NIR-Ex Analyzer

The 2060 *The* NIR-Ex Analyzer is the next generation of process spectroscopy instruments from Metrohm Process Analytics. With its unique and proven design from the inside out, it delivers accurate results every 10 seconds. It can provide non-destructive analysis of liquids and solids directly in the process line or in a reaction vessel by using fiber optics and contact probes. It has been designed to connect up to five (5) probes and/or flow-cells. All five channels can be configured independently from each other using our versatile embedded proprietary software.

Additionally, this analyzer is IECEx certified and fulfills the ATEX EU Directives. It has been designed with an approved purge/pressurization system together with intrinsically electronic devices, preventing any potentially explosive fumes or gases from the ambient air entering the analyzer enclosure. Furthermore, it is available in three other versions: the 2060 *The* NIR Analyzer, 2060 *The* NIR-R Analyzer, and 2060 *The* NIR-REx Analyzer.

