COMPARISON BETWEEN NIR/FT-IR AND 3RD GENERATION OP-NMR TECHNOLOGY

The on-line process analysers market is evolving quickly from discrete analysers into corelative ones. Correlative analysers provide an inherent advantage that multiple properties can be derived from a single measurement. Well known on-line process correlative analysers are the NIR /FT-IR/RAMAN, based optical methodologies. Lately, a new concept of an on-line process correlative analyser has emerged, the On-line Process NMR (OP-NMR) analysers

On-line Process Nuclear Magnetic Resonance (OP-NMR) analysers are beneficial in chemical and petroleum industries for qualitative and quantitative analyses of physical properties of process streams. NMR selectively specifies and quantifies hydrogen atoms with regard to the molecular structure of substances and their presence in mixtures. Its linear spectral response enables chemometrics to easily perform accurate linear correlation between provided spectral data and the physical properties to be determined. NMR process analysers are applicable to opaque and transparent solutions alike. This is highly beneficial for its application in process control in chemical process and petroleum industries.

Stability, reliability and accuracy are basic requirements for successful implementation of process analysers. Previous generations of NMR process analysers had significant issues moving from the lab to hostile production environments. This was predominately caused by a high sensitivity towards temperature fluctuations in production locations and input streams.

Process streams are characterised by different temperatures and flow properties. It is up to the analyser and the sampling system to eliminate any interference of these on analytical results.

A thorough engineering analysis of the first and second generation production units based on real-like deployments feedback was the foundation on which the 3rd generation on-line OP-NMR process analyser was developed. The challenge was to reduce its sensitivity towards the influence of temperature variations of process streams and to improve its reliability. This was achieved by entirely re-innovating its hardware and software. The third generation includes a new design of the magnet with an increase of the bore size to 30 mm and a newly developed measuring probe. Manually wrapped shim coils were replaced by new state of the art PCB cards. As a result of these improvements, enhanced long and short term stability, reduced sensitivity towards temperature variations, smaller footprint, improved SNR ratio, improved sensitivity and significant conditioning simplification have been achieved.

The 3rd generation is distinct from its previous generations by its low susceptibility towards temperature fluctuations, its high stability and its reduced cost of maintenance. Reliable measurements of transparent, dense and opaque process streams can be conducted without any impact from temperature differences between different streams. It can therefore benefit the chemical plants and refineries in their efforts to effectively monitor and control their entire processes. It prevents production of off-spec and borderline products and avoids the need for reprocessing. This in turn will definitely have its output on the plant economics.

Introduction

At present, refinery streams are predominately monitored by discrete process analysers, based on standard ASTM methods, and/or optical spectrometry based process analysers, such as NIR/FTIR. Standard method analysers are not dependent on crude quality and other factors. However, their response time is longer and their maintenance is expensive. Various optical spectroscopy analysers require close attention to the modeling efforts and are restricted to measuring transparent fluids only. Their reliability depends of the accuracy of the chemometric model, as well as the impact of the presence of hetero-atomic molecules which are present at fluctuating concentrations depending of the crude oil origin.

Principle of OP-NMR Analysers

NMR (Nuclear Magnetic Resonance) technology relies on the alignment of nuclei in a magnetic field. When spinning nuclei with an odd number of protons are placed in a magnetic field, they align with it, and their spinning generates small opposing magnetic fields, affecting the effective magnetic field at the nucleus. Neighboring protons, atoms, and chemical bonds have varying effects on this magnetic field, resulting in a unique shifting of the spectral signal for each proton, known as chemical shift. NMR spectrometry is a fundamental method that focuses on identifying the molecular structures of substances in a mixture, with spectral response correlating linearly with proton concentrations. This is different from optical spectroscopy, which relies on substance "fingerprints" and is impacted by signal variance, overlapping spectral bands, and a lack of linear spectral response.

The introduction of Fourier transform (FT) in NMR spectrometry has enhanced its sensitivity for measuring low concentrations. Multiple scans of the spectrum improve the signal-to-noise ratio and spectral resolution compared to continuous wave NMR spectrometers with similar magnetic strength.

NMR process analysers are designed to assign and quantify different types of hydrogen atoms in organic molecules or water, commonly found in distillates or crude oils. The linear spectral response accurately correlates with the hydrogen atom assignment to molecular species within the composition. NMR spectral peaks are influenced by neighboring chemical carbon-carbon bonds and non-carbon atoms in the molecular structure, allowing for the assessment of the chemical character of substances in crude oil or distillates. This enables identification of whether molecules are linear or branched paraffins, olefins, mono-aromatics, poly-aromatics, hetero-cyclic compounds, naphthenic compounds, acids, oxygenates, or water. This principle underlies the development of the first NMR analysers.

The On-line Process NMR (OP-NMR) technology was developed to enable expanding the scope NMR technology from the lab environment into the on-line process environment taking into consideration the special conditions and attributes of on-line streams, mainly in terms of temperature range, viscosity and opacity.

Applications of 3rd Generation OP-NMR Process Analyser in Process Control

The introduction of third-generation On-line Process NMR (OP-NMR) process analysers represents a significant advancement in the field of process control for chemical processes, refinery streams, and blending processes. Unlike optical spectrometry-based technologies like NIR analysers, OP-NMR analysers do not require process streams to be transparent for analysis. This makes OP-NMR technology applicable to a wider range of process streams, including those that are dense and opaque.

In the past, the first and second-generation NMR analysers faced issues related to stability, accuracy, and reliability, which led to skepticism among end users, particularly in refineries, about integrating these analysers into their process control systems. However, the third generation, the OP-NMR analysers has overcome these obstacles, making them suitable for

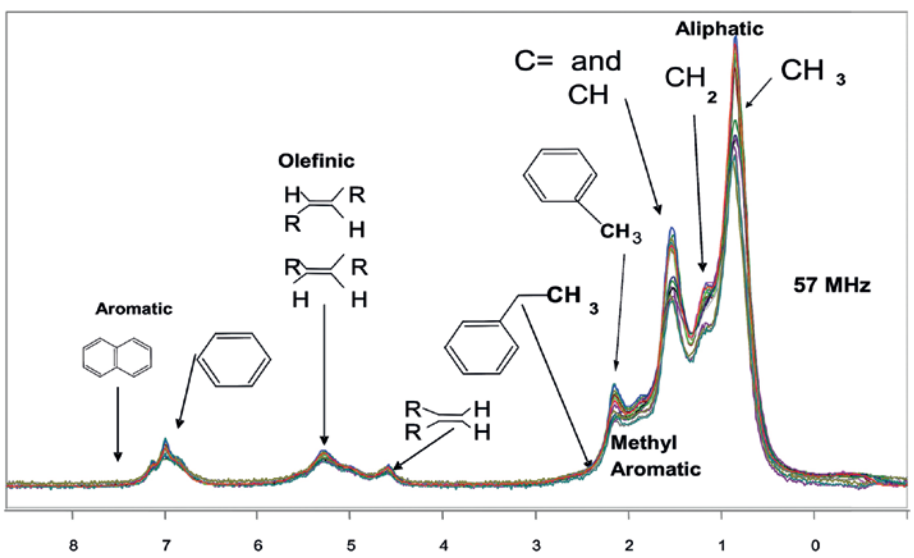

Figure 1: Clarity of various hydrogen types in gasoline NMR spectra [1].

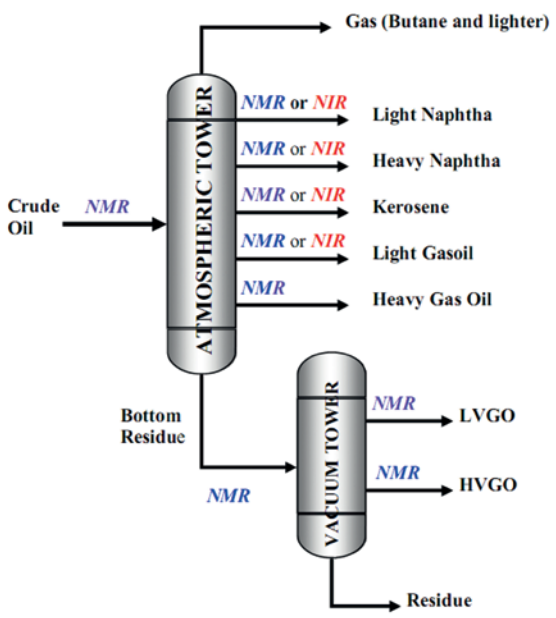

Figure 2: Implementation of NIR/FT-IR and NMR Analysers in Crude Oil Distillation

Table I - Comparisons between NIR and NMR Technology

Parameter	NIR/ FT-IR / RAMAN	OP-NMR
Applicable streams to measure	Raw Crude Oil Blended Crude Oil Desalted Crude Oil Light Naphtha Heavy Naphtha Kerosene Light Gas Oil Heavy Gas Oil Atmospheric Residue Vacuum Gas Oil Vacuum Residue Alkylation (name of the acid?)	Raw Crude Oil Blended Crude Oil Desalted Crude Oil Light Naphtha Heavy Naphtha Kerosene Light Gas Oil Heavy Gas Oil Atmospheric Residue Vacuum Gas Oil Vacuum Residue Alkylation Unit
Refinery applications	Crude Custody Transfer Crude Blending CDU (Partial) CDU (Full) FCCU Delayed Coker Alkylation Unit Light Product Blending	Crude Custody Transfer Crude Blending CDU (Partial) CDU (Full) FCCU Delayed Coker Alkylation Unit Light Product Blending
Modeling simplicity and robustness	Low (non-linear response)	High (linear response)
Sample lag time	Immediate (Fiber optics, optical switching)	Deployment specific (tubing, streams switching)
Sample Conditioning complexity	Higher (Water removal, higher temp sensitivity)	Lower
Deployment complexity (civil work)	Lower (fiber optics)	Higher, deployment specific (fluids tubing)
Maintenance overhead	Higher	Lower

implementation in refining and process industries.

OP-NMR technology can be applied to any process stream involving organic molecules, allowing for correlations between the physical properties of process feeds and product streams. It provides an effective means of making real-time adjustments to process conditions, which is essential for optimising process unit utilisation.

Physical properties of process streams result from the combined properties and concentrations of individual components. Optical methods like NIR/FT-IR/RAMAN spectrometry offer the advantage of measuring at distant locations via fixed field probes or flow cells connected by fiber optics. However, their applicability is limited by the transparency of the process stream, and they rely on chemical composition "fingerprints" without molecular structure specificity.

In contrast, NMR distinguishes between molecular structures and chemical bonds precisely, enabling quantitative and qualitative assessment of molecular structures with high certainty. Its linear response allows accurate correlation between spectral data and physical properties, even for compositions not included in the calibration curve of the chemometric model.

Optical spectrometric methods require chemometric models to encompass a wide range of expected compositions to enhance accuracy due to overlapping and weak spectral bands and a lack of linear spectral response. NMR's linear response allows extrapolation for quantifying physical properties of compositions not included in the model.

Crude oils contain various hetero-atomic substances at different levels depending on their origin. These substances can partially distill alongside distillation products, impacting the accuracy of analytical results with optical methods like NIR/FT-IR. NMR spectrometry, as a fundamental method, is not affected by the presence of these hetero-atomic molecules and can specifically assess hydrocarbon molecules. This is crucial for its application in crude oil distillation, covering crude oil, naphtha, diesel, kerosene, heavy distillates, vacuum distillates, and bottom products.

Figure 2 illustrates the application of NMR process analysers in a crude distillation unit of a refinery. Light distillates can be measured by NIR/FT-IR or OP-NMR analysers. Monitoring of kerosene and diesel can also be performed by both, but under the restrictions that process streams are transparent, and that crude switching is omitted. Otherwise, NMR is the method of preference. Heavy distillates, vacuum distillates and bottom product can only be monitored by NMR.

Full monitoring of all refinery streams is essential to the most efficient performance of the crude unit. However, temperature differences between distillate streams prevented previous generation of NMR analysers to switch between the distillate streams without losing accuracy. The enhanced temperature insulation between magnet and probe in the third generation eliminated these drawbacks.

Analysis of feed and product streams by the same analytical method and the same analyser is the preferred strategy to accurately correlate between physical properties of process streams. Boiling ranges of different distillates partially overlap. Efficient and stringent adjustment of the temperature profile in the distillation to optimise cut points between distillates increases its production capacity of the most required distillates. It enables the optimisation of its capacity towards the distillates that will have the highest profit on the market.

Crude switching is a common practice in many refineries. Implementation of NMR process analysers reduces the impact of the transition period, until optimised process conditions are restored.

Beside petroleum industries, chemical process industries can benefit from OP-NMR process analysers. NMR technology can provide accurate information about the substances available in the process stream. As a molecular determining method, NMR distinguishes between and enables quantification of raw materials, intermediates and final products. It provides an efficient tool for analyses of reaction proceedings and failure analyses in chemical processes. NMR spectra can be analysed by chemist throughout the entire production process.

Other applications of NMR analysers can be found in the pharmaceutical industries, the food industries, fermentation processes in biotechnology industries, in all other processes, where organic substances are available with NMR distinguishable chemical compositions.

Process NMR can be applied for at many locations within refinery processes. Its ability to not be restricted to transparent streams provide an effected tool to continuously monitor the feed and product streams of refinery units, especially those units where optical spectrometry methods fail.

In other process chemical industries, NMR technology can provide accurate information about the substances available in the process stream. As a molecular determining method, NMR enables quantification of raw materials, intermediates and final products.

The incorporation of NMR analyser in process stream monitoring prevents the production of border-line and off-spec materials and avoids the investment of time and money to upgrade these products.

Summary: Comparison between NIR and 3rd Generation NMR Technology

A comparison between the characteristics of NIR and third generation NMR technology is summarised in table I.

Conclusions

The successful application of on-line process analyses is dictated by its stability, its feasibility to provide reliable analytical results process streams and its capability to switch without any impact between different process streams.

Previously, its high sensitivity towards temperature fluctuations, its lack of stability of the magnetic systems and its deficient reliability harmed the reputation of NMR process analysers in refineries and process industries. The conclusions of a thorough and all including failure analyses of first and second generation on-line NMR process analysers were implemented in the entirely new design of the third generation. Incorporation of innovative hardware and software has eliminated the drawbacks of previous generations and increased its stability accuracy and reliability. The cost of human resources required for calibration and maintenance is reduced. It will benefit chemical industries and refineries to effectively monitor and control its entire process. It enables the entire production unit to run at maximum efficiency and profitability.

Stability, Reliability and accuracy of the third generation of NMR process analysers is the major challenge in restoring the reputation of NMR technology for process control in the chemical and petroleum industries.

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