The research and applications of on-line near-infrared spectroscopy technology in Chinese petrochemical industries

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Introduction

In China, the NIR analytical technology has been studied and applied in several fields since 1991, especially in the petrochemical industries. For on-line process analysis, NIR technology provides essentially real-time analyses and is capable of multi-stream and multi-property applications. The capital and operating cost benefits are very attractive when compared to traditional approaches. Our NIR R&D group in the Research Institute of Petroleum Processing of SINOPEC was established in 1995. Since then the group has been devoted to the research and development of packaged on-line NIR technology for petroleum products.

On-line NIR platform technology

The Online NIR-6000 Analyzer is composed of light source, multiplexer, grating monochromater, CCD detector, and various accessories, such as optical fiber and flow cells, or probes with different pathlengths.[1] A number of applications have proven that those analyzers can satisfy most of requirements for measuring light-colour liquid samples such as gasoline, diesel fuel, and kerosene. The sample conditioning system for light oils includes filtration, flow control, temperature control, pressure control, water removal, and outlier sample auto-grabbing.

A friendly and easy-to-use software package in native language has been written in Microsoft VC language, which has been updated to version 3.0. The software package consists of instrument control, chemometrics, database, and communication module via Modbus protocol.

Applications

The on-line NIR technology has been used in several petrochemical units in China, such as the catalytic reforming unit, steam cracking unit, MTBE unit, and gasoline blending unit.

Catalytic reforming unit

The catalytic reforming process is one of the most widely used and important processes in refineries and petrochemical industries for the production of mixed aromatics, high-octane-number components for gasoline, and high purity hydrogen. In our institute, the on-line NIR analyzer has been used to monitor eight sets of pilot-scale catalytic reforming units via optical fiber multiplexers for determining five chemical and physical properties (RON and aromatic compositions) of reformates simultaneously.[2] The five properties in reforming gasoline are accurately predicted with RMSEP of 0.29 for RON, 0.25 wt% for benzene, 0.56 wt% for toluene, 0.55 wt% for xylene, and 1.11 wt% for total aromatics. Those RMSEPs are quite good compared to the corresponding reproducibility standard deviation of the reference methods.

The on-line NIR analyzer has also been applied in the advanced process control (APC) system of an industrial catalytic reforming unit in SINOPEC Guangzhou Petrochemical Company. Good results have been achieved in operation. The analyzer can provide all real-time accurate analysis data required for feed naphtha and reformate, such as octane number and PONA compositions for the advanced process control system. This has solved a difficult technical problem for the APC application. By optimizing the process operation conditions in the system, the operation stability has been improved, the labor intensity of operators reduced, and the unit can operate at the maximum capacity to improve the product yield, and reduce energy consumption.

Steam cracking unit

The composition and properties of the feed naphtha are very important factors in the operational stability and profitability of a naphtha thermal cracker. However, current operations of naphtha thermal crackers depend on daily or even weekly laboratory tests of feed naphtha. As a result, the operating conditions are normally held at conservative values instead of optimal values to ensure safety, because on-line property and composition data are not available.

An on-line NIR analyzer has been installed on the feed naphtha to a steam cracking unit in SINOPEC Yanshan Petrochemical Company, which provides detailed PIONA analysis and some physical properties, such as density and distillation points, every two minutes, for input into APC/optimization (SPYRO) packages. Accuracy of property measurements by on-line NIR is in line with the reference methods. According to the quality of the feed stocks, the operating conditions of the furnace, such as outlet temperature of the cracking furnace (RCOT), dilution steam ratio, feed rate, and other parameters, are adjusted almost in real-time. Optimization of the operation of the cracking furnace has been realized.

MTBE unit

Methyl tertiary butyl ether (MTBE) is an important compound, that can be added into gasoline to raise the octane number and to reduce carbon monoxide emissions for protecting the ozone layer. It is also used as the raw material for producing pure isobutylene in the rubber industry. MTBE is synthesized under catalysis by methanol and isobutylene. In the MTBE production plant, the feedstock of MTBE production unit is the mixture of methanol and the C4 fraction from the refinery. The molar ratio between methanol and isobutylene (MRMI) is very important to the operation of the MTBE production unit. Traditional on-line GC is difficult to apply for the determination of

this parameter, due to the time-per-test, and the complicated maintenance for its sample preparation system.

The on-line NIR analyzer has been used in an MTBE unit of SINOPEC Yanshan Petrochemical Company to determine the contents of methanol and isobutylene in the feedstock of the MTBE unit and its MRMI. Calibration models for methanol and isobutylene were established using PLS, and the MRMI parameter is calculated by methanol content and isobutylene content, as predicted by NIR. Good application results are obtained. Since the on-line analyzer was put into use in the routine operation, the reference GC method has been used, only when outliers have been suspected, or tests for validation of NIR tests have been carried out.

To the best of our knowledge, this is the first NIR application in the world in a MTBE unit to determine the molar ratio between methanol and isobutylene of feedstock. The on-line analytical results are communicated via 4 ~ 20 mA analog signals to DCS to realize a closed loop control, and a real economical benefit of ten million RMB has been obtained by the plant per year.

Gasoline blending unit

Gasoline blending is a complex refining process required, to meet fuel quality and legislative targets, while operating at the lowest possible costs. To meet these operating targets, typical properties that are measured and controlled for both blend components and product gasoline include research octane number (RON), motor octane number (MON), density, Reid vapor pressure (RVP), % Aromatics, % benzene, % olefins, and % oxygenates.

In a new project of gasoline blending unit in SINOPEC Guangzhou Petrochemical Company, the on-line NIR analyzer has been applied to measure five blending component streams and three grades of finished gasoline streams. The analyzer determines eight properties simultaneously: RON, MON, density, RVP, % aromatics, % benzene, % olefins, and % Oxygenates. During the past 18 months, robust calibration models have been developed, and good predictions obtained. The analytical results are transported via Modbus protocol to DCS and to the optimization system, which was also developed by our institute.

The main goals of the new gasoline blending unit have been reached, due to the real-time measurement and optimization system, including enhancement of quality especially for RON, optimization of blend recipes, avoiding reblends, and reduction of future storage-capacity requirements. The annual benefit is about $2.5 million, which ensures rapid payback for the whole system.

Conclusion

Based on our national requirements, we have developed a turnkey NIR technique including analyzers, chemometrics software and calibration models. Through our work and efforts, more and more technicians in Chinese refineries know the NIR technology, and understand gradually what work it can do and how to use it. As a consequence, the acceptance of the NIR technique among Chinese refineries has steadily increased. Several on-line NIR analyzers based on our technology have been applied in refinery units for process control, such as steam cracking units, reforming units, gasoline blending units, and MTBE units, which has brought refineries large economic benefits.

References

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