Rapid Analysis of Gas & Liquid Phase Using NR800 Near-infrared Analyzer

- Application to Petrochemical Process such as Ethylene Plant and Chemical Process -

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Yokogawa's NR800 near-infrared analyzer can measure both liquid and gas samples and is applicable for various petrochemical processes such as ethylene plants and chemical process. Gas chromatographs are commonly used for measuring gas compositions such as those broken down by naphtha crackers. However, they take about five to ten minutes, so faster measurement methods are required. This report introduces an application of NR800 to such gas composition measurement that realizes rapid measurement and control cycle of about one minute.

INTRODUCTION

Yokogawa Electric Corporation released the NR500, Japan's first analyzer for process use in 1995, and the near-infrared analyzer NR800 [(1)] in 2001, which offers high-resolution and long-wavelength measurements with excellent reliability. Thanks to the customers' trust in our products, the NR800 has been used by a wide variety of customers for semiconductor and liquid crystal panel production processes as well as in the petroleum and petrochemical industries [(2), (3), (4)].

Conventionally, the liquid and gas components such as those broken down by naphtha crackers have been measured by a process gas chromatograph (PGC), and its measurement values have been used for control. However, it takes five to ten minutes for analysis, and faster analyzers are desired. Since the NR800 can measure the components of both liquid and gas at high speed, it can be applied to petrochemical processes such as naphtha cracking furnaces in ethylene plants and chemical processes. Yokogawa has applied the NR800 to those processes and has achieved high-speed measurement and control with about one minute cycle. This report describes the application of the NR800 focusing this.

OVERVIEW OF NEAR-INFRARED SPECTROANALYSIS

This section describes the features of near-infrared spectroanalysis and quantification method using it [(5)].

Features of Near-infrared Spectroanalysis

The near-infrared analyzer is a relatively new analyzer, introduced in the 1970s, and employs a wavelength range (approximately 900-2500 nm (11000-4000 cm^{-1})) close to that of visible light among infrared light.

Near-infrared light is absorbed less than mid-infrared light with longer wavelength and allow longer path lengths (distance of light transmission through the sample) to be used for measurement, thereby reducing concerns such as obstruction of measuring parts when applied to online measurement.

Because C-H, N-H, and O-H bonds show absorption in the near-infrared range, almost all organic substances can be measured as target in near-infrared spectroanalysis. Even ions in aqueous solutions with no absorption band in the near-infrared can be indirectly quantified because they influence the spectrum of water, the solvent [(3)].

Quantification using Near-infrared Spectroanalysis

Though quantitative analysis is based on the Lambert-Beer's law like general absorptiometry, it enables complex multi-component measurement by using multiple absorption points (occasionally several hundred points) instead of a single absorbance of peak absorption point.

The Lambert-Beer's law shows that the absorbance of solution is proportional to its concentration.

$$A = -\log(I_{out} / I_{in}) \quad \ldots\ldots (1)$$

$$A \propto C \bullet L \quad \ldots\ldots (2)$$

where, A: Absorbance, I_{in}: Intensity of irradiating light, I_{out}: Intensity of penetrating light, C: Concentration, L: Path length

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When the path length is constant, the following simple relation is obtained:

$$C = b \bullet A \qquad \ldots\ldots (3)$$

b: Constant

However, the concentration quantified in this expression is limited to the simple case of only one solute for the solution. In case of multi-component measurement, the absorption peaks of components interfere with each other, and the concentration cannot be calculated from a single absorbance. To measure multiple components, it is necessary to use an extended calibration model equation using multiple absorbances as shown below.

$$C = \sum_{i=1}^{n} b_i \bullet A_i \qquad \ldots\ldots (4)$$

To create this extended calibration model equation, near-infrared spectra of multiple samples whose concentrations C are known are measured and constant b_is are derived by solving the equation (4) using multiple combinations of the concentration and spectrum A_i. Once the constant b_i is determined, the concentration C of an unknown sample can be calculated using its spectrum.

The calibration model can be created for quantities or qualities other than the concentration. As long as the quantities or qualities to be measured, such as density, viscosity, octane number of gasoline, acid number of ester reaction, and sugar content of fruits, are correlated with changes in the molecular structure or amount of ingredients.

Thus, the near-infrared analyzer is capable of various measurements by using calibration models.

APPLICATION TO ETHYLENE PLANTS

Overview of Petroleum Refinery Processes and Ethylene Plants

Figure 1 shows an overview of the petroleum refinery processes [6], and Figure 2 shows a block diagram of the ethylene production processes [7] using naphtha as material, which is the final product of the petroleum refinery process.

The crude oil is first separated into several kinds of intermediate materials via the atmospheric distillation unit (distillation tower) depending on each boiling temperature. The final products of the factory are shown on the right of the figure. To satisfy high demand for gasoline, the heavy components of oil are reformed and resolved to increase the light intermediate materials and thus increase the gasoline fraction. Naphtha, like gasoline, is produced from relatively light components, and supplied to ethylene plants as a raw material.

In ethylene plants, carbon bondings of naphtha are broken (cracked) in the cracking furnace (cracker), and the gas produced by the cracker is distilled, reformed, separated, and refined into single components. The most important components are ethylene and propylene, which are used as raw materials for many industrial products. As indicated by the red circle in the figure, a near-infrared analyzer can quickly measure concentrations at any point. This report shows the measurement results at the inlet (liquid) and outlet (gas) of the naphtha cracker.

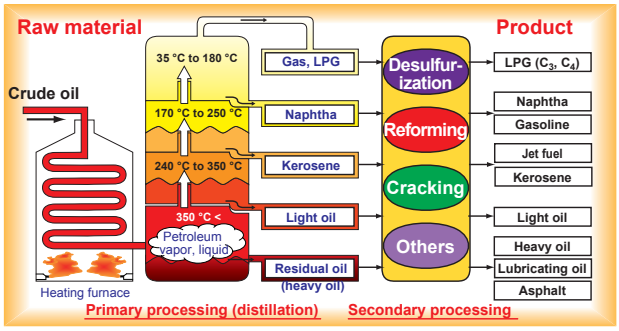


Figure 1 Overview of Petroleum Refinery Processes

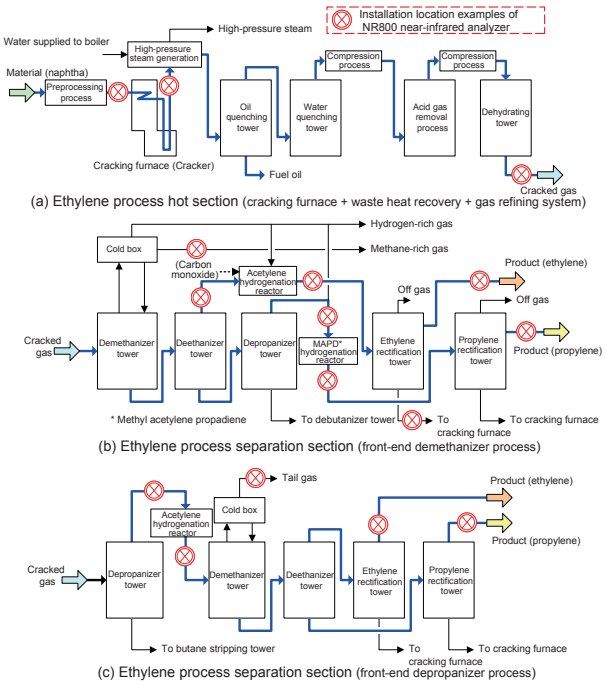


Figure 2 Block Diagram of Ethylene Production Process

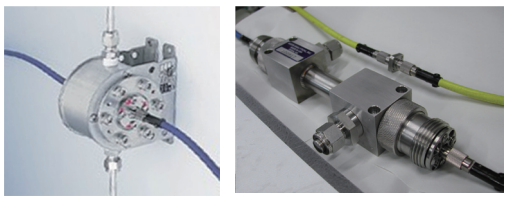
Installation Example of NR800 Near-Infrared Analyzer

Figure 3 shows an installation example of the NR800 near-infrared analyzer. The analyzer is installed in the analyzer house in the vicinity of the cracker and samples from the inlet and outlet of the cracker are conducted to it. Preprocessing such as filtering, defoaming and temperature adjustment is performed before they arrive at the flow cell for measurement so that the disturbance to the measured value is minimized. The near-infrared analyzer is operated in measurement cycle of about one minute far shorter than the analysis cycle by PGC (five to ten minutes), and this merit is highly evaluated. In addition, the near-infrared analyzer does not need to evaporate samples, and thus provides numerous merits for maintenance when used at the inlet of the cracker where many high-boiling-point components exist.

Figure 3 Installation Example of NR800 Near-Infrared Analyzer

A flow cell for measuring samples at the inlet of the naphtha cracker is shown at the lower left of Figure 3. NR512 whose path length is 10 mm is employed for the flow cell. The NR512 is the NR510, shown in Figure 4 (a), equipped with a constant temperature water pipe around it, which can maintain the liquid temperature of the sample constant and is used together with the insulation jacket.

Spectrum measurement of a gas requires a cell with a longer path length, about 100 to 500 mm, than those for a liquid. An example of a flow cell with a path length of 100 mm is shown in Figure 4 (b).



(a) NR510 (b) FFV-315 (Axiom product)

Figure 4 External View of the Flow Cells

Inlet side analysis of the naphtha cracker (liquid analysis)

The naphtha supplied to the naphtha cracker consists of carbon hydride with a carbon number of one to eight, and components such as methane, which are gas phase at ordinary temperature and pressure, are dissolved in it.

Figure 5 shows the near-infrared absorption spectrum of the naphtha. The spectrum was measured by preparing 175 samples including those collected from the naphtha cracker during operation and those produced by adding some reagents. The peak corresponding to the molecular structure of the constituent component is found and it shows that the absorbances of their peaks differs by sample.

Figure 6 shows the benzene calibration model created by using the 175 samples. The calibration model with a good correlation was obtained where the correlation coefficient was 0.999 and the prediction error was 0.025 wt% [2]. The prediction error is the standard deviation of the difference between the NR800 measurement result and the laboratory analysis result.

In addition to benzene, calibration models have been created for the following 24 items with reasonable results.

- Density
- Distillation point (initial, 50%, 70%, end)
- Paraffin (total, C3&4, C5, C6, C7, C8)
- Isoparaffin (total, C3&4, C5, C6, C7, C8)
- Naphthene (total, C5, C6)
- Aromatics (total, C6, C7, C8)

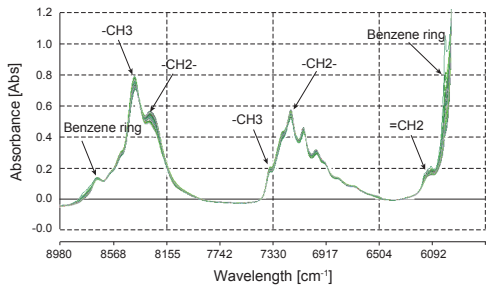


Figure 5 Near-infrared Spectra of Naphtha

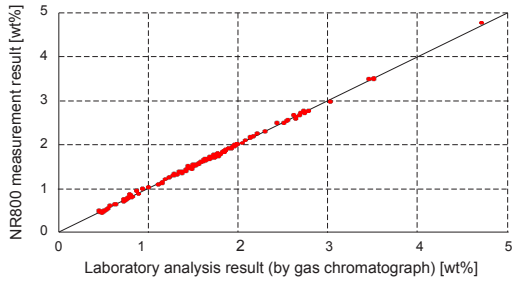


Figure 6 Result of Benzene Calibration Model at the Inlet of the Naphtha Cracker

Analysis at the outlet of the naphtha cracker (gas analysis)

Measurement at the outlet of the naphtha cracker is important in order to grasp the component ratio and the resolved residue of heavy components, and for optimum control of the cracking furnace operation. The combination of this measurement and the analysis result at the inlet side realizes further optimum control of the operation.

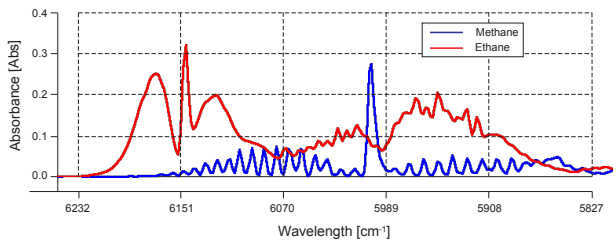


Figure 7 Near-infrared Absorption Spectra of Methane and Ethane

Because the spectrum of a gas is easily affected by temperature and pressure, it is crucial to accurately control temperature and pressure. However, the procedure for creating calibration models using the spectrum of the sample and the reference values (laboratory analysis values) is identical to that for a liquid. Figure 7 shows spectra of methane and ethane as examples of near-infrared absorption spectra of gas. It

shows sharper peaks compared with the spectra in Figure 5, and many small peaks due to molecular spin can be seen for methane. The NR800 analyzer can observe these peaks without being influenced by noise with its advantage of low noise characteristic. In addition, the calibration models can be created using the same procedure as for a liquid.

To create the calibration model at the outlet of the naphtha cracker, 33 samples were prepared by the same procedure as at the inlet. Though a small amount of acetylene, butane, benzene, or the like could be measured, the verification was conducted focusing on the most important seven components, methane, ethane, ethylene, propane, propylene, i-butane and n-butane.

Figure 8 (a) shows the created calibration model of propylene. Good results, a correlation coefficient of 0.996 and a prediction error of 0.22 wt%, was obtained. Figure 8 (b) shows the measurement results of the NR800 and PGC at the outlet. During the measurement, the values of the NR800 and PGC are close enough in time zones from 0:00 to 10:00 and 23:00 to 24:00. Though the value of the NR800 is slightly higher than that of the PGC from 10:00 to 23:00, both trends more or less match, causing no practical problem. Though the verification period is short and the examination is not sufficient, this result suggests the feasibility of high-speed control of the cracker in future.

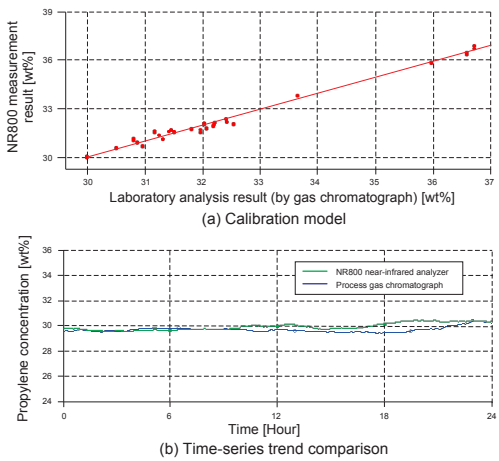


Figure 8 Calibration Model at the Outlet of the Naphtha Cracker and Time-series Trend

APPLICATION TO A CHEMICAL PROCESS (BUTYL RUBBER PRODUCTION PROCESS)

The respective components distilled and refined in an ethylene plant are used for manufacturing chemical products in various fields. The following explains an example of application to a butyl rubber production process using isobutylene, isoprene and methylene chloride. The NR800 was installed in the process to continuously collect the spectra of the sample gas employing a cell with a path length of 500 mm. The data from PGC at the same location were used as reference, and more than 1000 samples were collected over several weeks. Figure 9 (a) shows an isobutylene calibration model with a correlation coefficient of 0.991 and a prediction error of 0.19 wt%, and Figure 9 (b) compares the time trends of the NR800 and PGC indications. Because the data update cycle of the NR800 is shorter than that of the PGC, it can detect a concentration change earlier. In the future, it will be possible to control the isobutylene concentration more stably through the control by the NR800.

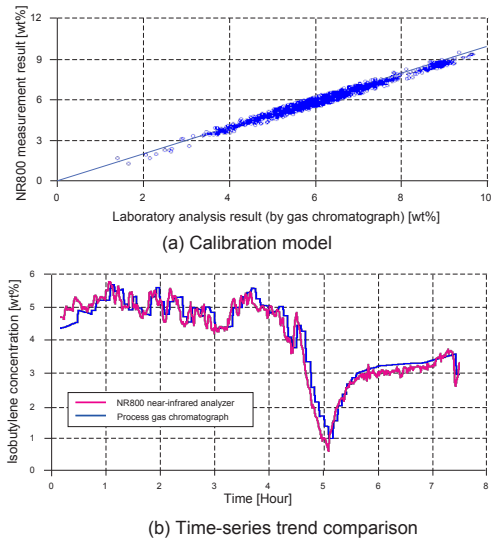


Figure 9 Isobutylene Calibration Model and Time-series Trend

CONCLUSION

Though the near-infrared analyzer is used as a liquid analyzer for various industrial processes, in recent years it has begun to be applied to gas analysis and is attracting attention as a means of realizing rapid and simultaneous measurement of multi components in both liquid and gas samples. In the field of petrochemical processes including ethylene plants and the field of chemical processes, various efforts to improve the stability of control by utilizing the features of the near-infrared analyzer have been made. Yokogawa will aggressively participate in such efforts, improve its products, and contribute to enhancing the efficiency of customers' plants.

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