Technical Information

InfraSpec NR800 Fourier Transform
Near Infrared Analyzer (FT-NIR)
(Applications Volume)

TI 12Y03A03-01E

Contents

YOKOGAWA ◆

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1. Overview

1.1 What is Near Infrared and What is a Near Infrared Analyzer?

Near Infrared refers to the region (between 0.75 and 2.5 μm) that is close to the visible range in the infrared spectrum (see the figure 1.1).

A near infrared analyzer is a new analyzer that uses events such as transmission absorption and scattering caused by emitting a near infrared beam toward an object, and that has features that are not available in conventional infrared analyzers (that use the middle infrared region).

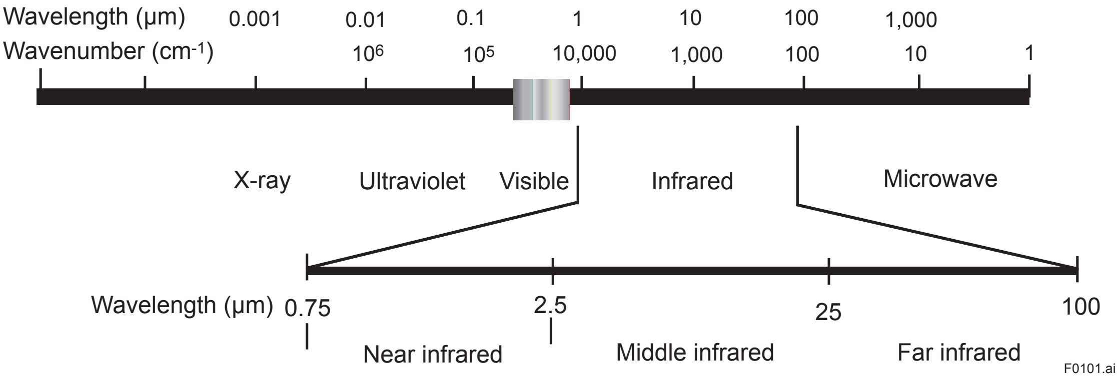

Figure 1.1

Features of Near Infrared Analyzer

A near infrared analyzer is the only analyzer capable of performing continuous nondestructive measurement of multiple components and properties of organic liquids.

	Near Infrared Analyzer	Middle Infrared Analyzer (Conventional Infrared Analyzer)
Objects of measurement	Liquids (organic liquid and water solution), solids, powder, and gas.	Gas
Contents of measurement	Component concentration and physical properties and physical quantities (e.g. density).	Component concentration
Measuring range	Several hundreds ppm - %	Several ppm - %
Fiber optic cable	Available Remote measurement is enabled by installing a measurement cell in the field.	Not available
Multi-point measurement	Possible	Possible
Continuous measurement	Possible	Possible
Calibration	Calibration model	Standard gas

Near Infrared Analyzer Applications

Type of Industry	Process & Application Example
Chemical & petrochemical	Component concentration
	Organic silicon compound
	Hydroxyl value
	Moisture content
	Molten polymer & ethylene concentration
	Resin
	Synthetic rubber
	Acid value
	Laboratory and others
Petroleum refinery	Topper, blender & octane value, steam pressure, distillation points, density, cetane value, flash point, CFPP, CP, PP, etc.
	Laboratory and others/oil determination, etc.
Foodstuff & pharmaceuticals	Edible ester, fermented milk, organic acid, ethanol, fermentation chemical, etc.
Paper & pulp	Causticizing efficiency
LCD & semiconductor	Cleaning fluid control, component concentration measurement
Other	—

1.2 InfraSpec NR800 Fourier Transform Near Infrared Analyzer (FT-NIR)

The Yokogawa FT-NIR analyzer technology is a combination of Yokogawa's experience in spectroscopic analysis technology, and many years of experience producing high quality process and measurement control systems.

The InfraSpec NR800 was developed based on the field track record of demonstrated reliability of its previous-generation model NR500 and achieved high-performance and functions with its newly developed interferometer and detector, as well as enhanced data processing. Its high resolution, wide wavelength scanning range, and a rich lineup of a desktop model and explosion-proof model for process use enable the NR800 to be used in a broad range of applications from laboratory to process scale.

Calibration model transfer to and from the NR800s (Note), software optimized for applications, and remote maintenance have achieved ease of use for customers.

A rich lineup of accessories and attachments such as measurement cells and fiber optic cables for measurement enable customers to use the InfraSpec NR800 to build analysis systems to suit their specific projects.

Note: A model cannot be transferred to and from the NR800s if the samples are different and if different optical systems are used.

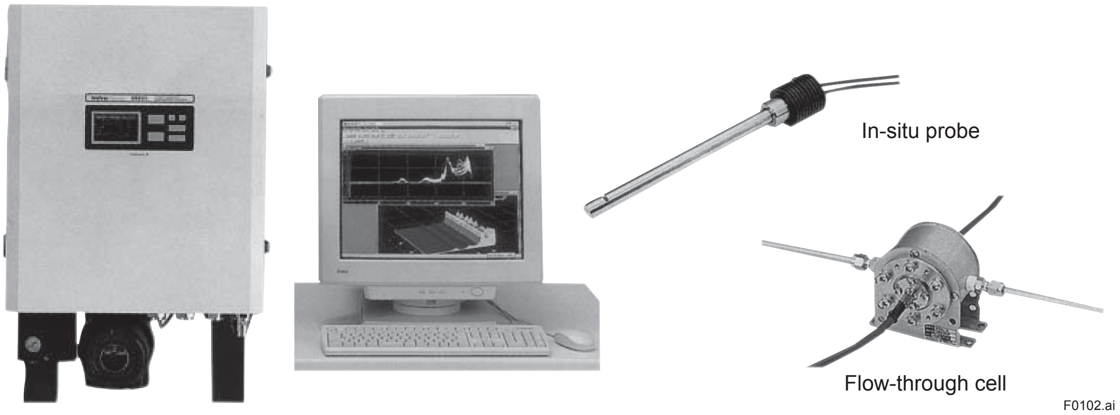

Figure 1.2

Features

High Stability and Reliability

The NR800 including the interferometer was developed from the beginning as an analyzer specifically to be used in processes.

In addition to the well-known features of FT-NIR of high throughput and fast response time, the NR800 employs a unique interferometer with no sliding parts, and its vibration-resistant mechanism ensures even more reliable and stable operation.

The NR800 does not need a PC for measurement and continuous operation. In addition to the improved reliability of the system as a whole, its variety of self-diagnostic functions and hardware reliability prediction analysis fully meet the requirements for process equipment.

Extended Measurement Wavelength Range Enables the NR800 to Be Used for a Broader Range of Applications (a Single Detector Covers a Wide Wavelength Range)

The measurement wavelength of the NR800 was extended from 900 nm to 2500 nm. Specifically, the extended measurement wavelength range makes it possible to measure OH-values, apply the NR800 to a broader range of applications, and perform high precision measurement.

High Resolution: Wavelength Resolution of the NR800 is from 4 cm^{-1}.

Calibration model generation with a best-fit wavelength range ensures high precision measurement. High resolution is especially useful for foodstuff and pharmaceutical applications.

High-Speed, Simultaneous, Continuous Multi-Stream Measurement on up to 4 Channels

The NR800 provides multiple channels for multi-stream applications. Up to 4-point samples can be measured simultaneously and continuously. The multi-channel optical system with no mechanical moving parts ensures maximum reliability and high speed measurement.

An external unit to switch up to 16 streams for measurement is also available as an option.

Seamless Transition from Laboratory to Process

High precision and stable hardware enables calibration models to be transferred to and from the NR800s. In addition to the model for process, a desktop model (used in laboratories) was added to the product lineup to facilitate a seamless transition from laboratory to process.

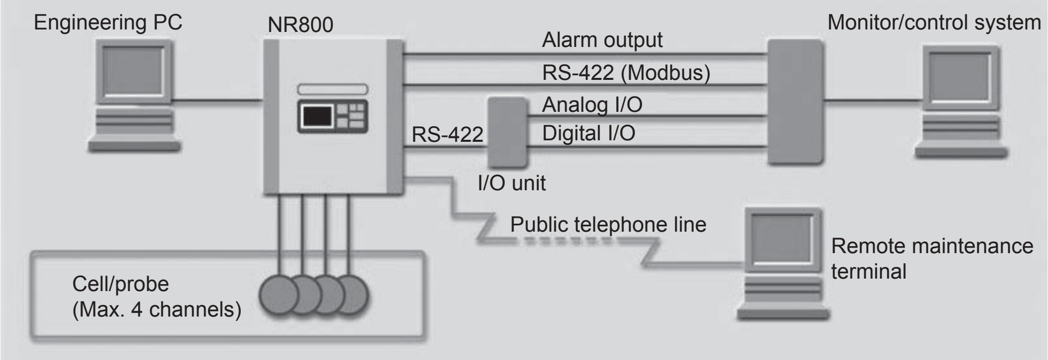

Figure 1.3 System Configuration Example

1.3 Explanation of Terms

The following explains the main terms that are used in the application examples.

■ Absorption Spectrum

This is fundamental data for the near infrared spectroscopic analysis, which shows the absorption characteristics in the near infrared region of a measurement sample by displaying the absorbance on the vertical axis and the wavelength (or wavenumber: inverse number of wavelength) on the horizontal axis.

The characteristic of the absorption spectrum depends on the component that makes up a sample and its concentration. Therefore, it is possible to calculate the component concentration and property values of a process sample by measuring the absorption spectra of that process sample and using that data and calibration model.

Calibration models are generated in advance by using the spectral data of standard samples and the corresponding laboratory analysis values.

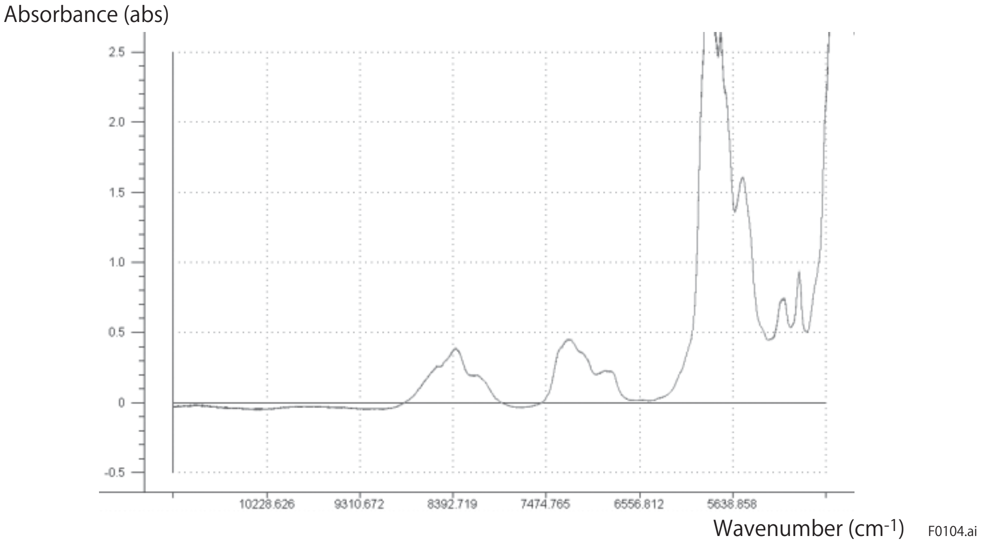

Figure 1.4 Near Infrared Spectra

■ Absorbance

$A = \varepsilon C L$

A [abs]: Absorbance (a quantity of light absorbed by a sample in the measurement cell)

ε: Molecular absorbance coefficient (a unique value of each of the components that make up a sample)

C [mol/liter]: Component concentration (concentration of a component that makes up a sample)

L [cm]: Optical path length of the measurement cell (thickness of a measurement sample through which the near infrared beam passes)

The absorption spectra represent the total of the absorbance values of components of a measurement sample.

Standard Sample

A standard sample refers to a sample that represents the conditions (component, concentration, temperature, etc.) of a process sample for which the laboratory analysis values of the measurement items (component concentration, physical quantity, property value, etc.) are known. Calibration models are generated using the spectral data and laboratory analysis values of this standard sample by using calibration model generating software.

The calibration model generation software runs on Microsoft Windows.

To generate a calibration model, 10 to 50 standard samples that cover the changing range of a normal process are required.

What is a Calibration Model?

A calibration model refers to an equation of measurement items (component concentration, physical quantity, property value, etc.), y, which represents the sum of the products obtained by multiplying the absorbance, A_i at several wavenumbers or wavelengths (λ_i) by the coefficient, b_i.

The calibration model is represented by the equation below.

$$\begin{aligned} y &= b_0 + b_1A_1 + b_2A_2 + \cdots\cdots + b_nA_n \\ &= \sum_{i=1}^{n} b_iA_i + b_0 \end{aligned}$$

b_i is called the regression coefficient or coefficient b.

Calibration Model Generation

Calibration model generation means obtaining this coefficient b by using the laboratory analysis values of a standard sample, the spectral data, and calibration mode generation software.

There are regression analysis methods for this purpose, such as MLR (Multiple Linear Regression), PCR (Principal Components Regression), and PLS (Partial Least Squares), and the InfraSpec NR800 employs the PLS method.

Accuracy of Calibration Model

Whether or not a calibration model is worth using is determined by whether or not the accuracy at the time of generation and that at the time of use are equivalent. When the accuracy at the time of use is lower than that at the time of generation, a calibration curve cannot be generated.

The accuracy of a calibration model is determined by the error of prediction that is represented by the equation below.

Residual error = Calibration model indicated value – Laboratory value

Error of prediction = Obtained by dividing the square root of the sum of squares of the residual error by (the number of data – 1)

$$= \sqrt{\left(\sum^{n} (\text{residual error})^2\right)} \,/\, (n - 1)$$

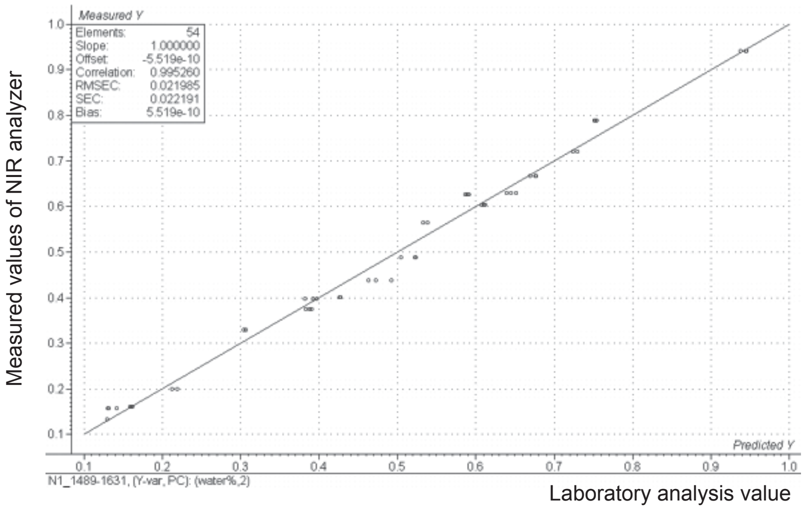

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Figure 1.5

Error of prediction is called as follows depending on the stage of evaluation. However, the name is not standardized yet. Be careful when comparing the data from various sources.

At the stage of calibration model generation:	SEC (Standard Error of Calibration)
At the stage of calibration model validation:	SEP (Standard Error of Prediction)
At the stage of calibration model alternate validation:	SEV (Standard Error of Validation)

2. Petrochemicals and Chemicals

2.1 Measurement of Polyol Molecular Weight (OH Value)

● On-line measurement to monitor the process reaction with high-speed off-line measurement

- ■ Applicable process: Polyurethane process
- ■ Object of measurement: Polyol OH value

Note: An OH value is an OH weight at the end of the polyol and an indicator of the molecular weight.
The OH value is the most important parameter to identify the end point of the process reaction.
Polyol: HO-C-C-...-C-OH

- ■ Application:
  - ○ Reaction progress control: On-line continuous measurement
    - Consumption situation of raw material
    - Checking of the reaction end point
  - ○ Quality control of product: Off-line measurement
    - Checking of the product specification (remaining -OH)
- ■ Feature: Example of measurement of the hydroxyl value of the polyol

Purpose of Introduction	NR800 NIR Analysis	Conventional Analysis (Titration Method)
Fast response time	1 minute (nondestructive analysis)	3 to 4 hours (with pretreatment)
Measurement variations among operators	Do not occur	Occur
No pollution	Chemical pretreatment is not required	Reagent (pyridine) is required
Go on-line	Continuous automatic measurement is easy	Automation is difficult

- ■ Analyzer configuration:

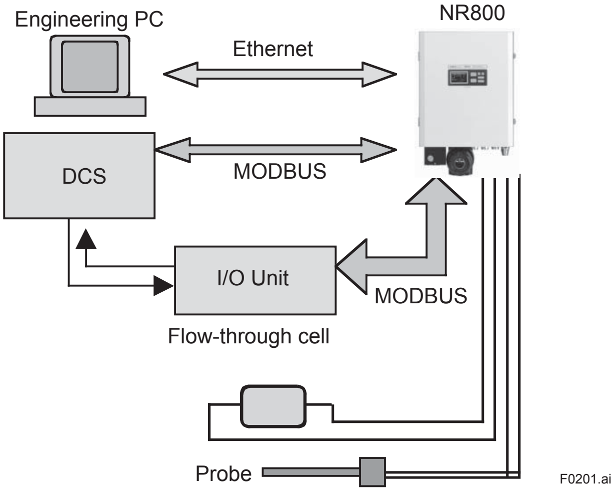

Figure 2.1

- ■ Measurement method: An OH value calibration model is generated using the NIR spectral data and OH value laboratory analysis data

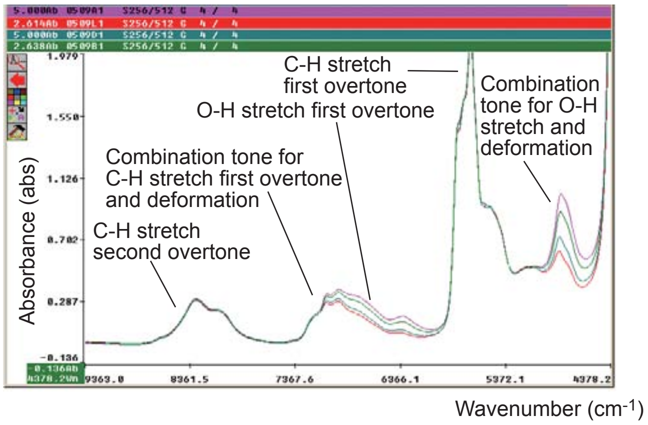

Figure 2.2 Example of NIR Measurement Spectra of the Polyol

- ■ Measurement precision varies depending on the process.

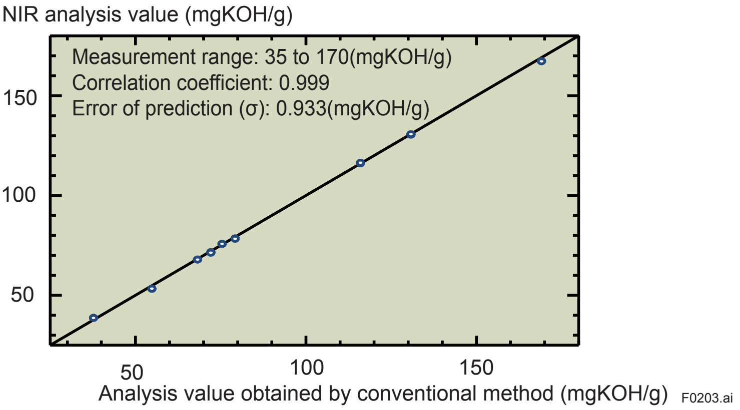

Figure 2.3

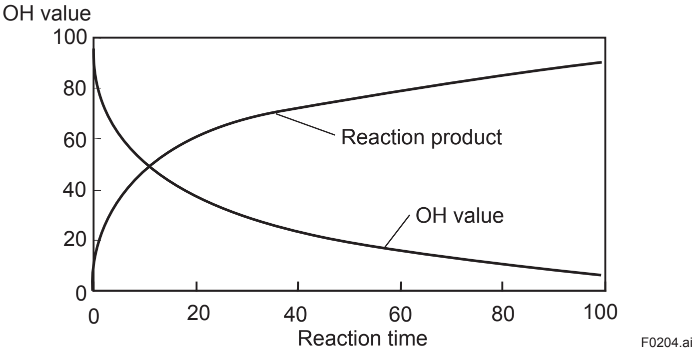

Figure 2.4 Illustration of On-line Continuous Measurement

2.2 Hydroperoxide Measurement in Organic Solvents

Hydroperoxide is the generic name given to the class of peroxides denoted by (R-O-O-H), and are typically used as oxidizing agents, polymerization catalysts, bleaching agents as well as other applications.

Peroxides readily decompose and produce oxygen and in concentrated form can form very violent reactions with hydrocarbons.

Keeping a close eye on the peroxide concentration is therefore a safety critical issue as well as quality control of a process, but most traditional direct-contact measuring principles like gas chromatography cannot be used as they require heat for separation.

As a result, there is no other method but to use the titrating method for analysis, but it is difficult to speed up analysis and save energy with this method.

By contrast, NIR analysis does not require the heating of the sample as is required by chromatography as the pretreatment for analysis, and NIR analysis is safe because it does not unnecessarily activate the sample.

Furthermore, when compared with the titrating method, NIR analysis does not require chemical pretreatment, so it is able to decrease the analysis time and perform real-time analysis.

NIR analysis just needs to emit a near infrared low energy light toward an unstable sample and is capable of performing nondestructive and high-speed analysis, thus enabling safe and high-speed on-line analysis to be performed.

High-speed, real-time on-line analysis is extremely useful for correcting the differences between the actual plant status and operation control target and running the plant stably and efficiently.

Upon requests of customers, Yokogawa is currently performing testing to determine whether or not hydroperoxide can be measured. The results including the laboratory data cannot be made public yet. The following uses the publicly available information to present an example of concentration analysis of hydroperoxide in organic solutions and proposes concentration analysis of hydroperoxide using the NIR analysis method.

● Example of a report for hydroperoxide measurement in organic solutions

According to the report, 21 organic solution samples with an ethylbenzene hydroperoxide (EBHP) concentration in the ethylbenzene ranging from 0 to 1.91% were prepared and their NIR spectra were measured. (Literature 1)

Figure 2.5 shows the NIR spectra in the report. A hydroperoxide concentration peak can be clearly observed near the wavelength of 1,463 nm (6,835 cm^{-1}) in the measured spectra.

Near infrared absorption in this wavelength region is often the O-H group stretch first overtone, so it can be estimated to be the O-H group absorption of the hydroperoxide.

In the report, this single wavelength is used to obtain the correlation between the hydroperoxide concentration and NIR spectra by employing the least square method. Figure 2.6 shows the resulting correlation.

As observed in the figure, the concentration and NIR values of prediction are well correlated with a correlation coefficient of 0.999 and with the standard error of prediction (SEP) = 0.03%.

Literature 1: Muller KL: Fresenius J. Anal. Chem. Vol 343, No.8, 1992

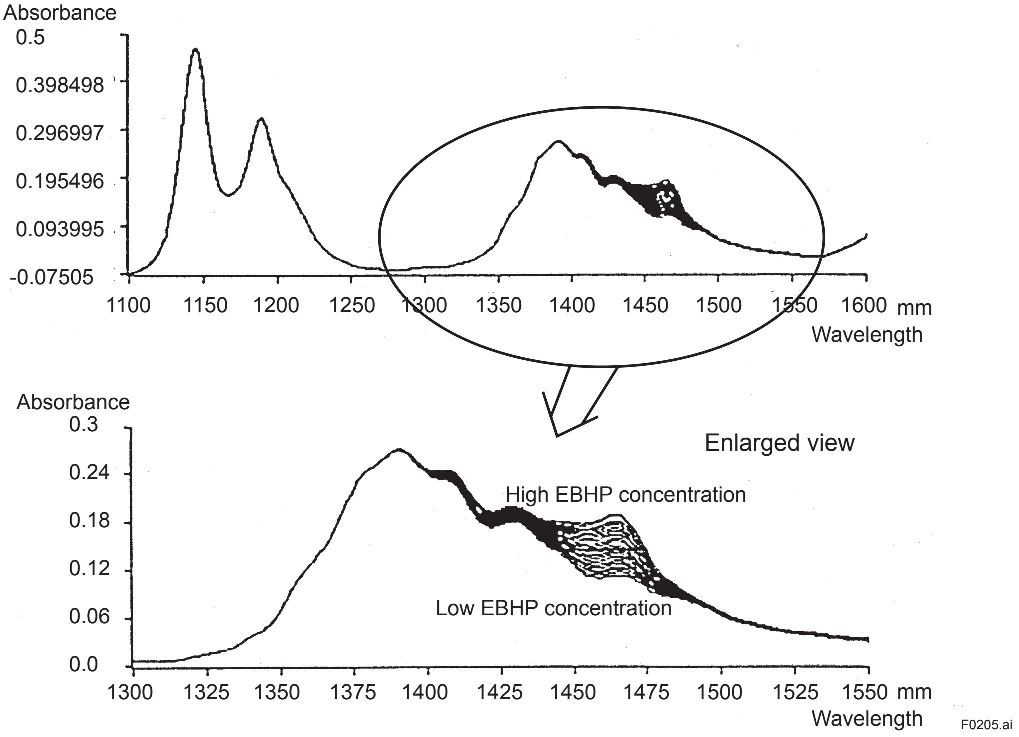

Figure 2.5 NIR Spectra of Ethylbenzene Hydroperoxide (EBHP) in Ethylbenzene

This demonstrates a high accuracy of approximately 1.5% over the measurement range, thus it is possible to conclude that concentration analysis of hydroperoxide using the NIR analysis method provides a high accuracy and can be practically used satisfactorily.

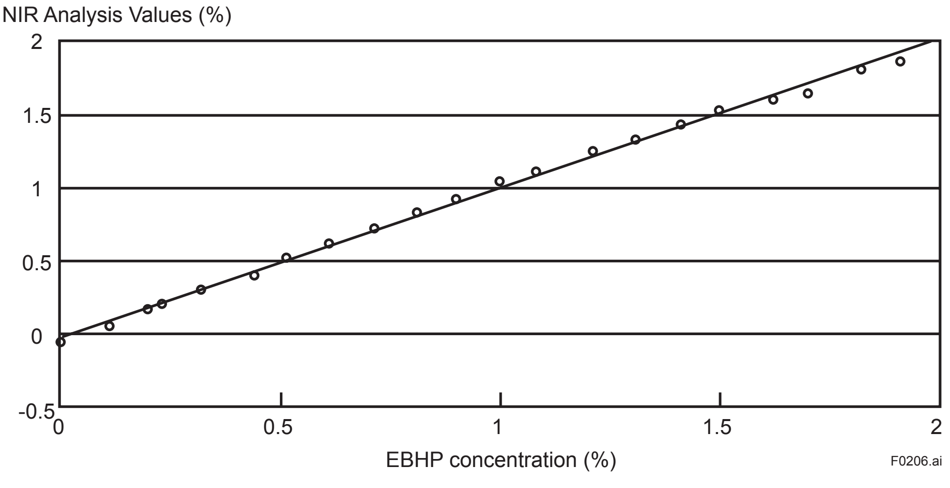

Figure 2.6 Correlation between Ethylbenzene Hydroperoxide (EBHP) Concentration and NIR Analysis Values

2.3 Isocyanate Measurement in Organic Solvents

Polyurethane, which is used as the raw material of polyurethane foam and polyurethane fiber, is synthesized by the reaction of isocyanate and alcohol.

At the present time, isocyanate concentration analysis is performed using the titrating method.

However, isocyanate is unstable and easily transforms to another compound so measurement must be performed at high speed. In addition, it has an irritating odor that induces tears, so an automated measuring method without the interaction of humans would be preferred.

Therefore, it is almost impossible to analyze an ever changing small amount of isocyanate concentration in real-time using the titrating method.

Compared with the titration method, NIR analysis does not require chemical pretreatment, and allows real-time analysis because it emits the near infrared light toward the sample and analyzes the concentration based on the absorbance. It also allows on-line remote sensing via fiber optic cable, so it can significantly reduce work hazards to workers.

The following presents an example of analysis of a small amount of isocyanate concentration and proposes isocyanate concentration analysis using the NIR analysis method.

Example of a Laboratory Test of Analysis of a Low Concentration of Isocyanate in Organic Solution

Several samples of organic solvent (monochlorobenzene) with a hexamethylene diisocyanate concentration ranging from 0 to 10,000 ppm were prepared and their NIR spectra were measured. Measurement took approximately 20 seconds per sample.

Figure 2.7 shows the measured NIR spectra. Although the measured spectral component changes are very small, changes of absorbance linked to the changes of concentration can be observed in the wavelength region near 5,680 cm^{-1} at the peak of the methylene that is bonded to the isocyanate.

This wavelength region was used to obtain the correlation between the isocyanate concentrations and NIR spectra by employing the partial least square method (PLS regression method). Figure 2.8 shows the resulting correlation.

The regression results show that the concentration and NIR analysis values of prediction are well correlated with a correlation coefficient of 0.998 and error of prediction (1σ) = 220 ppm.

This demonstrates a high accuracy of approximately 2% over the measurement range, thus it is possible to conclude that analysis of a small amount of isocyanate concentration using the NIR analysis can be practically employed satisfactorily.

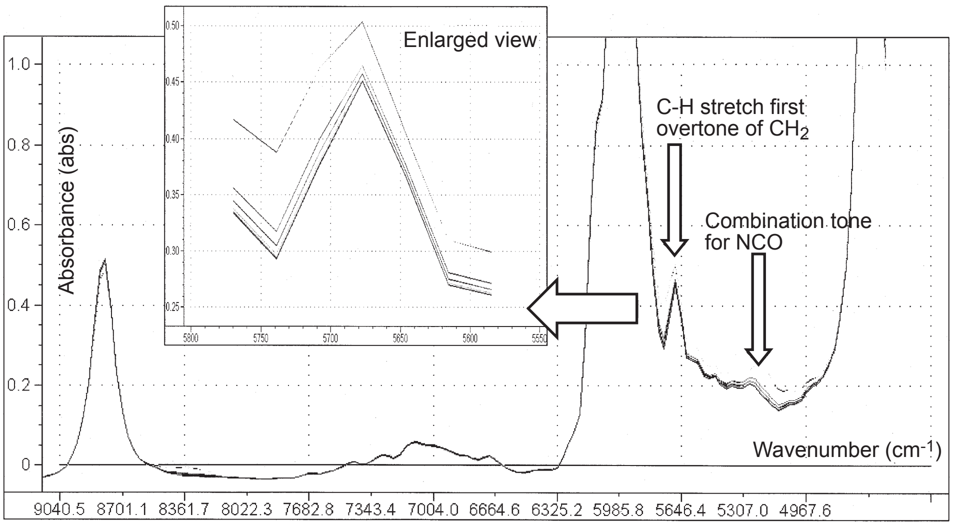

Figure 2.7 NIR Spectra of Hexamethylene Diisocyanate in Monochlorobenzene

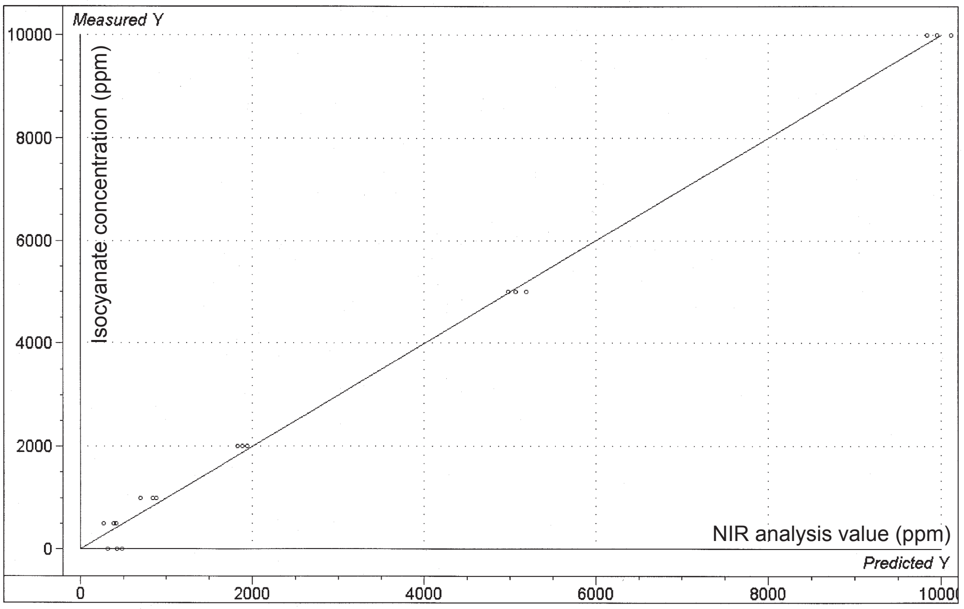

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Figure 2.8 Correlation between Isocyanate Concentration and NIR Analysis Values

2.4 Process Monitoring of Styrene Concentrations

Styrene, which is used as the raw material for many petrochemical products, is made from ethylbenzene and refined through the dehydrogenation, distillation, and rectification stages.

The following shows estimated concentrations of the styrene and ethylbenzene between processes.

(1) Dehydrogenation reactor vessel – Distillation column
    Styrene: Intermediate concentration
    Ethylbenzene: Intermediate concentration

(2) Distillation column – Rectification column
    Styrene: High concentration
    Small amount of ethylbenzene, polymerization inhibitor, etc.

(3) Distillation column → Product
    Styrene: 99% or more
    Polymerization inhibitor: Small amount

In the styrene manufacturing process, the styrene concentration in solutions is measured at each connection point between the processes to determine the difference between the measured values and control target values to gain an understanding of the operation efficiency of each piece of equipment, the remaining time until the next maintenance, or prevent nonconforming products from being sent to the back-end process.

High-speed on-line real-time analysis of this kind is very effective for operating a plant reliably and efficiently because it is able to eliminate the differences between the control target and actual operation.

The following presents an experiment using the InfraSpec near infrared analyzer and flow-through cell and an application example of NIR analysis, and proposes a styrene concentration measurement system.

Experiment of Mixed Solution of Styrene and Ethylbenzene

Solution samples with different mixing ratios of styrene and ethylbenzene were prepared beforehand and their NIR spectra were measured. Figures 2.9 and 2.10 show respective chemical formulae and spectra, respectively. Absorbance intensity changes were observed at multiple peak points in the measured spectra due to the different mixing ratios. The peaks at 6170 cm^{-1} and 5677 cm^{-1} where significant changes are observed belong to the CH stretch first overtone of $=C=CH_2$ of the styrene and to the CH stretch first overtone of $-CH_2-$ of the ethylene group of the ethylbenzene, respectively.

These wavelength regions were used to obtain the correlation between the styrene/ethylbenzene concentrations and NIR spectra by employing the partial least square method (PLS regression method). Figures 2.11 and 2.12 show the resulting correlations. The values measured by employing the gas chromatography and NIR analysis values are very closely correlated with the correlation coefficients of 0.993 for styrene and 0.994 for ethylbenzene. The measurement accuracy (error of prediction) also was approximately 2% over the measurement range, respectively, and so it was confirmed that the InfraSpec can be practically used satisfactorily as an on-line analyzer.

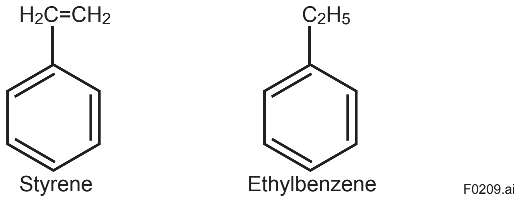

Figure 2.9 Chemical Formulae of Styrene and Ethylbenzene

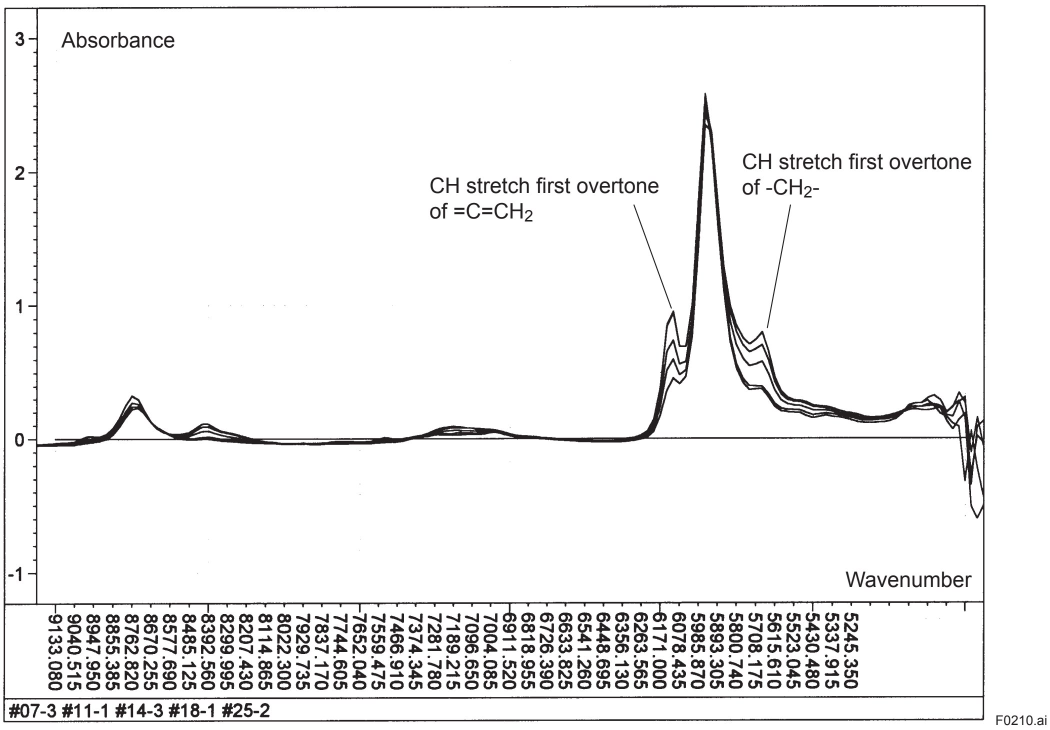

Figure 2.10 Mixed Solution of Styrene and Ethylbenzene

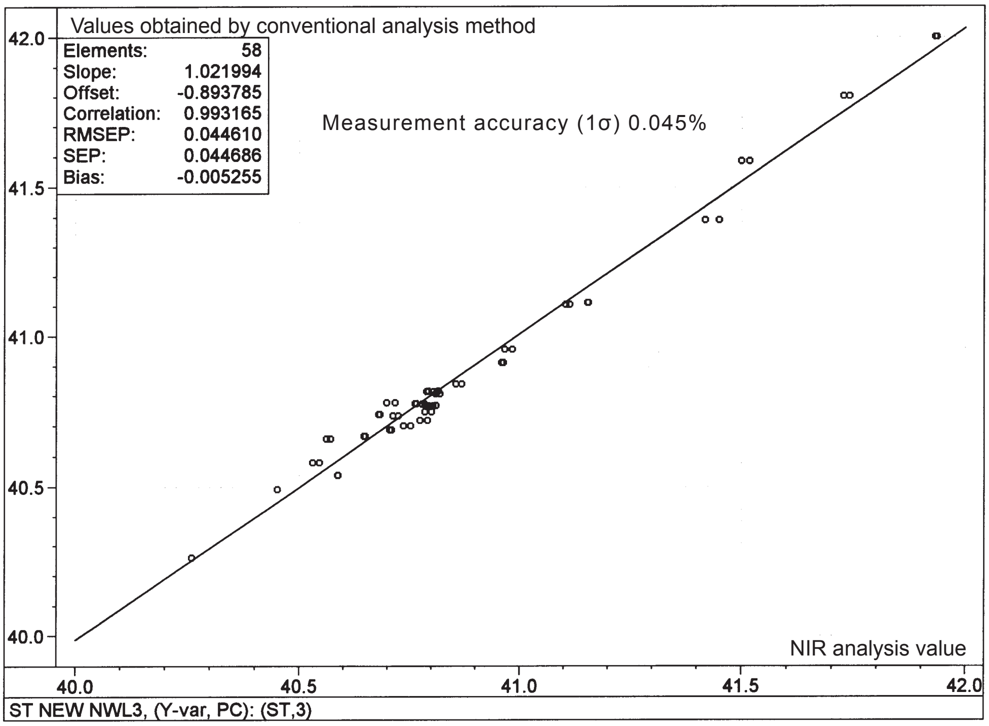

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Figure 2.11 Concentration Measurement of Styrene

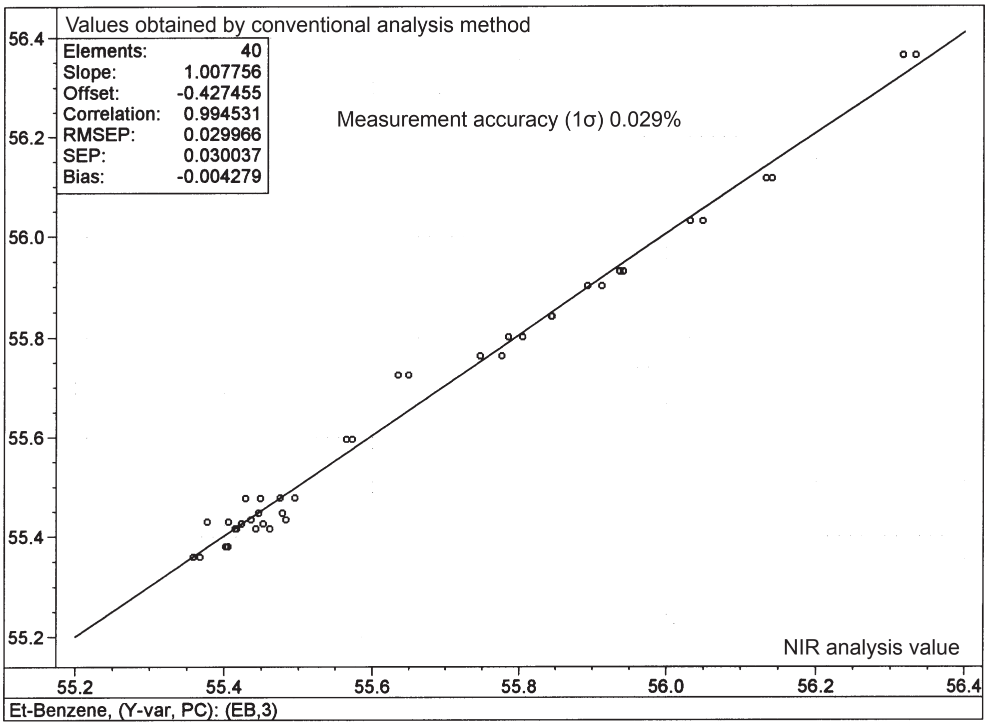

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Figure 2.12 Concentration Measurement of Ethylbenzene

Process Installation System

Figure 2.13 gives a typical layout of equipment used for manufacturing processes.

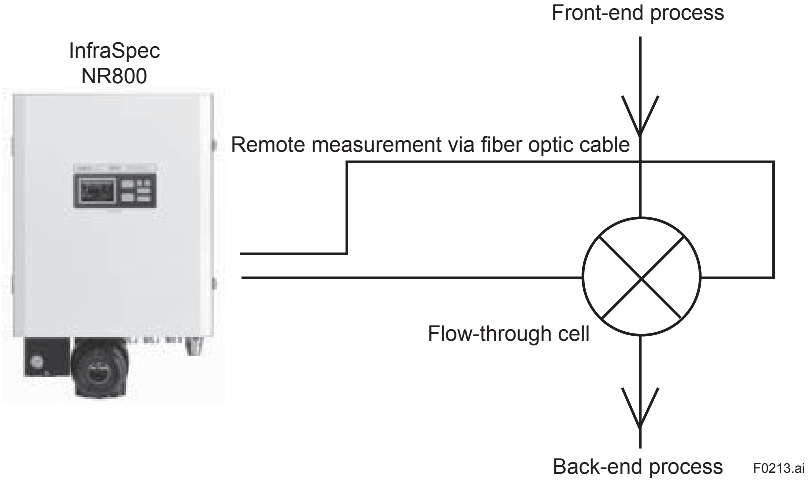

Figure 2.13 Installation System Overview

A continuous flow through cell can be installed either directly in between the front-end and back-end processes or on a small bypass loop.

The consumable supplies used in this system are just a near infrared light source lamp and HeNe laser oscillator for waveform calibration, and it is easy to replace them and the replacement interval is approximately once every 6 months.

The InfraSpec is capable of performing a remote measurement via fiber optic cable. Furthermore, an optional explosion-proof unit enables the InfraSpec to be installed in the field with a shorter fiber optic cable. The InfraSpec can be installed freely considering the installation and maintenance conditions.

Conclusion

This application is traditionally done using on-line gas chromatography which while accurate in determining trace concentrations of impurities suffers from a tendency for the styrene to polymerize as well as the cycle time being in region of 10-15 minutes per stream.

The InfraSpec NIR analyzer for the process presented in this document has the main features of high-speed continuous measurement and ease of maintenance, and so it is expected to be used as an easy-to-use process analysis system for measurement points, where there were many problems that could not be solved with the conventional analysis methods.

2.5 Naphtha Cracker Monitor

Naphtha is the lighter distillate of crude oil (number of Carbon is around 3 – 9). After few steps of distillation, cracking and refining, it will become basic material of petrochemical industry, such as ethylene or propylene. (See Figure 2.14)

For on-line monitoring of naphtha crackers, gas chromatographs have been commonly used, but their measurement cycles are around 10 minutes, which are too long as naphtha cracker monitors. Using NIR enables rapid control and also enables to measure density and distillation points which require stand-alone analyzers.

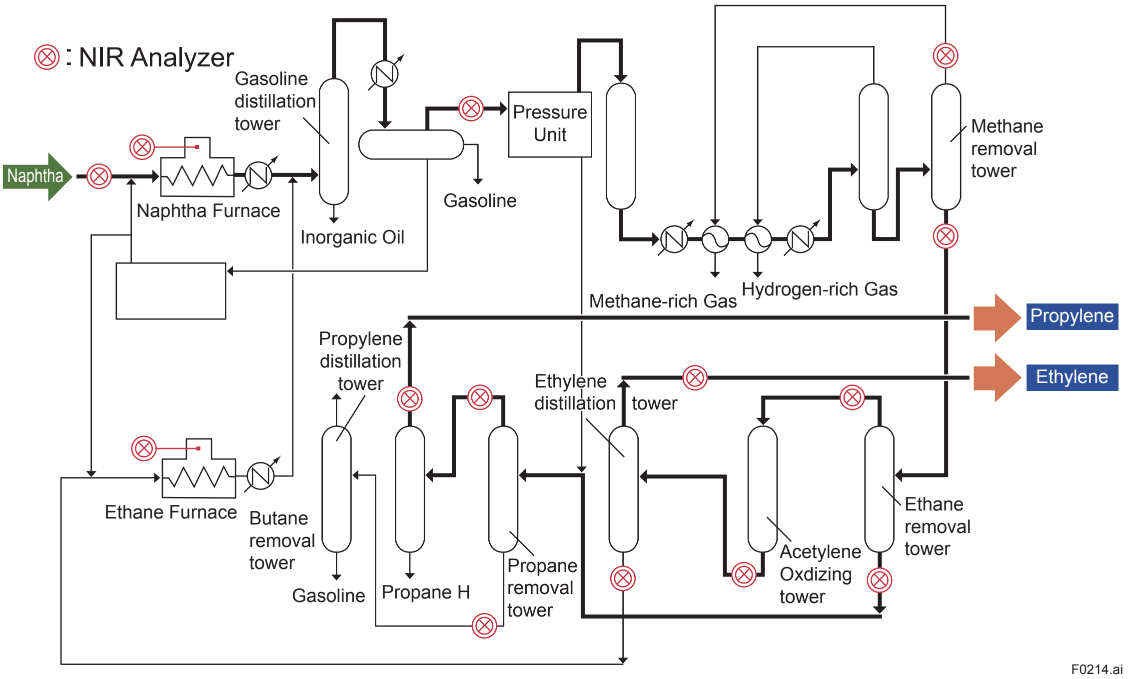

Figure 2.14 Naphtha Cracker

Calibration Modeling

Samples were corrected from the naphtha cracker at site and NIR spectra were measured in the lab. For liquid measurement, small amount of light component was added to the samples from at site to increase the number of samples. The number of samples was 125 for liquid and 33 for gas.

For lab value measurement, a gas chromatograph was used for concentration, a distillation meter was for distillation points, and a densitometer was for density.

(1) Liquid measurement

24 models shown below were made.

- Density
- Distillation Point (IBP, 50%, 70%, EP)
- 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 2.15 shows the example of C6 aroma model.

(2) Gas measurement

23 models shown below were made.

- C1 (Methane)
- C2 (Ethane, Ethylene, Acetylene)
- C3 (Propane, Propylene, Propadiene, Methyl-acetylene)
- C4 (Iso-butane, Butane, Butene, Iso-butene, Butadiene, etc.)
- More than C4 (Total, Benzene, Toluene, etc)

Figure 2.16 shows the spectra from compressed gas cylinders. Peaks caused by molecular rotation can be seen clearly. Unlike liquid, there is no interference between each peak in gas spectrum because the distance between molecular is further than the liquid. And because the pressure and spectra absorbance is proportional, it is easy to obtain desirable sensitivity by adjusting pressure. These characteristics make modeling for gas easy.

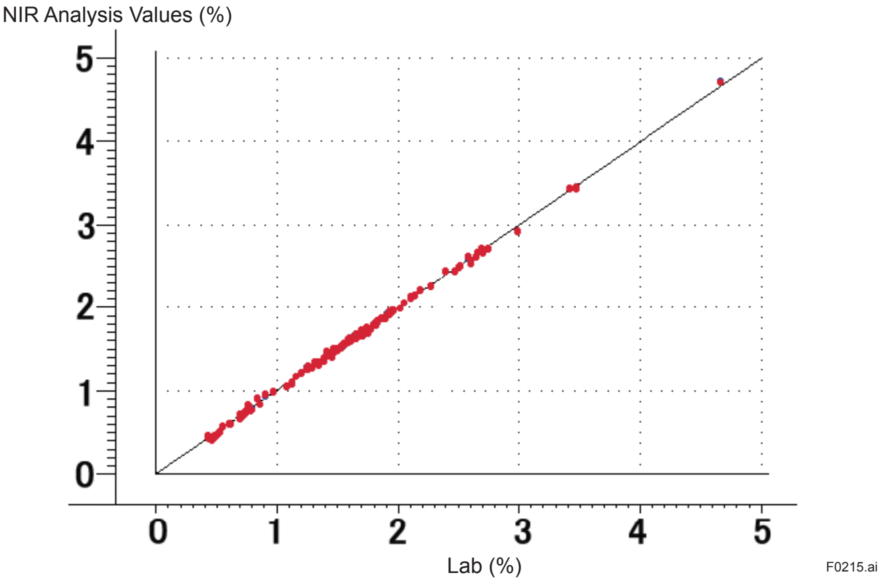

Figure 2.15 Model for Aroma C6 (Benzene)

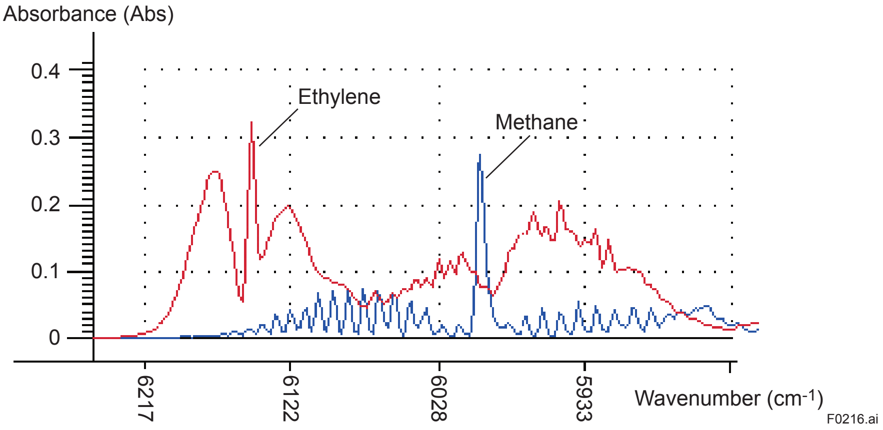

Figure 2.16 Spectra of Ethylene and Methane

2.6 Naphtha Steam Cracker Optimization

Overview

Naphtha steam crackers are one of the most commonly found petrochemical plants in the world today. This is because they are usually the first step in the production of all other petrochemicals and plastics such as polyethylene, polypropylene, polystyrene etc.

The fact that production of ethylene worldwide is very large gives rise to the situation that feedstock naphtha has to be very varied and flexible.

This and the large throughput of a typical cracker is what has made these plants highly suitable for process automation and optimization and particularly the use of on-line gas chromatograph to improve process operation, conditions and throughput.

Naphtha Steam Cracker Description

A typical steam cracker can be divided into two sections.

1 – Cracking Furnaces

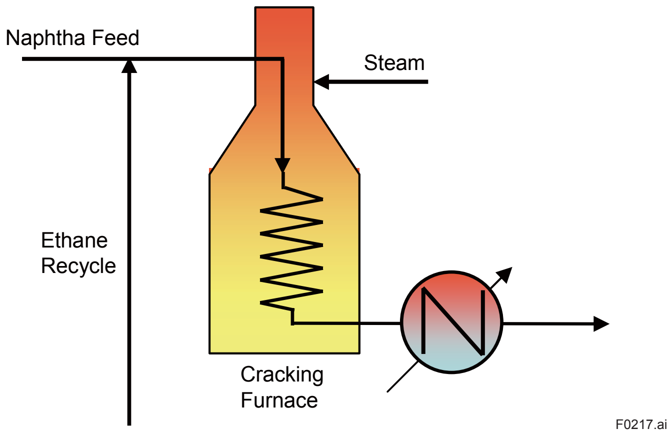

Figure 2.17

Naphtha feedstock is reacted with steam at 850-900ºC inside a tubular furnace.This pyrolysis process converts the heavier hydrocarbon into lighter fractions, primarily ethylene and propylene, by removing the hydrogen molecules. The hot gas effluent from the furnace is then passed through the quench section where it is cooled to retard further cracking and to condense heavy fractions. The heavy fractions are subsequently processed into fuel oil, light cycle oil and pygas (pyrolysis gasoline) by-products.

2 – Fractionation and cleaning section

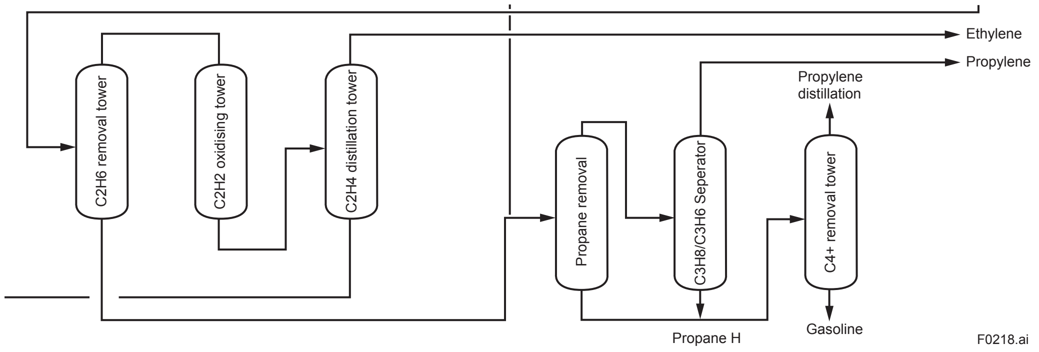

Figure 2.18

The cooled gases are then compressed, treated to remove acid gases (ie. H_2S), dried over a desiccant and fractionated into separate components at low temperature through a series of refrigeration / distillation processes. Hydrogen and methane are removed by way of a compression / expansion process. The methane removed is distributed as fuel gas for use in the furnaces, boilers and co-generation power plants. Hydrogen is collected and further purified in a pressure swing unit for use in the hydrogenation process. Polymer grade ethylene and propylene are separated in the cold section. The separated ethane and propane streams are recycled back to the furnace for further cracking while the mixed C4 stream is hydrogenated prior to recycling back to the furnace for further cracking.

The final products, ethylene and propylene are purified and go to the next plant, either polyethylene, polypropylene or so other.

Plant optimization

Naphtha crackers are sometimes known as "dustbins" as they take all forms of left over naphtha from refineries, and cheap spot naphtha loads from the open market. Therefore, naphtha feed quality can be extremely variable. This effects not just the furnace crackers, but also downstream seperation efficiency as well, so on-line analyzers play a useful role in monitoring these streams.

1 – Analytical monitoring for the naphtha cracker furnace

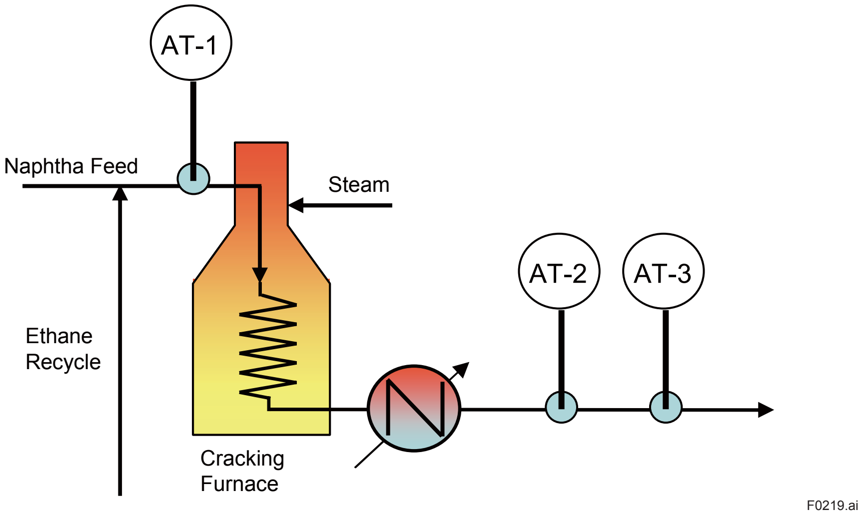

Figure 2.19

AT-1 – Naphtha Feed Analysis

On-line measurement of naphtha feed quality is one of the most important measurements. Traditionally, this has been done with a process gas chromatograph to measure paraffins, olefins, iso-paraffins, naphthalenes, aromatics (PIONA) and other distillation properties, with a cycle time usually around 90 minutes.

A faster way to do the same analysis is to use the NR800 FT-NIR which can do the same analysis of PIONA and as many other properties as are required in under one minute.

Direct Benefits of fast on-line Naphtha feed analysis:
A feed forward control strategy on each cracker can be implemented. Not only does this stabilize the reaction as to maximize ethylene yield but can be used to increase overall reactor throughput. (see Figure 2.20).

The cracking process inevitably yields methane which has to be removed in demethanizer compressors after the reactor. These have a maximum throughput, so each cracker throughput is largely influenced by this maximum demethanizer throughput.
The flow rate through the cracker is set, so that any change in feed quality that suddenly yields more methane can be countered in time before it reaches the maximum allowed. This is called a "constraint" or a "safety-margin".

By on-line fast monitoring, and an effective feed forward control strategy, this constraint can be reduced as any methane "excursion" can be picked anticipated sooner, and measures taken.

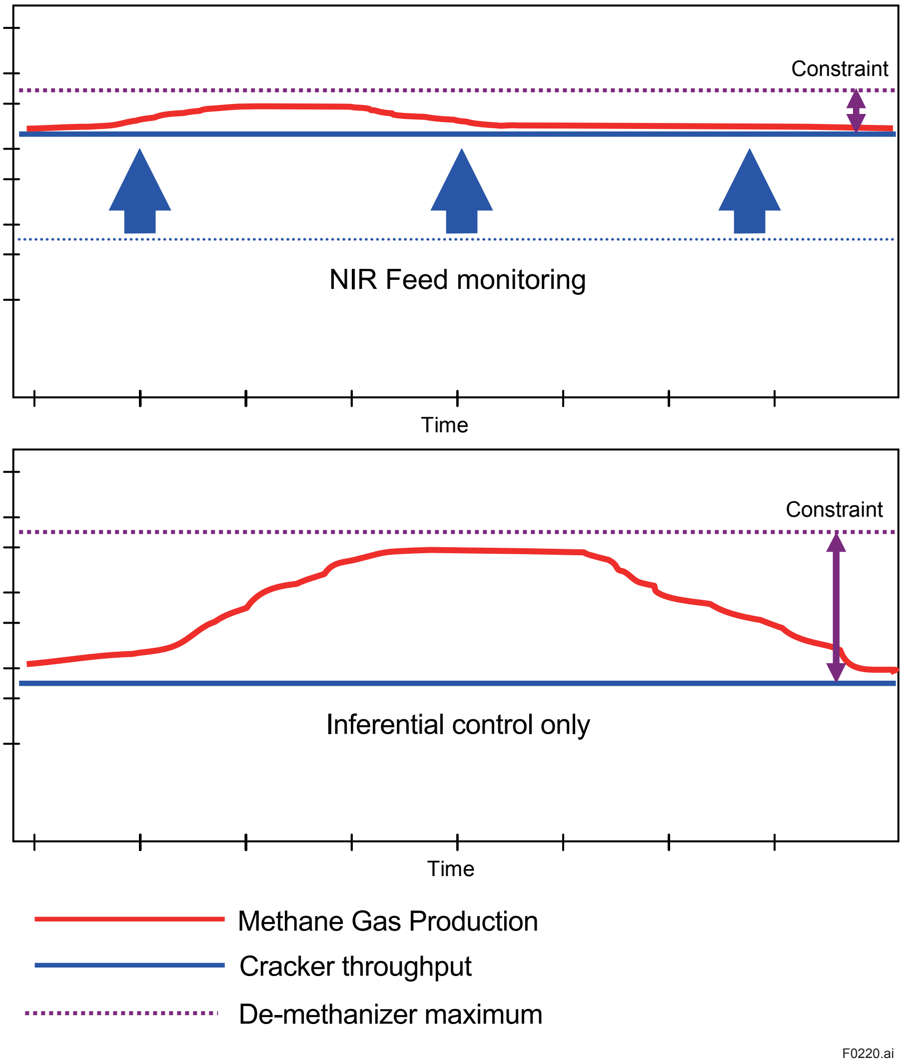

Figure 2.20 Naphtha Feed Analysis

AT-2/3 – Downstream from Pyrolysis cracker

AT-2 and AT-3 are at least two points of downstream measurement, partly because there are likely to be many analyzers measuring different things, but also several stages of cooling and even H_2S removal.

These measurement points are traditional filled with GC's and these are used to measure concentrations of ethylene, ethane, propylene, propane, C4's and above, as well as H_2S and other components.
These measurements give a good indication of cracking "severity" or whether the reactor is "under-cracking" or "over-cracking".

The primary analysis point for this measurement is the exit from the transfer line cooling exchangers after the cracker, and then a specialized sample probe called a "reflux" or "pyrolysis" probe is used, as it prevents tars and contaminants from entering into the analyzer which is doing the measurement. Traditionally, several GC's are employed per furnace to provide as fast as possible analysis of C2's and C3's.
Then a second more thorough analysis is done on the furnace effluent in parallel to the first high speed one. The cycle time on this second analyzer is not as urgent as the first C2,C3 analysis.

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Figure 2.21 FT-NIR Gas measurement cell

Gas chromatographs measuring C2's and C3's usually have a best cycle time of 2-3 minutes. Attempts have been made in the past to use faster analysis techniques such as NDIR (Non-dispersive Infrared) analyzers. These analyzers while fast, employ a filter wheel method for wavelength selection and are therefore subject to large cross-interferences to other components.

The NR800 FT-NIR now has a gas cell capable of measuring these components at high speed, and without the cross-interference problems suffered by conventional NDIR analyzers. As all infrared wavelengths in the range 900-2500nm can be measured with far better resolution, individual measurement of C1's to C5's and above can be done very quickly and reliably. (see Figure 2.22)

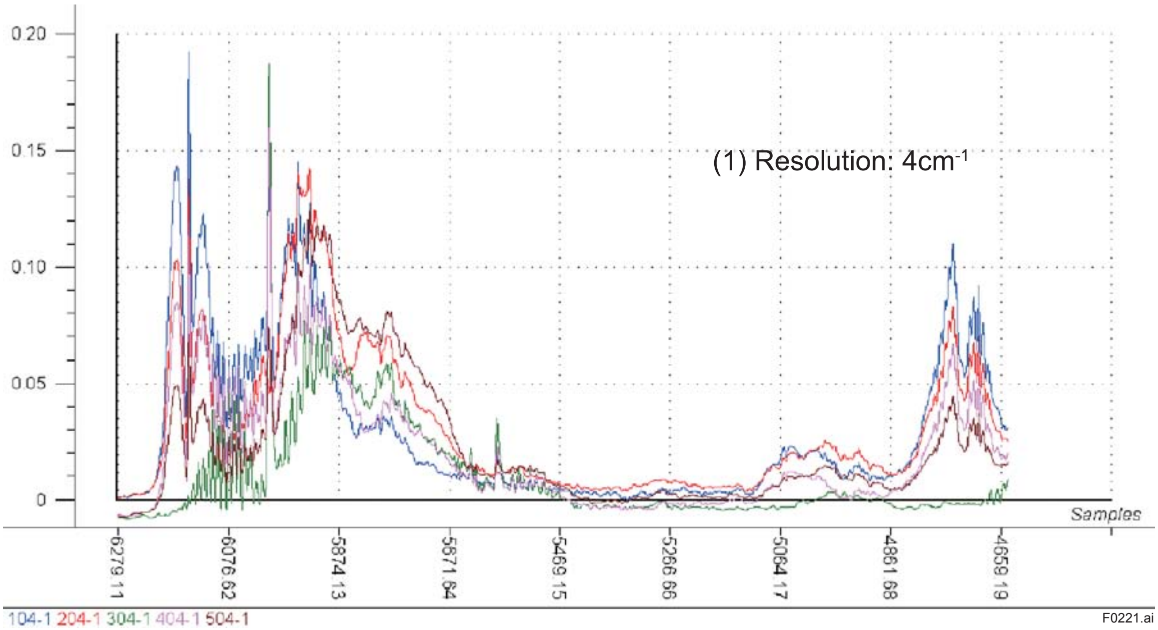

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Figure 2.22

Fractionation train

Fractionation and separation of the mixture into pure components and recycle is a deceptively energy intensive process in it's own right, and therefore analysis of column overheads and bottoms products by the selective use of GC's or NIR measurements can significantly improve separation efficiency.

Consequently many of the GC's employed on ethylene plants also find their way in the fractionation part of the process.

Other benefits to on-line monitoring of Furnace reactors

All furnaces at some stage have to go through a decoking phase. The reactor coils eventually coke up over time, and this affects the overall performance of the reactor.
By constantly monitoring cracker severity and conversion rates, down-time and de-coked schedules can be managed more effectively.

Complete Ethylene cracker plant Schematic with possible measurement locations using either

1) NR800 FT-NIR analyzer

2) GC1000 MarkII Process Gas Chromatograph

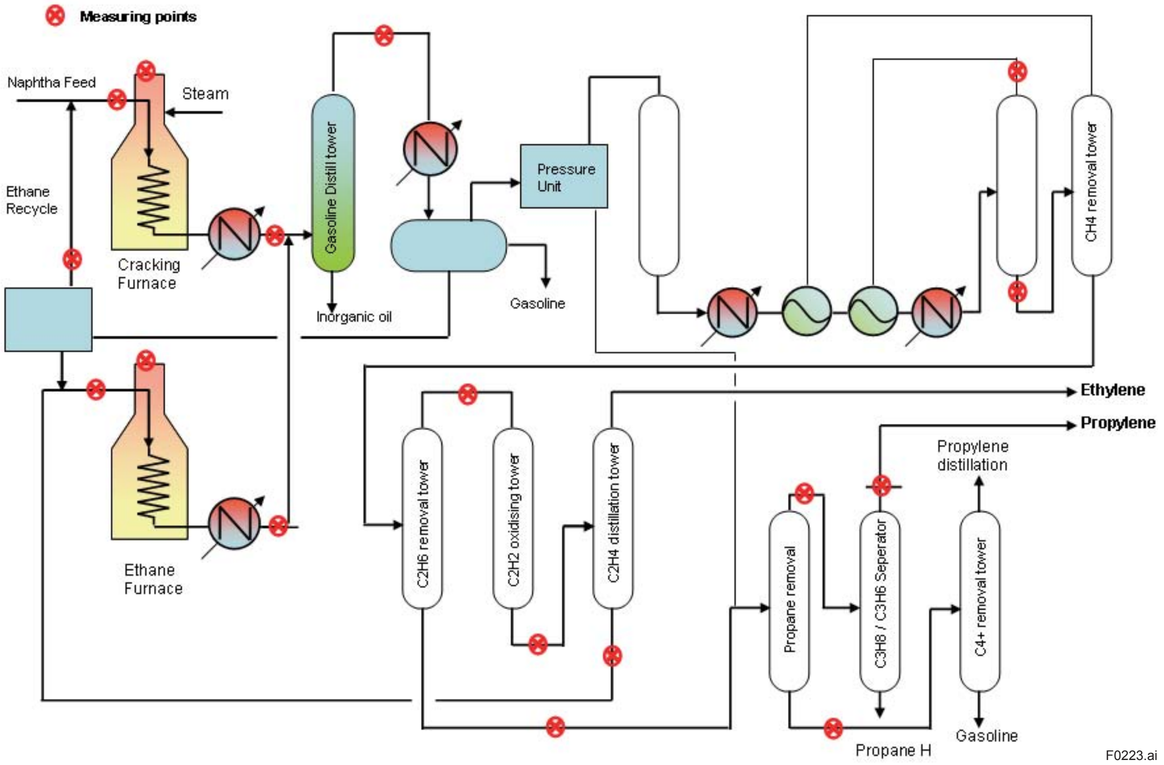

Figure 2.23

Conclusions

Naphtha cracker plants remain to this day ideally suited for fast stream analysis and process optimization, and based on their large throughputs and variable feed and operation parameters offer significant pay-back time compared to initial capital investment outlay and maintenance.

Yokogawa offer highly reliable FT-NIR and GC hardware platforms and combined with effective project management and highly skilled personnel, can ensure that such profitable strategies can be implemented as effectively as possible.

2.7 On-line measurements in Ethanol Fermentation Plants

Background

Ethanol alcohol has been used as a motor fuel for over two hundred years. In recent years, it has become the 'oxygenate of choice' in the production of reformulated gasoline in the United States, and demand continues to grow exponentially worldwide, as countries recognize the need to develop alternative bio-friendly fuels and decrease their dependence on oil.

Production

World production of Ethanol is 40-50 Billion litres per year on one of three ways :-

1) 60% is produced through sugar crop fermentation, (sugar cane & sugar beet)
2) 33% is produced from other fermentable products, the largest being corn/maize
3) 7% is 'synthetic alcohol' and is produced directly from crude oil and gas

Sugar crops are the most direct way to fermentation, but with improvements in enzyme and process technology corn fermentation is increasing in efficiency.

Corn/ Maize Dry milling Fermentation process

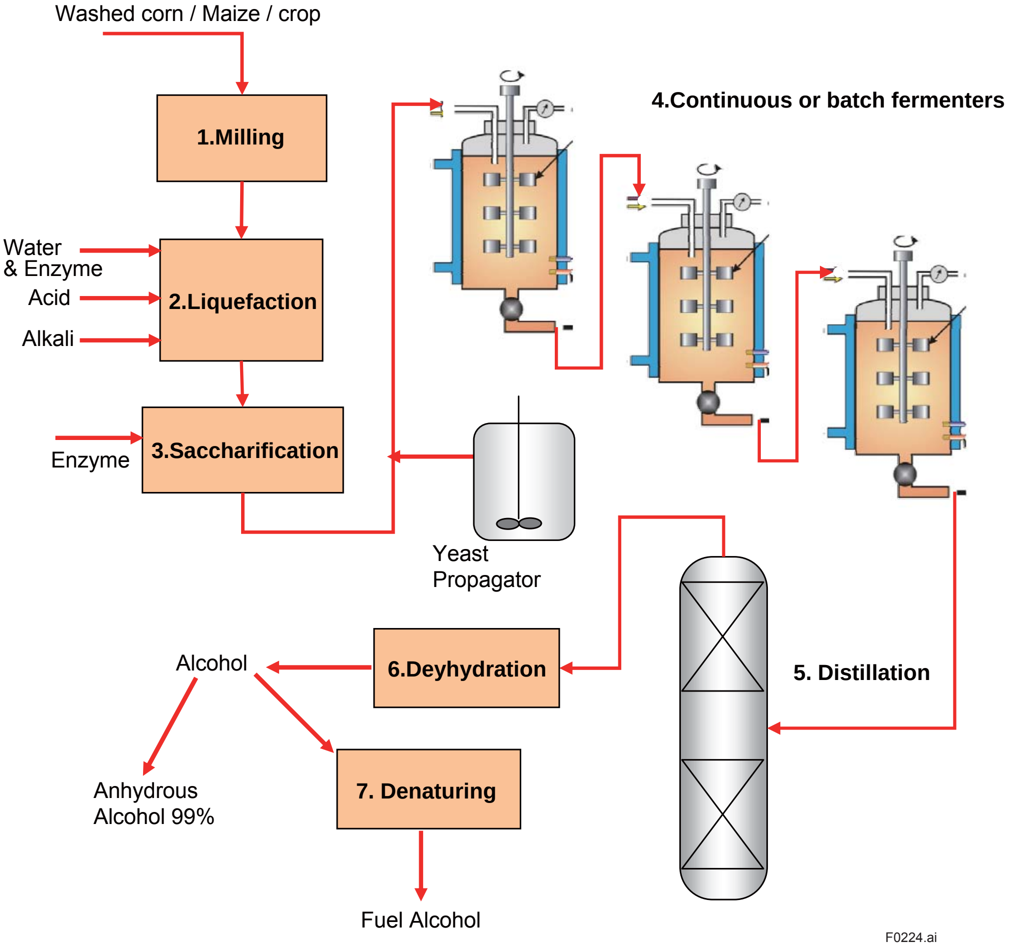

Figure 2.24

■ Description of Process

1) Cleaning and Milling

After the corn is cleaned, it passes first through hammer mills which grind it into a fine powder.

2) Liquefaction

The powder is mixed with water and an enzyme(alpha-amylase) is added. Then mash passes to cookers operating at 120-150°C where the starch is liquefied, and the viscosity of the mass consequently reduced. This allows the total dissolved solids level to be increased thereby increasing process efficiency.

Sulphuric or sodium hydroxide are also added to keep the mix pH neutral. A holding tank at 95°C is also used to reduce bacteria levels.

3) Saccharification

The liquefied mash is cooled, and another industrial enzyme gluco-amylase is added which directly converts the liquefied starch to fermentable sugars. Care must be taken to prevent bacterial contamination at this stage.

4) Fermentation

Yeast is added from a yeast propagator tank and the mash is fed through a series of continuous reactors or in the case of a batch reactor ferments for approximately 48 hours before the mash is fully fermented containing around 10% ethanol.

5) Distillation

The fermented mash, or "beer" as well as all the non-fermentable solids from the corn and yeast cells goes to a multi-column distillation system where the alcohol will be removed from the solids and water. 96% pure ethanol comes off as overhead from the column, and the residue mash from the bottoms of the column is sent to the co-product processing area.

6) Dehydration

Vapor molecular sieves are used to remove the remaining 4% water to yield 'anhydrous alcohol' which is almost 100%.

7) Denaturing

For ethanol which goes up to make fuel, up to 5% of methanol, gasoline or other product is added to make it unfit for human consumption.

■ Process Improvements

Compared to gasoline production, ethanol is still a relatively expensive fuel to product. Over recent years dramatic process improvements have been made to reduce energy costs and maximize the conversion of starch in the mash to ethanol:-

- Molecular sieve dehydration. With the advent of vapor molecular sieve, secondary and tertiary distillation was no longer necessary and harmful solvents such as cyclohexane or benzene were no longer required.
- Combination of yeast propagation, saccharification and fermentation process. This maximizes yeast contact time with the liquefied mash, improving yields, reducing bacterial contamination and reducing storage problems with yeast.
- Improved enzymes which are pH tolerant and improve liquefaction and saccharification and fermentation processes.
- Ever improving distributed control systems DCS which allow fine tuning of process parameters and better control of the plant.

Continuous On-line process measurements using NR800

With the implementation of DCS systems in ethanol plants, there have been improvements in plant efficiency, but further enhancements are possible by using real-time real composition data from the reactors using the NR800 NIR Analyzer.

Applications – Liquefaction cooker monitoring

During liquefaction where the enzyme is breaking down the solid starches in the cookers and dissolving them in solution (see Figure 2.25), monitoring the solution content gives a very good indication of the endpoint of this process and also helps to optimize the liquor with a maximum concentration of dissolved starches, further improving the fermentation process. This can be monitored in real-time using NIR analyzer and can help to ensure that the maximum amount of yeast-fermentable products are drawn from the solids and into solution, with the optimum amount of energy consumption during this cooking process.

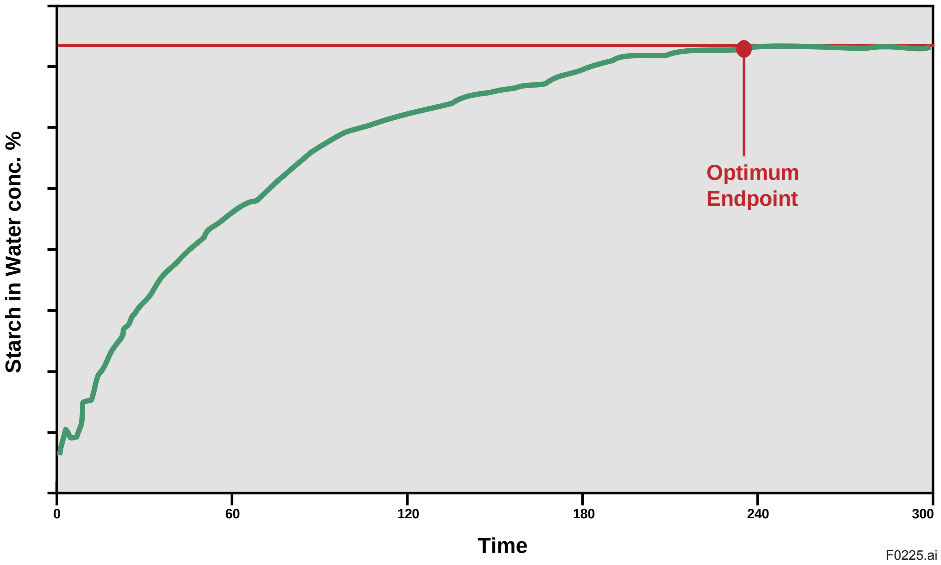

Figure 2.25

Additional Applications – Fermenter and Saccharification monitoring

For many plants, saccharification, fermentation and yeast propagation are consolidated into one process to reduce the risk of bacterial contamination, maximize yeast contact, and generally increase yield (SSYPF – Simultaneous Saccharification Yeast Propagation and Fermentation).

Using NIR analyzer to monitor sugar concentration and ethanol concentration continuously and simultaneously in the fermenter (see Figure 2.26) allows the fermentation endpoint to be monitored very carefully, saving on unnecessary extended batch runs where no more ethanol is being fermented, and the risk of bacterial infection will also increase.
Monitoring total dissolved fermentable sugars and ethanol thereby reduces energy usage and increases ethanol yield by being able to run optimized batch runs.

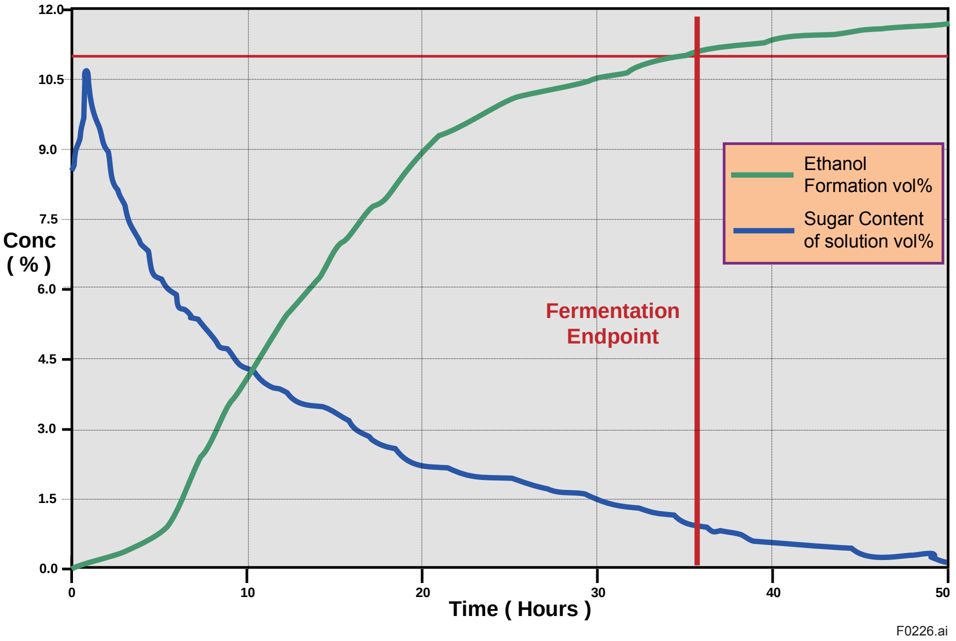

Figure 2.26

Sample Handling

Analytically, it is not difficult to measure concentrations of sugars reactants and ethanol product, but handling the mash sample has always been a problem for any kind of sensor or detector.

Different approaches have been tried in the past :-

- Insitu transmission probes. Give a good signal, but the path gap clogs very easily and cleaning is a problem. In addition, the mash consists of solids and liquids at various states of dissolution. Analyzers like to see homogenous samples, and the mash typically is not giving very unstable readings.
- Reflectance probe measurements. Do not suffer the same clogging problems as path gap probes, but the reflected signal is good only for ethanol property determination. As with transmission probes, sample presentation of a not-quite homogeneous mash can be a problem.
- Extractive systems. Have similar problems to above with clogging of the cell or filters (if present).

Yokogawa have developed a highly stable and reliable batch cleaning filter system which is able to take the raw 'beer' product and filter it to produce clear liquid. This clear liquid will contain the total dissolvable sugars that the enzymes and cooking have trying to produce therefore conveniently giving a clean and correct solution for monitoring in transmission mode. By being able to use a 2mm transmission cell, sugar content can be quantified unlike a reflective measurement.

Cost Benefit Analysis

Cost of production per litre of ethanol varies greatly on many factors such as size of plant and the economizes of scale that can be introduced, but also external factors such as location to crop suppliers, CO_2 users, or farm silage distributors.

Over time, the cost of ethanol production has dropped largely due to a less energy intensive process and improved molecular sieve design to around 30-50 Euro cents / litre.

The two applications above liquefaction monitoring and fermenter monitoring are designed to save money on energy used during these processes, and cutting down the number of extra hours used to ferment or liquefy the mash. Cost savings therefore occur in time saving between batches, reduced bacterial contamination and energy savings between batches.

One final application exists on the molecular sieve dehydration system.

Molecular sieve dehydration system

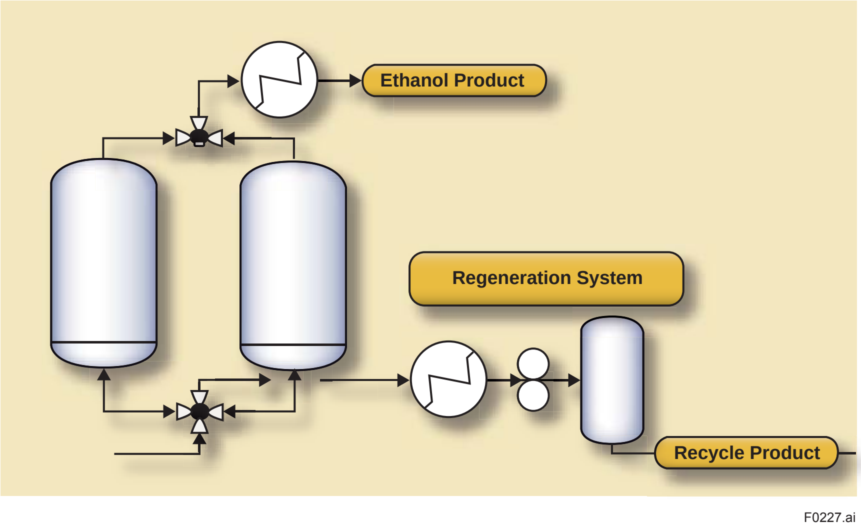

Figure 2.27

In order to produce 'anhydrous alcohol' quality at 99.5% pure alcohol, it is necessary to take 96.4% 'hydrous alcohol' and dry it. Further distillation is not possible unless it is azeotropic distillation but the energy used is too high.

Molecular sieve technology is so advanced these days that the alcohol can be dried to within 50ppm of water.

However, it is possible to save money, by rediluting the ethanol from 99.99% purity to 99.0% purity which is still classified as 'anhydrous alcohol'.

For an average ethanol plant producing 100 Million litres / year ethanol.

With an average cost of production of 45 Euro-cents/litre give annual cost of 45 million Euros / year. With a saving of 1% ethanol by diluting with water there is a cost saving of :-

(99.99 / 99.0) x 0.45 Euro/ litre = 0.4455 cents / litre.

0.45 – 0.4455 cents / litre saved x 100 million litres / year = **Euros 445K**

In addition, molecular sieve driers normally operate in pairs, with one drier being regenerated (dried) while the other is in service. Monitoring the ppm levels of moisture in the anhydrous alcohol can make the changeover and regeneration of filters more efficient minimizing the risk of water breakthrough to the anhydrous product.

Conclusions

The last ten years have seen the continuous improvement in efficiency of ethanol fermentation plants by the employment of technology and control.

Other factors such as political climate vary per country and region, and costs of corn of cereal prices will all effect profitability.

By the introduction of fast multi-channel infrared technology, together with our unique sample system design will allow the user to increase his plant efficiency with a choice of one of three applications :-

1) Liquefaction monitoring
2) Fermentation and saccharification monitoring
3) Molecular sieve active ethanol concentration control.

A total project cost for the NIR including services and hardware is around Euros 150K.

Therefore with the third application alone, it is possible to obtain somewhat near a 3-6 month payback.

The analyzer itself is multi-channel and links remote locations via. Fiber optics so it would be possibly to install one unit on site to control all three applications simultaneously.

2.8 Propylene Oxide, Styrene Monomer Plant Optimization

Overview

Styrene (vinyl benzene) is a very useful monomer that polymerizes readily to give many different forms of plastics such as polystyrene, ABS, styrene-butadiene rubber (SBR), SIS, S-EB-S, S-DVB and polyesters.

Traditional ways of producing styrene have centered around the catalytic dehydrogenation of ethyl benzene. Whilst this has a reasonable conversion of between 60-70%, one of the biggest issues is that separating the unreacted ethylbenzene from styrene is energy intensive and difficult.

This is mainly because styrene & ethylbenzene have similar boiling points (145 & 136ºC) so distillation requires tall towers with high reflux ratios.
To complicate matters further, styrene has the tendency to polymerize at these temperatures.`

A more energy efficient method is the propylene oxide process. Although the limitation on production of styrene seems to be how fast propylene oxide can be sold.

The two distinct phases of production are shown below:-

1) Ethylbenzene production by Alkylation

In all the styrene production plants the main reactant chemical required is always ethylbenzene. This is formed from the alkylation of benzene and ethene at a high temperature (380-420ºC) reaction and moderate pressures using any of a variety of solid catalysts. Benzene is typically sourced from a refinery platformer unit and ethene from a steam cracking unit.

The alkylation reaction is straightforward and proceeds with 100% conversion. However the ethylbenzene product is more reactive than the original benzene so additionally polyethyl-benzenes are also produced.
These are reconverted back to mono-ethylbenzene in a 3rd trans-alkylation reactor.

2) Ethylbenzene to Styrene

This involves more stages than the direct dehydrogenation method as follows:-

First ethylbenzene is reacted with oxygen to form ethylbenzene hydroperoxide

$C_6H_5CH_2CH_3 + O_2 \rightarrow C_6H_5CH_2CH_2O_2H$

The EB-hydroperoxide is then used to oxidize propylene to propylene oxide which produces phenylethanol.

$C_6H_5CH_2CH_2O_2H + CH_3CH{=}CH_2 \rightarrow C_6H_5CH_2CH_2OH + CH_3CHCH_2O$

This is the dehydrated to yield styrene and water

$C_6H_5CH_2CH_2OH \rightarrow C_6H_5CH{=}CH_2 + H_2O$

In practice there are a number of separation and recovery steps and various purge streams are formed which must be disposed of.

1 – Initial Reaction – Converting Benzene to Ethylbenzene

The alkylation process of converting benzene to ethylbenzene is already well established. This process must also be well controlled to avoid excessive polymerization of ethylbenzene.

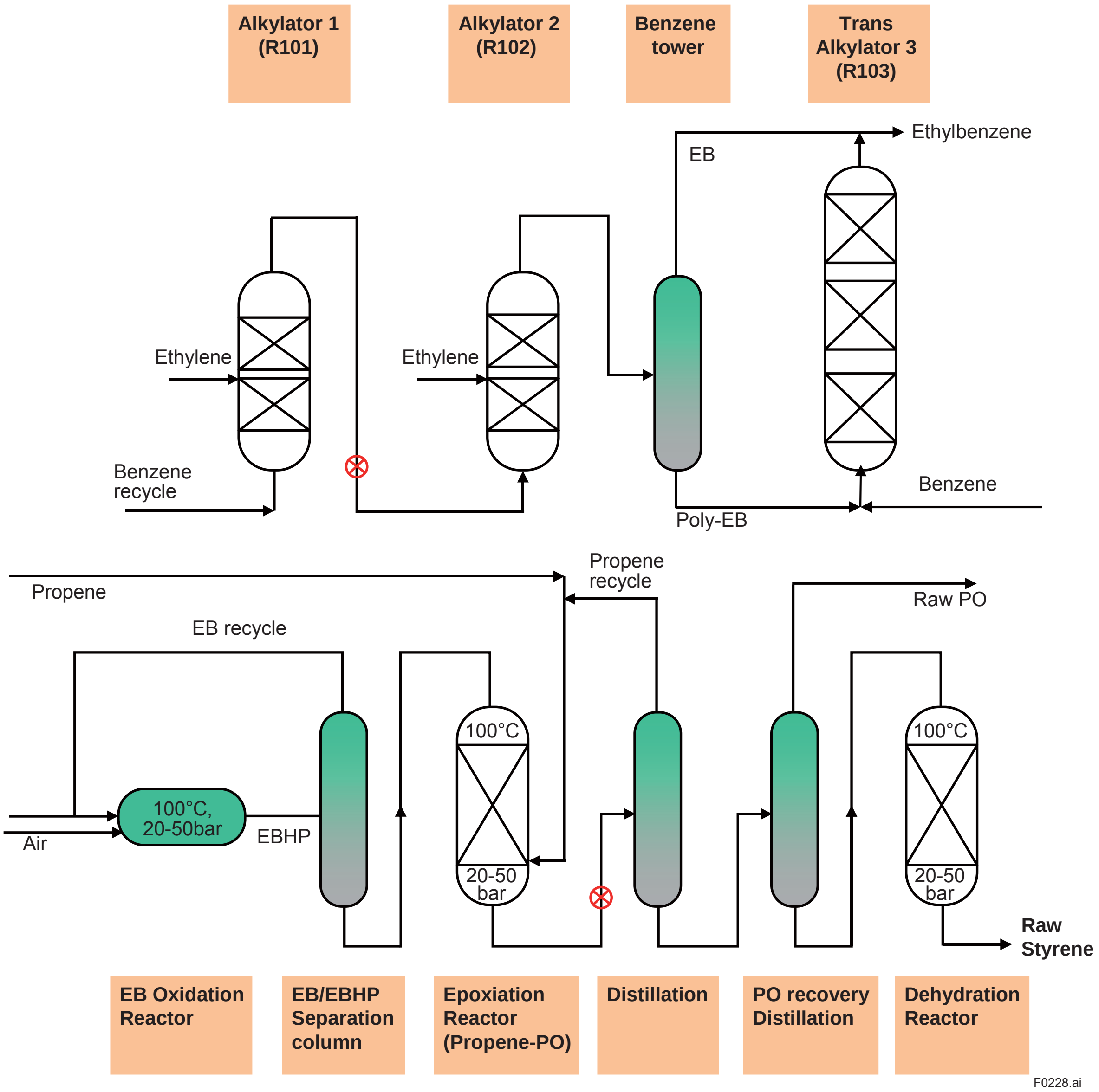

Figure 2.28

2.9 Measuring On-line Monoetylene Glycol (MEG) Concentration

■ Background

Natural Gas Liquids is natural gas that has been pressurized and cooled to liquefy for ease of transportation by pipeline and storage.

Natural Gas, the source of Natural Gas Liquids is a natural mixture of gaseous methane its chief component, methane, usually makes up from 80% to 95% its composition.
The balance is composed of varying amounts of ethane, propane, butane, up to C6 and higher with CO_2, CO and N_2.

From off-shore to an on-shore treatment facility, the gas is separated from entrained condensate and processed before sending to distribution.

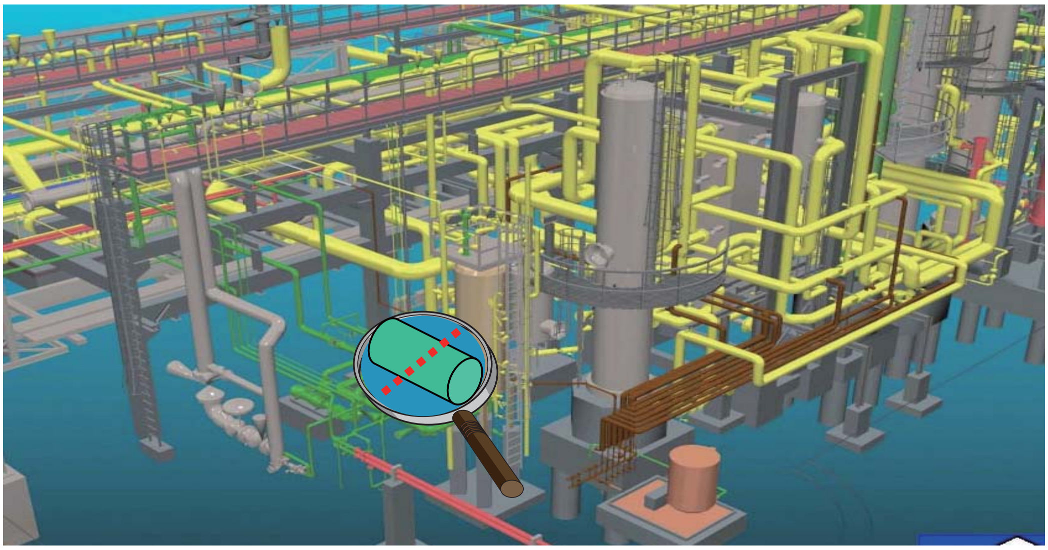
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Figure 2.29

■ NGL Pre-treatment

Feed is sent to the degassing drum and then on to the feed gas separator. In this separator, condensate and MEG are separated from the gas mixture.

This gas is sent to the condensate system.

The off-gas is fed to a feed gas filter separator where solids and residual droplets are removed to protect the downstream plant. This feed gas then goes off to the downstream processing plant.

The recovered condensate goes through a liquid expansion valve, and to avoid hydrate formation in this valve, a mixture of monoethylene glycol (MEG) and water is added.

This liquid is combined with the condensate from the feed gas separator and goes to the condensate system.

MEG/Water mix is separated and recovered from this in the condensate system and recycled.

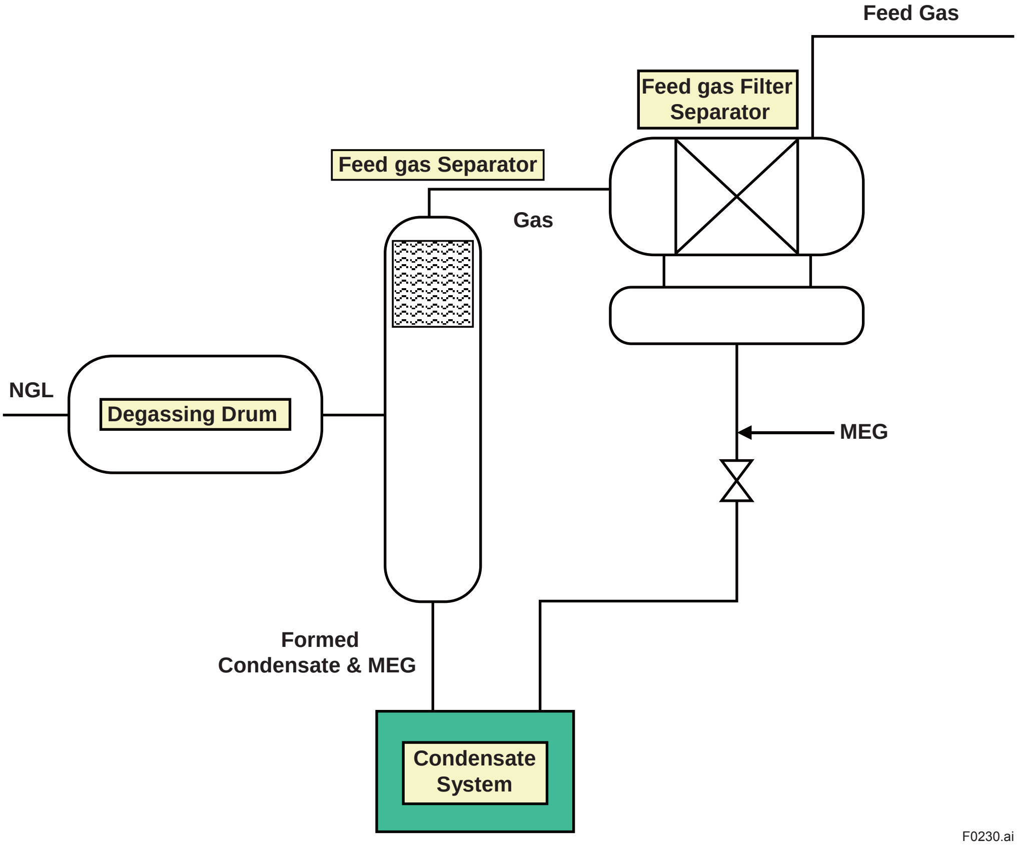

Figure 2.30

MEG Recycling

The MEG is recycled and reprocessed and sent back to the gas separation plant.
The problem is, the MEG concentration must be fairly accurate.

Too much MEG in water, and the MEG runs the risk of freezing out.

Too little MEG and the MEG is not effective to stop hydrate formation in the liquid expansion valve.

Therefore, a viable application exists on the MEG blending plant to continuously monitor on-line the concentration of MEG in solution.

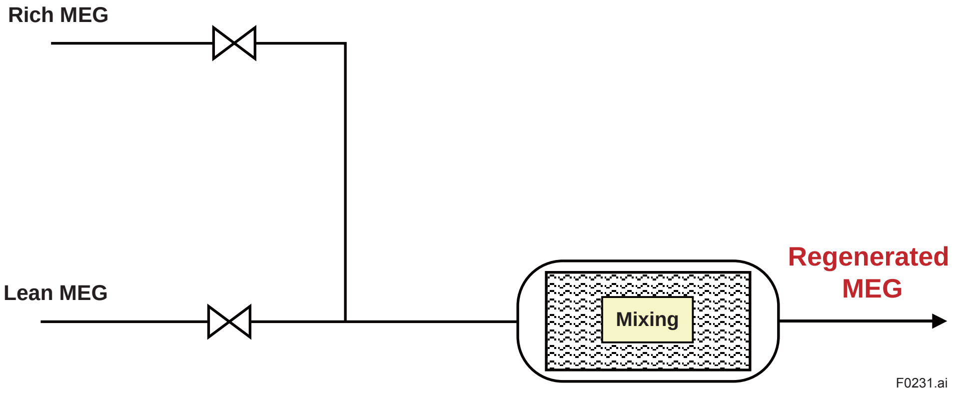

Figure 2.31

NIR Analysis

To get a real time on-line analysis of concentration of MEG in water can be done very effectively using NIR Analysis.

With a potentially dirty and changing process stream, a highly repeatable, non-invasive analytical technique is required.

The type of plant requires that the equipment used is highly reliable, with low maintenance and provides a stable reading, not affected by impurities,

The NR800 FT-NIR analyzer provides the best equipment for this application.

MEG responds favorably in the near infrared region. Below in Figure 2.32 is the NIR spectra of 20-30 samples of MEG in water ranging from between 60-100% MEG content.
The region highlighted by the magnifier proves to be the most suitable for correlating against MEG concentration.

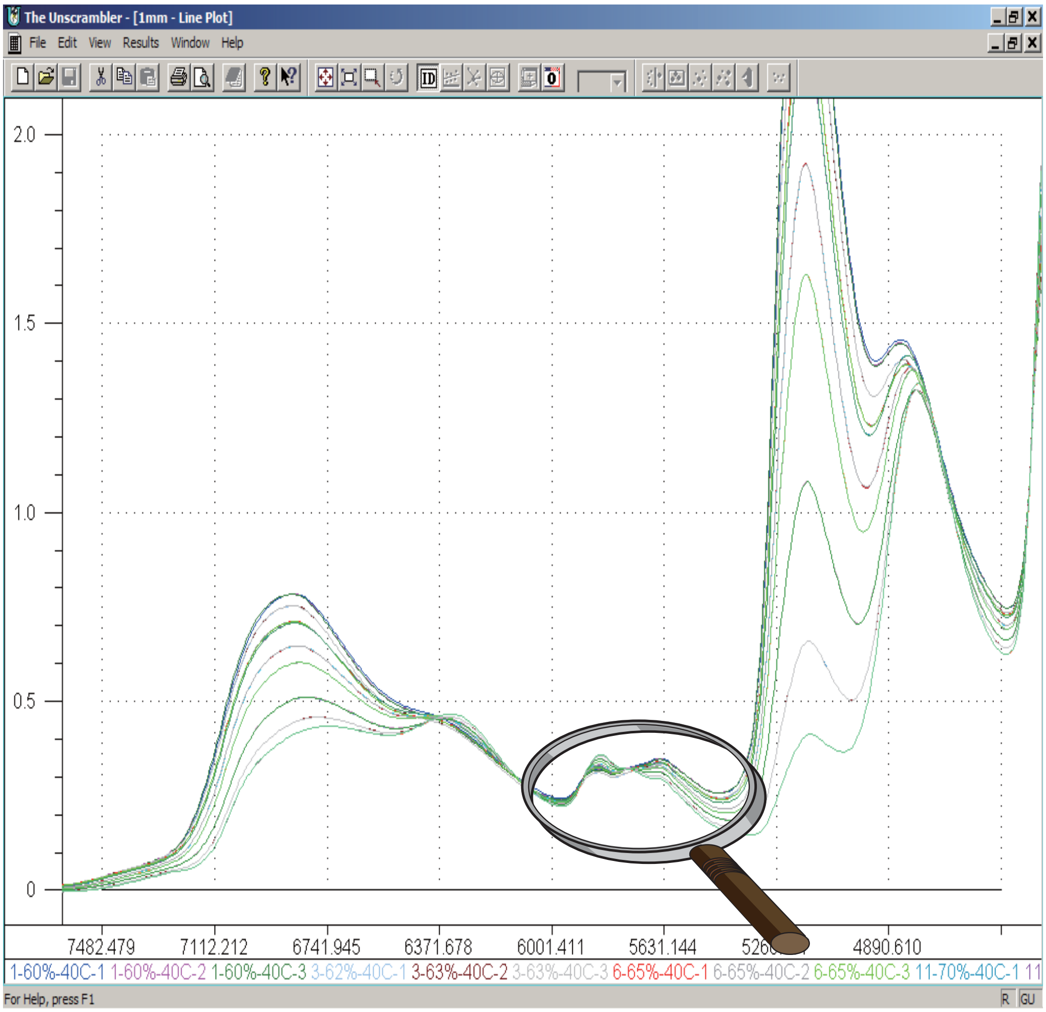

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Figure 2.32

It is very useful to have a full range of spectral information to look at. Other filtometer infrared systems are able to measure MEG in water at discrete chosen wavelengths, but fail to take into account temperature, and impurities concentrations such as inorganic salts which have an affect of shifting the spectrum. These errors cannot be accounted for in simple non-dispersive filter based systems.

Correlation of NIR Spectra and MEG Concentration

Diagram Figure 2.33 below shows that a good correlation exists between MEG conc% and spectral data.
The RMSEC Value describes the root mean square error of calibration as a way of cross-validating the model for performance.
This value represents 1 Standard deviation of error, so for 95% confidence in prediction, we used 2 x Standard deviations to determine accuracy of the model.

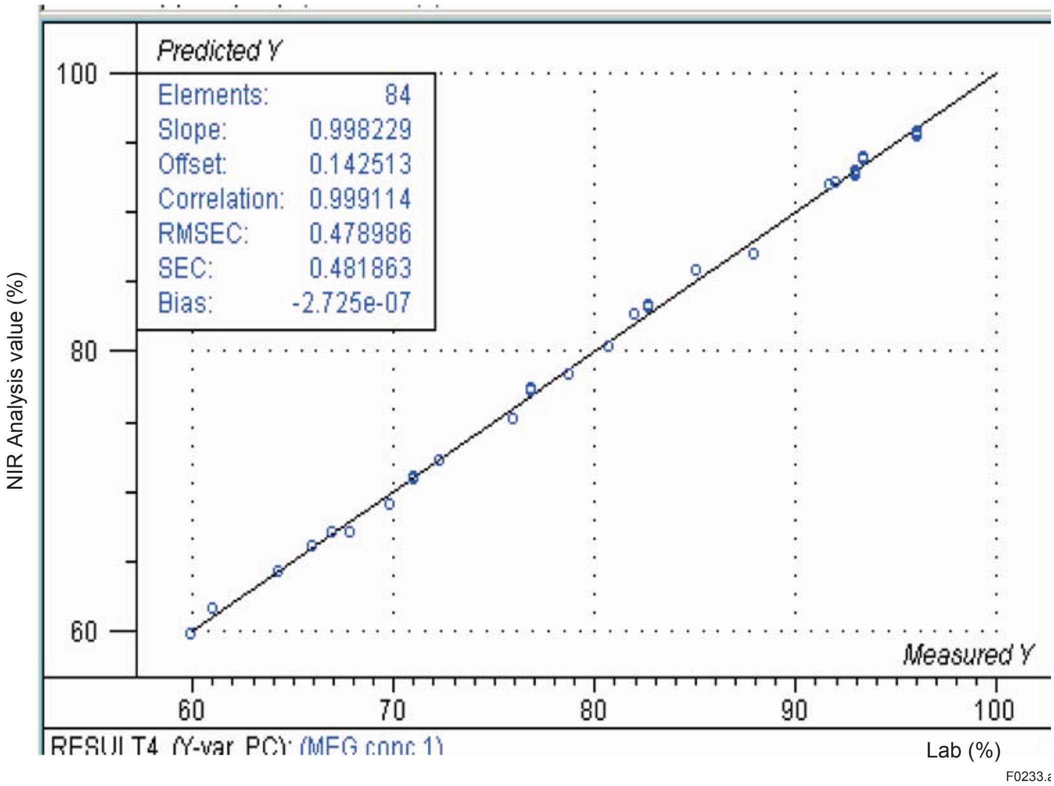

Figure 2.33

Conclusions

Hydrate formation or MEG freezing within the condensate recovery facilities of a NGL reprocessing plant are both costly problems to correct.

The investment of FT-NIR technology with it's low maintenance and high reliability will improve overall plant performance and eliminate the possibility of these problems occurring in the future.

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3. Petroleum Refinery

■ Petroleum Refinery Process

NIR analyzers are used on-line in many processes. The following presents an example of the NIR analyzers used in the petroleum refinery process.

In the petroleum refinery process, measuring instruments based on a variety of principles are used in the testing room and on-line to measure the properties and concentrations in stages such as crude oil acceptance, distillation/fractional distillation, modification, cracking, blending, and so on.

If multiple properties and concentrations of multiple components can be measured on-line with high speed by using the NIR analyzer, labor in the testing room and maintenance work for a variety of measuring instruments can be reduced.

Moreover, the optimized control of each stage will result in great investment benefits such as give-away reduction for the whole refinery plant.

Figure 3.1 shows the installation locations of NIR analyzers before and after the blender and the configuration of the optimal property control system. Properties of base materials are measured and the flow rate of each base material is controlled by the feed-forward loop of the optimal property control. On the other hand, the NIR analyzer after the blender controls the property of products to be shipped and corrects the optimal property control model by feeding back the measured values.

Points to keep in mind for on-line measurement include disturbance elements such as pipeline rust, bubbles, water cloudiness, and temperature changes in the flowing sample. There are methods to deal with such disturbance elements; for example, removing or stabilizing them in the sample pretreatment device before measuring the spectra, or reducing disturbances by performing a pretreatment calculation of each spectrum. The most suitable method should be applied to each specific process. Furthermore, in general, the temperature and pressure are high on the site, so a probe that withstands high temperature and pressure and that is easy to maintain is required.

The only maintenance required is cleaning the measurement window approximately once every 1 to 3 months.

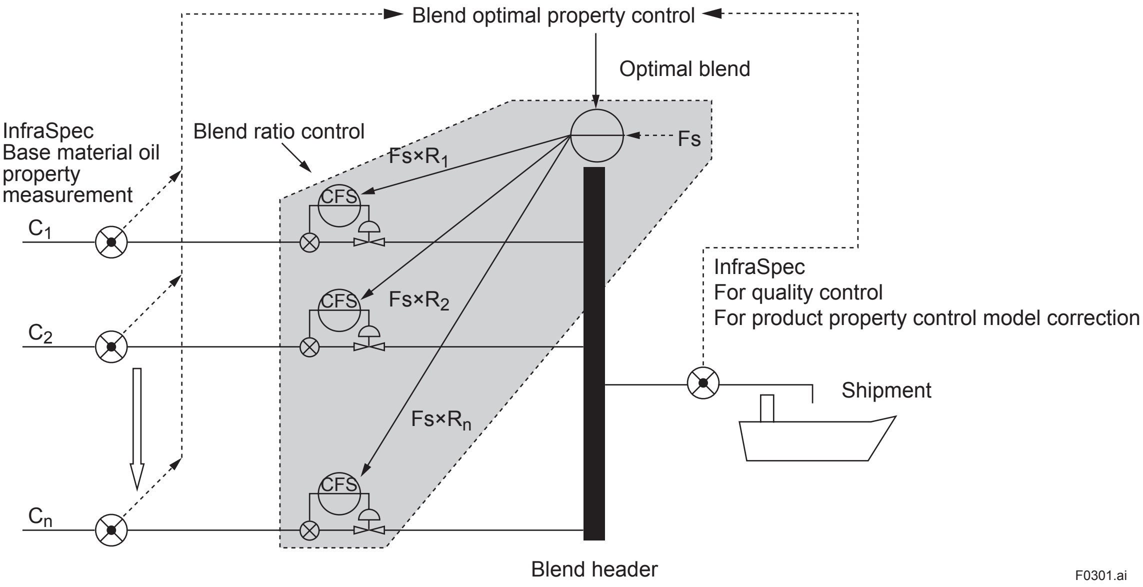

Figure 3.1 Blender Optimal Property Control System

Figure 3.2 shows an example of gasoline spectra. Figure 3.3 shows an example of on-line measurement after the gasoline blender that was continued over 1.5 months. The accuracy of prediction (SEP) was an octane value of 0.15.

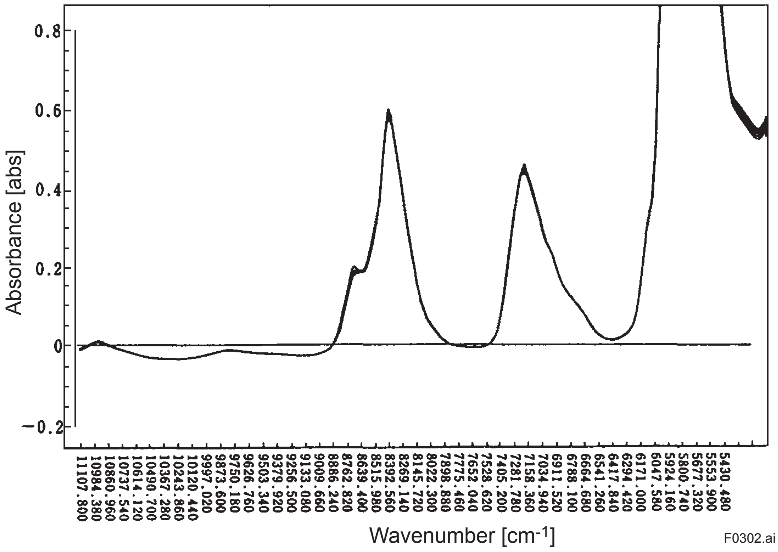

Figure 3.2 Example of NIR Spectra of Gasoline

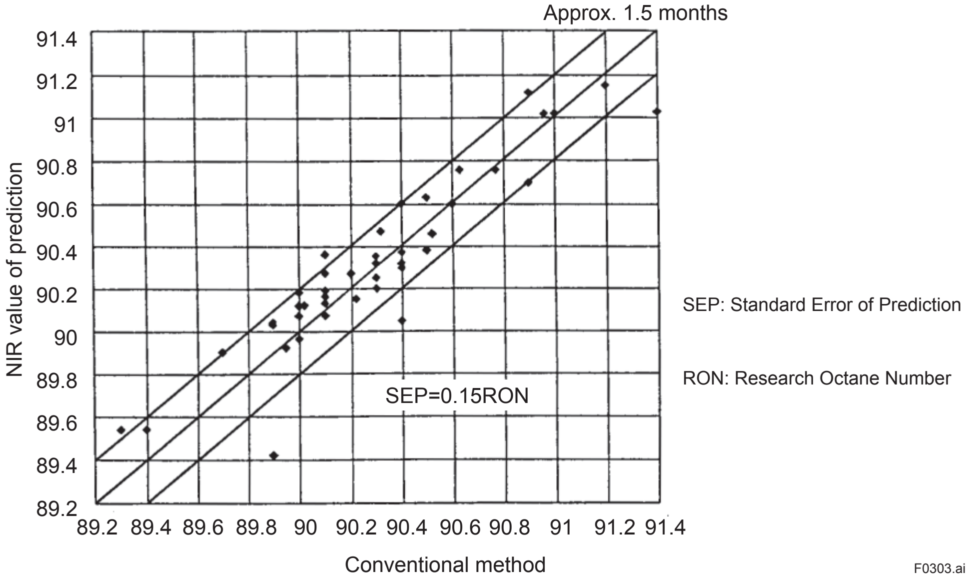

Figure 3.3 Example of On-line Measurement of Regular Gasoline

With the low benzene gasoline requirements due to the environmental health regulations, petroleum refinery plants are measuring the amount of benzene of gasoline base material to reduce the benzene content.

Needless to say, other aromatics must be separated for measurement, so the chemometric method is a choice for this kind of measurement. Figure 3.4 shows an example of concentration measurement of benzene in gasoline base material. The accuracy of prediction (SEP) is 0.12%.

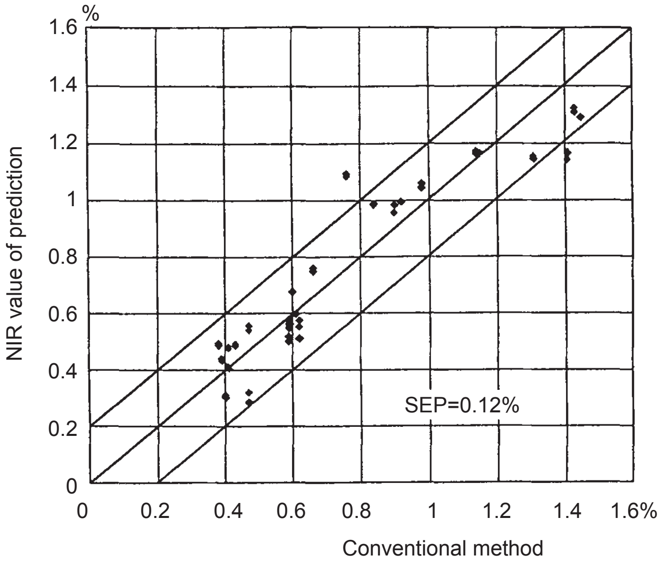

Figure 3.4 Example of Benzene Measurement of Gasoline Base Material

Figure 3.5 shows an example of cloud point measurement of light oil. A high accuracy of prediction (SEP=0.59°C) was achieved.

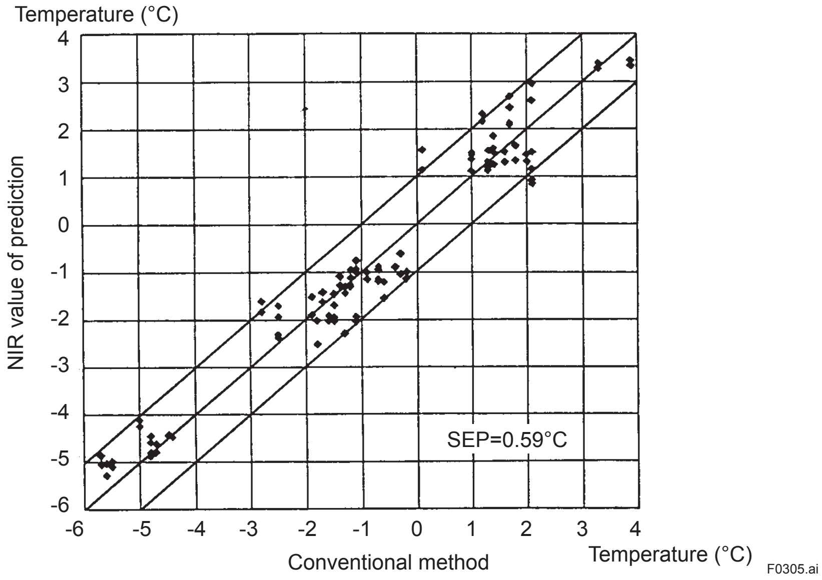

Figure 3.5 Example of Cloud Point Measurement of Light Oil

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4. Food and Pharmaceuticals

■ Iodine Value Measurement of Unsaturated Fatty Acid (Cooking Oil)

The iodine value is one of the control items for the cooking oil process. The iodine value refers to the number of grams of iodine that is absorbed by 100 grams of fat. If this value is large, the content of the unsaturated fatty acid in the sample is high, or the unsaturation level of the fatty acid is high.

In the production process, the iodine value is usually measured in the testing lab with employing the titration method; however, the titration method requires pretreatment of the sample, so it takes much time to determine the iodine value for one sample. Therefore, measurement needs to be simplified and speed up.

The following reports on an experiment to simplify the sample treatment and decrease the measurement time employing the NIR analysis method.

● Experiment and Equipment

The sample was set into a cuvette holder for 10-mm thick samples and the transmission method was used for measurement.

Figure 4.1 shows the NIR spectra of a known sample that was measured to obtain the iodine values by employing the conventional method, and Figure 4.2 shows the enlarged view of spectra.

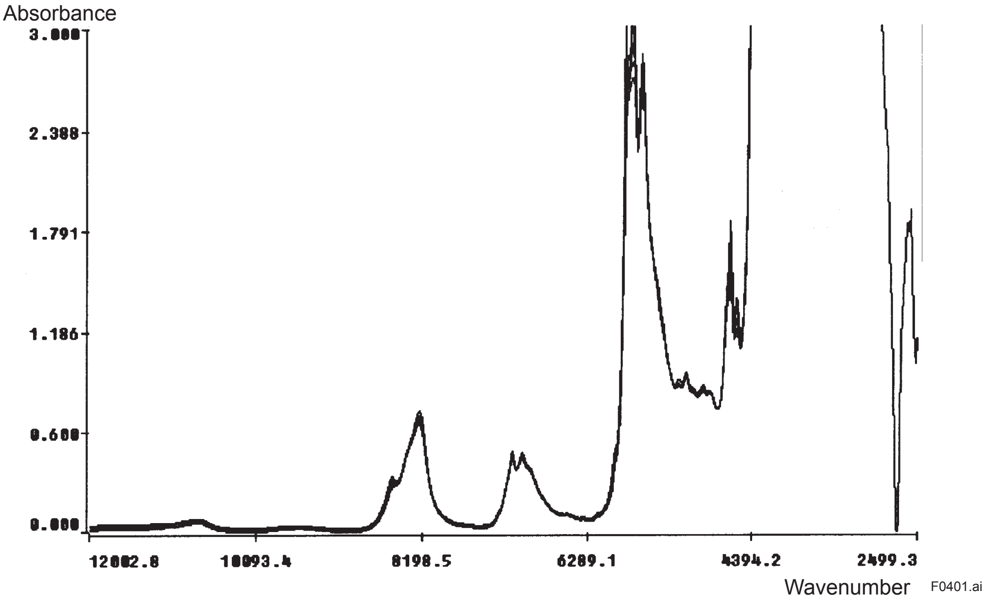


Figure 4.1 NIR Spectra of Vegetable Oil

A peak of absorption intensity changes linked to the changes in the iodine value is observed in the wavelength region from 4490 to 4750 cm^{-1} of the spectra in Figure 4.2.

The peak of the significant changes observed belongs to the combination tone for the C-H and C = C stretch vibrations of the double bond (C = C-H) between the carbons of an unsaturated compound that is correlated with the iodine values.

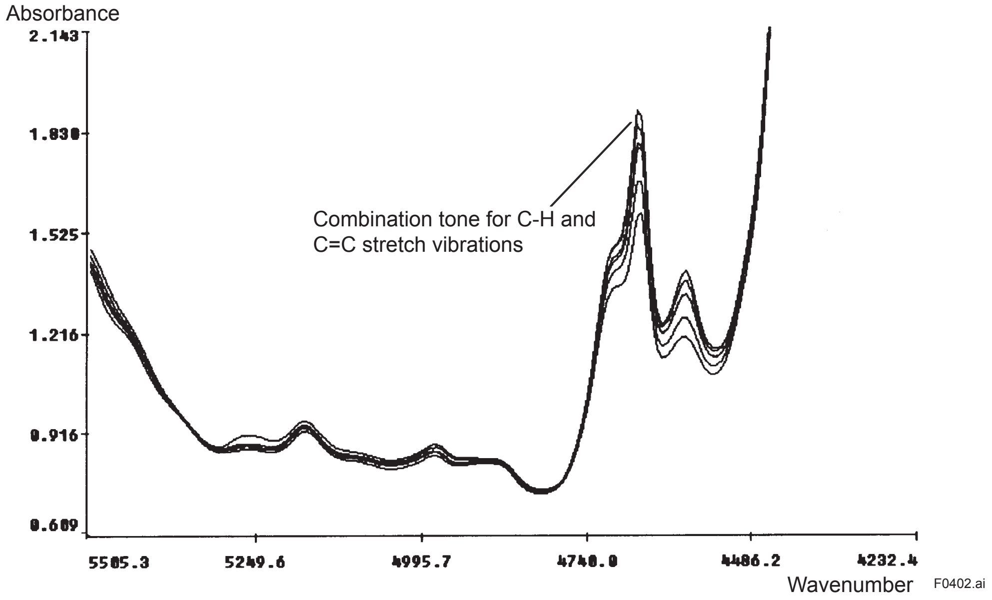


Figure 4.2 Enlarged View of Spectra

Figure 4.3 shows the correlation of the iodine values obtained by employing the conventional method and the above-mentioned wavelength region with the NIR spectra that was obtained by employing the partial least squares method (PLS regression method).

The calculation results were positive with a correlation coefficient of 0.999 and error of prediction of 0.3% over the measurement range.

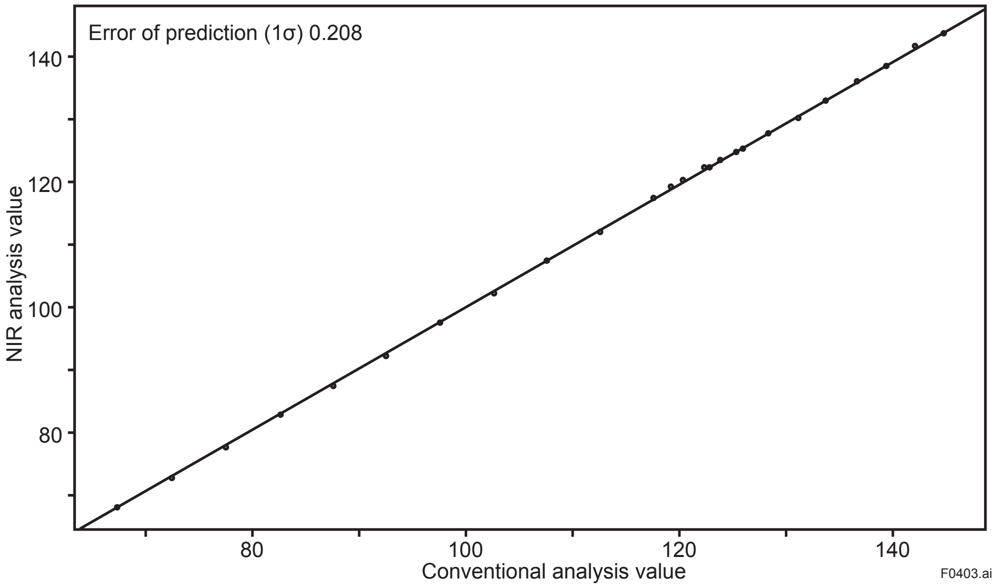


Figure 4.3 Correlation between Values Obtained by Conventional Analysis Method and Values Obtained by NIR Analysis

Conclusion

Unsaturated bond in the unsaturated fatty acid can be observed by using the NIR spectra and the iodine value can be determined by using the absorption wavenumber region.

By using the NIR method, the pretreatment can be simplified to just taking the sample into the cuvette, and the analysis can be speed up with the measurement time being reduced to approximately 1 minute.

5. LCD and Semiconductor

■ Concentration Control of Cleaning Liquids

● Features

- In-line continuous measurement without any chemical reagents
- No contamination (NIR analysis)
- Trace moisture (0 to 10 ppm) can be analyzed

● Applications

Semiconductor wet process and liquid crystal substrate manufacturing process

- Concentration and moisture control of cleaning liquids
- Control of trace moisture in resists
- Etching liquid concentration control
- Stripping liquid concentration control and moisture control

Lithium ion battery manufacturing and lithium ion battery electrolyte manufacturing processes

- Organic chemical concentration control
- Control of trace moisture percentage

Organic chemical recycling equipment

- Organic chemical concentration control
- Control of trace moisture percentage

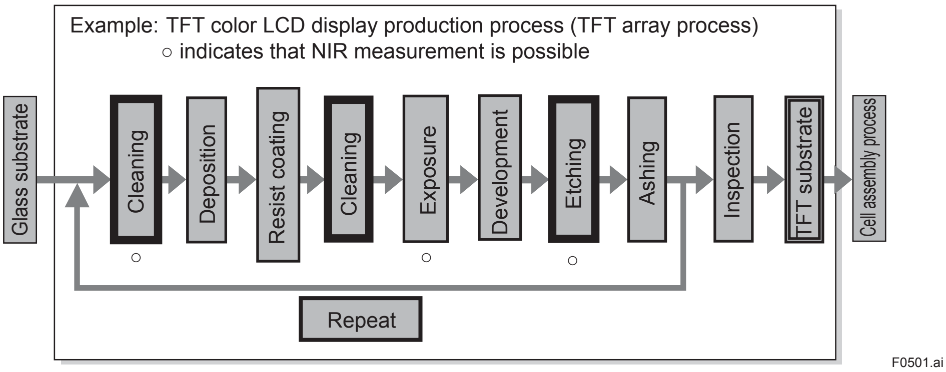
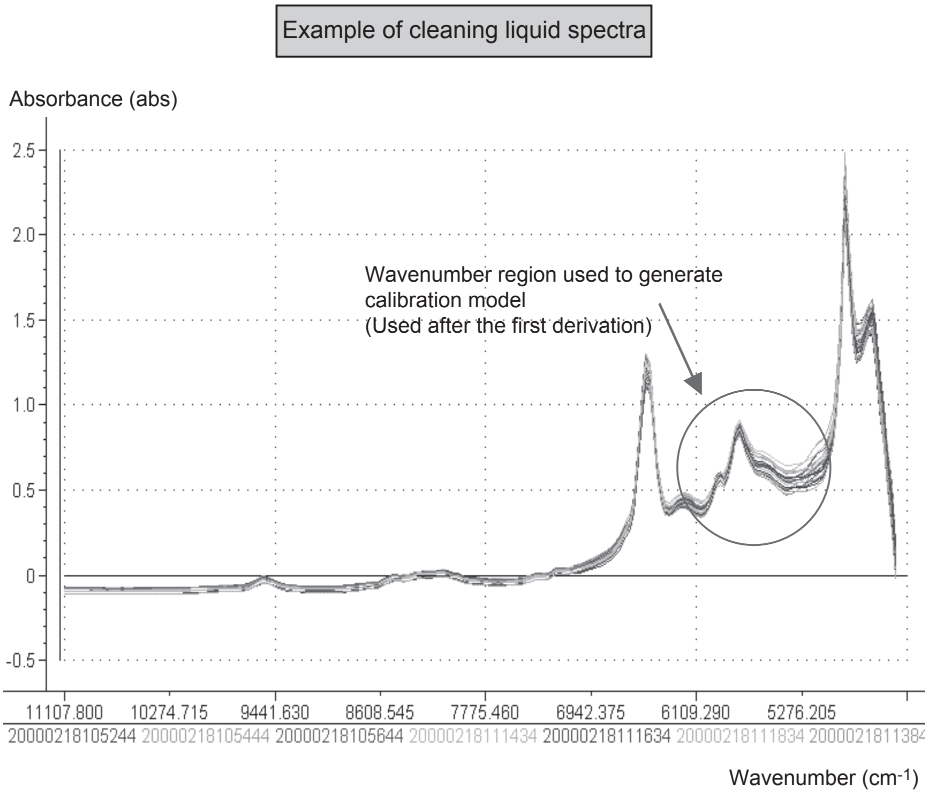


Figure 5.1

<Comparison with conventional methods>

	NIR Method	**Conventional Analysis (Titration Method, etc.)**
Continuous measurement	○ (Possible)	X (Not possible)
In-line measurement	○ (Possible)	X (Not possible)
Multi-component simultaneous measurement	○ (Possible)	Δ (Difficult)
Sample pretreatment	○ (A little)	Δ (A lot)
Nondestructive analysis	○ (Possible)	X (Not possible)
Reagent and waste liquid	○ (Not required)	X (Required)
Maintenance frequency	○ (Not frequent)	X (Frequent)



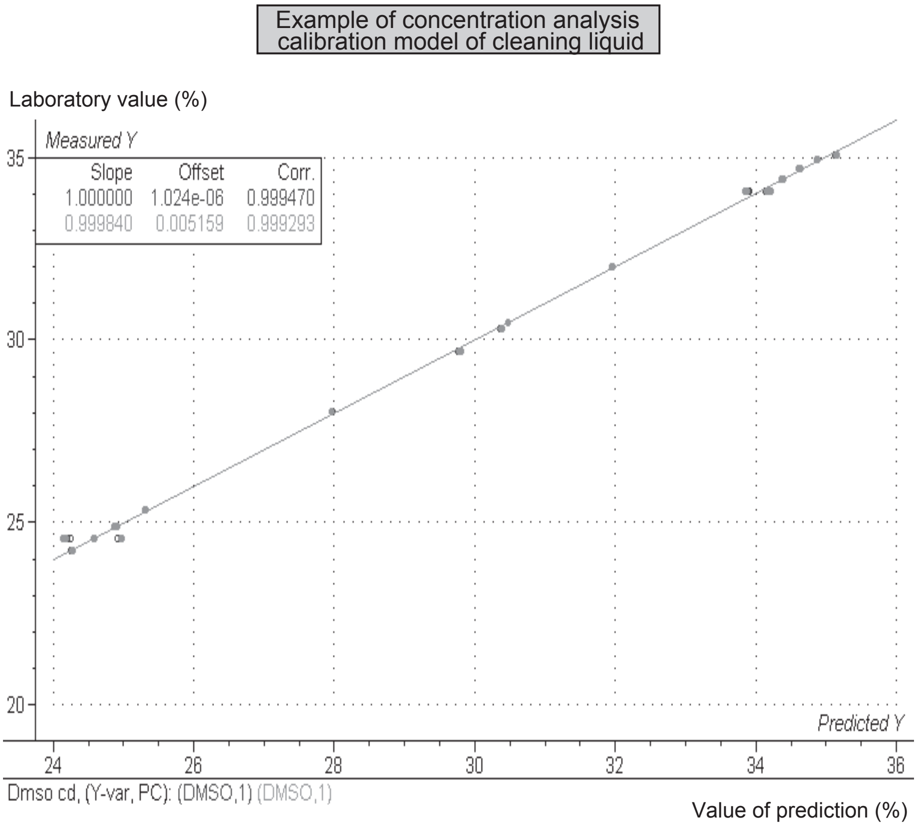


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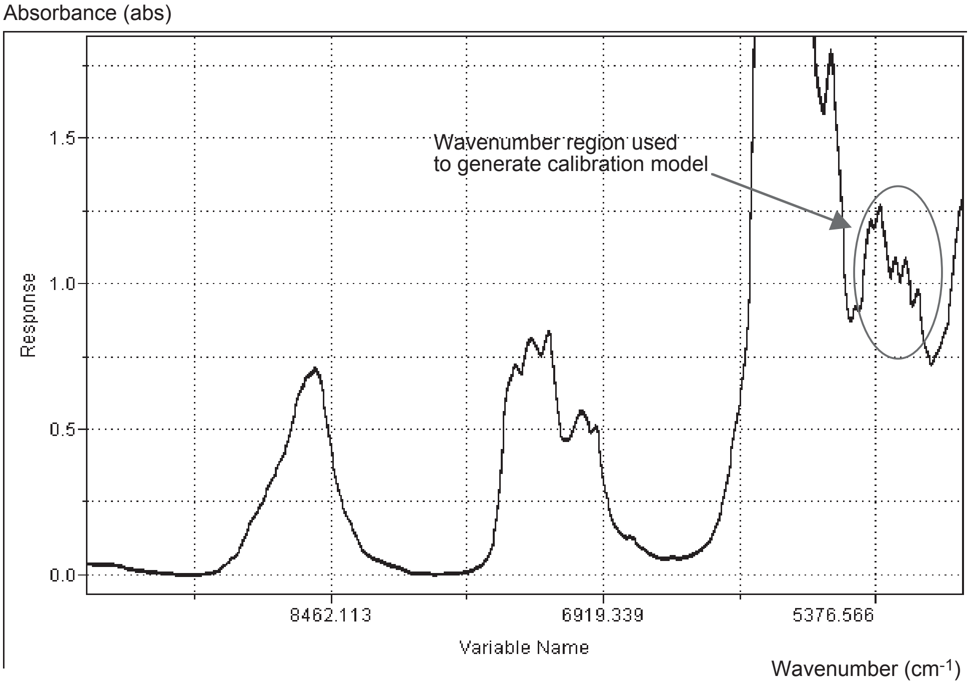
Figure 5.2 Example of cleaning liquid

Example of lithium ion battery electrolyte spectra



Example of calibration model of trace moisture in lithium ion battery electrolyte

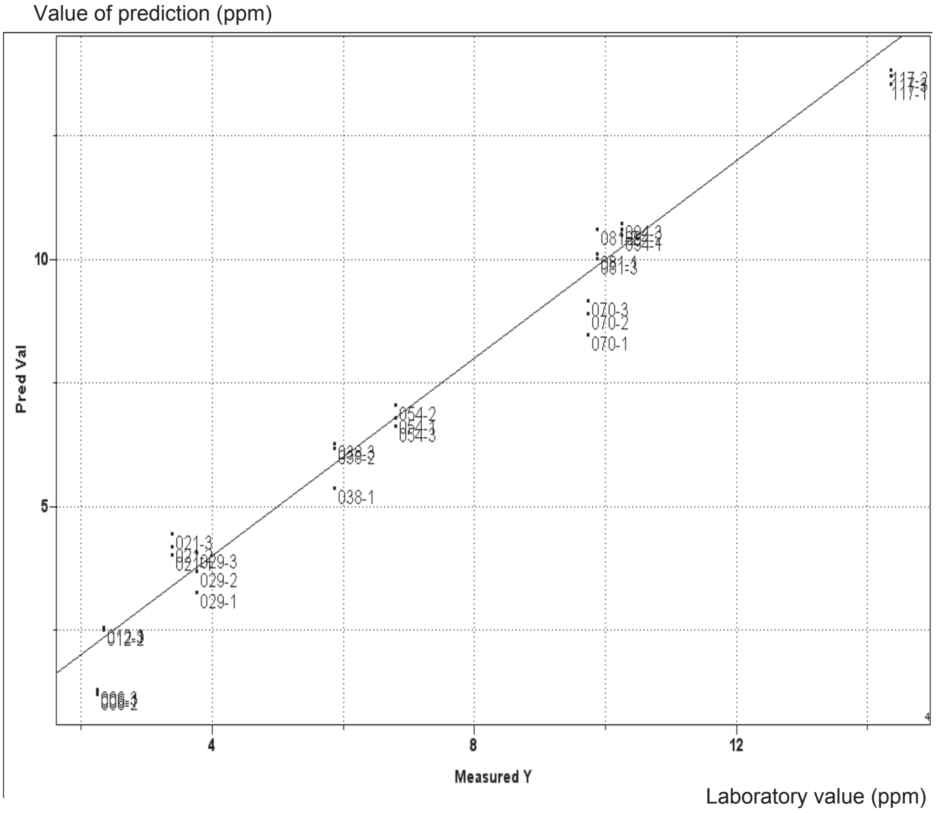


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Figure 5.3 Example of lithium ion battery electrolyte

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6. Pulp and Paper

Figure 6.1 shows the block diagram of pulp & paper process. The NR800 is used for measuring the concentration of white, green and black liquor.

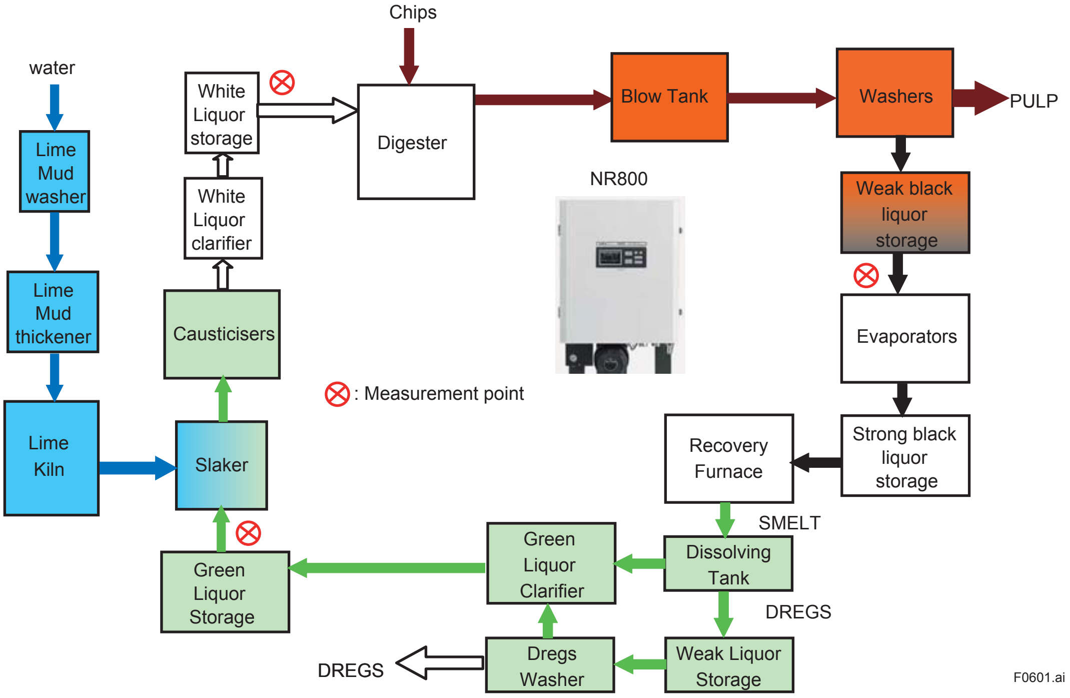


Figure 6.1

■ Alkali Measurement by Using NIR Analysis

Causticizing efficiency is a parameter to determine the pulping efficiency in the kraft pulp process. The causticizing efficiency is obtained based on the caustic alkali concentration in alkali water solution.

Caustic soda used in the digester is recovered and reused. If it is used as is, the pulping efficiency decreases. Therefore, caustic alkali is input in the causticizing process again to generate a reaction and increase the causticizing efficiency.

In the causticizing process, alkali content needs to be measured to determine the required quantity of caustic alkali and reaction time. Up to the present time, caustic alkali concentration of this kind was analyzed in laboratories by using titrating analysis.

However, the titrating method has the downside that measurement variations among operators are unavoidable.

It also needs a pretreatment using a reagent so analysis takes several minutes; therefore, it is difficult to use the titrating method for the feedback and feed forward control because of the lack of a fast response and real-time capability.

It is also hazardous for workers to work with a strong alkali solution.

Automatic titrating units for automatic measurement are available in the market. However, dissolved alkali that has adhered to the valve or other components causes trouble, thus making maintenance extremely difficult.

By contrast, NIR analysis does not need a chemical pretreatment so that it can speed up analysis. It also does not need to dispose of the used samples and reagents, so it has less impact on the environment.

Furthermore, it is capable of performing continuous on-line analysis, and analysis does not require the involvement of human operators, so there are no measurement variations among operators.

Causticizing efficiency analysis by using NIR analysis is able to save labor in laboratories and reduce hazardous work substantially, so it can be expected to be an analysis method that can go on-line easily.

The following presents a measurement example of caustic alkali solution and proposes Near Infrared causticizing efficiency analysis.

Example of an experiment of near infrared causticizing efficiency analysis

Water solution containing 3 different components, NaOH, Na_2S, and Na_2CO_3 was prepared for this experiment.

Several water solution samples with different alkali concentrations were prepared and their NIR spectra were measured. Figure 6.2 shows the measured NIR spectra.

As observed in Figure 6.2, the spectral characteristics vary depending on the causticizing efficiency; however, the peaks of each of the alkali components cannot be clearly distinguished.

This wavenumber region was used to obtain the correlation between the NIR spectra and the concentrations of each of the alkali components by employing the PLS regression method. Figures 6.3, 6.4, and 6.5 show the correlations of NaOH, Na_2S, and Na_2CO_3, respectively.

The amount of each of the components can be determined with an error of prediction (1σ) of 1 g/liter or less.

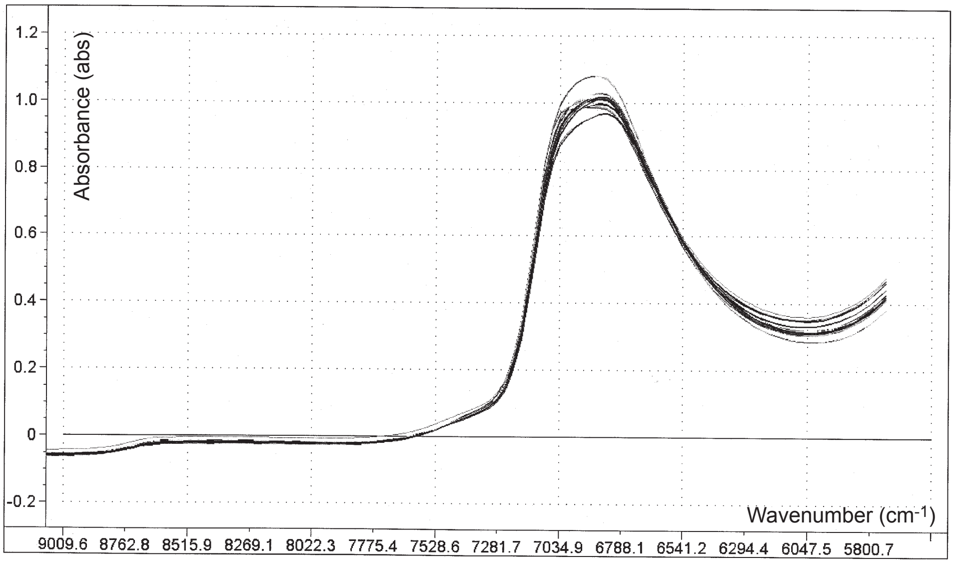


Figure 6.2 Spectra of Water Solution with Different Alkali Concentrations

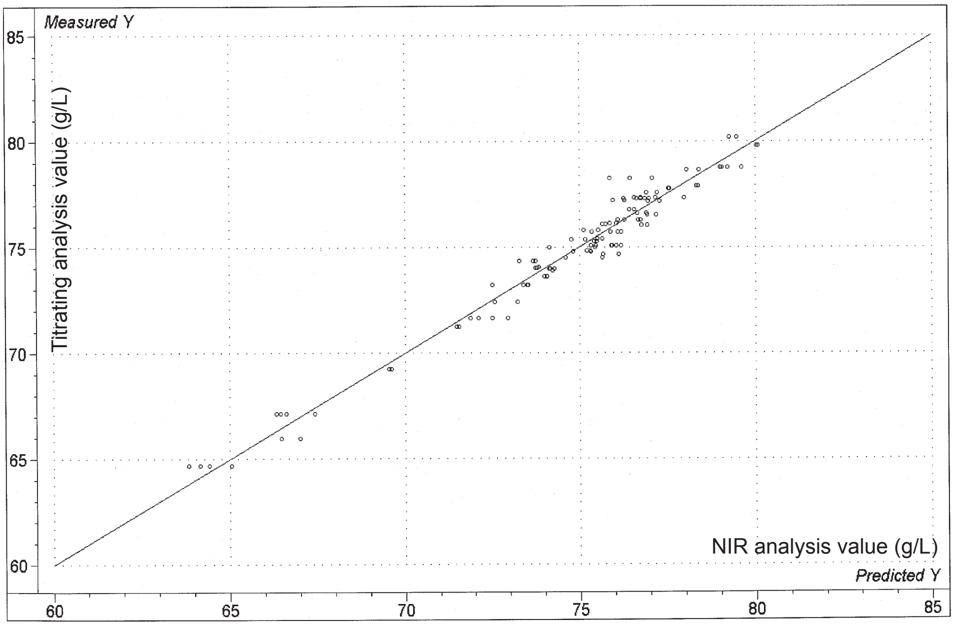


Figure 6.3 Correlation between NaOH Content and NIR Analysis Values

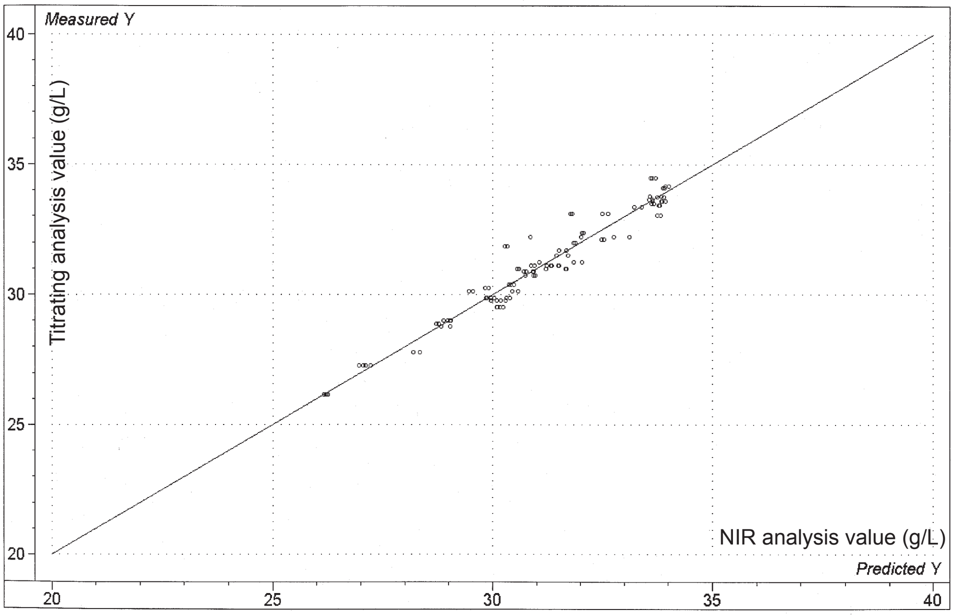


Figure 6.4 Correlation between Na_2S Content and NIR Analysis Values

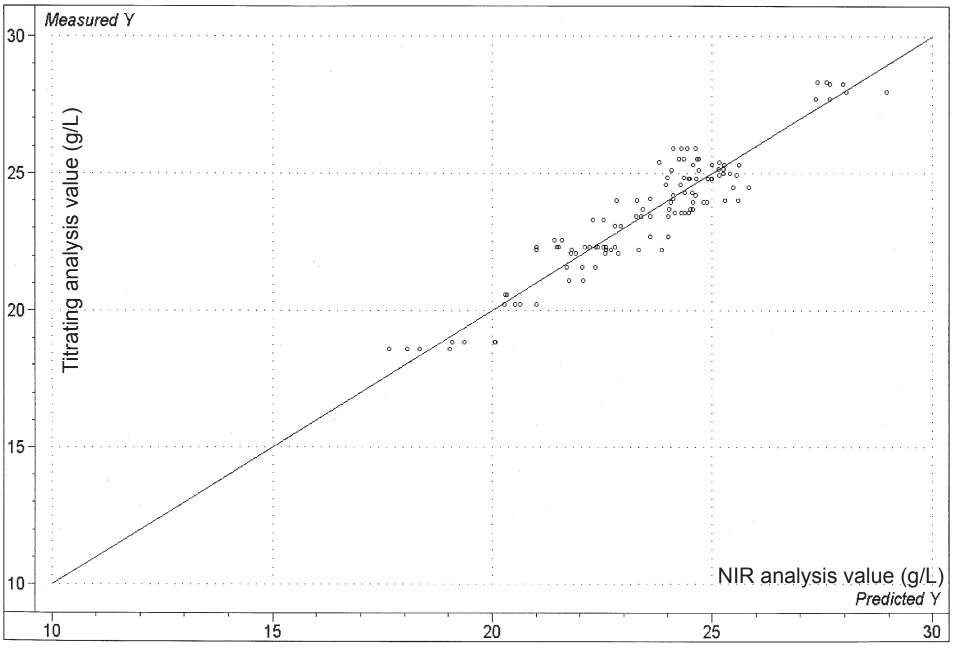


Figure 6.5 Correlation between Na_2CO_3 Content and NIR Analysis Values

Figure 6.6 shows the output of continuous measurement. The trends in the figure drop abruptly as the samples were diluted by water to forcefully lower the alkali concentrations.

The indicated values show the correlations well, and so it could be confirmed that causticizing efficiency analysis by employing the NIR analysis method can be practically used satisfactorily.

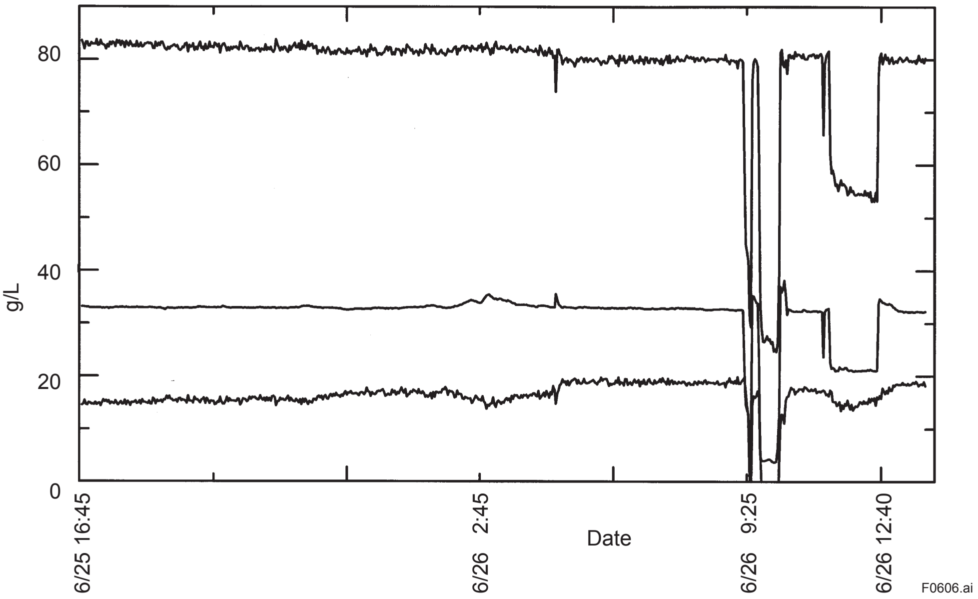


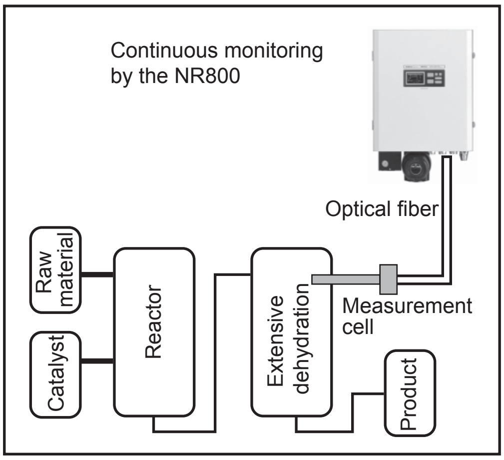
Figure 6.6 Continuous Output Trends of 3 Alkali Components

7. Measurement of Trace Moisture Content

■ Purposes

- The purpose is to perform continuous monitoring of the removal of moisture containing interfering substances such as catalyst poison and cut costs by speeding up the startup and controlling the limit of allowable moisture concentration.

  (Operation control to keep the concentration close to the upper or lower control limit
  ➡ Reduce the frequency to replace the catalyst)



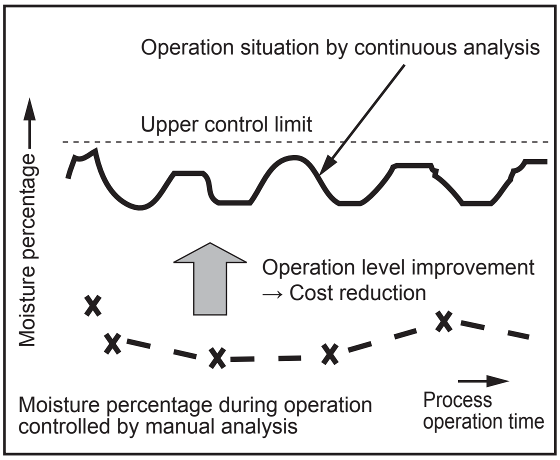


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Figure 7.1 Installation Example of Chemical Process

Figure 7.2 Changes of Process Operation Time and Moisture Concentration

- Ensure product quality (keep the moisture percentage within the specified range, prevent the hydrolysis, etc.)
- Control for preventing the corrosion in processes and equipment (monitor for pin holes on pipes)

■ Objects

Capable of measuring trace moisture in various chemical processes.

Simultaneous continuous measurement of multiple major components is also possible.

Measurement Object Classification	Main Component of Measurement Object
Acid	Acetic acid, formic acid, etc.
Alcohol	Methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, isobutyl alcohol, polyol, hydroquinone
Aldehyde	Acetaldehyde
Ester	Ethyl acetate, vinyl acetate, butyl acetate, phosphoric acid ester, methyl methacrylate, acrylic acid ester
Saturated hydrocarbon	Hexane, heptane
Aromatic	Benzene, toluene, xylene, styrene, cumene, chlorobenzene
Halogenated hydrocarbon	Carbon tetrachloride, methyl chloride, methylene chloride, chloroprene, trichloroethane, ethylene dichloride (EDC) in VCM plant
Others	Propylene oxide, tetrahydrofuran, acrylonitrile, acetonitrile, etc.

7.1 Points of Measurement of Trace Moisture by Using the NR800

■ Introduction Benefits of the NR800 Compared with Conventional Measurement Methods

Introduction Benefits	NR800 (NIR Analysis)	Conventional Analysis (Karl Fisher's Method)
Fast continuous monitoring achieved (Note)	On-line continuous measurement Data update period: Within 1 minute Multi-component, simultaneous measurement possible	Off-line intermittent measurement Measurement time: Several minutes Measurement of other components not possible
Measurement variations among operators	Do not occur	Occur. Error due to moisture absorption or other errors occur.
Environmental load reduction	Nondestructive analysis without needing no reagent	Using reagents (disposal of toxic and hazardous chemicals required)

Note: Not only the moisture but also other components in the sample can be measured simultaneously (high-speed, simultaneous, multi-component measurement).

■ Features of NIR Spectra of Water

The NIR absorbance is very large and a clear absorption peak appears even if the amount is small. ➡ The NIR suits the measurement of the concentration of trace moisture.

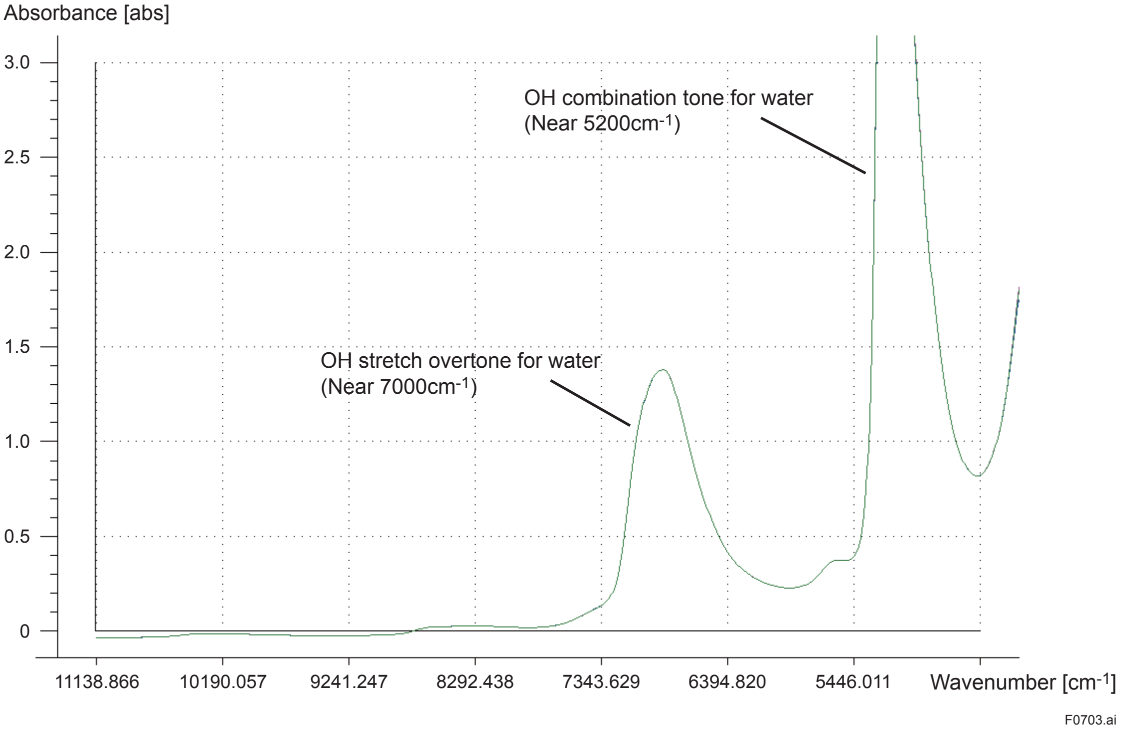

Figure 7.3 Example of NIR spectra by using the NR800 (Path length = 1 mm)

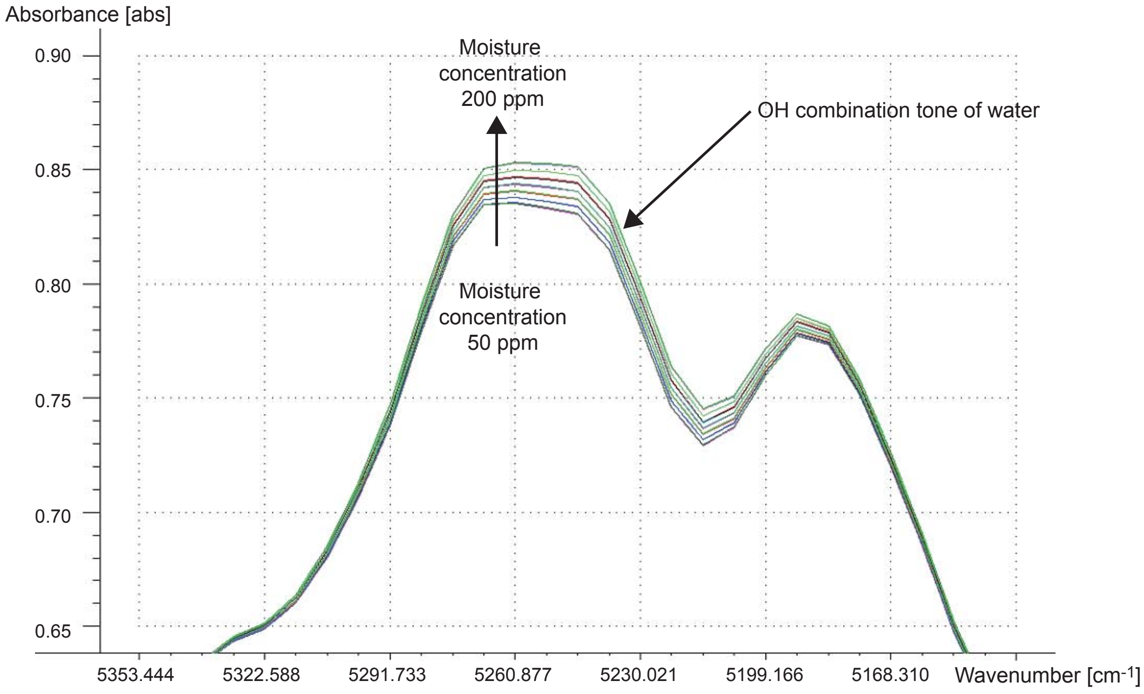

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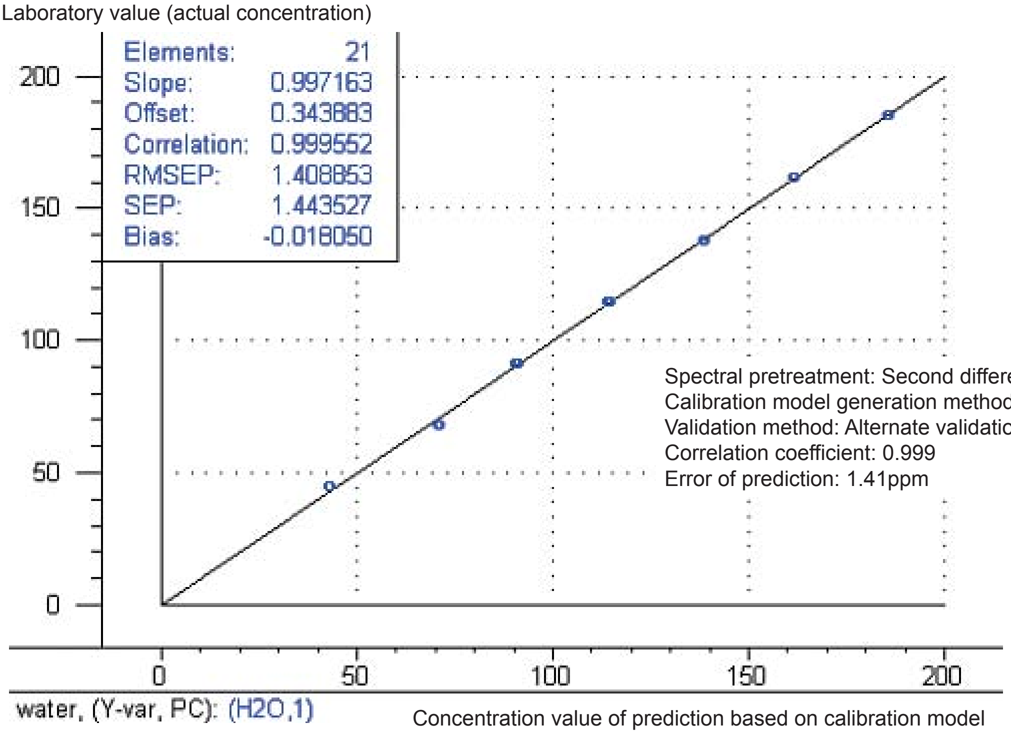
Figure 7.4 Example of Measurement Spectra of Trace Moisture (OH combination tone of water)



Elements: 21
Slope: 0.997163
Offset: 0.343883
Correlation: 0.999552
RMSEP: 1.408853
SEP: 1.443527
Bias: -0.018050

Spectral pretreatment: Second differentiation
Calibration model generation method: PLS1
Validation method: Alternate validation
Correlation coefficient: 0.999
Error of prediction: 1.41ppm

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Figure 7.5 Calibration Model of Trace Moisture (Measurement Range: 0 to 200 ppm)

7.2 Example of NR800 Application to Actual Plant

- Realizing a stable and accurate continuous monitoring of water concentration that solves a moisture absorption problem and eliminates variations such as those among operators.
- Understanding the factors of changes such as switching the pump and inputting chemicals and improving the process by the on-line measurement of trace moisture.

■ Overview of a Process to be Implemented and the Purpose of Introducing the NR800

- Purpose of Introduction
  - Monitoring sea water leaking into the process from the condenser
  - Monitoring steam leaking into the process
- Overview of a process to be implemented

  Off-line analysis was performed in check tanks A, B, and C by using a conventional analysis method to check the product specification ($H_2O \leq 100$ ppm).

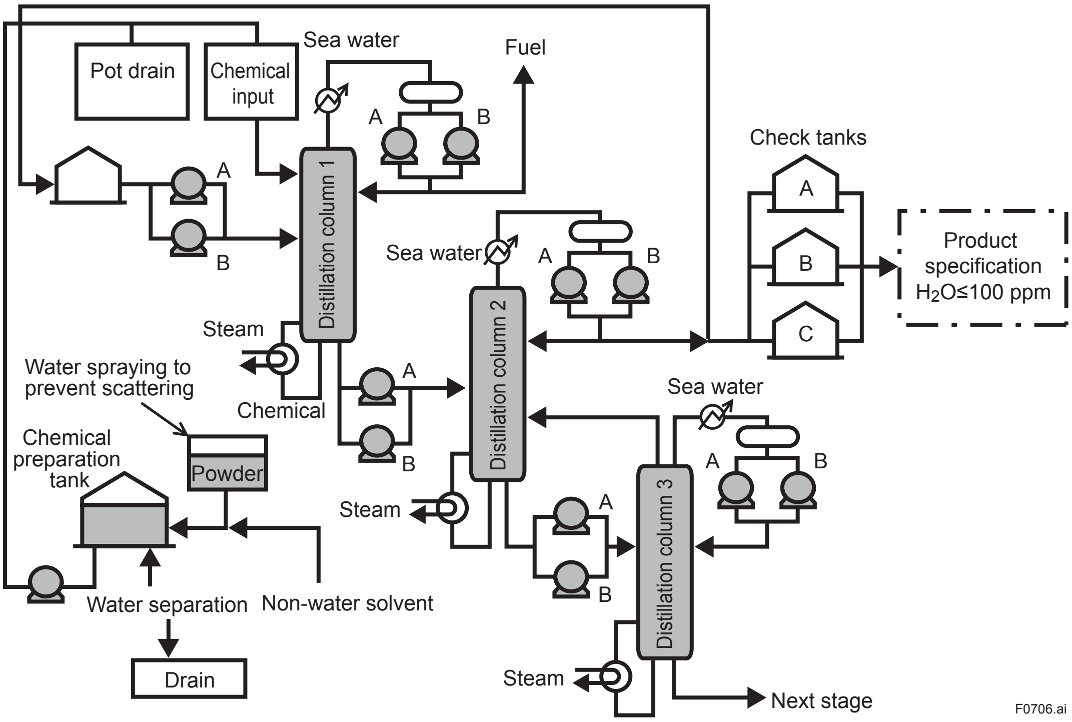

Figure 7.6 Off-line analysis of conventional analysis method

■ Reasons for choosing the NR800

The conventional analysis method is an intermittent measurement so the frequency of analysis must be increased to meet the introduction purposes. It also has problems that need to be addressed; for example, the effect of moisture absorption during sampling must be removed, an analysis engineer must be assigned, and the increase of hazardous waste must be dealt with.

In contrast, the NR800 has the following features.

- Fast and continuous monitoring and on-line continuous measurement (data update period within 1 minute)
- No variations among operators and no effect of moisture absorption
- The analysis engineer just generates calibration models and performs maintenance.

  No engineer needs to be present at all times during on-line continuous measurement.
- No chemical waste (nondestructive analysis without needing reagents)

■ Advantage of the measured values of NR800 over the analysis values of the conventional analysis method

Compared with the measured values of the NR800, the analysis values of the conventional method were relatively high, and high concentrations that seem to be blamed on moisture absorption were observed.

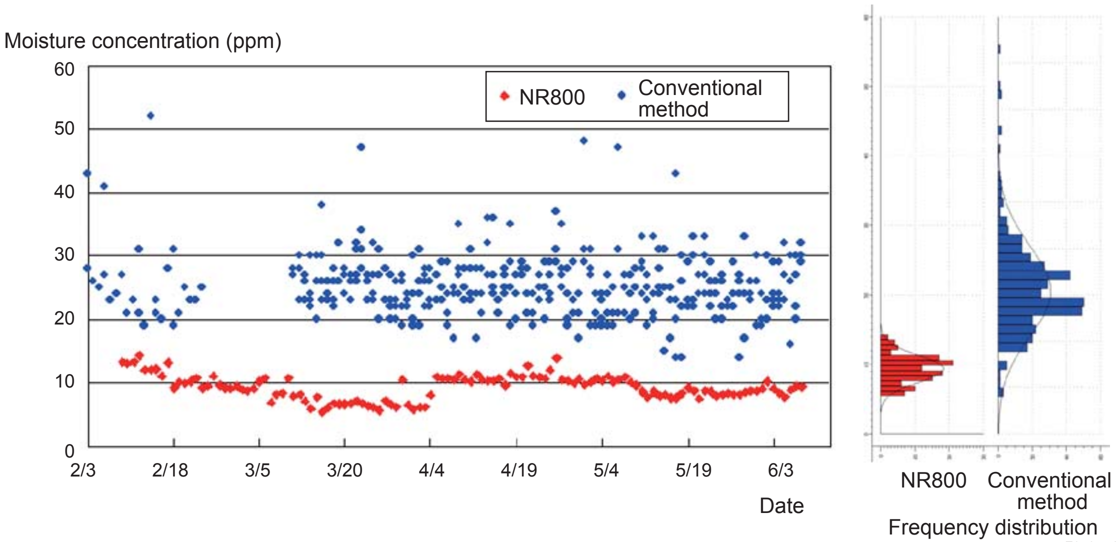

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Figure 7.7 Comparison of Analysis Results of Moisture Concentration in Products

■ Examples of Process Improvement by Performing On-line Continuous Measurement

- The cause of the increase in the moisture concentration caused by switching the pump was identified and the yield was increased by preventing the occurrence of nonconformity.
- The cause of the increase in the moisture concentration caused by inputting the chemical was identified and the yield was increased by preventing the occurrence of nonconformity.

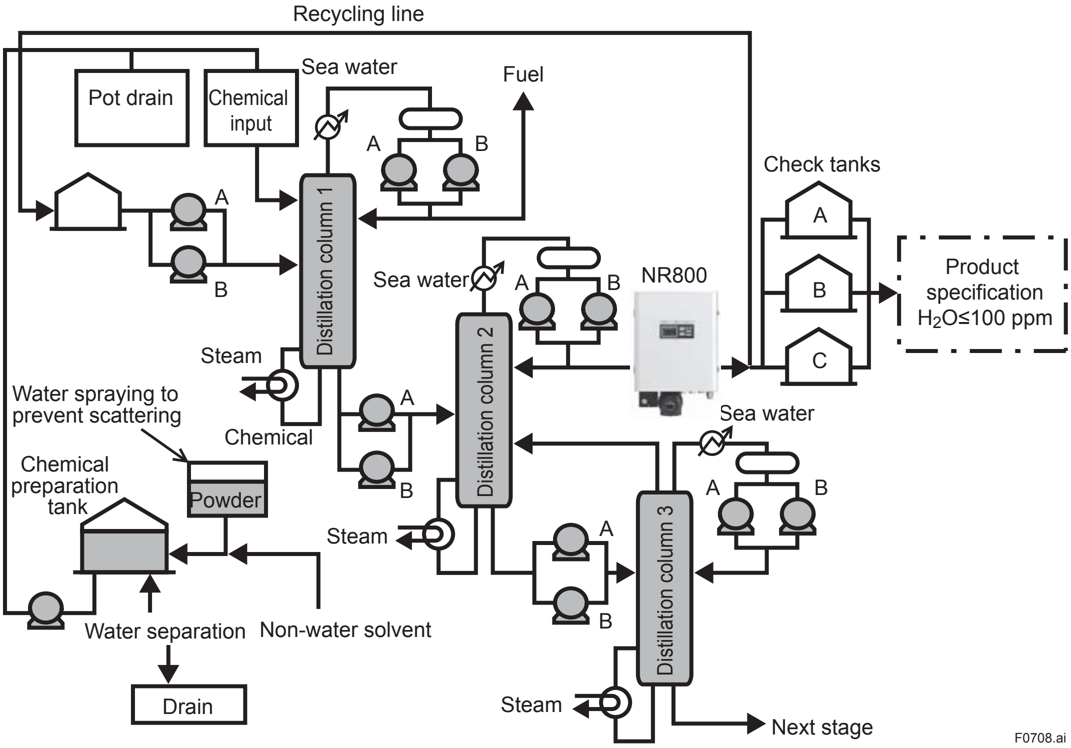

Figure 7.8 Flow chart of the implemented process and the locations of moisture concentration measurement by NR800s

- The cause of the increase in the moisture concentration caused by switching the pump was identified and the yield was increased by preventing the occurrence of nonconformity.
  - Problem: Occurrence of moisture concentration nonconformity
  - Moisture measurement by the NR800 detected that the moisture concentration increased when the pump was switched.
  - Cause of the occurrence of nonconformity:
    Nonconforming liquid that remained after cleaning the pump or nonconforming liquid that was input remained in the pump line.
  - Improvement: Switching and running all the pumps when the process is started, and purging the remaining nonconforming liquid out of the pump line.
  - Effect: Nonconforming moisture concentration in the product can be corrected at the time of starting the process, and the amount of nonconforming products could be reduced, and as a result, the yield increased.

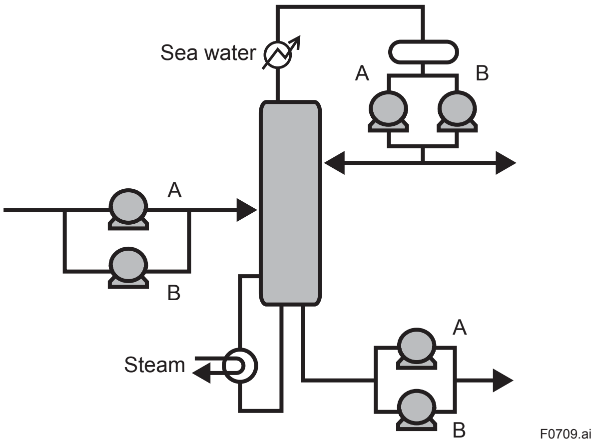

Figure 7.9

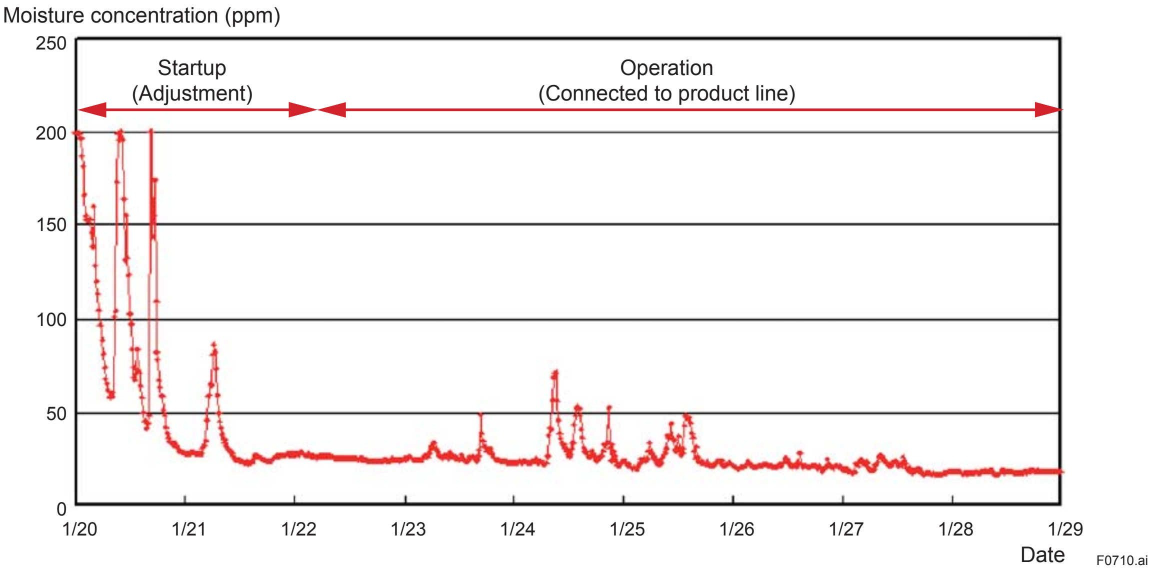

Figure 7.10 Change of moisture concentration in the product after the improvement

- The cause of the increase in the moisture concentration caused by inputting the chemical was identified and the yield was increased by preventing the occurrence of nonconformity.
  - Problem: Occurrence of moisture concentration nonconformity
  - Continuous measurement by the NR800 detected that the moisture concentration in the product increased when the chemical was input.
  - Cause of the occurrence of nonconformity:
    Water that was sprayed to prevent the scattering of the chemical was brought into the process when the chemical was input, and as a result, the moisture increased.
  - Improvement: The chemical solution is left standing for a while after it is prepared to separate the water from the solution, and a drain pot was added to prevent the water from being brought into the process.
  - Effect: The increase in the moisture concentration when the chemical is input can be prevented, and the amount of nonconforming products could be reduced, and as a result, the yield increased.

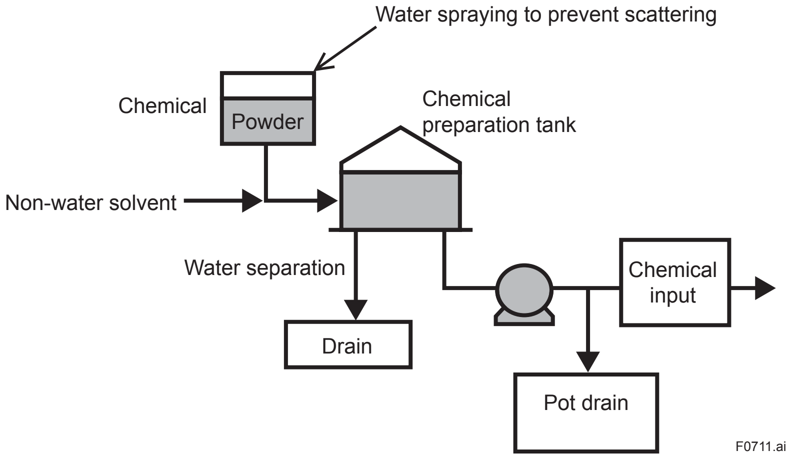

Figure 7.11

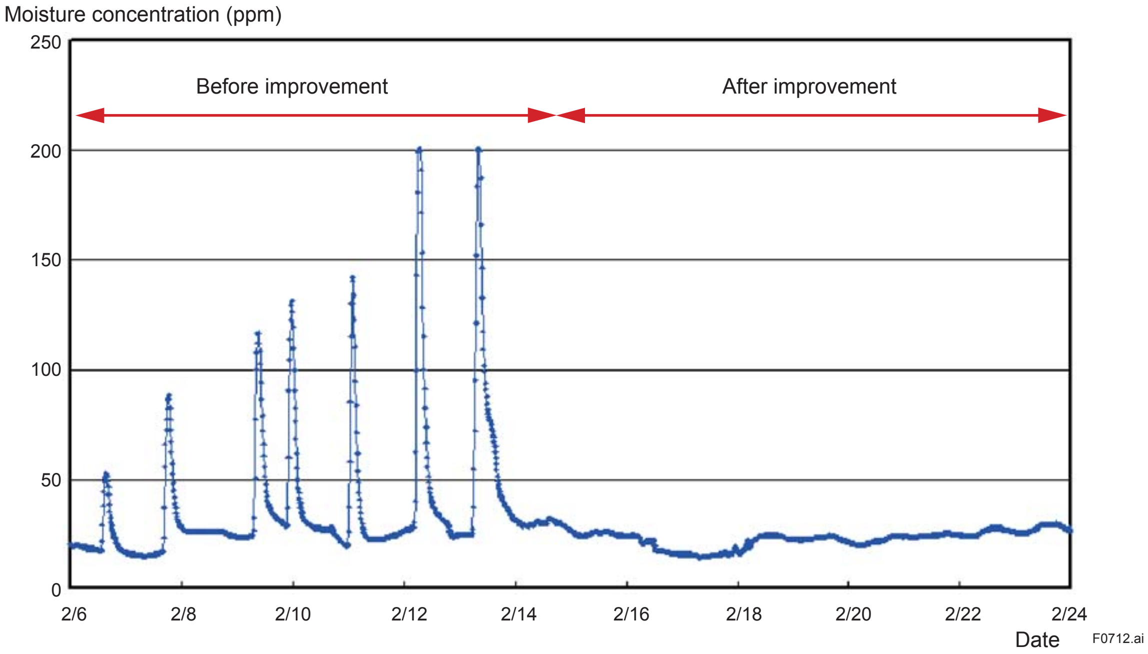

Figure 7.12 Change of moisture concentration in the product after the improvement

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