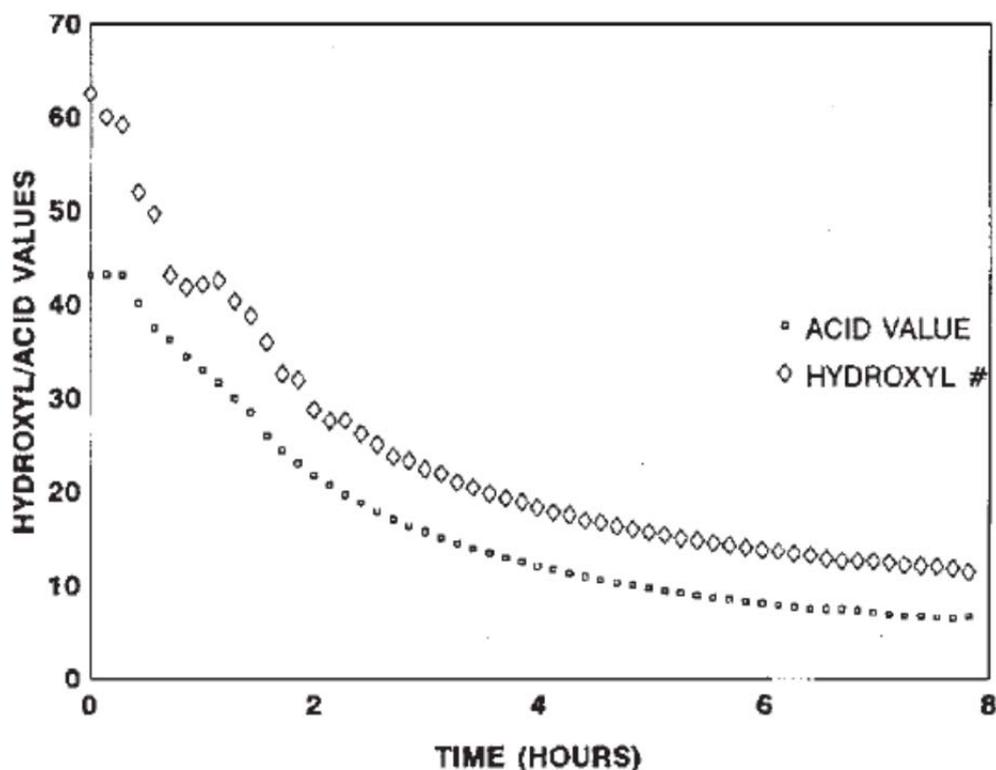


Near-infrared analysis of polyols: process monitoring in a hostile environment



During polymerization, real-time determination of hydroxyl and acid numbers of polyols provide important information about the molecular weight and the reaction end point. This Application Note sheds light on the practical aspects of process monitoring in a polyol batch process using NIRS methodology. Real-time process monitoring with NIRS is the key to lower production costs and better product quality.

Method description

Introduction

Polyols are long-chain polymers which can be produced through reactions involving organic oxides, acids, and multi-functional alcohols. Varied uses for the polymeric material include polyurethanes, surfactants, paint additives adhesives, and foams. The particular use of the polymer is dependent on the molecular weight of the polyol product (which is inversely related to the hydroxyl number of a given amount of polyol).

Polyol products are typically produced in a batch reactor process under severe conditions ($> 260\text{ }^{\circ}\text{C}$, nitrogen sparging, and turbulent mixing). In addition, suspended particles are typically found in the reactor. These conditions are normally prohibitive to in vivo sampling of the polyol reactor. Typical analysis of the polyol reaction must be performed in the laboratory using titration methods. Also, polyol samples can be difficult to handle in a laboratory due to their inherent physical characteristics (i.e., high melting point and high viscosity).

Near-infrared (NIR) laboratory methods have been developed as a rapid alternative and yield results which are equivalent to those obtained by the reference laboratory method (see also AN-NIR-6, «Near-infrared analysis of polyols»). The flexibility of NIR spectroscopy has also made it possible to develop NIR methods for the process environment. Through the use of a fiber-optic sampling interface, NIR spectroscopy provides real-time (within one minute) process monitoring of the hydroxyl and acid number endpoints in a polyol batch reactor process.

Experimental

Polymer samples ranging from 0 to 80 in hydroxyl numbers and from 0 to 80 in acid numbers were analyzed during a batch process with the temperature of the reactor held constant at $260\text{ }^{\circ}\text{C}$. All NIR spectra were collected in the transmission mode (1100–2500) using an FOSS' Process Analytics Polyol Analyzer. Since this instrument is not available anymore, the NIRS XDS Transmission Optiprobe Analyzer with sample heater is recommended. In vivo sampling of the reactor was accomplished with a fiber-optic sampling interface consisting of an anhydroguide fiber bundle and a stainless steel intercontact immersion probe. The probe end tip was set to a gap of 3 mm providing a total optical pathlength of 6 mm. Sample scans were generated from 32 co-added scans of each sample and referenced against 32 co-added scans of an internal fiber reference.

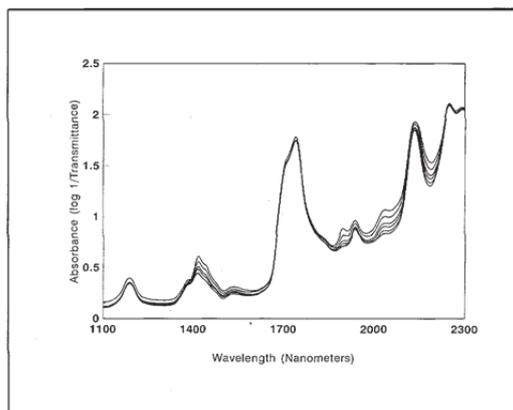


Figure 1. Raw NIR absorbance spectra of the polyol production process.

Results and discussion

The absorbance spectra ($\log 1/T$) for the polyol samples collected in a batch reactor at $260\text{ }^{\circ}\text{C}$ are shown in Figure 1. The variations in the wavelength regions around 1400–1500 and 1900–2100 nm are related to the polymeric O-H first overtone and O-H combination bands, respectively. To enhance subtle spectral features and reduce baseline variations caused by scattering differences (due to suspended solids and nitrogen bubbles), the second derivative spectra were calculated and plotted in Figure 2. Note that the second derivative has the effect of converting peak maxima into peak minima.

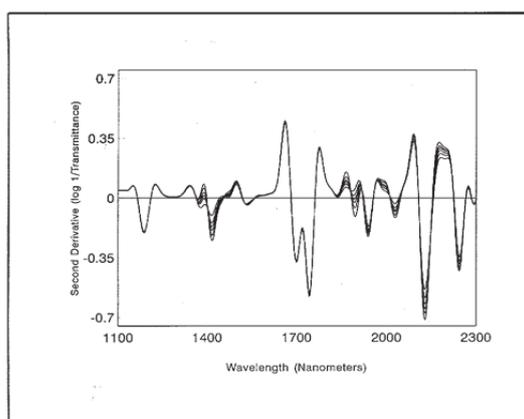


Figure 2. Second derivative spectra of the polyol production process.

Method description

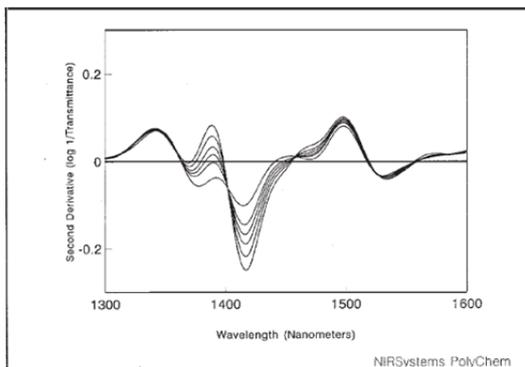


Figure 3. Expanded second derivative spectra of the polymeric first overtone O-H band. Variation around 1420 nm corresponds to changes in the hydroxyl number.

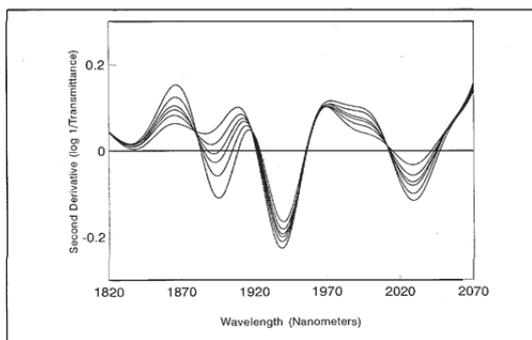


Figure 4. Expanded second derivative spectra of the polymeric combination O-H bands. Variation around 1900 nm corresponds to changes in the acid value, 1940 nm to changes in the moisture content, and 2030 nm to changes in the hydroxyl number.

Figures 3 and 4 represent enlargements of the second derivative spectra. Notice that the bands at 2030 nm (hydroxyl combination band) and 1418 nm (hydroxyl overtone band) are decreasing with decreasing hydroxyl number. It is also evident that the band at 1898 nm (the O-H combination band for a carboxylic acid) is decreasing with decreasing acid number.

In order to accomplish process monitoring of the hydroxyl and acid number in a polyol batch process, a calibration model must first be developed. A multilinear least-squares regression (MLR) was calculated using the second derivative spectra and the known hydroxyl and acid numbers for each sample.

The calibration equation developed for the online analysis of hydroxyl number in the polyol production process is given in the following equation:

$$[\text{Hydroxyl number}] = K(0) + K(1) [A \lambda(1418/1522)]$$

This two term model provided a correlation coefficient of 0.999 and a standard error of calibration (SEC) of 0.41. The laboratory determined hydroxyl numbers versus those obtained using NIR analysis have been plotted graphically in Figure 5. It should be noted from Equation 1 that a second wavelength was used as a denominator wavelength. The denominator term normalizes for multiplicative scatter effects caused by effective pathlength variations for the sample matrix (due to suspended solids and reactor turbulence).

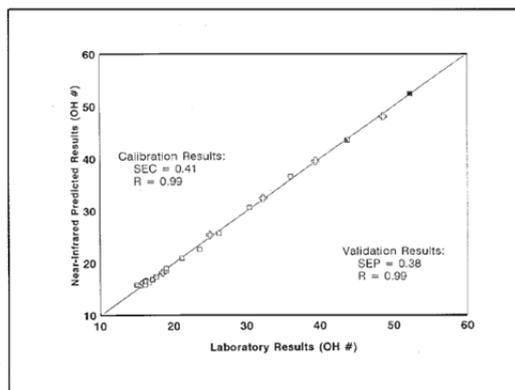


Figure 5. Hydroxyl number scatter plot.

An MLR calibration equation determined for the online analysis of acid number in the polyol production process is given in the next equation. Once again a multiplicative scatter correction was used in this model. A correlation coefficient of 0.999 and a SEC of 0.28 were obtained. A plot of the calibration equation fit (laboratory value vs. NIR value) is shown in Figure 6. In both cases (hydroxyl number and acid number), the NIR method provides a relative error of 1.5% of the mean laboratory value.

$$[\text{Acid number}] = K(0) + K(1) [A \lambda(1898/1978)]$$

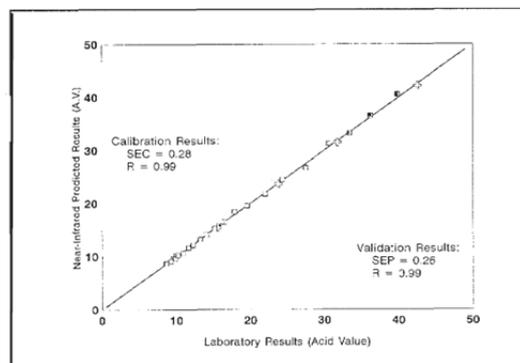


Figure 6. Acid value scatter plot.

Method description

Real-time process control

Having derived suitable spectroscopic models for hydroxyl number and acid number, the NIR method was now applied to real-time process monitoring. The results attainable using NIR spectroscopy for real-time polyols process monitoring are shown in Figure 7.

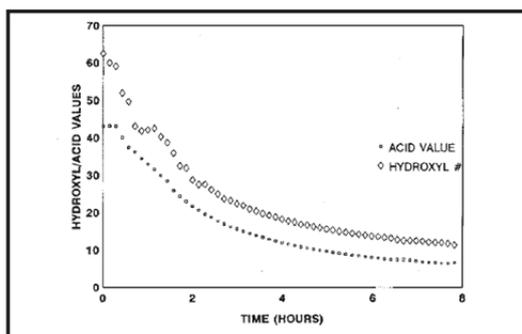


Figure 7. Summarized results from the application of NIR spectroscopy to the application of real time polyol process monitoring.

The results, summarized from an 8 hour reaction process, illustrate how the hydroxyl number and acid value change with reaction time. The rapid (results back to the user within a minute) and accurate (comparable to the primary method) results possible using NIR spectroscopy allow the process engineer to determine the reaction endpoints more rapidly for the polyol batch process. This analysis will save the plant 3–4 hours of sample residence time and decrease the energy needed to keep the reactor at temperature. Real-time NIR spectroscopy will also improve the reproducibility of the final product and decrease the risk of «overcooking» the polyol sample.

This paper has demonstrated the potential of NIR spectroscopy for monitoring the hydroxyl and acid number in a batch reactor process. Other NIR measurements of interest for polyol manufacturers include the analysis of mixed polyols (polyols made from propylene and ethylene oxides), the methyl substitution rating of a polymer backbone (by using a ratio of the methyl absorption due to propylene to that due to both propylene and ethylene), the determination of moisture (typically higher than 100 ppm), residual oxide, and primary and secondary amine levels in substituted polyols.

Conclusions

Real-time process monitoring of polyol production is possible with NIR spectroscopy. Analysis of hydroxyl and acid number readily provides molecular weight information and reaction end point determination. Benefits of NIR process monitoring of polyols production include increased production, lower production costs, and better product quality control.