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On-line analysis of chemical composition using an FT-Raman spectrometer in the near-ir

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ABSTRACT

Newly commercialized Fourier transform Raman spectroscopic instrumentation provides a simpler alternative for vibrational spectroscopic analysis. Instrument vendors currently design for laboratory use, but there are many potential process applications of these stable, easy to use instruments. Raman spectroscopy is highly suited to analysis of aqueous samples. Near infrared excitation minimized fluorescence interference and allows for remote operation via fiber optic probes.

The Department of Energy has funded research at the Measurement and Control Center to establish the utility of this method for on-line composition analysis in distillation columns. Laboratory evaluation and instrument employs an air-cooled laser and a thermoelectrically cooled detector. The device is mounted on a three by three foot cart for convenient location in control rooms. Current fiber optic extension cables allow for analysis in a cell thirty five meters from the instrument.

Application of the device to an acid recovery column at Tennessee Eastman Corporation in Kingsport, Tennessee will be discussed. Sensor placement is critical to optimal application of any on-line device. Potential energy savings and product throughput increase will be detailed.

1. SYSTEM DESCRIPTION

During this project a multiple point measurement system was constructed and tested.^{1,2} This was accomplished by routing the excitation light from a diode pumped YAG laser to the measurement points with optical fibers and returning the Raman scattered light to the spectrometer with optical fibers. An optical multiplexer was designed to time-share the light in both paths. The excitation light wavelength was in the near infrared range, thereby reducing the possible fluorescence of the samples to be analyzed.

The spectrum of the Raman-scattered light was measured by use of an interferometer-based spectrometer (Perkin-Elmer 1700). The entire system is controlled by an IBM compatible computer. The computer initiates a scan of the spectrum of the chemical stream, gathers the spectral data from the spectrometer and estimates the composition of the constituents. The calibration of the system is done by a "training" process in which multiple samples with different typical concentrations of the constituents of the chemical stream are analyzed and their spectra stored. Next, the unique set of orthogonal functions making up the experimental data are found. Finally an empirical mathematical model of the relation between spectral features and composition is formed based on multiple linear regression of the weights of the orthogonal functions against the known concentrations of the constituents. The accuracy goal of the project was a measurement of composition of each constituent of a process chemical stream within 3 minutes with a root-mean-square (rms) uncertainty of less than 2%. The final system achieved an error of about 1% rms in 3 minutes for the constituents composing the chemical stream in the first field trial test site, Tennessee Eastman Corporation of Kingsport, Tennessee.

Various composition analysis methods have been considered, in the past, for use in column process control. Many of these have been utilized with varying degrees of success due to inherent limitations in these techniques. A critical concern in determining potential energy savings utilizing composition control is the universality of the on-line analyzer. Raman spectroscopy was chosen for this development effort as the most appropriate for the control of a broad range of distillation separations. Of the three common optical spectroscopic methods in use today, fluorescence spectroscopy, absorption spectroscopy, and Raman spectroscopy, we chose Raman because of its narrow, distinct spectral features and relative insensitivity to the presence of water in the sample.

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One important aspect of composition based control systems is the relationship between the composition measurement location and the required measurement resolution. One feature of the Raman based composition analyzer is that it can be used to measure compositions in the tray section of the column. (Conventional process analyzers are typically applied to only product streams). This offers several advantages for addressing the control and energy reduction problems. The first advantage is demonstrated in Figure 1, where the sensitivity of the composition profiles to changes in the reflux and steam is plotted for each tray location. Note that product ends (where conventional analyzers are applied, if applied at all) have very little sensitivity. The leverage in controlling composition is orders of magnitude greater if the measurement is made inside the column. This is a characteristic of the TEC azeo column, but it is also a general characteristic of most distillation processes. If composition information is to be used in controlling a column, it needs to be well selected internal composition and not product compositions.

2. ECONOMIC ANALYSIS

The project economic analysis quantified the improvements in the TEC azeo column control that would be possible if the control system were based on composition measurements instead of temperature as at present. This preliminary study was

Figure 1
Acetic Acid Composition Sensitivity vs. Tray Location

conducted on a simulation of the proposed field test column and included two relatively simple composition control strategies. The results of the study indicate that there is a clear advantage to composition based control. Both composition

control schemes significantly reduced the variation in the product composition. Reducing variation saves energy by allowing operation of the column much closer to the minimum energy requirement without jeopardizing the product specification.

Not specifically addressed in this economic analysis is the cost of the analyzer vs. the anticipated energy savings. The general feeling is that the cost of the components in the prototype system does not accurately reflect the price tag which would be on an industrialized, commercial unit.

However, this study demonstrates that the high resolution and mechanical sampling requirements placed on present industrial analyzers are not necessary. High resolution and sampling both contribute to the capital as well as the maintenance costs of current process analyzers. A commercial Raman based analyzer should compete quite favorably with these existing technologies in both price and maintenance. Also, it should yield much higher control performance. The control performance advantage offered by the Raman based analyzer is that it can be applied with relatively little difficulty to determine the internal composition of the column.

3. REFERENCES

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