On line Applications in Phosphorous Chemical Industry

Non-destructive optical monitoring of chemical composition can be accomplished using Raman Spectroscopy. Raman spectra can be utilised to distinguish differences in chemical bond structures. This is particularly useful in applications where reactions could progress towards either a desired product or an undesired by-product. The Raman spectrum indicates when local conditions exist which favour one reaction path over another. This qualitative measurement can be developed into a tool to monitor process conditions.

Application

A basic ingredient used in the synthesis of inflammable products and fertiliser production is PCl3, the naturally favoured reaction product of phosphorous and chlorine. However, the production of PCl3 can follow several reaction paths based on the ratio and the concentrations of the starting materials. It is possible to introduce the phosphorous at a rate faster than the chlorine can be consumed, allowing the pyrophoric phosphorous to pool on the bottom of the reactor and causing the system to go into an uncontrollable state. Likewise, the reaction path can favour the formation of highly toxic PCI5 should the chlorine content become excessive. To avoid either of these problems, proper control must be maintained at all times of operation by controlling the raw material supply rates.

Periodically, the process must be halted for reactor maintenance. The shutdown procedure dictates stopping the phosphorous flow and monitoring for the first signs of PCI5, indicating full consumption of the phosphorous.

The monitoring methodology should indicate this full consumption as early as possible to avoid excess formation of the undesired PCI5.

Set-up

The Raman spectra are collected on-line using a JobinYvon HE industrial Raman analyser incorporating a laser. Its high throughput spectrograph is directly coupled via optical fibres to four remote Raman probes allowing simultaneous monitoring of four different sampling points. A high performance air-cooled CCD multichannel detector is used to detect and separate the four different signals. The rugged and compact design of this spectrograph makes it ideally suited to industrial environments.

Before the Raman technique was proven, batch analysis was useful to determine the level of elemental phosphorous in PCI3. The batch analysis used either a calorimetric measurement of the heat of reaction between the dissolved phosphorus and liquid bromine dissolved in carbon tetrachloride, or gas chromatographic analysis using an SE 30 column. The involvement of human operators in the measurement contributed to slow turnaround time, operator error, and possible safety hazards.

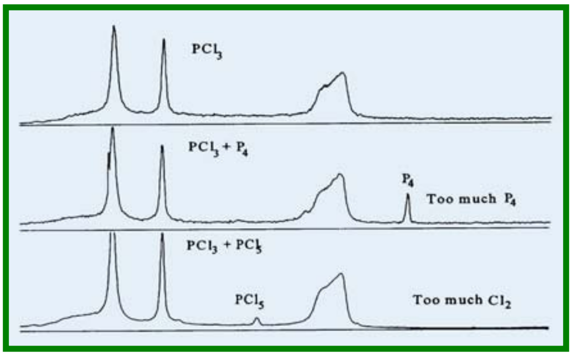

Figure 1. PCl3 reactor products

Results

The Raman lines of the components are very distinct and well separated, as shown in the spectra. By simply monitoring the peak heights of the PCI3, P4, and PCI5, the necessary safety margins can be maintained. Monitoring full reaction at shut-down is also met within the required time frame.

Wavenumbers in Raman spectroscopy are equivalent to wavenumbers in IR absorption spectroscopy. They are inversely proportional to wavelength and directly proportional to energy.

Comparison

The data collected on the JobinYvon HE dispersive system using a Class IIIb laser require less than 10 mW of power and 10 seconds integration time. An alternative method using interferometric-based FT/Raman spectroscope involves a class IV laser with more than 1 Watt of power and 5 minutes integration time. The following table summarises the differences of the two methods

Technique	Dispersive	Fourier Transform (FT)
Acquisition Time	10 seconds	300 seconds
Wavelength	800 nm	1064 nm
	Visible Beam	Infrared, Invisible Beam
Laser Power at Source	0.008 watt	≥1.0 WATT
Laser Class	Type IIIb	Type IV
Moving Optics	None	Interferometer

Conclusion

Dispersive Raman spectroscopy is successfully applied to this process application. The system quickly and clearly monitors the reaction. This insures safer and more efficient formation of the desired product. The technique also guides the process shut-down for maintenance without any additional hardware. In this application the dispersive Raman spectroscopy technique returns higher quality data in less time and with less laser power than FT methods.

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