

FT-NIR Analysis of the Hock Process for the Production of Phenol and Acetone

Chris Heil, Thermo Fisher Scientific, Madison, WI, USA

Introduction

The Hock process to produce phenol and acetone from low cost reagents, oxygen, and sulfuric acid was discovered by Hock and Lang in 1944. The phenol produced by the Hock process approaches 99.99 wt % with total impurities of only 60 ppm. The process starts with cumene being oxidized to form an intermediate compound called cumene hydroperoxide (CHP) (Figure 1). The cumene hydroperoxide then goes through a cleavage reaction to form phenol and acetone. Cumene (isopropylbenzene) is an aromatic hydrocarbon that can be easily synthesized from benzene and is found in crude oil and refined fuels. Phenol can be used in aspirin, billiard balls, dyes, deodorant, and phenolic resins used in adhesives and plastics, while acetone finds use in plastics and solvents.

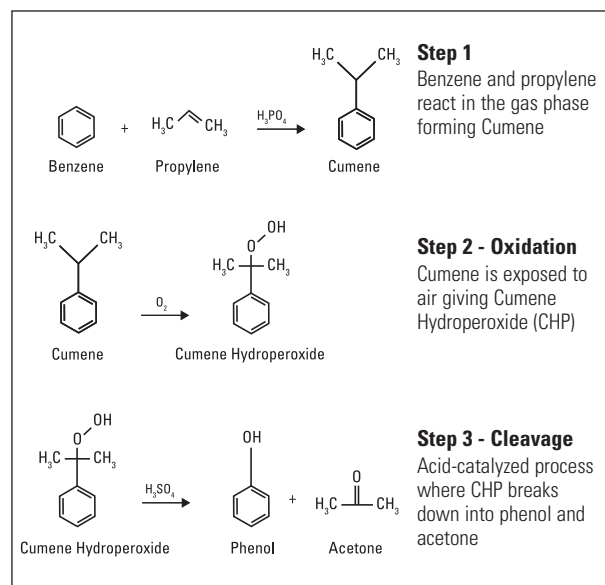


Figure 1: Chemistry of the Hock Process

The chemistry of phenol production is a two-step synthesis. First, cumene is reacted with oxygen to form an intermediate compound, cumene hydroperoxide (CHP). Second, the CHP is decomposed with sulfuric acid to form the phenol and acetone co-products. Monitoring the process for CHP concentration is very important since CHP is the critical intermediate as a product of the oxidation step and as a reactant in the cleavage reaction. The oxidation reaction is accomplished in a series of towers with each successive tower producing a higher % of CHP. The CHP is then concentrated in a series of distillation columns to produce a stream that is over 80%. Samples can be grabbed

at each oxidation tower and distillation column to track the concentration of CHP. The primary analysis method for determining CHP concentration is titration. The initial step in the titration is the reaction of CHP with potassium iodide to produce a stoichiometric quantity of I_2 . Step 2 is to titrate I_2 with thiocyanate to a colorless endpoint. The delay in results from grab samples run by titration is 30 minutes.

An analysis by Fourier transform near-infrared (FT-NIR) is several orders of magnitude quicker than by traditional wet chemistry methods such as titration (Table 1). High volume, continuous flow production facilities like the ones using the Hock process are ideal candidates for real-time in-process analysis by FT-NIR. Real-time analysis will indicate when any step in the process is not at an optimum condition and allow adjustments to be made quickly before a large quantity of out-of-specification material is produced. Due to its hazard-certified enclosure, the Thermo Scientific Antaris™ EX FT-NIR process analyzer (Figure 2) is well suited for real-time analysis in explosive, corrosive, and wet and dirty environments. The Antaris EX can measure several process points simultaneously with probes installed directly in tanks or pipes.

Titration Time	Lab NIR Time	In-line NIR Time
30 minutes	5 minutes	20 seconds

Table 1: CHP analysis time for different techniques



Figure 2:
Antaris EX FT-NIR
process analyzer

Key Words

- Antaris
- Chemical
- Cumene
- Cumene Hydroperoxide
- FT-NIR
- Hock Process

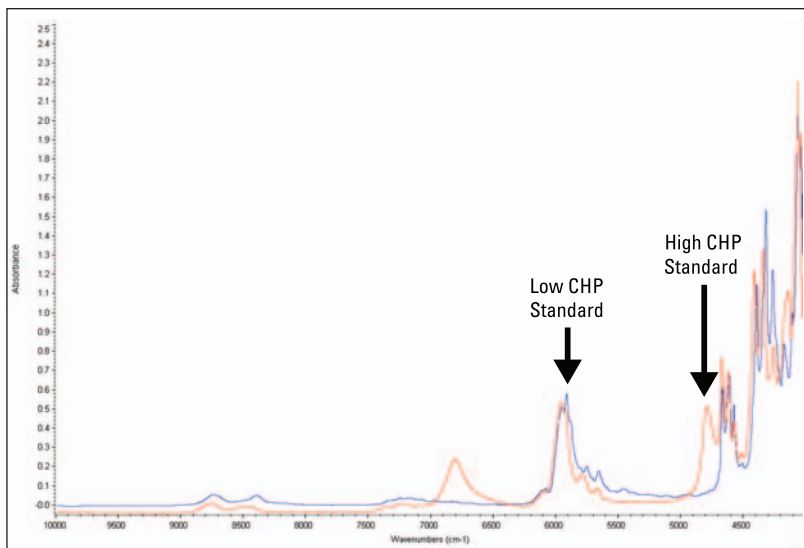


Figure 3: Spectral differences for low and high CHP standards

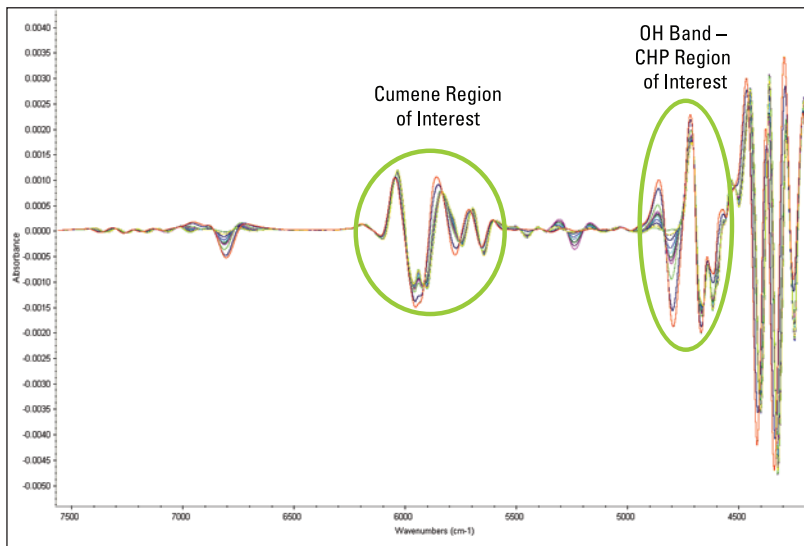


Figure 4: 2nd derivative standard spectra showing the regions of interest for calibration development

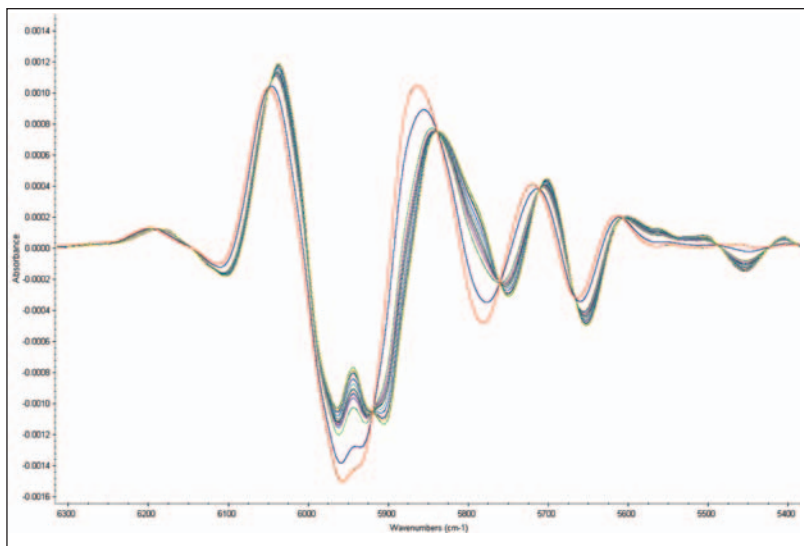


Figure 5: 2nd derivative spectral region of interest for cumene

Experimental

The samples for this application were run on a fiber optic probe with a 1 mm optical pathlength. The relatively small optical pathlength ensured that total absorption did not occur in any part of the spectral region used for this application. The peak of interest for CHP is at lower frequency (4800 cm^{-1}), a longer pathlength could have excluded the use of this peak. Spectra were collected with a fiber optic probe because real-time in-line analysis is much more valuable than lab analysis on a dynamically changing process. Spectral collection parameters were 32 co-averaged scans at 8 cm^{-1} resolution. This resulted in a 20 second spectra collection time for each standard. A background scan was taken of air from a clean and dry probe before spectra collection. This allowed any environmental effects, including interaction of the source light with the probe, to be factored out of the spectra.

For CHP, we can see two distinct peaks at 6800 cm^{-1} and 4800 cm^{-1} which are not present in the cumene. Figure 3 shows a pair of spectra, one that is low in CHP (high in cumene) and one that is high in CHP (low in cumene). The peaks at 6800 cm^{-1} and 4800 cm^{-1} are due to the OH group in the peroxide component of CHP. For cumene, we see the most spectral difference vs. CHP in the region between 6000 cm^{-1} and 5600 cm^{-1} (Figure 3). In Figure 4, we see the 2nd derivative plot with regions of interest for calibration development for cumene and CHP marked. The regions of interest in this 2nd derivative plot correlate to the regions referenced in Figure 3. The 2nd derivative enhances spectral differences that can be obscured in the raw spectra. This is most evident in the region from 6000 cm^{-1} to 5600 cm^{-1} where small differences in the raw spectra show up as distinct absorbance and peak shape changes in the 2nd derivative plot (Figure 5).

Results and Discussion

The calibrations for cumene and CHP showed good correlation and accuracy across large concentration ranges from 0-80% for CHP (Figure 6) and 6-100% for cumene (Figure 7). For any method of analysis to be successful for a mixture of different compounds there cannot be inter-correlations or interferences between the compounds in the mixture. As discussed earlier, spectral peaks unique to cumene and CHP were easily identified in the spectra for this study. A partial least squares (PLS) model was developed using spectral regions of 5272 to 4671 cm^{-1} for CHP and 6000 to 5457 cm^{-1} for cumene. The spectra were processed with a 2nd and Norris derivative filter with segment length = 11 and gap between segments = 0. The 2nd derivative served not only to enhance hidden spectral difference but also to eliminate small baseline shifts seen in the samples.

The root mean square error of calibration (RMSEC) for CHP was 0.169% (Figure 6) and for cumene was 0.323% (Figure 7). For CHP the RMSEC was very close to the root mean square error of cross-validation (RMSECV) of 0.362% (Figure 8). The RMSECV is a better metric than RMSEC to gauge the accuracy of a method applied to unknowns since it is an error computed from predictions made on standards not in the calibration model. The calibration plot for cumene displays validation samples (+) with the same accuracy as the calibration samples (\circ) based on how closely the validation samples are to the best fit line of the calibration samples. The low RMSECV for CHP and accuracy of validation samples for cumene indicate a calibration model that is robust and does not lose accuracy when predicting samples not in the calibration set.

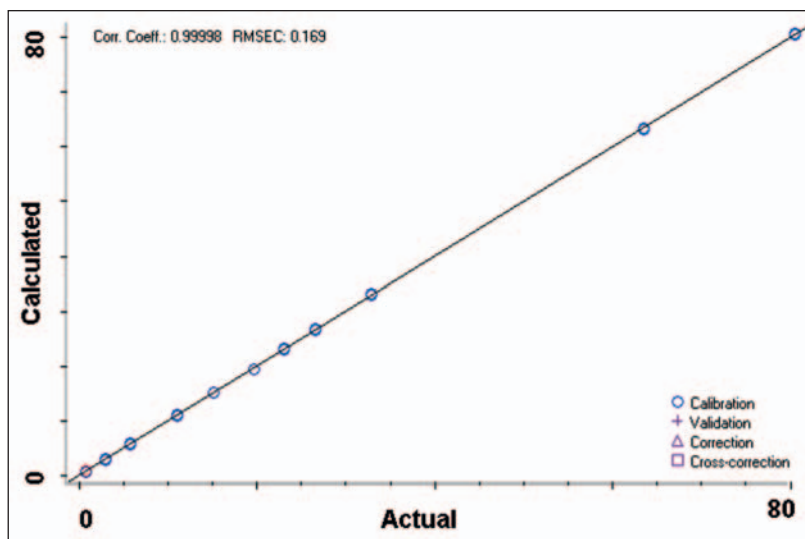


Figure 6: Calibration plot for CHP

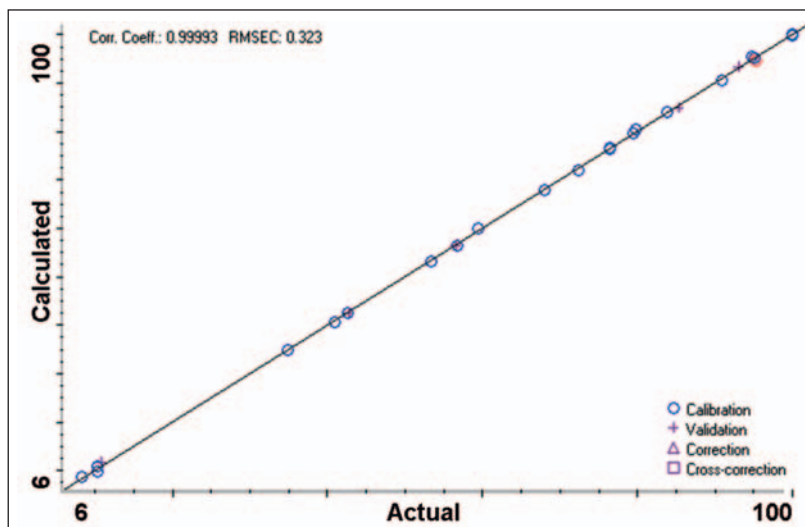


Figure 7: Calibration plot for Cumene

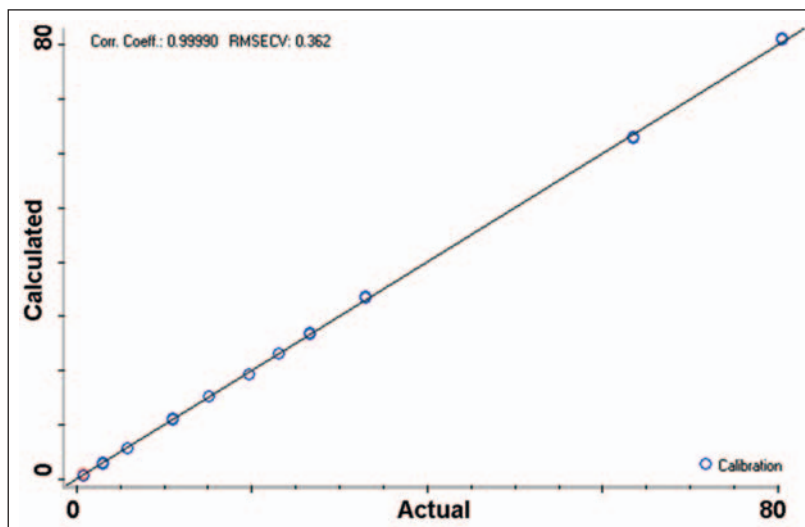


Figure 8: Cross-validation plot for CHP

The PLS model developed to monitor the Hock process only needed 3 factors for CHP and 4 factors for cumene. PLS models that achieve low calibration error and good correlation with few factors are more ideal than models requiring many factors since they run less risk of using irrelevant spectral data when predicting unknowns. PLS uses factors for concentration and spectral variation in the calibration standards. The Predicted Residual Error Sum of Square (PRESS) plot visually shows the relationship between the number of factors and the RMSECV. The PRESS plot is key in determining the optimum number of factors, since it shows when the minimum cross-validation error has been achieved. As stated earlier, the RMSECV is an indicator of model performance independent of the samples in the calibration. A PRESS plot that has an initial dramatic drop in RMSECV shows that the spectral and concentration variation is easily correlated to one another and is not affected by other sources of variation in the calibration samples. For the PRESS plot of both CHP and cumene (Figure 9), the minimum RMSECV is achieved with very few factors.

Conclusion

The capability of the Antaris FT-NIR analyzer to perform multi-component analysis quickly is invaluable when monitoring high-volume continuous flow processes such as those often found in the chemical industry. The application of the Antaris MX or EX FT-NIR (Figure 2) analyzers for real-time in process analysis allows for even shorter analysis times by using truly simultaneous analysis of multiple process points. For the cumene-to-phenol process, this allows monitoring of all serial oxidation towers and distillation columns at the same time. The simultaneous analysis gives a snapshot of the process at any given time with the ability to communicate the results to a process control center. The streaming real-time data from Antaris FT-NIR allows for easy trending, closed loop control, or sounding of an alarm whenever the CHP concentration is not inside acceptable limits.

The return-on-investment for a fully automated in-line FT-NIR analyzer is rapidly achieved when factoring the savings from decreased out-of-specification product, reduced laboratory analysis time and the cost to perform the primary analysis. Table 1 summarizes the time of analysis for a typical CHP titration including getting the sample to the laboratory. By moving away from time-consuming tests, like titrations, lab personnel can concentrate on more value-added projects. Plant operators can focus on optimizing the process using the wealth of critical component concentration data continuously flowing to their control center console from the in-line FT-NIR analyzer.

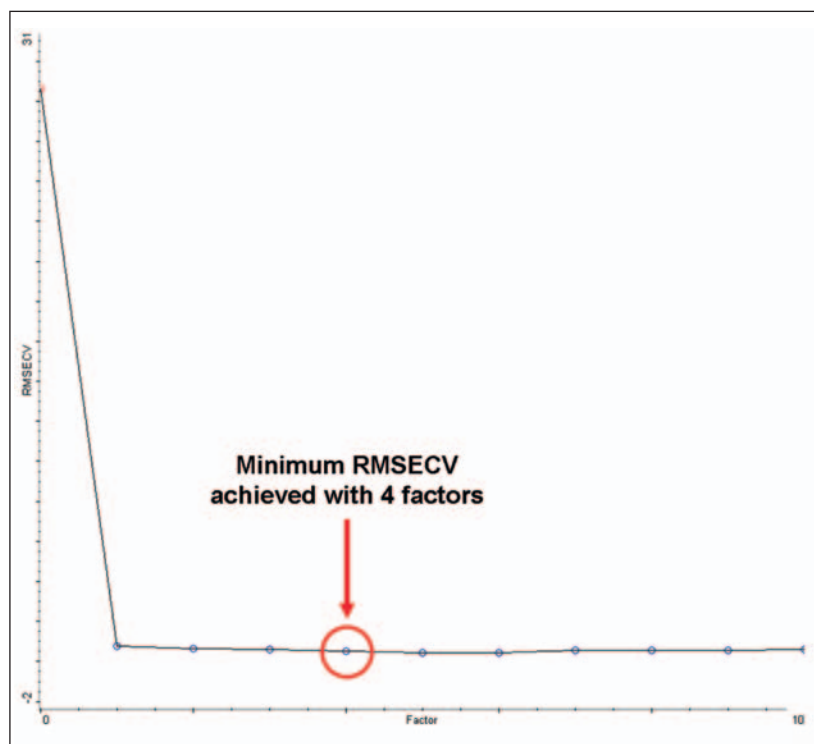


Figure 9: PRESS plot for cumene

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa
+43 1 333 5034 127

Australia
+61 2 8844 9500

Austria
+43 1 333 50340

Belgium
+32 2 482 30 30

Canada
+1 800 530 8447

China
+86 10 8419 3588

Denmark
+45 70 23 62 60

Europe-Other
+43 1 333 5034 127

France
+33 1 60 92 48 00

Germany
+49 6103 408 1014

India
+91 22 6742 9434

Italy
+39 02 950 591

Japan
+81 45 453 9100

Latin America
+1 608 276 5659

Middle East
+43 1 333 5034 127

Netherlands
+31 76 579 55 55

South Africa
+27 11 570 1840

Spain
+34 914 845 965

**Sweden/Norway/
Finland**
+46 8 556 468 00

Switzerland
+41 61 48784 00

UK
+44 1442 233555

USA
+1 800 532 4752

www.thermo.com



Thermo Electron Scientific Instruments LLC, Madison, WI
USA is ISO Certified.

AN51711_E 10/08M

©2008 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.