

STEAM CRACKER PERFORMANCE OPTIMIZED BY PROCESS MRA

Magnetic Resonance Analysis Gives BASF AG a Consistent, Low-Maintenance Method to Accommodate Fluctuating Feedstocks. **By John C. Edwards**

Two Spyro steam crackers from Technip/KTI are the heart of the BASF AG Ludwigshafen integrated chemicals site in Germany. BASF operates the crackers mainly for captive use, as logistically they are at the end of the pipeline.

The crackers produce in excess of 610,000 metric tons of ethylene and other products mainly for internal consumption. The company aims for 365 days per year operation with extended cracker shutdown every five years. Feed characterization in the form of gas chromatography has been used for proper unit operation for a number of years.

With a measurement time of more than one hour, the existing gas chromatographs (GCs) were slow to respond and had high maintenance overhead. More frequent analysis and lower-maintenance technology was required to allow constraints to be filled, reduce coil outlet temperature and severity variability, optimize the yields of the most valuable products, and, in time, allow greater feed variability and flexibility.

A feasibility study investigated a number of options. A process magnetic resonance analyzer (MRA) system was chosen due to its measurement linearity, fast-track project execution, and high availability.

BASF purchases naphtha of variable feed specification (Figure 1), depending on strategic or tactical requirements. More than 140 naphtha types are regularly used. With tank stratification and regular feed tank changes, good monitoring of feed quality is essential to minimize lost production during feed transitions and to maintain stable operation in the case of a slug of high-variability naphtha potentially violating a constraint. Heavy naphthas could violate the coil outlet temperature, causing excess coking or tube wall damage. A light naphtha could exceed the downstream compressor loading limit.

Working in partnership with BASF, Invensys Process Systems GmbH supplied a feedstock analyzer system that has been successfully extended to both crackers, including naphtha recycle streams. The measurements cover some 29 components plus four calculations from C4-C11, including paraffins, isoparaffins, naphthenes, and aromatics.

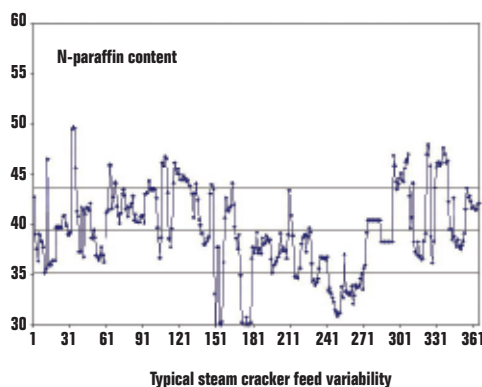
The Process MRA System

The MRA analysis system uses high-resolution FT-NMR proton spectra in conjunction with partial least-squares modeling techniques to obtain highly linear and robust predictive models. Modeling requirements are limited, with single predictive models applied across the entire variability range of each property.

The technique, developed in the 1950s, reveals the hydrocarbon structure of a fluid without temperature or chemical preconditioning. When a hydrogen proton is introduced into a homogeneous magnetic field, the magnetic moments of the protons align with the field; these magnetic moments can be described as vectors.

If the sample is then given a short-duration radio-frequency pulse at the proton resonant frequency of 58 MHz, the vectors will rotate. A 90° rotation yields optimum signal strength. Once the radio frequency pulse has caused a 90° rotation, the RF pulse is turned off and the vectors relax back to the origi-

FIGURE 1.
FEED VARIES



BASF AG PURCHASES MORE THAN 140 TYPES OF NAPHTHA. TANK STRATIFICATION AND REGULAR FEED TANK CHANGES MAKE GOOD MONITORING ESSENTIAL TO MINIMIZE LOST PRODUCTION AND MAINTAIN STABLE OPERATION.

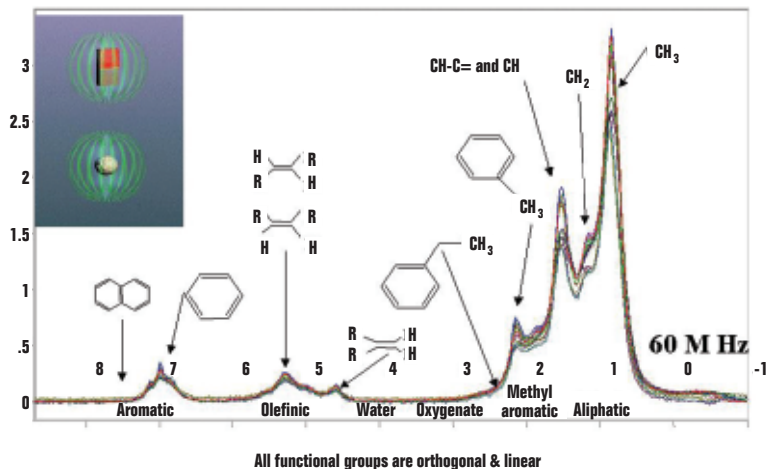
nal state in a manner characteristic of the proton location within the molecular structure.

When a Fourier transform is performed on the decay, the structural information is revealed in the resulting spectrum and is commonly known as chemical shift. These shifts have textbook locations (Figure 2), and with partial least-square chemometric software, the chemical compositions are correlated.

The installation included integration of feed characterization from analytical and optimization software Process MRA, plus ROMeO Optimization software to improve the operational efficiency and reliability of this site-critical operation. Availability has been high (greater than 98%) with prediction models updated remotely (typically once per quarter) as part of an inclusive three-year support agreement.

FIGURE 2.

SORTS HYDROCARBONS



A TYPICAL MAGNETIC RESONANCE ANALYSIS SPECTRUM REVEALS STRUCTURAL INFORMATION BASED ON THE LOCATIONS OF PROTONS IN THE MOLECULES.

Project Execution

Since September 2000, the process MRA system has been functioning online, providing feed-forward stream characterization to the steam cracker reactor model.

Implementation of the process MRA took place over a period of about 22 weeks. During the first two weeks, BASF was provided with an MRA that measured a starter set of some 100 naphtha samples spanning the expected operational range. Fewer than 50 were incorporated into the final model.

In the next 16 weeks, an online system was installed and online model development commenced. Another 75 samples were gathered prior to the decision to run the validation phase.

During the last four weeks, a validation phase was conducted (Figure 3) and the unit was accepted and transitioned to operations.

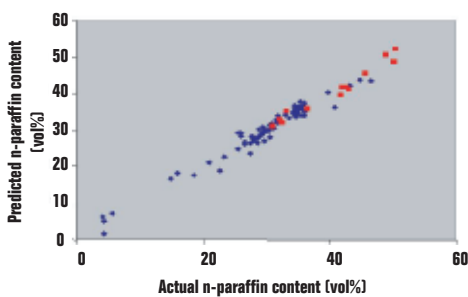
The system was installed and commissioned without any disruption to production and within the operational constraints of the local maintenance, engineering,

and laboratory staffs.

Since the sampling requirements are straightforward, the system was integrated into the established shelter for other ana-

FIGURE 3.

INTERNAL VALIDATION



ONLINE MAGNETIC RESONANCE ANALYSIS PROVIDES A LINEAR AND ROBUST MODEL TO ADJUST THE STEAM CRACKERS FOR VARYING NAPHTHA FEEDSTOCK N-PARAFFIN CONTENT.

lytical equipment associated with the crackers. No water removal is required and the filtering was set at 100 microns to prevent valve seat damage only (the sample passes through a relatively wide-bore

6 mm tube). For the multistream sampling, an inline heater is preferred to clamp stream-to-stream temperatures within $\pm 5^\circ\text{C}$.

Performance on the Line

An important measurement of the naphtha feed is the quality index (QI), often expressed simply as:

$$QI = 2 \times nP + iP + N + 2 \cdot A$$

Where nP is normal paraffin content, iP is iso-paraffin content, N is naphthene content, and A is aromatic content.

Running rigorous test cases has shown that this simple model does not fully express the value available for capture. Process MRA makes available a higher-fidelity measurement, superior in terms of accuracy and precision to that previously available.


Comparison of MRA-predicted values with GC analysis showed very good results:

- For total normal paraffin with a mean value of 34.10%, the standard error of prediction was 0.78%, and the correlation coefficient was 0.98.
- For total iso-paraffin, the equivalent values were 32.01%, 0.66%, and 0.97.
- For total naphthene, 20.4%, 0.63%, and 0.98.
- For total aromatics, 6.66%, 0.17%, and 0.99.

Additional daily full chemical analysis was conducted during the project phase. However, since the system has gone closed-loop, the on-stream time has been very high (greater than 99%), with minimal maintenance required from the cracker department.

The system required a single model update after installation to achieve results to BASF's specifications. Invensys has responsibility for support of the system for three years from validation, and to date has replaced a couple of selection valves, made a software release update, and adjusted the models on average once per quarter.

BASF will not disclose the bottom-line improvements except to say the

payback is within the return expected of a capital project, along with soft benefits such as a direct reduction in maintenance and in the laboratory support for full GC analysis work. 

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