Hydrofluoric acid alkylation

ABB and ConocoPhillips develop a critical new process analysis tool

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The ABB Process Fourier Transform Infrared (FTIR) Analyzer for HF (Hydrofluoric Acid) Alkylation Refinery Process Unit Optimization, jointly developed with ConocoPhillips, helps petroleum refineries to operate their HF alkylation units more efficiently and safely, while making a significant contribution to operational and environmental risk mitigation.

In the early days of petroleum refining, back in the 1920's and 30's, most of the pool of gasoline blending components was made up of straight-run material taken directly from the crude oil distillation unit. Refineries were essentially rather simple oil boilers. The first conversion units were uncomplicated and aimed at thermal reforming of straight-run naphthas to yield higher octane blending components for improved product quality.

The situation was given a significant boost during World War II when there arose, for obvious reasons, a desperate need for high-octane aviation gasoline (military aircraft at that time were mainly equipped with reciprocating piston engines fuelled by high-octane gasoline, rather than jet engines fed on kerosene).

One of the responses to this need for high-octane gasoline was the development of a refinery conversion unit – the hydrofluoric acid (HF) alkylation unit.

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The HF alkylation unit (HFU) remains of key importance to this day. It plays a critical role in providing one of the most important feeds to the final product gasoline blending pool. Its significance has grown side by side with the increasing number of fluid catalytic cracking (FCC) units in refineries. The FCC adds value to the heavy end of crude distillation by catalytically cracking heavy feeds into lighter products such as light cycle oil and FCC gasoline, which can be used either directly or after hydrotreating in final product blending operations. The downside of this process is that light olefins, typically butene and propene, are also produced in FCC operations. These are essentially worthless as feedstock. Similarly, in any crude distillation process an excess of light end products such as butane tend to be produced that are of limited use. N-butane can easily be converted to iso-butane, and in this form it joins the FCC c3 or c4 olefins (butene or propene) as the combined feeds to the HF alkylation unit.

The HF alkylation unit performs the important role of upgrading these byproducts to high-value alkylate, which is used as a gasoline blending component. This economically invaluable task of sweeping up the c4 olefins from the FCC and the c4 isoalkanes from the crude oil distillation unit and converting them, through the catalytic HF alkylation process (a modified Friedel-Crafts reaction), to iso-octanes, continues to be of major importance in petroleum refining.

Iso-octanes (alkylates) are the gold-standard of gasoline blending feedstocks in today's context of clean fuels and environmental concerns. They have high RON and MON (Research and Motor Octane Numbers), low-sulfur, low Reid Vapour Pressure (RVP) and near zero aromatics. They are the perfect gasoline component.

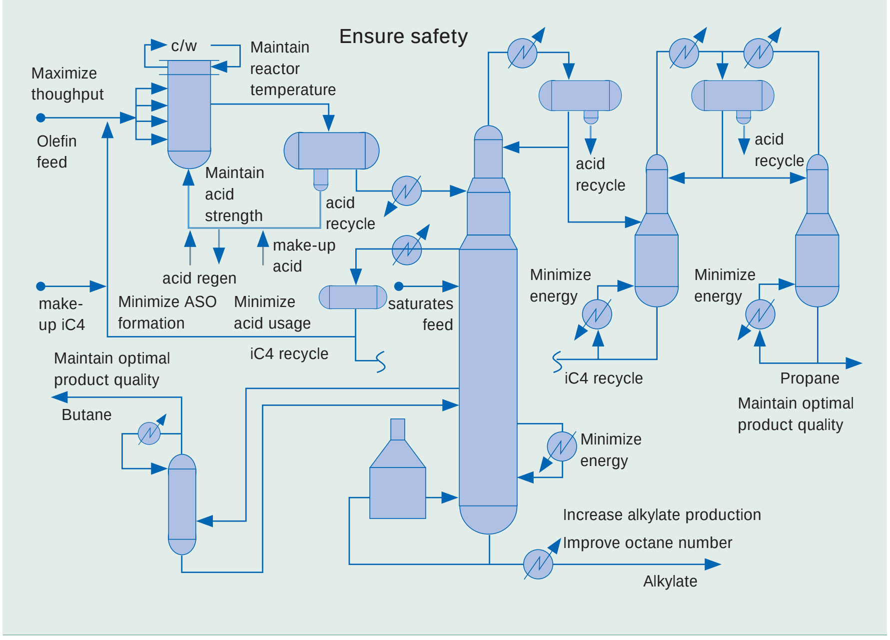
Over the past 15 years, gasoline formulation requirements, as driven by government environmental agencies in most regions of the world (but led by the European Union and the United States), have been significantly sharpened. Requirements for lower sulfur, lower benzene, lower aromatics, lower RVP and lower Driveability Index (a combination of fuel distillation properties) severely restrict the options for refiners in their final product gasoline blending operations.

The two most recent changes that have probably had the biggest impact on the gasoline pool are the removal of MTBE (methyl tertiary-butyl ether), because of its contaminating impact on groundwater, and the addition of bio-ethanol for its carbon-neutral status. MTBE is a lower vapor pressure high-octane blending component for gasoline. Although ethanol is equally high-octane it makes a substantial contribution to RVP, which essentially prevents straight butane from being used to any large extent in the same blend recipe. Thus, alkylate produced by the HFU is of exceptional value to refineries in their struggle to meet environmental and other legal constraints on their operations 1.

HF alkylation operating issues

Consequently, refiners operating HF alkylation units are under increasing pressure to maximize unit throughput, improve product quality and yields while operating safely and with low environmental impact. Ever tightening legislation on gasoline quality and increasing public and regulatory scruti-

1 The HF alkylation unit operational objectives



ny of the use of hydrofluoric acid combine to make reliable and efficient operation of HFUs of critical importance to the overall reputation and profitability of petroleum refineries.

The efficient operation of an HFU is a difficult task and subject to the most testing of operating regimes. This is due to a number of industry-specific constraints and operating issues that stretch the processing capability of the plant.

Operating issues

- HFUs must be able to deal with feedstocks that routinely vary in contaminant levels, hydrocarbon composition and volume due to upstream operating complexities.
- Operators have the difficult challenge of minimizing iC4 recycling and associated utility costs while producing alkylate of the desired quality with minimum acid consumption.
- The units must be operated in a safe manner despite the ever-present potential for acid runaway, accelerated equipment corrosion and associated HF release.

The demands on HF alkylation units are further increased by ongoing trends within the petroleum refining industry.

Industry trends

- The ongoing expansion of FCC units and the introduction of new cracking catalysts to satisfy gasoline growth also result in the production of more alkylation feedstock.
- The continuing trend of increased residue cracking and upgrading capacity produces more complex and problematic alkylation feedstock.
- There is an increasing interest in C5 olefin processing as a means to return volatile components to the gasoline pool while increasing product volumes.
- The continual tightening of legislation concerning gasoline quality further restricts the use of some current blend components.

Each of the above requires the HF alkylation unit to be more flexible in handling increased and varying feedstocks while maintaining unit efficiency and alkylate quality. The ideal blending characteristics of alkylate make it a critical element in meeting refinery profit targets and complying with fuel quality legislation.

Operational targets

- Alkylate quality optimization: the RON, RVP and distillation properties of the alkylate product of the HFU are critical for its use in downstream gasoline blending. These parameters are influenced by HF catalyst purity, and specifically by water content, which must be optimized within a suitable operating window. The water content of the HF acid recycle stream is vulnerable to feed contamination events, and these must be picked up and acted upon promptly.
- Corrosion mitigation: corrosion mitigation places severe lower limits on HF acid purity and upper limits on water content. Keeping within defined operational windows extends HFU turnaround times, significantly reduces maintenance costs and limits the risk of HF release into the environment.
- HF acid consumption: correct operation of the HFU depends on the successful separation of hydrocarbon product from the acid catalyst in the acid settler. If there is a build up of acid soluble oil (ASO) by-product and HF acid is consumed (thereby reducing acid strength), the process can fail, with the resulting rapid consumption of the remaining acid – a so-called acid runaway event. Such an event is extremely costly, but is an inevitable risk of HFU operation. A close watch on acid strength and the percentage of ASO byproduct can significantly reduce the likelihood of this happening.

The ABB-ConocoPhillips partnership

Recognizing the need for improved online HFU process monitoring and control in the mid-1990's, Phillips Petroleum (now ConocoPhillips) sought a process analytical instrumentation partner to jointly develop a solution that would improve the monitoring and optimization of these complex process units. ABB was an established supplier of online process FTIR analytical solutions in gasoline blending and downstream petrochemical applications, and a productive partnership between ABB and ConocoPhillips Factbox was formed to jointly develop an analytical solution.

At the time, monitoring the key process parameters of HF alkylation units was not straightforward. It relied on expensive, slow and potentially hazardous manual sampling of the recirculating hydrofluoric acid catalyst for laboratory assessment of its strength and the level of critical contaminants such as water and fluorination by-products (known as acid soluble oils).

HF acid purity determination is the key control parameter for HFU control and optimization, provided it can be delivered quickly enough to detect process unit upsets, such as transient shifts in acid strength and contamination events caused by upstream disturbances in, for example, FCC operation.

> As of December 2006, the online acid analysis system is installed in almost 20 HF alkylation units worldwide and has a combined operating history of more than 40 years.

ABB began working with the ConocoPhillips R&D laboratory at Bartlesville, Oklahoma in 1996 to develop an online acid analysis system. Two years of testing and development followed on HF alkylation pilot scale units. This included sample system design, metallurgy considerations and model development. The analyzer was then installed at the Phillips Petroleum refinery in Sweeny, Texas in May 1998. Two more years of successful onsite testing ensured the technology was ready for industry-wide implementation. The online acid analyzer was then launched for the HF alkylation market at the 2000 Phillips licensee symposium.

As of December 2006, the online acid analysis system is installed in almost 20 HF alkylation units worldwide and has a combined operating history of more than 40 years. The systems are installed in both ConocoPhillips and UOP licensed units in North and South America, Europe and the Middle East, and in sites operated by other major refining companies.

The ABB–ConocoPhillips solution

The key breakthrough in the creation of a robust and useful process FTIR analytical solution for HFU monitoring and optimization came with the development of an accurate and precise pre-calibrated chemometric model for the required process variables (HF acid strength, water % and ASO %) 2.

The traditional laboratory reference techniques for these measurements are poor, and in contrast to the usual methods of analyzer calibration, do not provide a reliable basis for the development of a precise calibration model. Fortunately, the HF acid recycle stream is of relatively simple composition. This allowed ConocoPhillips to develop the required universal calibration model on the basis of a gravimetrically prepared calibration standard and run it in a laboratory scale pilot alkylation reactor under real-life process conditions – but without any olefin feed in order to maintain exact acid composition during the run.

> The successful development and market introduction of the ABB process FTIR HF acid analyzer is the result of a very fruitful cooperation between ABB and ConocoPhillips.

The data obtained were essential and subsequently formed the basis for a successful patent registration under which ABB offers the HF process FTIR alkylation analyzer solution under license.

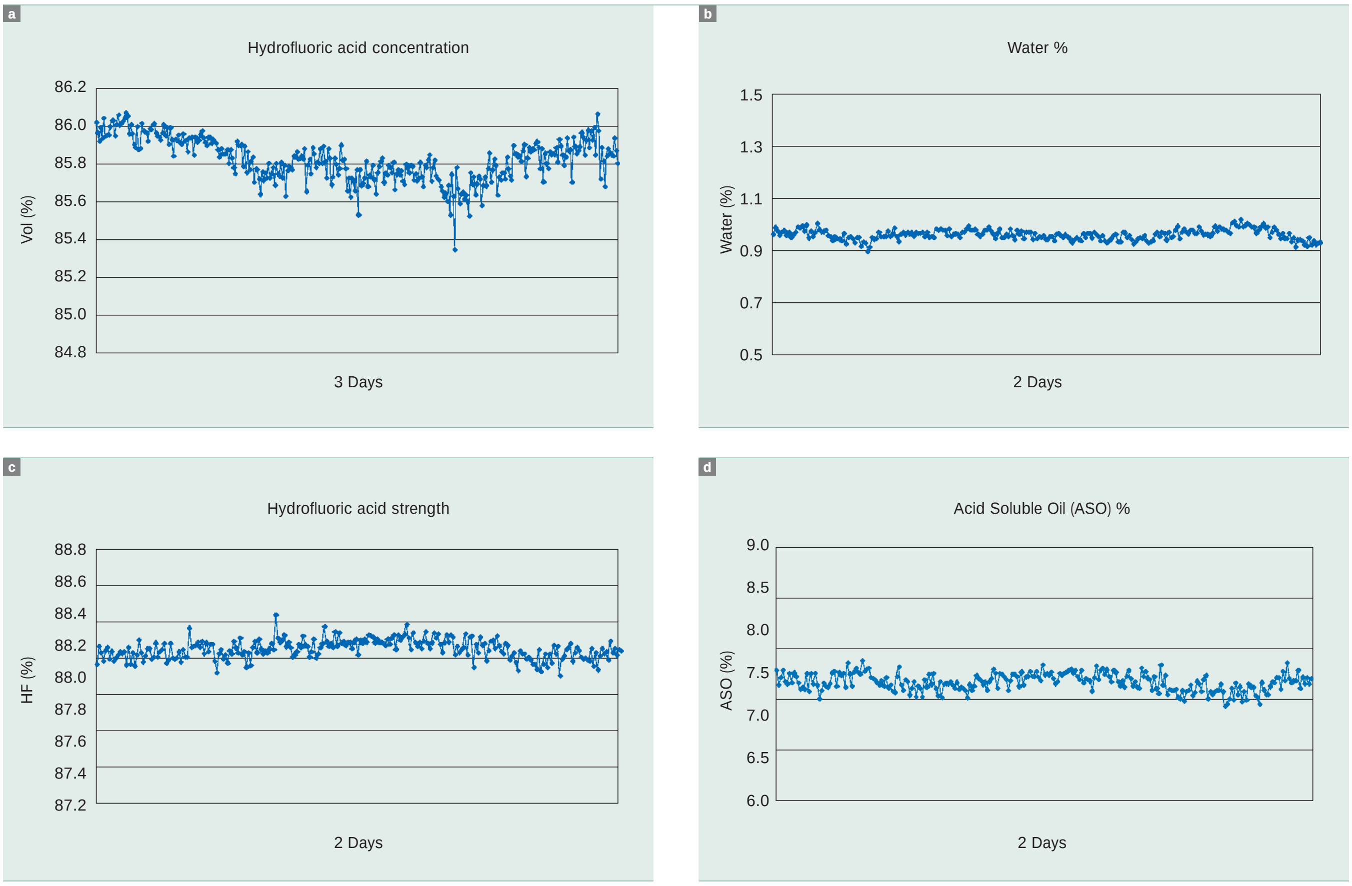
A major part of ABB's contribution to the project was the development of a safety-engineered field sample panel that is low maintenance and requires minimal field intervention inside the acid area (which in an HFU requires full C-suit personal safety equipment).

FTIR analyzer technology

ABB's fiber-optic-based multichannel process FTIR analyzer is ideally suited for this type of application. It allows a remote field-based acid-area sample flow cell and associated safety and sample conditioning system to be physically separate from the analyzer optics station (which is normally located in a control room or similar safe area). This arrangement is essential when dealing with the online analysis of an exceptionally hazardous process stream such as HF acid.

An additional benefit of ABB's FTIR technology is its ability to monitor multiple process streams with a single analyzer. In HFUs this enables two acid streams to be monitored (for example, the main acid recycle and the acid regeneration overhead) in real time, which significantly improves HF acid purity control and regeneration efficiency 3.

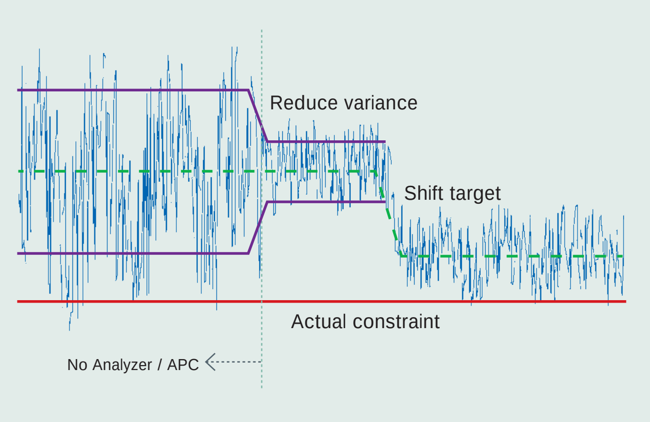
2 Run-time data from ABB's Process FTIR HF Acid Analyzer



Process collaboration

In addition to these benefits there are other exciting process control options for the HFU process FTIR analyzer. Besides the HF acid catalyst monitoring role, there are many important hydrocarbon streams in the HFU that benefit from reliable, low-maintenance and rapid compositional analysis. The olefin feed stream and the iC4 recycle stream from the iso-stripper are the most important. Together, these two streams directly influence the feed purity to the HFU, which in turn has a direct impact on HF acid consumption. Real-time process data on these streams, along with the HF acid purity measurement, provide a significant improvement in unit operational stability.

3 Real-time process monitoring with APC



> ConocoPhillips brought a key understanding of real-life process monitoring requirements and critical process variables to the partnership.

In summary, the ABB–ConocoPhillips solution for HFU reactor optimization offers ABB multivariable control technology underpinned by a unique capability for rapid online characterization of HF acid, recycle iC4, olefin/iC4 makeup feeds and alkylate. The solution delivers the following significant operating improvements to HF alkylation reactors:

- Feed rates, alkylate yield, and alkylate octane are maximized to an economic optimum, subject to operating constraints
- Isobutane:olefin (I:O) ratio and energy consumption can be reduced while meeting alkylate quality and yield targets with minimum acid consumption.
- Isobutane makeup rate can be optimized while respecting iC4 inventory constraints
- Acid quality is maintained in the optimum operating range for HF, ASO and water content. This leads to:
- Less frequent approaches to runaway conditions
- Lower acid inventory, as acid makeup requirements are reduced
- Alkylate octane enhancements are possible as the water content of the catalyst can be increased in a controlled manner. One of the major licensors reports that an increase in water content from 1.0 – 2.0 wt% can deliver more than $1 million in benefits for a 10,000 bpd unit operating at the typical I:O ratio of 10
- Less aggressive regenerator operation and lower acid losses
- Higher quality alkylate and yields
- Acid:hydrocarbon ratios and reactor temperature are controlled to improve product quality and suppress ASO production
- Reactor conditions are optimized to manage variations in fresh feed compositions.

Factbox ConocoPhillips

Headquartered in Houston, Texas, ConocoPhillips is the third-largest integrated energy company in the United States – based on market capitalization, oil and gas proved reserves and production – and the second-largest refiner in the United States. The company operates in more than 40 countries, has 38,700 employees and is known worldwide for its technological expertise in deepwater exploration and production, reservoir management and exploitation, 3-D seismic technology, high-grade petroleum coke upgrading and sulfur removal. For more information, please refer to www.conocophillips.com

An extended portfolio

The successful development and market introduction of the ABB process FTIR HF acid analyzer is the result of a very fruitful cooperation between ABB and ConocoPhillips.

As one of the principal HF process licensors, ConocoPhillips brought to the partnership a key understanding of real-life process monitoring requirements and critical process variables. Through their R&D department they also brought the capability to develop the crucial universal analyzer pre-calibration necessary for successful commercial exploitation.

ABB was able to contribute state-of-the-art process FTIR technology and expert field sample system design engineering. Together, these inputs have produced a result of significant benefit to both parties. ConocoPhillips is able to offer a key process analytical tool to its many HF process licensees, as well as benefiting from the direct implementation of the technology in its own refining operations. ABB has been able to add a significant and unique building block to its portfolio of refinery process FTIR analytical solutions.

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