ABB MEASUREMENT & ANALYTICS | WHITE PAPER

Hydrofluoric acid alkylation (HFU) unit optimization

The use of robust pre-calibrated on-line analyzer technology for the measurement of HF acid purity

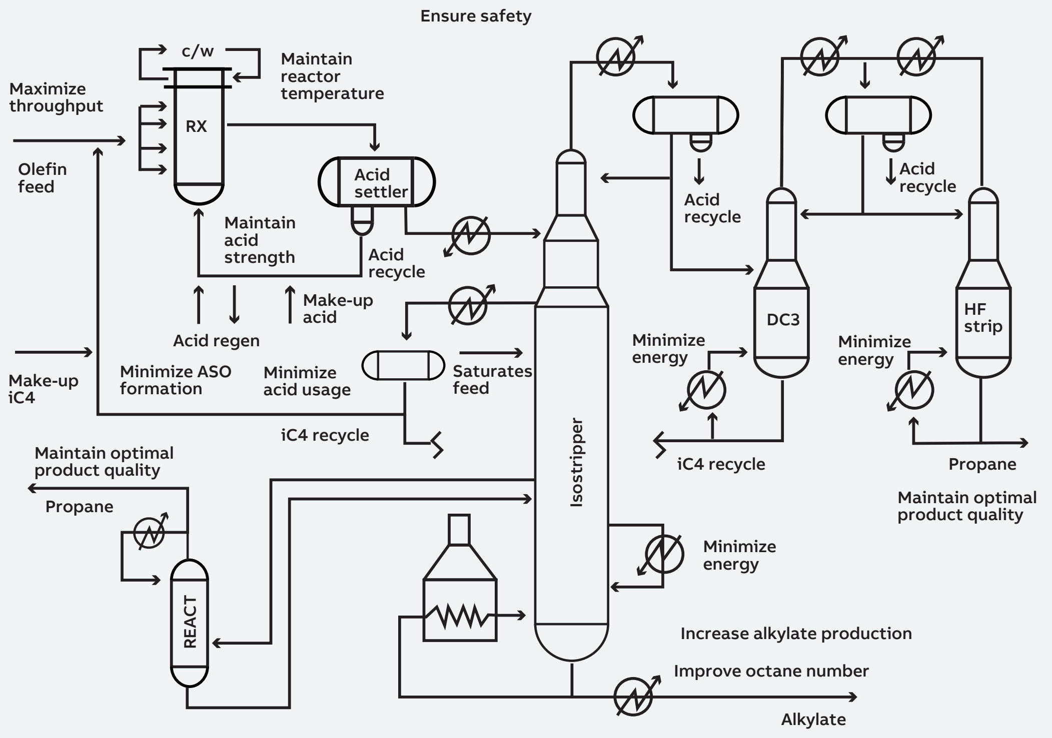
This white paper aims to illustrate how the fast response times and excellent repeatability of an on-line FT-NIR analyzer, when coupled with a robust field sample system and reliable pre-calibrated model for HF acid purity can be used to provide complete and safe real-time data when optimizing the operation of hydrofluoric acid alkylation units.

Measurement made easy

—
Refinery

In the earliest days of petroleum refining, most of the pool of gasoline blending components was made up of straight-run material taken directly from crude oil distillation units. Refineries were essentially simple oil boilers. The first conversion units were uncomplicated and aimed at the 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, for obvious reasons, there arose a desperate need for high-octane aviation gasoline (military aircraft at that time were equipped with reciprocating piston engines fueled by high-octane gasoline, rather than with jet engines fed on kerosene). One of the answers to this need for high-octane gasoline was the development of a refinery conversion unit – the hydrofluoric acid (HF) alkylation unit, producing alkylate, which is composed mainly of c7 and c8 isoalkanes that have excellent gasoline blending properties, high octane and zero aromatics content.

Dr. Michael B. Simpson
Industry Manager, Refining and Petrochemicals
ABB Measurement and Analytics



The HF Alkylation Unit processes olefin feed and isobutane to create high-value alkylate product

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 products of 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 hydro-treating, 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 isobutane, 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 then 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 HF alkylation process, to isooctanes, continues to be of major importance in petroleum refining.

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 drivability index (a combination of fuel distillation properties) severely restrict the options for refiners in their final product gasoline blending operations. 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.

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

ABB TALYS ASP400-Ex FT-NIR Analyzer with HF Acid Area Field Sample System

Monitoring the key process parameters of HF alkylation units is not straightforward. Historically, it relies on expensive, slow, and potentially hazardous manual sampling of the recirculating hydrofluoric acid catalyst for laboratory assessment of its strength and 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.

Fiber-optic up to 300m run

Analyzer in safe area

Field sample system in HF acid area

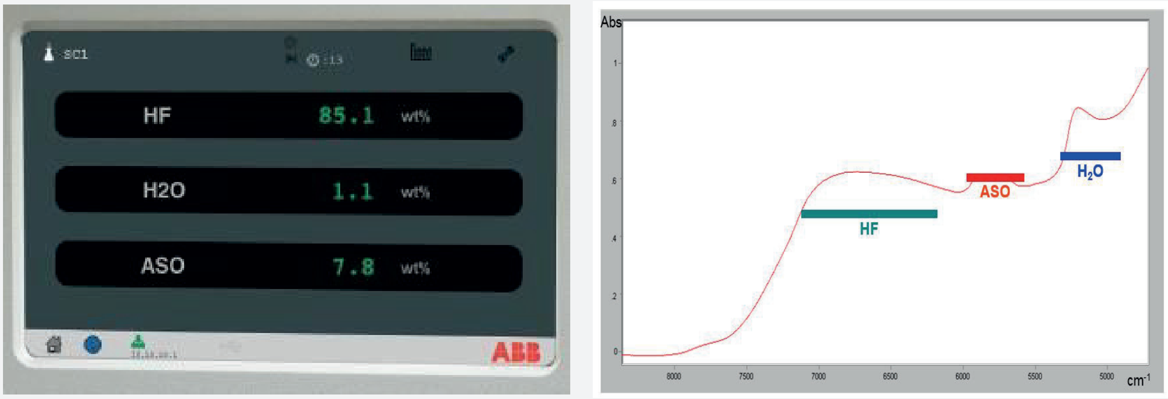
Operational targets

- **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) byproduct 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 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%).

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 the development of the required universal calibration model on the basis of a gravimetrically prepared calibration standard run in a laboratory scale pilot alkylation reactor under real-life process conditions—but without any olefin feed, to maintain exact acid composition during the run. This method, pioneered by Connoco Phillips in the 1990’s, yields a highly reliable pre-calibration for the ABB HF Alkylation analyzer, which is always supplied fully pre-calibrated without the need for any further on-site model development.

A major part of the success of this application was the development of a reliable 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).



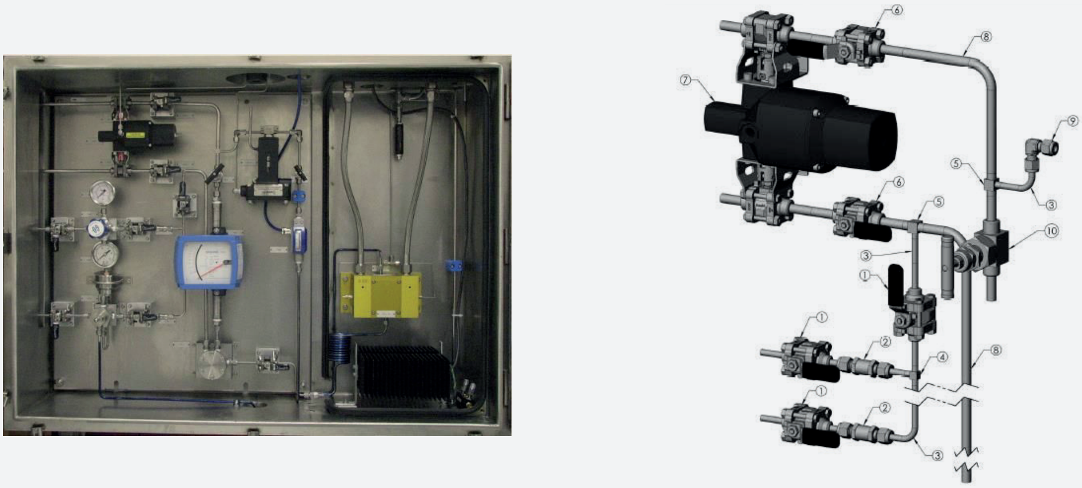
SC1

HF 85.1 wt%

H2O 1.1 wt%

ASO 7.8 wt%

The TALYS-HF on-line process analyzer measures complete HF acid purity



HF acid field sample system detail, showing welded fast-loop sub-assembly, Hasteloy C and sapphire sample flow cell, and HF leak detection with auto-emergency-shutdown system.

The use of a fiber-optic-based 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 be expanded to monitor multiple process streams with a single analyzer. In some HFUs, this enables a requirement for 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.

In addition to these benefits, there are other useful 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 isostripper 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.

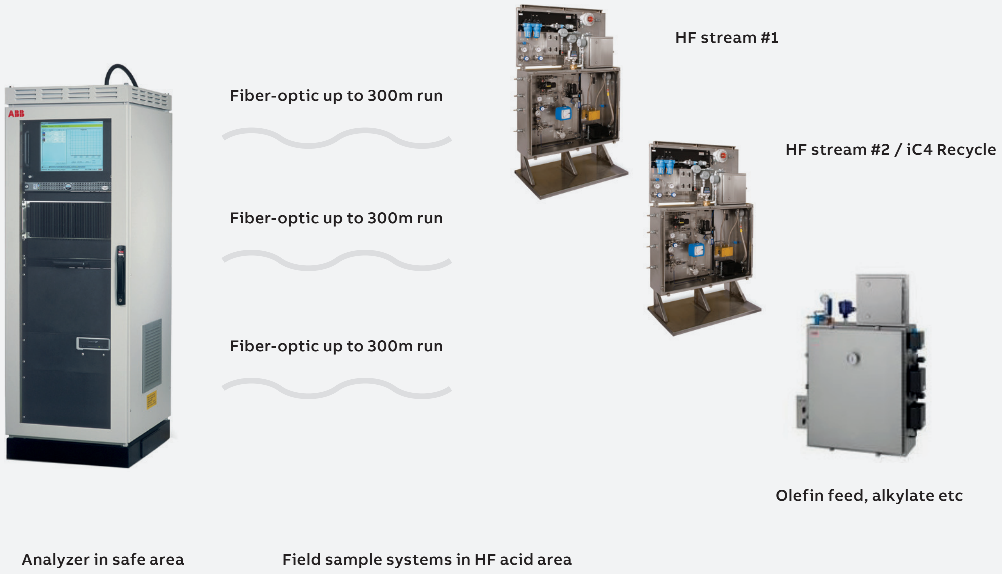
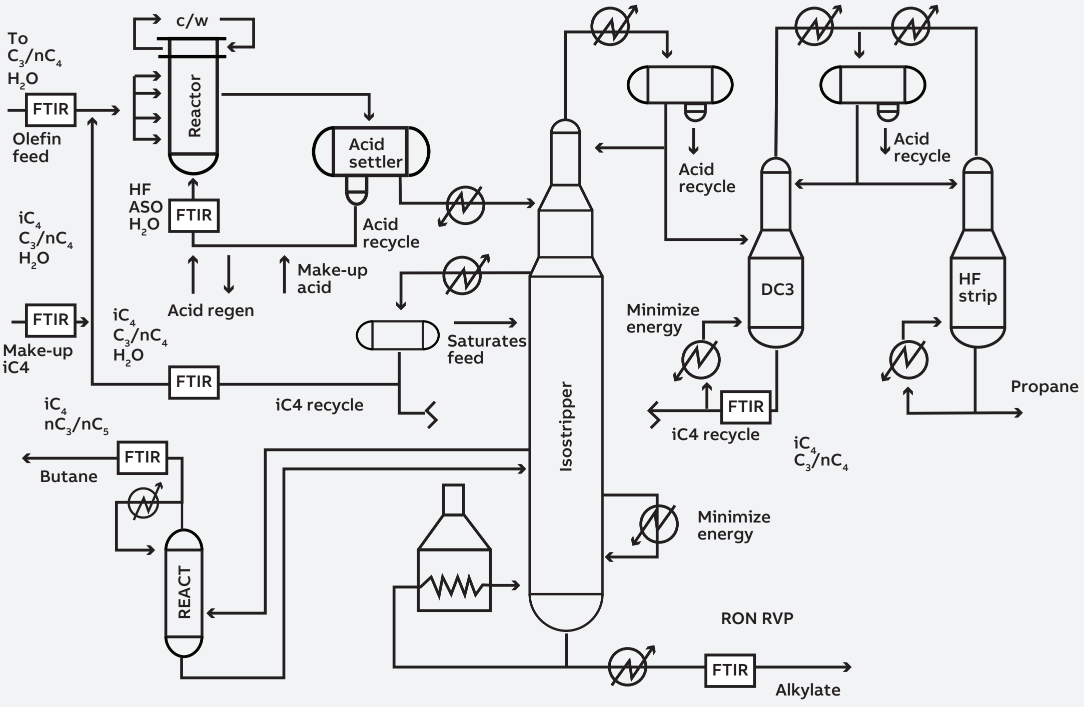


ABB FTPA2000-HP20 multi-channel system for full HF Alkylation Unit optimization



Examples of FT-NIR analyzer measurement points for full HF alkylation unit optimization

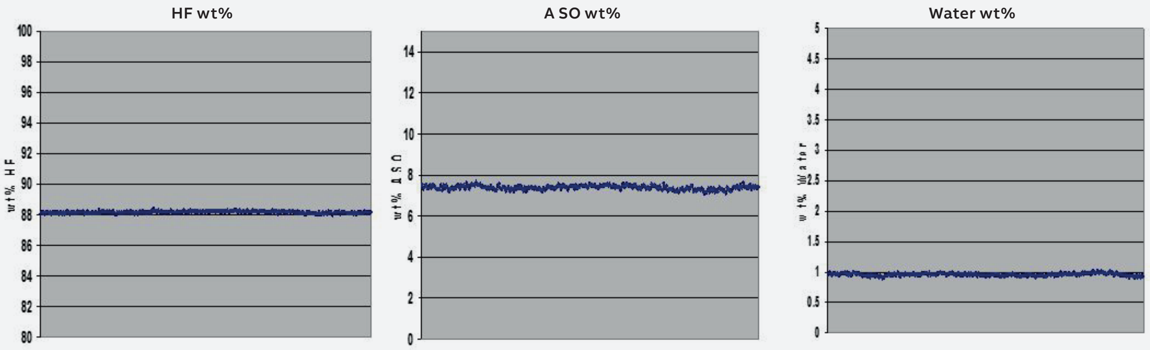
In the multi-channel version of the analyzer system, typically one stream is dedicated to the most important HF acid recycle analysis (HF stream #1) and a further field acid area sample system can be used either for a second HF stream, for example the HF regeneration overhead on some units (HF stream #2) or further HF-tainted hydrocarbon streams such as the iC4 Recycle. Furthermore, HF-free hydrocarbon streams (olefin feed or alkylate product) can be added using sample systems with conventional metallurgy, which may be located outside the unit acid area.

Overall:

- Feed rates, alkylate yield, and alkylate octane are maximized to an economic optimum, subject to operating constraints.
- Isobutane-to-olefin ratio (typically around 10:1 to reduce side reactions, but limiting yield) 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 made possible as the water content of the catalyst can be better managed
- 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.
- Less aggressive regenerator operation and lower acid losses
- Higher quality alkylate and yields
- Acid-to-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
- There is a major reduction in the risk of unanticipated unit corrosion due to better acid strength control.



Run-time data from ABB on-line FT-NIR HF Alkylation Unit analyzer: 2-days steady-state conditions HF%, Water% and ASO%
Measurement ranges are HF 80–100 wt%, ASO 0–15 wt%, water 0–5 wt%

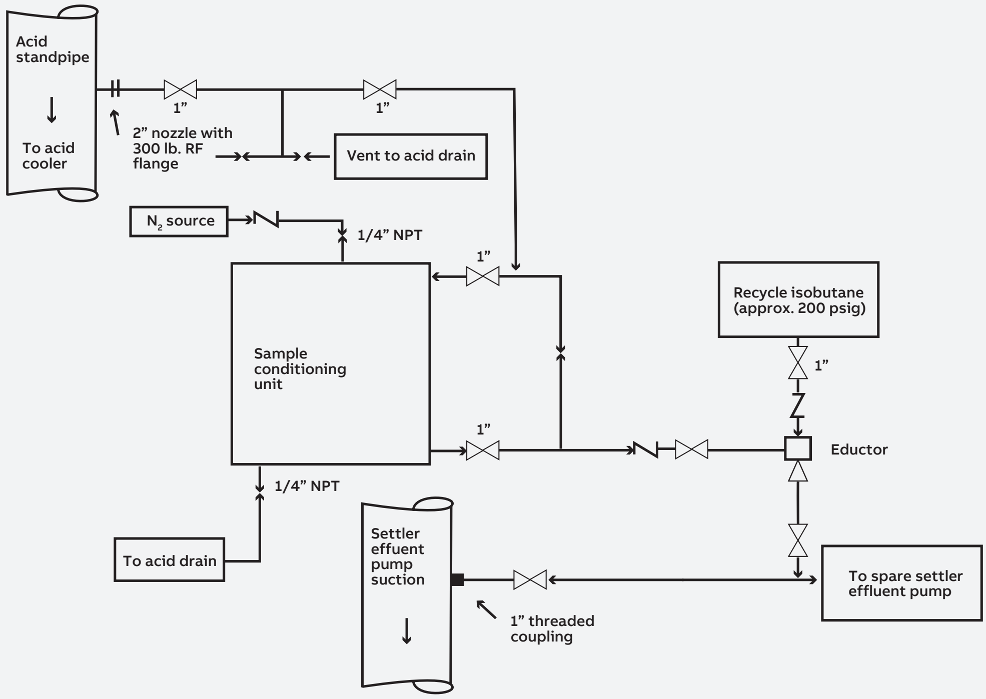
Note the significantly improved precision of the on-line analyzer compared with equivalent laboratory test results. Repeatabilities are 0.1% for HF% and ASO% and 0.03% for H2O% (absolute) by the on-line FT-NIR method versus 5× to 10× worse by standard test methods (acid-base titration, gravimetric and Karl-Fischer titration).

In this white paper we have reviewed the use a pre-calibrated on-line process FT-NIR analyzer system for monitoring HF acid purity in the HF acid catalyst recycle stream for HF alkylation units. The important impurities in the acid recycle stream (acid soluble oil [ASO] and water) have significant impacts on key process parameters such as alkylate octane and unit corrosion rates. Moreover, rapid deterioration in HF acid quality can occur due to upstream process unit (and therefore HFU feed) upsets.

The traditional analytical control for the unit was based on frequent (daily) manual field sampling for HF acid samples and laborious laboratory work-up using standard chemical methods. These techniques exposed refinery personnel to the potential of HF release and had both poor precision and were slow to execute. The on-line analyzer system therefore provides much more rapid, significantly more precise and very much safer data for unit optimization.

References

1. NPRA, Annual Meeting, San Antonio, TX, “Advances in Hydrofluoric Acid Catalyzed Alkylation”, March 23-25, 2003



Typical Piping diagram & Sample Take-off Arangement - Sample take-off from acid cooler downpipe and return to iC4 recycle pump-suction via eductor or other low-pressure return where available.

ABB Inc.
Measurement & Analytics
3400, rue Pierre-Ardouin
Québec (Québec) G1P 0B2
CANADA
Tel: +1 418-877-2944
1 800 858-3847 (North America)
E-mail: ftir@ca.abb.com

abb.com/analytical

WP/HFUUNIT-EN 11.2017