

Acid Strength Control in a Sulfuric Acid Alkylation Unit

Joseph N. Congiundi
Equistar Chemicals, a LyondellBasell company
8280 Sheldon Road
Houston, TX 77530
P.O. Box 777 (77530-0777)

Stephen G Finlayson
Applied Manufacturing Technologies
3200 Wilcrest Drive
Westchase III Suite 400
Houston, TX 77042

Prepared for Presentation at the 2010 Spring National Meeting, San Antonio Tx,
Session T7 - 13th Topical Conference on Refinery Processing (#15),
Model Predictive Control (MPC)

Copyright LyondellBasell/AMT LP
April 2010

AICHE shall not be responsible for statements or opinions contained in papers or printed in its publications.

Summary

Sulfuric acid alkylation units are characterized by the interaction between two very different and competing process behaviors: the hydrocarbon side, where iso-butane and C3/4 olefins are reacted to form alkylate; and the sulfuric acid side, which acts to catalyze the reaction. On the hydrocarbon side the reaction occurs very quickly, while the acid side literally takes days to settle-out after a load change.

Alkylation units where feed compositions and rates vary require constant manipulation of the acid to control both the acid material balance and the strength of the acid that has been spent (spent acid). The long response times make it difficult for operations to run these units at the optimum acid consumption, while at the same time controlling the acid strength and the acid inventories. Unit conditions can change in a few hours, making it challenging for the operator to account for these changes on the acid side of the process, which results in higher than necessary acid consumption.

Introduction

A large number of alkylation units in industry today use a sulfuric-acid-based process technology. The sulfuric acid is used to catalyze the alkylation reaction at a relatively high hydrocarbon-to-acid ratio. Sulfuric acid contacts the hydrocarbons in a once-through fashion, and then it must be regenerated typically by a third party. Fresh acid purchase is expensive and represents one of the large components of the operating costs for this type of unit.

A DMCplus controller has been developed for LyondellBasell's Channelview alkylation unit to control the spent acid strength. The alkylation unit has two trains (A&B); each train contains three contactor/settler systems operating in series with respect to acid flow and parallel with respect to the hydrocarbon flow. The multi-variable control (MVC) application controls the spent acid strength from each train and the acid interface level in each settler. There are four acid flows to control three levels and the spent acid strength resulting in a fully determined 4x4 system. The fresh acid flow rate sets the series acid strength through the first two contactors in each train and the final spent acid strength from each train. Levels are controlled by adjusting the series acid flows from each of the first two settlers as well as the spent acid flow from the last settler in each train

This paper discusses the application of MVC to this sulfuric acid unit. The application was designed to minimize acid consumption, stabilize spent acid strength, and manage acid inventories. The challenges presented by this unique process, as well as methods used to exploit dynamic and steady-state process behavior are discussed.

Process Overview

The alkylation unit is a low-temperature process where olefins are reacted with iso-butane in the presence of a sulfuric acid catalyst. The resulting product is a branched, paraffinic, high-octane blending component. There are two alkylation reaction units running in parallel – "A-train" and "B-train" – which produce the alkylate product.

The olefin feed is a combination of butylenes from various sources, including an MTBE unit, and a refinery FCC C4 stream. Isobutane is consumed in the alkylation reaction and must be continually made up in order to maintain the desired iso-butane to olefins ratio (I/O).

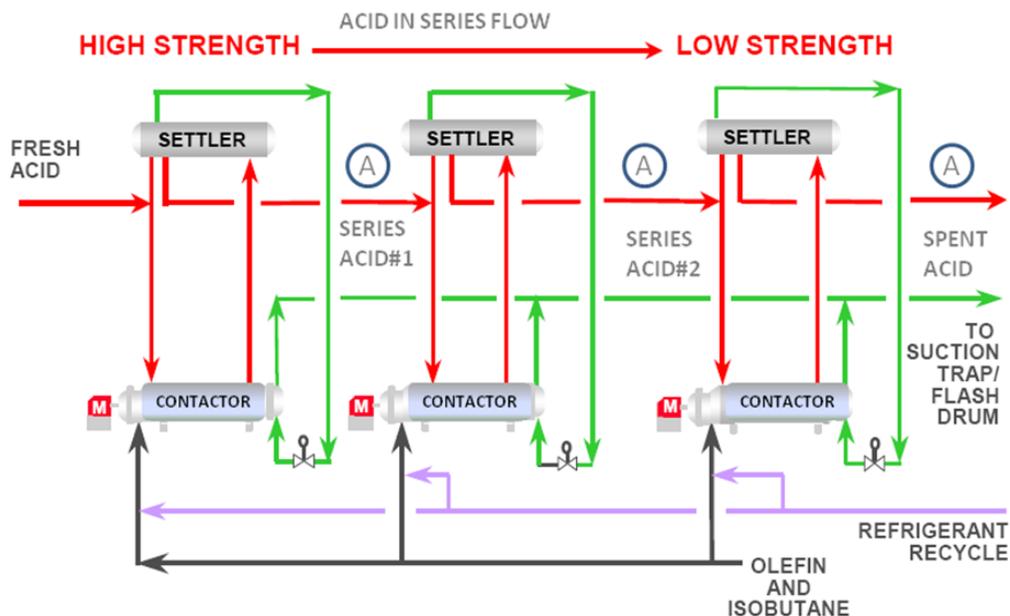


Figure 1: Single-train Process Flow

Each contactor is fed a stream of mixed olefins and iso-butane at an I/O ratio of roughly 8:1. The contactor/settler systems contain a very large volume of sulfuric acid which acts as a catalyst for the alkylation reaction. In each contactor/settler system, the acid/hydrocarbon mixture/emulsion is flowing from the contactor to the settler; once the acid has separated, it flows back to the contactor. Fresh acid at a concentration of (98 wt %) is pumped into the first contactor in each train. The series acid from the first settler is sent to the second contactor/settler pair; the series acid from this contactor/settler pair is sent to the final contactor/settler pair.

The alkylation reaction is a function of acid activity. Higher acidity increases isobutane solubility, but enhances polymerization reactions. The limits on suitable acid strengths generally range from 99.5% to 90%. Below the minimum, olefin buildup in the acid increases greatly. Fresh acid flows are adjusted to maintain the spent acid strength from the last contactor of each train to a minimum of 90%.

Consequently, series #1 acid strength is typically around 96% or greater, and series #2 acid strength is typically around 93% or greater. The series acid flows and the spent acid flows are adjusted to control the acid/hydrocarbon interface levels in each of the settlers.

Controller Objectives

The MVC controller has been designed to minimize acid consumption by controlling the spent acid strength against a low limit. To do this, the controller will adjust all four acid flows in each of the A and B trains, and control settler acid interface levels as well as spent acid strength.

The controller has been designed specifically to:

- Maintain settler levels within specified range by manipulating fresh, series, and spent acid flow rates.

- Account for the impact of feed and acid concentration changes, ambient conditions, and total olefins feed rate changes to each contactor.
- Control the spent acid strength leaving the third contactor in each train.

Controller Design

The process is fairly simple in terms of the independent and dependent variables. The controller design is also quite straightforward. The fresh acid, series, and spent acid flows are manipulated to control the three contactor levels and the spent acid strength. The feedforward disturbance variables are the calculated feed rate of the olefins to each of the contactors, the ambient temperature, and the series acid strength analyzer readings that are coming from the first and second settlers.

Olefins component feed flow is the most direct way to measure the amount of reaction occurring in each contactor. Calculating the olefins fed to the contactor, rather than just the overall feed rate, was found to be the best way to capture the feed rate changes and olefins composition shifts on each contactor. On-line analyzers in the feed system are available for the calculation of olefins feed rate.

The series acid strength analyzers measuring the acid strength leaving the first and second settlers provide an indication of any disturbances that will affect the spent acid strength. However, these analyzers are not independent of the acid flows or the olefins feed flows and, as such, they cannot be used directly. For each of the upstream contactors, models were developed that predict the series acid strength based on the independent variables from the associated contactor. The prediction errors from these models are then used as feed-forward variables in the final acid strength prediction for each train. This provides a reliable way to capture any unmeasured disturbances that originate with the fresh acid strength/quality or enter the system via the olefins feed system.

Ambient temperature has been included because it was found that ambient temperature affected the level indications in each of the settlers. As the daytime temperature increases the settler level (acid/hydrocarbon interface level) indication increases.

General Operating Issues

This process is characterized by vessels with very large hold-up or volume operating with relatively low acid throughputs. Due to the very large hold up, response times for the acid interface levels are uncharacteristically long. Further, the level responses have very different dead-times for acid entering the contactor versus acid leaving the associated settler.

The long residence time also results in an extremely slow response for the spent acid strength, making it difficult for operations to control the acid strength tightly. Each contactor has an on-line acid strength analyzer that measures the strength of the acid leaving the contactor. Although these cannot be used directly in the controller, they were used to predict the effects of unmeasured disturbances on acid strength that occurred in the first and second contactors. The measured strength using these analyzers had to be conditioned to reject the hydrocarbon carry through effect. This is discussed later in the analyzer signal conditioning section.

Plant Testing

During the plant test, the data was examined and the move frequency was regularly reduced to the point where moves were being made on a 12 to 24-hour frequency.

After analysis of the initial test data, the response time for each of the contactors was found to be in the range of 24 to 30 hours. When combined in series, the overall response time of the three systems in series was just over three and a half days.

With the acid/hydrocarbon levels open, each contactor could be tested separately. With the extremely long acid response relative to the moderately long level response, a strategy was required to manage the levels while getting the long response moves on the acid flows. During the first week of plant testing, the unit was monitored closely by the application development team. Once the strategy was understood and the operations team was comfortable with the testing technique to be used, the test was turned over to operations for the remainder of the test period.

Measurement Issues: Analyzer Signal Conditioning Requirements

In order to use the series acid strength analyzer from the #1 and #2 series contactor/settlers for the spent acid strengths of the A and B train, the signals had to be properly conditioned.

Filtering the Acid Strength Analyzer Readings

The analyzer readings were subjected to significant and frequent oscillations or spiking in the strength measurement in all of the online analyzers. The analyzer readings were conditioned by applying very heavy filters to the acid signals. The figure below shows the raw and filtered acid strength signal for a typical acid strength reading. Filter times of 100 to 120 minutes were used on the acid strength signals in order to remove this higher frequency oscillation in the measurements.

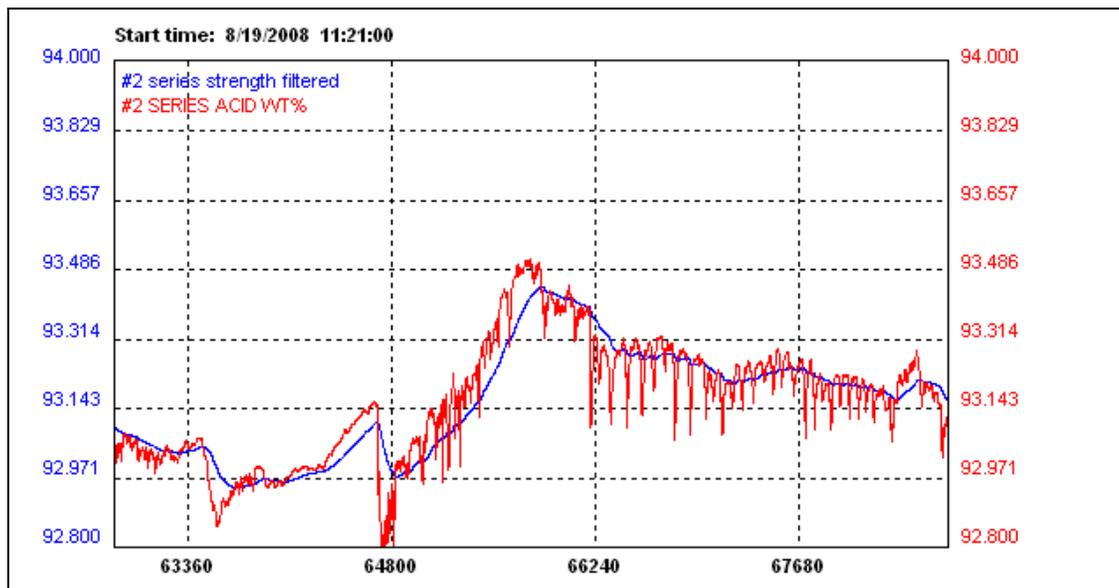


Figure 2: Raw and Filtered Acid Strength

The Series Acid Effect

Changes to the series acid flow out of any of the contactors were found to have an effect on the series acid strength as measured by the acid strength analyzer. This was thought to be caused by “carry-through” of hydrocarbons with the acid exiting each settler. The amount of acid “carry-through” changes proportionately with the acid flow rate; as the acid flow is increased the hydrocarbon content in the acid increases. The acid strength response from each contactor/settler was analyzed using the series

flow from that settler as one of the independents and a very consistent response was found for series flow versus acid strength.

Any hydrocarbon that is carried through from one settler to the next will settle out in the downstream contactor/settler system. Because the upstream analyzer reading contains this hydrocarbon carry-through effect, the upstream strength analyzer cannot be used directly in the downstream settler strength modeling and must be corrected prior to use in the online model. This was accomplished with an online application that subtracted the dynamic series flow effect from its respective strength analyzer reading prior to use in the controller model.

Acid/Hydrocarbon Level Signals

The level signals from the contactors were affected by ambient temperature and possibly internal equipment conditions in the settlers. Because these are controlled inside the DMC controller as integrating variables, the open loop prediction of the level can be impacted significantly by the erratic level indication. The erratic signal will cause the open loop prediction of each level to vary significantly.

The time to steady state associated with the acid strength is very long (3.75 days) while the response time of the levels is much quicker (120 minutes). This means that any unnecessary rotation of the level will significantly impact the controller performance. In order to minimize this effect, all levels signals were filtered with a standard first order filter using a 40-minute filter time. The plot below shows a typical level signal both filtered and unfiltered. In addition, level models in the online MVC Controller were tuned with a very low rotation factor of 0.01 to minimize rotation of the prediction due to erratic level readings. Note that usually such a low rotation factor will provide poor level control, but this was not the case due to the extremely good open loop prediction of settler levels.

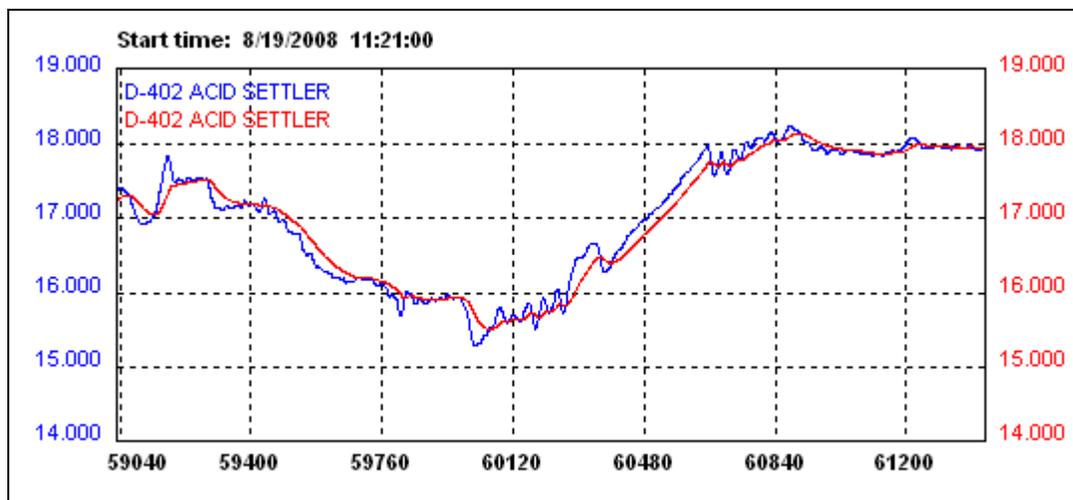


Figure 3: Raw and Filtered Level Signal

Implementation Details: Spent Acid Analyzer Lab Bias Updating

The A and B train spent acid analyzers must be biased based on the unit lab in order to eliminate the drift in the analyzer reading. The unit lab takes a measurement several times per day and these results will be used to update the bias in the analyzer. The strategy utilizes AspenIQ to validate the conditioned analyzer readings and then to carry out the bias updating with the lab. After commissioning it was

found that using the average of the last 20 lab samples minimized any oscillation induced by the lab analysis technique. Based on this average, an update of the analyzer reading is performed to bring the analyzer into agreement with the unit lab results.

Online Model Gain Adjustment

The gains obtained in the analysis of the plant test data represent a linear gain for the average acid and feed flow which occurred during the plant testing phase. As both of these flows change, the process gain of acid strength to a change in feed rate or a change in olefins feed can change considerably. Since the unit charge rate moves around significantly, using a constant gain across all expected operating conditions would not be possible. Partial differential equations for acid strength as a function of feed and acid flow were developed to estimate the change in the acid strength gains.

These calculations were implemented within the control application and the controller gains are adjusted online at every cycle of the controller. A simplified mixing model may be utilized to calculate the non-linearity of the acid strength gains.

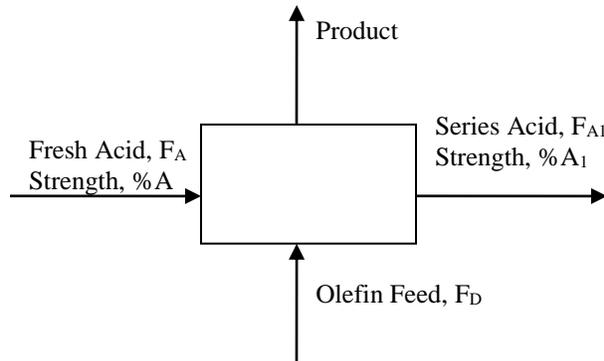


Figure 4: Simplified Mixing Model of Acid Settler and Contactor

By performing a material balance around the acid phase, the series acid strength may be estimated:

$$\%A_1 = \frac{F_A \cdot \%A}{F_D \cdot k + F_A} \tag{1}$$

The k constant is assumed to be a constant fraction of dilution of the olefin feed into the acid phase.

To derive the non-linearity, the partial derivative of the acid strength is taken with respect to the fresh acid rate and the olefin feed rate.

$$\frac{d(\%A_1)}{d(F_A)} = \frac{F_D \cdot k \cdot \%A}{(F_D \cdot k + F_A)^2} \alpha \frac{F_D}{(0.15 + F_A)^2} \tag{2}$$

$$\frac{d(\%A_1)}{d(F_D)} = \frac{-F_A \cdot \%A \cdot k}{(F_D \cdot k + F_A)^2} \alpha \frac{-F_A}{(0.15 + F_A)^2} \tag{3}$$

F_{DK} term in the denominator is assumed to be a constant value of 0.15 based on process data, since it is approximately 1 % of the fresh acid flow rate. The partial derivatives are then developed into gain multiplier equations which are used to alter the acid strength model gains online relative to base rate conditions.

Gain Multiplier for Series Acid Strength to Fresh Acid Rate:

$$\frac{F_D}{F_{DBase}} \frac{(0.15 + F_{ABase})^2}{(0.15 + F_A)^2} \quad (5)$$

Gain Multiplier for Series Acid Strength to Olefin Feed Rate:

$$\frac{F_A}{F_{ABase}} \frac{(0.15 + F_{ABase})^2}{(0.15 + F_A)^2} \quad (6)$$

Performance and Benefits

The benefits from the controller were two-fold. Due to the DMC model controlling the three settler levels in each train, the acid flows were substantially stabilized. Previously, the operators would constantly chase the settler levels, which would cause large dynamic swings in the intermediate acid and spent acid strengths. In addition, the level instrumentation would provide erratic readings during the heat of the day and swing between day and night, which would make it very difficult to manually control the settler acid inventory. Since the model was able to predict the levels extremely well, the controller tends to manage acid inventory exceedingly well, while not taking action on the erroneous level readings.

Fresh acid costs for a typical alkylation unit are approximately 15 – 20 million dollars a year, representing a significant percentage of a unit's operating costs. Therefore, minimizing acid consumption is very important and can provide substantial economic benefit. Since the application was able to stabilize the process, the controller was able to drive the spent acid strength much closer to the minimum, thus minimizing acid consumption. Results show that the acid consumption in the unit was reduced by an average of 8%, which corresponds to roughly \$1,500,000 per year in savings.

Refer to Figures 5 through 10 below to compare control of the settler interface levels and spent acid strength prior to and after implementation of the MVC application. Each of the three pairs of trends is on the same span and shows a fifteen-day window. The first pair of plots shows the settler acid/hydrocarbon interface levels in each of the settlers. The level control is greatly improved in the MVC Control plot (Figure 6) even though there is still spiking occurring in the level signals, which is discussed earlier. The controller is able to reliably control the levels and spent acid strength even though this type and severity of measurement error occurs routinely. These trends demonstrate the significant reduction in variability of the settler levels and the spent acid strength, as well as the reduction in acid flows.

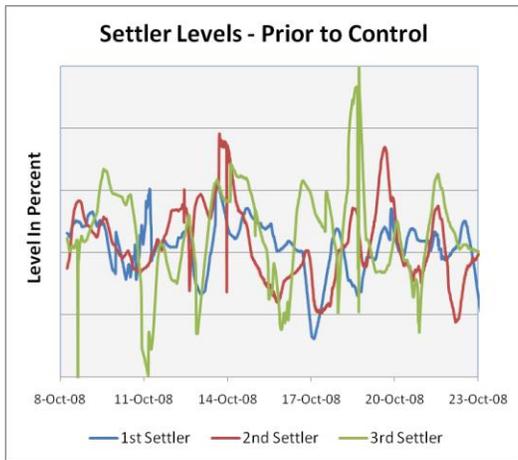


Figure 5: Settler Levels Prior to MVC Implementation

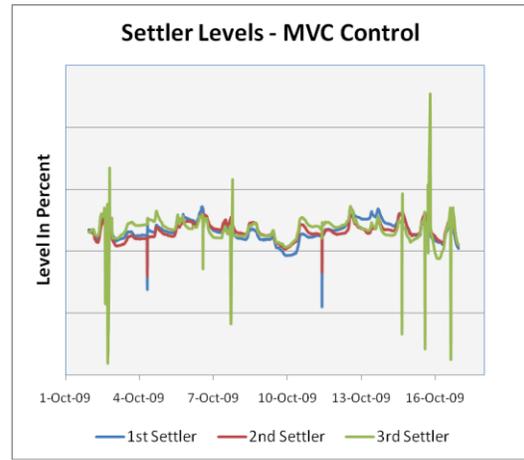


Figure 6: Settler Levels After MVC Implementation

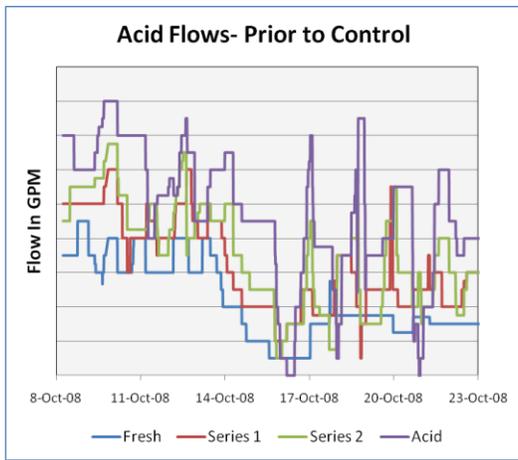


Figure 7: Acid Flows Prior To MVC Implementation

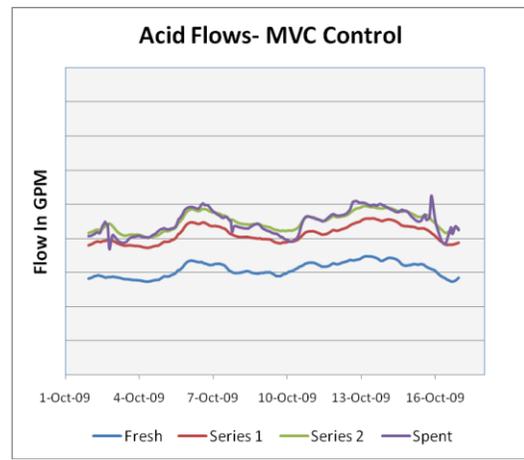


Figure 8: Acid Flows After MVC Implementation

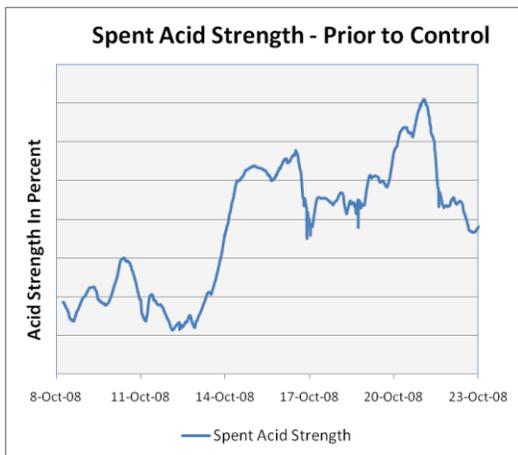


Figure 9: Spent Acid Strength Prior To MVC Implementation

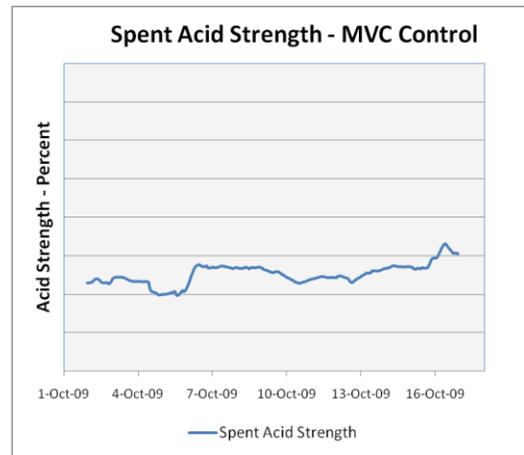


Figure 10: Spent Acid Strength After MVC Implementation

Conclusions

The acid strength controller was implemented successfully on LyondellBasell's alkylation unit in Channelview, Texas. Although there were several operating and measurement issues associated with this unit, they were successfully overcome during the development of the application. The application has been running for just over one year and has demonstrated significant value to LyondellBasell. By incorporating the operation's lab strength analysis into the online measurement, managing the levels in a much more reasonable fashion, and driving the acid consumption to a minimum, the controller has been widely accepted by the operators directly involved in running the unit. Significantly reducing the acid consumption and hence unit operating costs have resulted in strong support from plant management for the application. This application has demonstrated that the acid side of sulfuric acid alkylation units can be controlled using MVC technology, and the resulting application will have high operator acceptance and a high return on investment.

Acknowledgement

The authors would like to thank the management of LyondellBasell for providing them with the opportunity to develop this MVC application and allowing them to share the implementation details of the projects. A special thanks is also extended to the operations staff at the Channelview Complex who were directly involved in the model development effort and played a key role in making this project successful.

References

Introduction to Sulfuric Acid Alkylation Unit Process Design, Jeff Canton, Brian Racen, Greg Troutman, DuPont STRACO Clean Fuel Technology, 11350 Tomahawk Creek Parkway, Suite 200, Leawood, KS