Testing Catalyst Additives for Sulfur Reduction in Cat-Naphtha

María Paz Chiavarino

Axion Energy FCC Process Engineer

Collaboration: Uriel Navarro Uribe

PhD in W. R. Grace & Co Tech Service

REFCOMM RIO DE JANEIRO 29 Sept - 3 Oct 2014

CatCracking.com

AXION energy

GRACE

Enriching Lives, *Everywhere.*™

Kick Off

- Maximum Allowable Sulfur in Gasoline is getting lower all around the world. Upper limit in Latin America is moving towards 10-50 ppm range.
- Approximately 5-7% of FCC feed Sulfur ends up in FCC gasoline, impacting 80-90% of total sulfur in gasoline pool in every refinery.
- Axion Energy Argentina SA is getting ready in advance in order to have gasoline product under 50 ppm spec, minimizing alkylate utilization.

Summary

- In 2012 Axion Energy Argentina SA performed a test run in FCC unit replacing about 25% of equilibrium catalyst inventory by a Grace Davison's cat-naphtha sulfur reduction additive named GSR-5.
- A base case was established prior to the test setting unit operational conditions and laboratory analysis results for typical products.
- Mathematical expressions were developed by Uriel Navarro Uribe from Grace's Tech Service for naphtha properties and sulfur content. By using this equations we were allowed to estimate sulfur content without the additive and therefore, additive efficiency comparing against real lab results.

Summary

- The main objective was reducing as much as possible sulphur naphtha content. When maximizing LCO product, we capture additional incentives in gasoil pool, taking into account that some percentage of heavy cut naphtha goes to LCO.
- Additional effects were observed in propane & butane products. Sulfur species were removed from LPG and this impact with great optimization in caustic treatment.

Pre-Trial Planning

- Many lab analysis were done in order to understand product's quality variability and establish baseline.
  - Density, Distillation and Sulfur Content for feedstock, recycle to the reactor (HCO), gasoline, LCO, Slurry (Bottoms).

- E-cat samples were sent to Grace's USA Labs and to an alternative supplier for routine analysis (physical & chemical equilibrium catalyst properties).
  - **Vanadium** was used as the chemical marker to calculate the amount of sulfur reduction additive in the catalyst inventory. Any change in the Nickel content on the ECAT was used to review the amount of vanadium coming from the feed and to review the correlation developed for additive calculation.

Pre-Trial Planning

- A base case was developed during two months before the trial considering:

  – **Unit operation variables:** Reactor temperature, Preheat Temperature, Regen Temperature profile, Cat/Oil, CCR, air flow, stripping steam, Total Inventory and Catalyst Addition Rate.

  – **Product Properties:** Feed and FCC naphtha properties were used to develop the correlation.

Addition Rate Plan

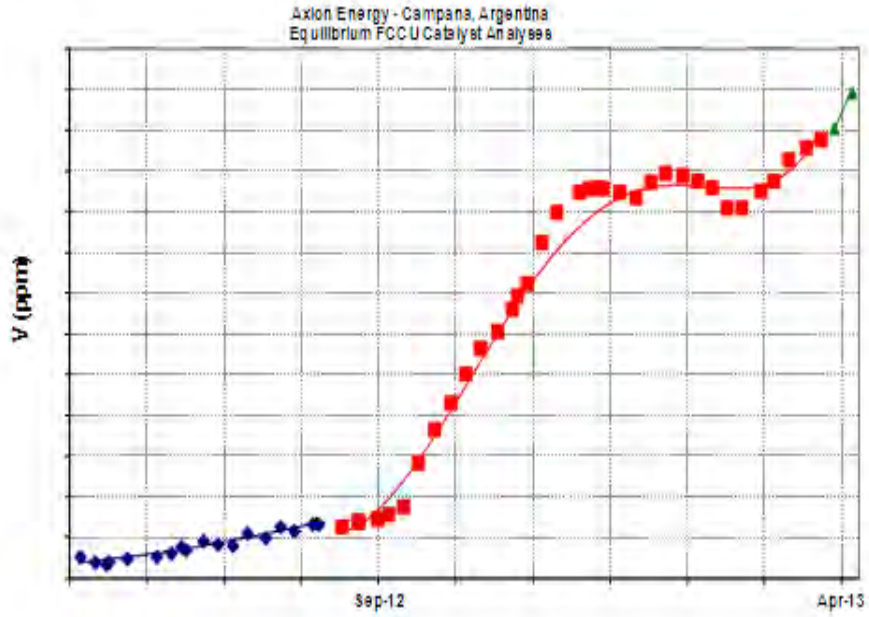
- Back to back inventory replacement was planned in two stages

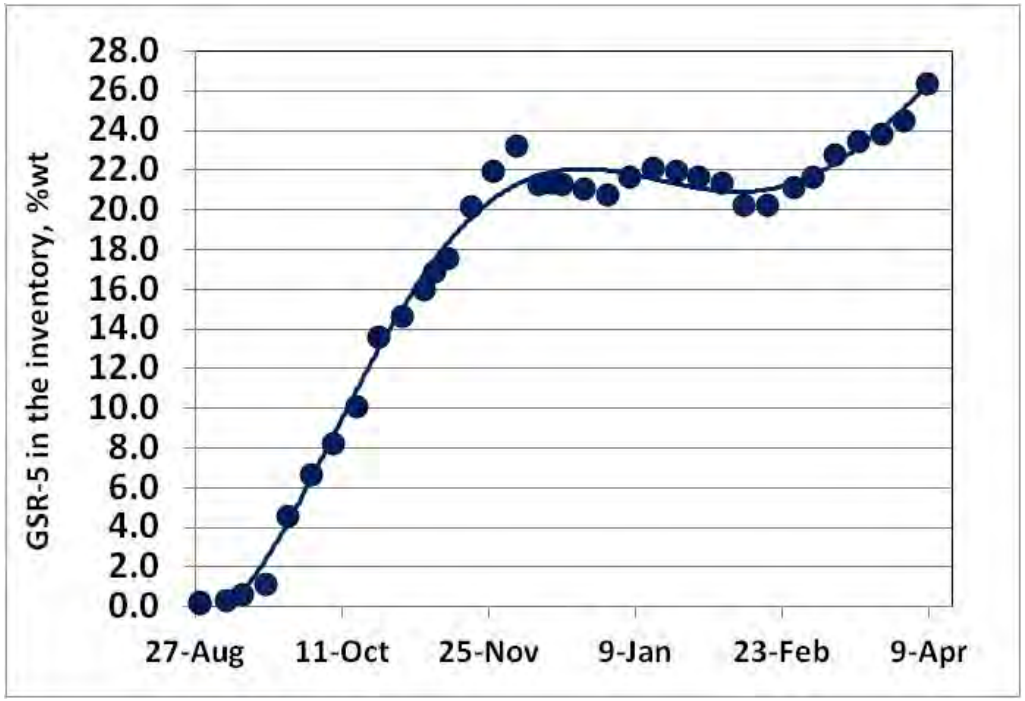
1. **Baseload**: 37% additive until reaching 25% of total catalyst inventory.
2. **Regular Additive Addition** 25% of total addition.

- GSR-5 additive functionality is based on GRACE DAVISON SuRCA technology and replaces 25% of fresh catalyst additions.
- Utilizes custom zeolite and matrix formulation. Axion informs slight yield change due to less activity in ECAT.
- Reduces 20 to 35% full range sulfur reduction.

Vanadium trend in ECAT

- As expected, vanadium content increased dramatically in equilibrium catalyst inventory during transition.
- This property allows to strictly adjust addition in order to reach desire GSR-5 content in the unit.

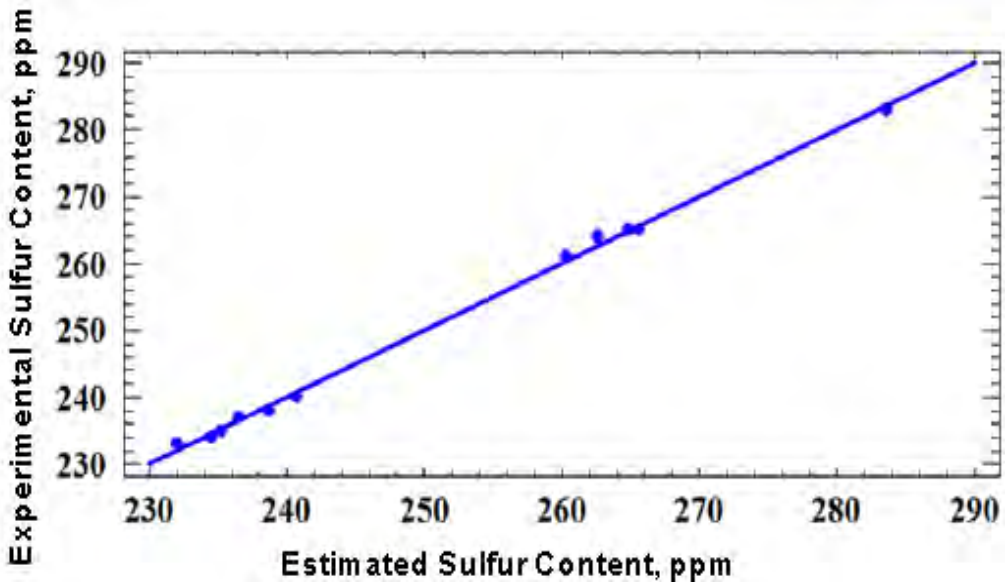




Base Case Results

Total Sulfur in cat-naphtha is dependent on:

1. Sulfur in feedstock
2. FCC-Naphtha FBP
3. FCC-Naphtha MeABP
4. FCC-Naphtha SpGravity



CatNaphta

$$TotalSulfur(ppm) = 3238.92 + 2.9523.FBP - 5336.83.SG + 2.6805.MeABP + 486.43.FeedSulf\ \%wt$$

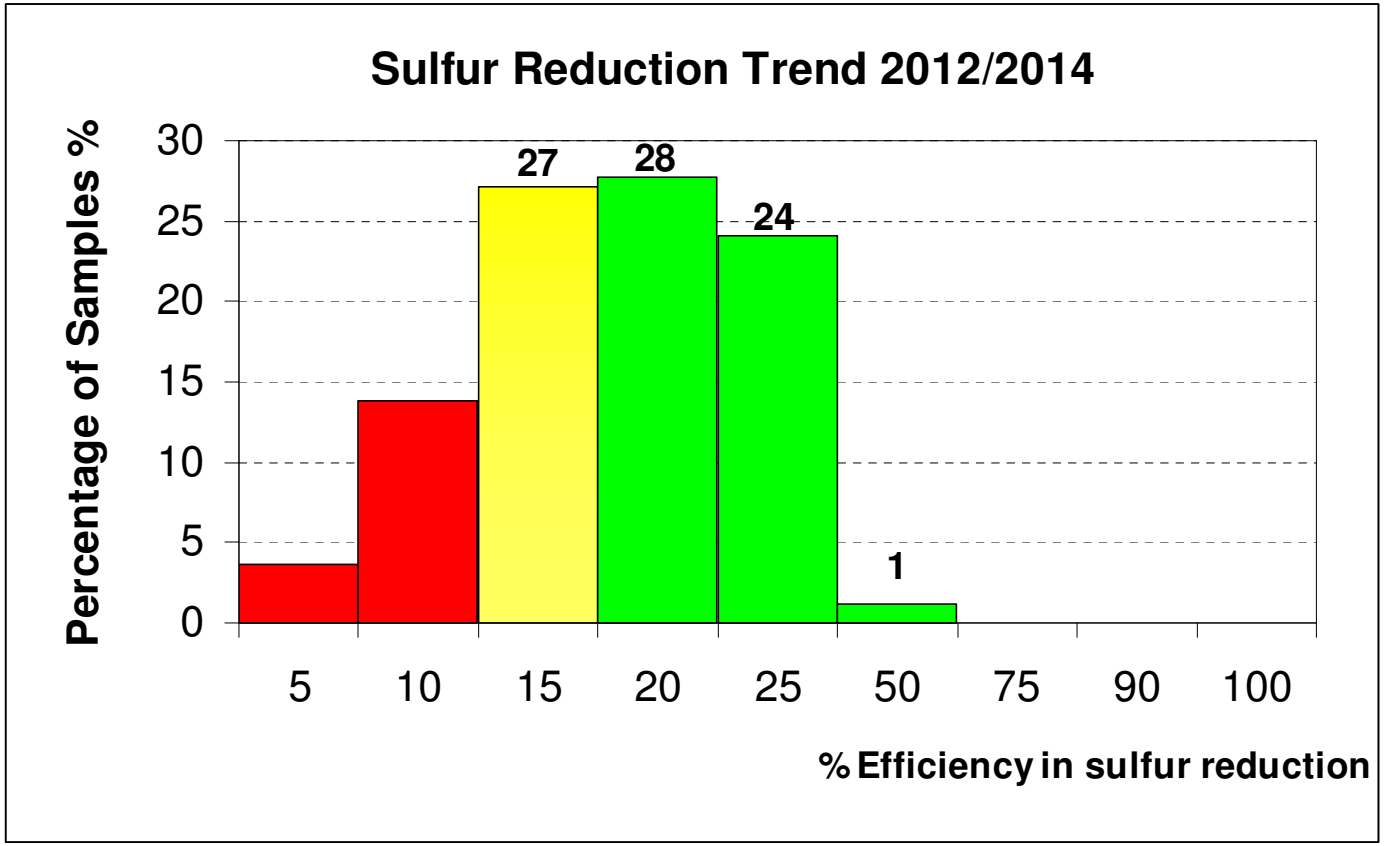
With this equation developed by Grace, was possible the sulfur content calculation in FCC naphtha.

Valid ranges in which applies:

Typical Sulfur Naphtha content varies between 230-285 ppm.

Typical FBP varies between 160-195 ℃ (320-353 ℉)

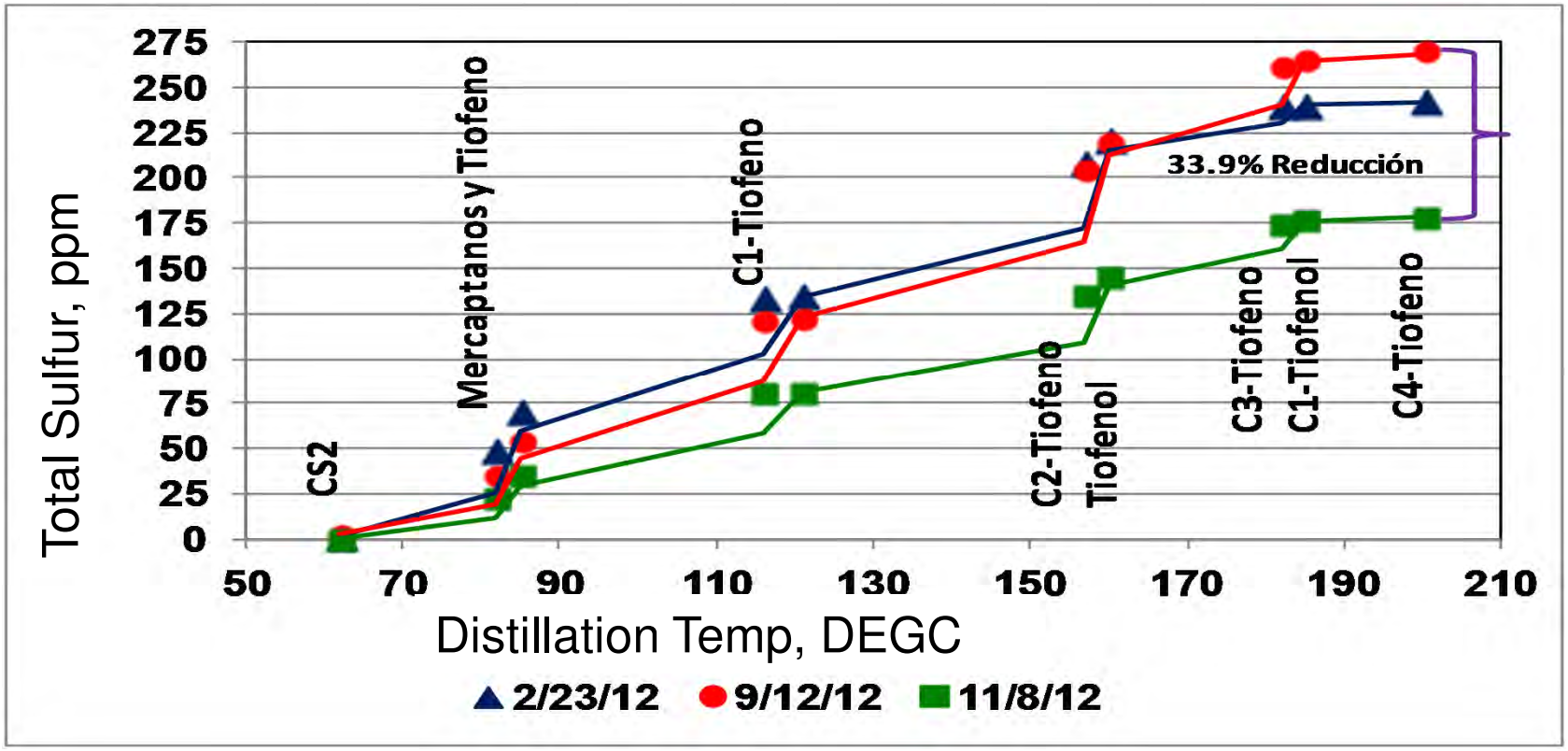
Sulfur Reduction Results in Gasoline



- 52% of samples above 20% sulfur reduction.
- 27% of samples between 10-15% sulfur reduction.

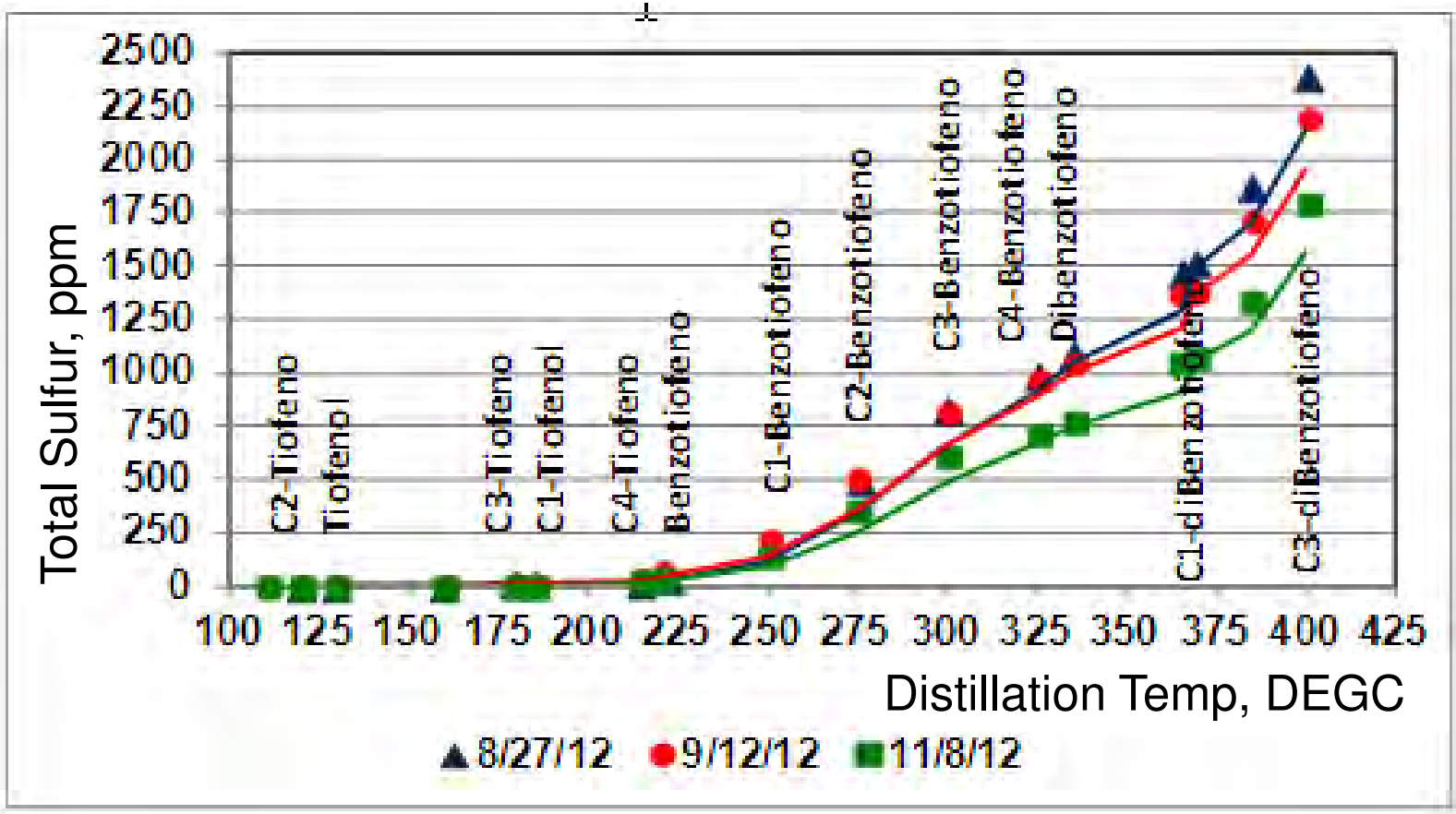
$$\text{Re}\,ductionEf = \frac{EstimatedSulfCont - LabSulfurContent}{EstimatedSulfurContent}$$

Sulfur Compound Distribution: Gasoline



- Cat-Naphtha sample taken on Nov 2012 shows 34% reduction in cumulative sulfur content.
- This results were provided by Grace Davison Labs, Maryland.

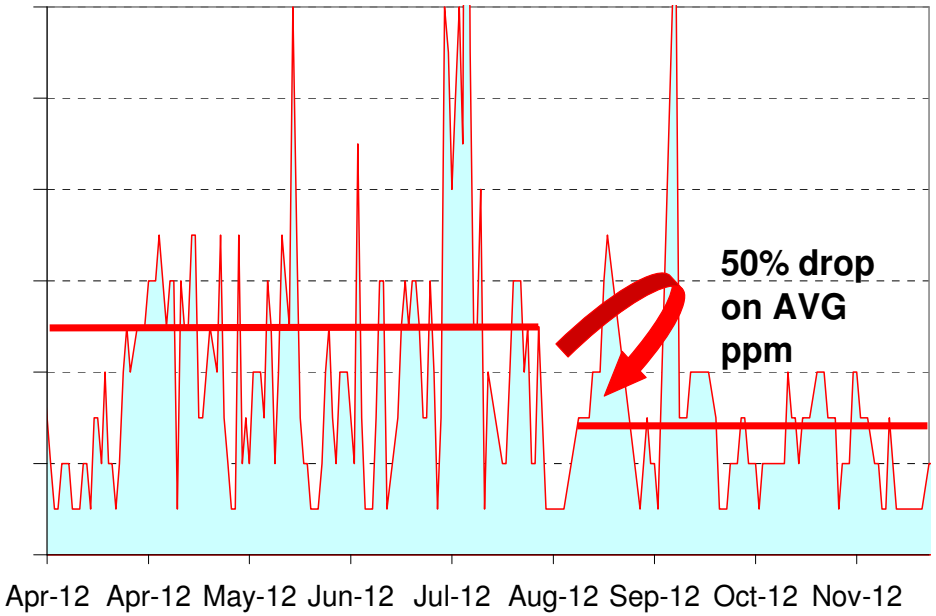
Sulfur Compound Distribution: LCO



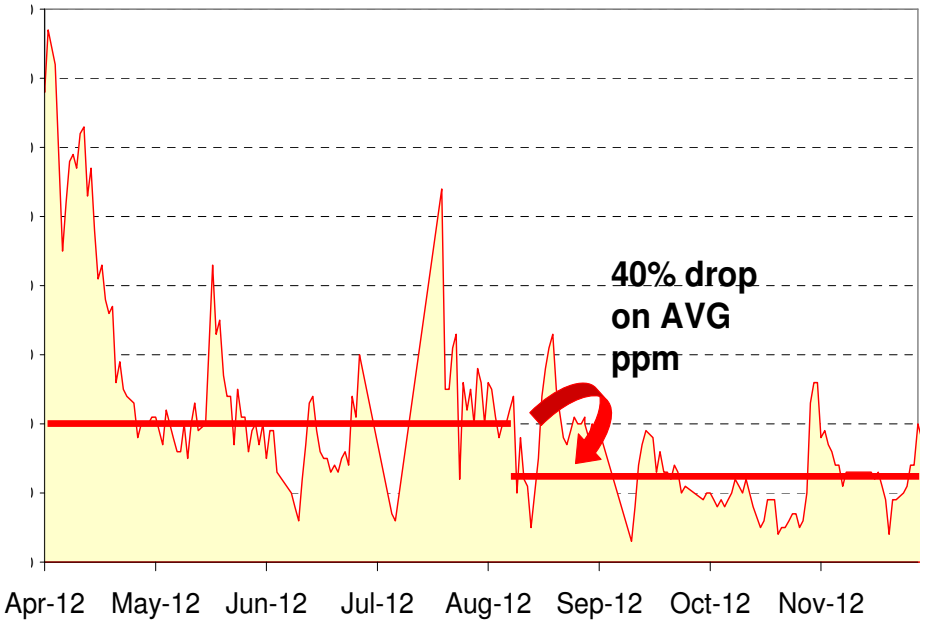
- LCO sample taken on Nov 2012 shows 34% reduction in cumulative sulfur content. This is due to 15-20% vol of gasoline in LCO withdrawal.
- This results were provided by Grace Davison Labs, Maryland.

Additional benefits: LPG sulfur reduction

Sulfur content in Propane



Sulfur content in butane



- By keeping constant caustic treatment Axion reduces 40-50% in sulfur content in LPG.
- Part of spent caustic volume is sent to external treatment. At constant LPG yield, by using GSR-5 we are able to reduce caustic consumption.

Thank you
Q&A

Contact Information
Mrs. Maria Paz Chiavarino
maria.p.chiavarino@axionenergy.com
+54 03489 492023
Axion Energy Argentina, Campana Refinery

Backup

Abstract

- In August 2012, Axion Energy planned a back to back inventory replacement for the FCC unit incorporating GRACE gasoline sulfur reduction additive. The main objective at that moment was reaching a legal limit of 50 ppm total sulfur in the gasoline pool by maximizing cat-naphtha volume and minimizing alkylate imports. Before the new additive was in the unit, a base case of study was performed. With that information, Grace Davison's technical support group developed mathematical expressions which allowed estimations for sulfur removal efficiency taking into account distillation curves, specific gravity and sulfur content in feedstock. In addition most operating variables were tracked, in order to understand how severity of the cracking reactions, conversion, temperatures and C/O ratio works with sulfur reduction. Cut-Point data from the main fractionator tower was also collected, understanding than the higher FBP of the product, the more difficult is to reduce the heavy sulfur species such as benzothiophenes is to achieve. Progressive effects were seen while content of sulfur additive was increasing in equilibrium catalyst inventory. 25 to 30% total sulfur reduction of FCC-naphtha was reached, with events of 40-45% at maximum severity in the unit. Some unexpected additional reductions were seen in LPG (propane and butane production before entering caustic treatment) getting margin improvements in spent caustic handling.