Low NOx Promoter Optimization at CITGO Petroleum Corporation’s Lake Charles Refinery

Summary

CITGO has successfully applied CP® P, Grace Davison’s third generation low NOx FCC combustion promoter, at their Lake Charles refinery. CP® P promoter replaced Grace Davison’s first generation low NOx promoter, XNOX®, and Grace’s second generation low NOx promoter XNOX® 2, and built on the successful application of these products.

CP® P promoter allowed CITGO to reduce regenerator excess O₂ levels by ~0.3% and improve CO emissions at similar NOx levels. Operating with lower excess O₂ provided additional operating flexibility in terms of feed rate and conversion. CP® P promoter steady state additions were 75% lower than the base XNOX® promoter, resulting in significant cost savings as well as improved product performance.

Table VI summarizes the results of the evaluation.
CP® P promoter has been successfully used in over ten FCC units to date, in addition to the FCCU’s at CITGO’s Lake Charles refinery. Commercial experience confirms that CP® P promoter has equal activity as a medium activity platinum CO Combustion additive like Grace Davison’s CP® 5 promoter. CP® P promoter is copper free. Unlike earlier generations of low NOx promoters, CP® P promoter does not require strict adherence to maintenance dosing. CP® P promoter can be used with immediate reduction in FCC regenerator afterburn and CO similar to traditional platinum-based promoters, but without lingering NOx emissions. Daily dosing of CP® P promoter, however, is recommended to achieve consistent CO, afterburn and NOx Control. 1

Background

CITGO Petroleum operates a 425,000 bpd sour crude refinery in Lake Charles, LA with three similar FCC units (A-Cat, B-Cat and C-Cat). All three FCCU’s are Kellogg Model II designs constructed in 1944 and have been revamped to include vertical risers, modern FCC feed nozzle and riser termination technologies. The FCC feedstock to each FCCU consists of sour vacuum and coker gas oils. Each FCCU operates in full combustion mode.

On October 6, 2004, CITGO agreed to a set of environmental operation parameters with the Environmental Protection Agency (EPA). CITGO installed wet gas scrubbers on each FCCU in 2005 and 2006 to meet SOx emissions limits of 25 ppm, 365 day and 50 ppm, seven day rolling average limits (25ppm/50ppm). CO limits of 100ppm/500ppm and a particulate limit of 1 lb/1000-lb coke were also established for each FCCU as part of the agreement.

CITGO’s agreement with the EPA also required that low NOx promoter and NOx reduction additives be used to establish long-term NOx limits. CITGO stopped Pt formulated CO promoter additions and evaluated several EPA approved low NOx promoters and NOx reduction additives in a series of short-term trials.

Grace Davison’s low NOx promoter, XNOX®, and NOx reduction additive, DENOX®, were identified as the best performing products during those short-term trials. CITGO then conducted an optimization evaluation with both products, followed by a demonstration period with the optimized addition rates.

During the demonstration period, it was evident that CITGO was successfully meeting EPA target NOx emission levels with the application of XNOX®, DENOX®, and tight control of flue gas excess O2. As a result, CITGO elected to stop the demonstration period and accept EPA standard NOx limits of 20 ppm/40ppm.

Low NOx Promoter Optimization

The use of combustion promoter is critical to meet FCC emission limits at CITGO’s Lake Charles Refinery. With NOX limits established, Grace Davison recommended that CITGO evaluate new, more active, non-platinum promoter additives available from Grace Davison.

The FCCU’s at CITGO operate within a narrow range between its NOx and CO emissions limits. CITGO typically minimizes flue gas excess O2 to inhibit NOx formation. However, as O2 is reduced, CO eventually begins to increase. CITGO is careful to add just enough combustion promoter to meet CO limits, but not excessive amounts that would risk elevated NOx formation.

Table VI
Low NOx Promoter Evaluation Data Summary

<table>
<thead>
<tr>
<th>Low NOx Promoter</th>
<th>Additive</th>
<th>NOx</th>
<th>CO (1)</th>
<th>O2</th>
<th>Afterburn</th>
</tr>
</thead>
<tbody>
<tr>
<td>XNOX®</td>
<td>Base</td>
<td>Base</td>
<td>Base</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>XNOX® 2</td>
<td>50% Base</td>
<td>~</td>
<td>Lower</td>
<td>Lower</td>
<td>~</td>
</tr>
<tr>
<td>CP® P</td>
<td>25% Base</td>
<td>~</td>
<td>Lower</td>
<td>Lower</td>
<td>~</td>
</tr>
</tbody>
</table>

(1) CITGO could have elected to operate at similar CO levels and lower NOx levels by re-optimization of the promoter additions and excess O2 levels.
has found that twice daily additions of CO combustion promoter are optimal to meet CO, NOx, and regeneration afterburn objectives.

After the conclusion of the test period, CITGO elected to further optimize promoter additions by testing a second generation low NOx CO promoter from Grace Davison, XNOX® 2, followed by Grace Davison’s newest low NOx CO promoter CP® P. CITGO and Grace Davison established a test plan which included product addition rates, data monitoring, and milestones.

**XNOX® 2 Combustion Promoter**

XNOX® 2 promoter is more active than XNOX® promoter and CITGO immediately reduced promoter additions by half, once they began using XNOX® 2 promoter.

CITGO noted a fundamental shift in the relationship between CO and O₂ in the FCC flue gas with XNOX® 2 promoter. Figure 22 shows that XNOX® 2 promoter shifted the CO vs. O₂ curve to a more favorable position. With XNOX® 2 promoter, CITGO was able to reduce excess O₂ for the same level of CO. By operating at lower excess O₂, CITGO was afforded additional operating flexibility in terms of rate and conversion within NOx emission limits and air blower constraints.

Flue gas NOx levels and Afterburn were maintained with XNOX® 2 promoter at half of the promoter additions as shown in Figures 23 and 24.
Data shown in Figures 22, 23 and 24 represents data from one of the three FCC units at the CITGO Lake Charles Facility. Similar conclusions were also made in CITGO’s other two FCCU’s.

**CP® P Combustion Promoter**

CITGO evaluated CP® P promoter after a successful application of XNOX® 2 promoter. CP® P promoter was more active than XNOX® 2 promoter and CITGO reduced additions of CP® P promoter by 75% relative to the base XNOX® promoter additions.

CP® P promoter was able to maintain the favorable relationship of CO versus O₂ that XNOX® 2 promoter provided as shown in Figure 25. As a result, CITGO continued to minimize excess O₂ without a CO penalty.

NOx production and afterburn continued to be controlled with CP® P promoter as shown in Figures 23 and 24.

**Acknowledgements**

The authors would like to thank CITGO Petroleum management for permission to publish this work.

**References**

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