

HP

Special Report

Clean Fuels

Y.-A. JOLLIEN, Tamoil S.A., Collombey, Switzerland; and
C. KEELEY, J. MAYOL, S. RIVA and V. KOMVOKIS,
BASF Corp., Iselin, New Jersey

Use an innovative cracking catalyst to upgrade residue feedstock

Tamoil S.A. is a major downstream organization active in Europe and Africa. This energy company has refineries in Hamburg, Germany, and Collombey, Switzerland, in addition to distribution networks operating in Italy, Germany, Switzerland, The Netherlands and Spain. The Collombey refinery operates a resid fluid catalytic cracking (RFCC) unit. The RFCC technology provides a cost-effective, flexible and reliable means to upgrade residue feedstocks to higher-value refined products.^a This unit processes a 100% residue feedstock with up to 7 wt% Conradson carbon residue (CCR) and a high contaminant metal level—the equilibrium catalyst (Ecat) nickel (Ni) is up to 6,000 ppmw and vanadium (V) is up to 6,000 ppmw.

Due to the adverse rare earth (RE) market conditions in 2011, Tamoil re-evaluated the operation of the Collombey RFCC unit.¹ At this refinery, the base catalyst in use was the best proposed solution offered by a competitor. The catalyst

was a residue catalyst with a high zeolite-to-matrix (Z/M) ratio and an average of 3.3 wt% of RE content. A trial was conducted using one of the competitor's low RE products with 2.6-wt% RE. This trial was abandoned due to poor performance, increases in the LPG yield (which was the unit's main operating constraint), bottoms yield, and catalyst addition rate. Since the driver for a catalyst change was still valid, Tamoil decided to trial a catalyst from another supplier.

THE TRIAL

Working with catalyst development companies, refiners can fine-tune operations. The evaluation requires a wide range of tools that when selectively used, based on specific refiners needs, ensure a flawless catalyst change. **FIG. 1** summarizes the key tools that were used at the Collombey refinery. Following appraisal activities, an innovative RFCC catalyst was selected to fit the Collombey operation and deliver the highest value.^b The

new catalyst combines the benefit of the distributed matrix structures platform with the proximal stable matrix and zeolite platform.²⁻⁴ This combination can achieve deep-bottoms conversion with low-coke make.

At the molecule level. The new RFCC catalyst has a unique catalyst pore architecture, providing optimized porosity for heavy-feed molecule diffusion with selective zeolite-based cracking. In addition, the catalyst has an ultra-stable and coke-selective matrix along with ultra-low sodium (Na) zeolite. The zeolite and matrix

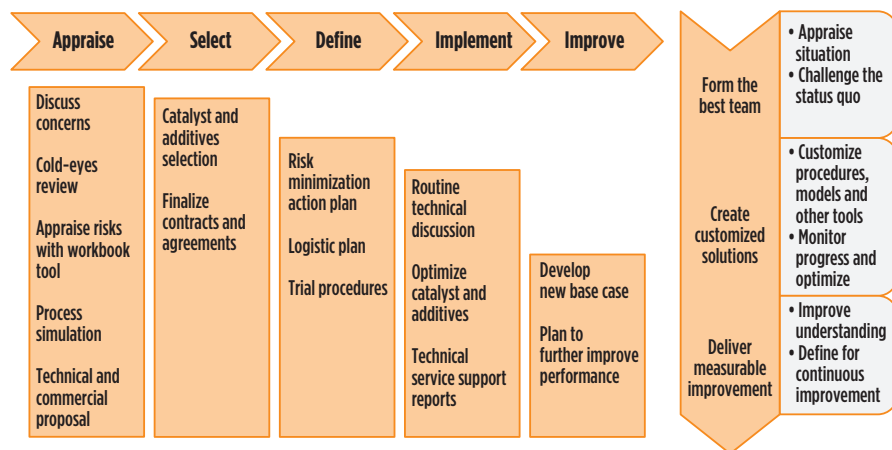


FIG. 1. The catalyst change management process.

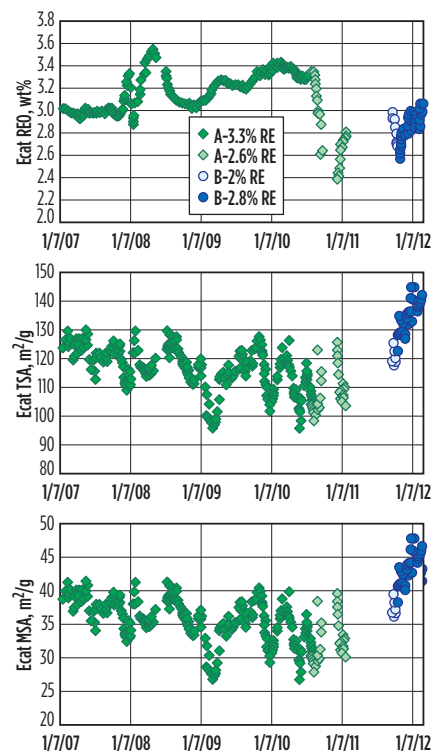


FIG. 2. Catalyst customization for the Collombey new RFCC catalyst trial.

are innovatively formed in a single manufacturing step. This catalyst design can provide refiners the flexibility to improve gasoline and light cycle oil (LCO) yields with low-coke make. It also improves metals tolerance and bottoms cracking.

To address Collombey's requirements, the RFCC catalyst needed customization. To minimize catalyst cost, the RE level was reduced (FIG. 2a). Even at low RE levels, the V contaminant metal tolerance was excellent because the metals passivation technology is not RE based, and the low-Na zeolite provides inherent V tolerance.^b To compensate for the loss of catalyst stability/activity when reducing the RE level, the zeolite surface area was increased (FIG. 2b). A unique in-situ catalyst manufacturing process allowed increasing the zeolite to higher levels without compromising the catalyst's physical strength. To substantially improve the

bottoms cracking, an active matrix was added; thus, the new design offers a higher matrix surface area (FIG. 2c).

During the define stage (FIG. 1), the catalyst provider worked closely with the Collombey refinery staff to develop a detailed catalyst change plan, logistics plan and trial procedures to minimize all risks. The technical review required input from Collombey's procurement, planning and operation specialists, and equivalent participation from the catalyst provider. Throughout the catalyst change, the RFCC unit was closely monitored, and process simulation was conducted to forecast the long-term performance and to optimize the catalyst. FIG. 3 shows the timing of the key value-added technical service before and during the catalyst change. During the catalyst trial, a wide range of unit processing throughput was explored, and the feed quality was com-

pared to past periods with feed CCR content ranging from 4 wt%–6 wt% (FIG. 4).

Using the data represented in FIG. 4a, periods of distinct operation can be singled out, as shown in FIG. 5. As illustrated in FIG. 5, the average feed CCR during the new RFCC catalyst trial was typical for the operating period. Comparing the RFCC catalyst trial to previous operating periods, for a similar fresh catalyst addition rate, the Ecat V levels were similar; the Ni was slightly lower; the Na level was definitely lower; and the Iron (Fe) was toward the higher range of previously experienced levels. The operating data is presented in FIG. 6.

Tremendous strides have been attained in catalyst technologies as demon-

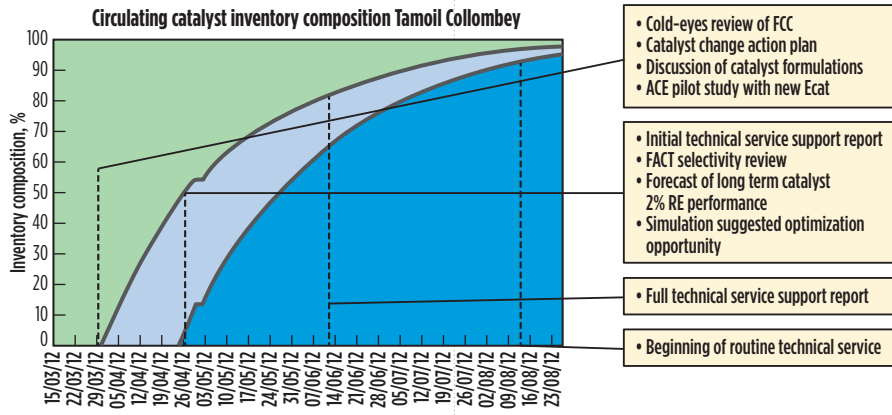


FIG. 3. Collombey catalyst change to new RFCC catalyst.

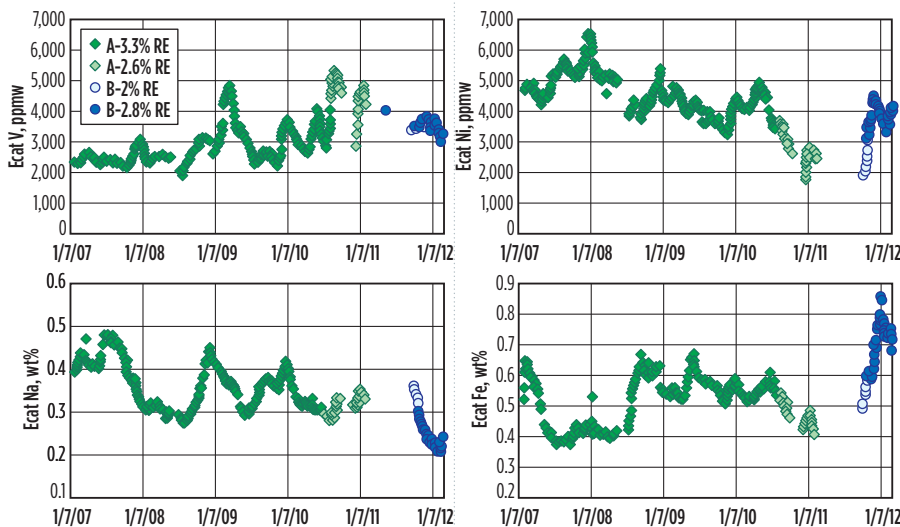


FIG. 6. New RFCC catalyst trial Ecat metals vs. previous operating periods.

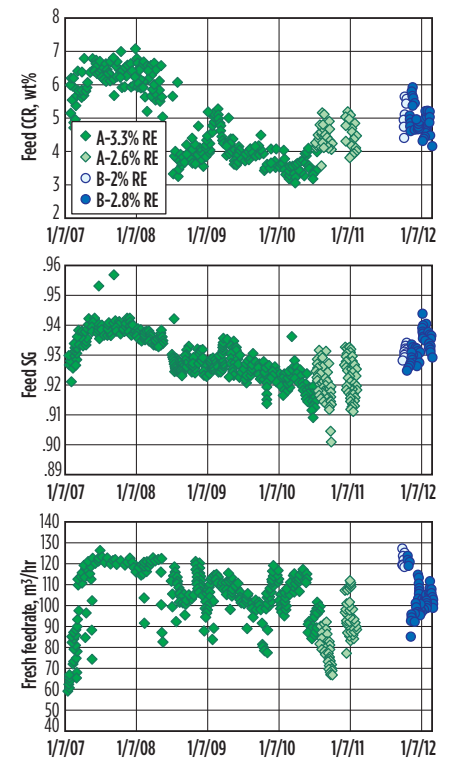


FIG. 4. New RFCC catalyst trial feed quality and unit throughput.

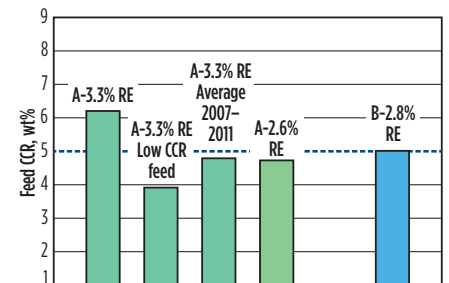


FIG. 5. New RFCC catalyst trial feed CCR vs. previous operating periods.

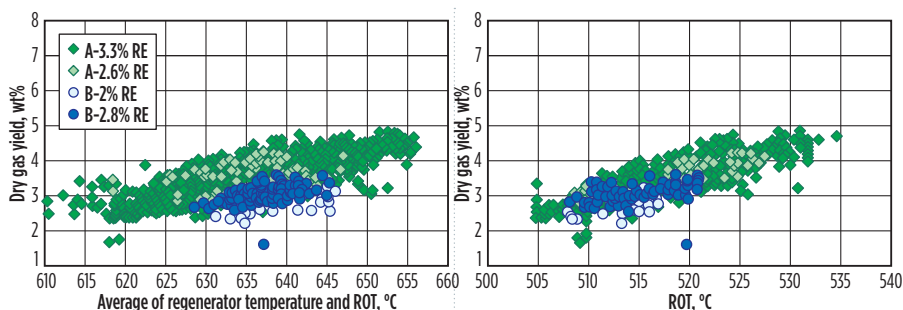


FIG. 7. New RFCC catalyst trial dry gas yield and ROT correlation.

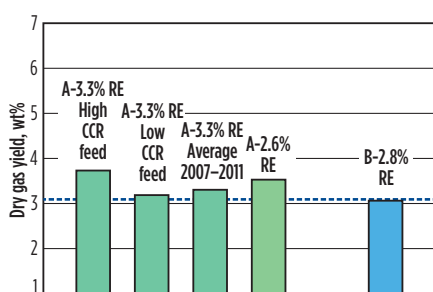


FIG. 8. New RFCC trial dry gas yield vs. previous operating periods.

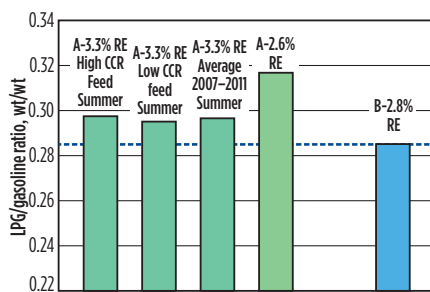


FIG. 10. New RFCC catalyst trial improved LPG/gasoline selectivity vs. previous operating periods.

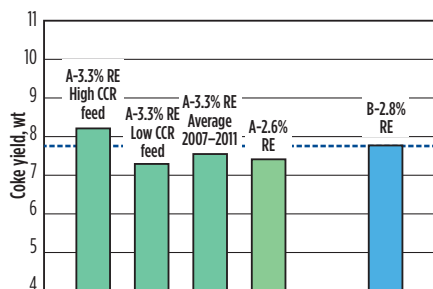


FIG. 9. New RFCC catalyst trial coke yield vs. previous operating periods.

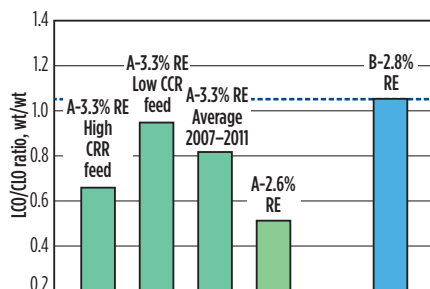


FIG. 12. New RFCC catalyst trial bottoms upgrading vs. previous operating periods.

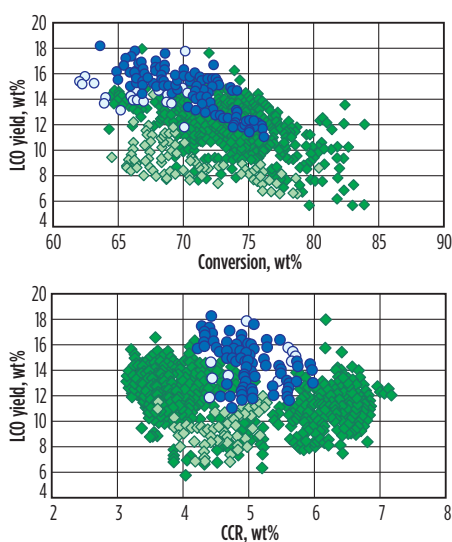
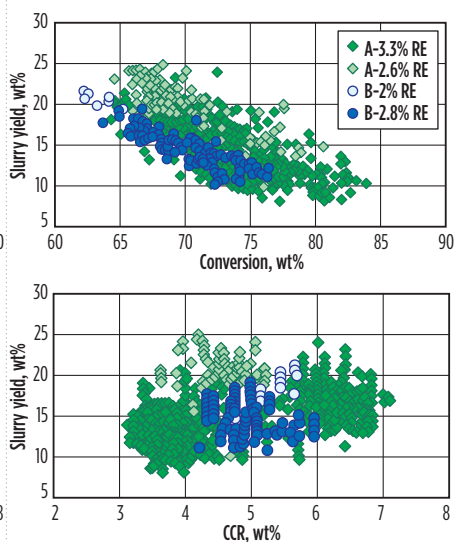


FIG. 11. New RFCC catalyst trial LCO and slurry yield.



strated with very low Na levels (FIG. 6c). It is well known that Na cations negatively impact zeolite stability.⁵ Accordingly, the new RFCC catalyst suffers less from Na acid-site neutralization and zeolite deactivation compared to other available catalysts. Since the fresh catalyst has low-Na content, the new RFCC catalyst has inherent V resistance. Furthermore, because of the low-Na content, hydrogen transfer reactions are minimized, thus preserving LCO quality at similar RE/Z levels.

FIG. 7 shows that the dry gas yield is a function of the mix-zone temperature, which can be estimated using the regenerator temperature and the riser operating temperature (ROT). Despite the much higher matrix surface area (FIG. 2c), the dry gas yield trended to the lower end of the range previously experienced, as shown in FIG. 7.

High levels of Fe were present in the unit feed during RFCC catalyst trial. Based on past experience, Collombey refinery was ready to use flushing Ecat to lower the Fe content of the circulating catalyst inventory. However, with new RFCC catalyst, there were no signs of catalyst surface sintering, dry gas selectivity deterioration or activity loss. Therefore, flushing Ecat was not necessary. The new RFCC catalyst has high porosity and, therefore, is resistant to Fe pore-plugging deactivation.

Furthermore, by comparing the dry gas yield to periods of distinct operation (FIG. 8), the new RFCC catalyst dry gas yield is similar to the average dry gas yielded with the base catalyst despite the lower RE level and much higher matrix content (FIG. 2c). FIG. 9 shows a similar result for the coke yield.

The LPG yield was controlled by the new RFCC catalyst despite the low RE level, and the gasoline yield remained similar. Thus, the LPG/gasoline selectivity was even better than the summer season performance of the base catalyst, as shown in FIG. 10. This significantly improved LPG/gasoline selectivity. The new RFCC catalyst removed the unit's main operating constraint. However, if a refinery needed to maintain the same LPG yield, then a lower RE/zeolite catalyst formulation, either on its own, or in combination with ZSM-5 additive could be used to convert the gasoline to LPG.

With the new RFCC catalyst, bottoms upgrading was improved. FIG. 11 shows in-

creased LCO yield and decreased slurry yield—also known as clarified oil (CLO).

FIG. 12 shows that this amount of bottoms upgrading is a record for the Collombey unit. When the trial results were considered along with the dry gas yield data (**FIG. 8**) and coke yield data (**FIG. 9**), the refinery data proved that the new catalyst's added active matrix truly can achieve coke-selective bottoms upgrading.

Final word. Tamoil's Collombey refinery worked very close with a new catalyst supplier to remove the main operating constraint and significantly improve the unit profitability. Several project goals were set and attained. The performance of the customized new RFCC catalyst, despite the low RE content and higher matrix surface area, exceeded Collombey's expectations. For similar fresh feed quality and feedrate, and similar fresh catalyst addition rate, compared to the base catalyst, the new RFCC catalyst:

- Was 0.5 wt% lower in RE content
- The plant LPG/gasoline selectivity was improved
- The dry gas yield was similar or in

the lower range

- The coke yield was similar
- An outstanding improvement in the bottoms cracking was achieved with record LCO yield and significantly reduced slurry yield.

The customized new RFCC catalyst with 2.8 wt% of RE substantially improved the unit's profitability, which is estimated using standard feed, product and utility prices to be:

- +1.2 \$/bbl vs. the competitive low RE catalyst with 2.6 wt% RE
- +0.4 \$/bbl vs. the competitive high RE catalyst with around 3.3 wt% RE. **HP**

NOTES

^a The RFCC technology installed at the Collombey refinery is the R2R process offered through the FCC alliance between Axens (technology developer and licensor), IFP Energies Nouvelles (R&D), and Technip/Shaw (licensing and engineering innovation).

^b BASF's Aegis catalyst, introduced to the market in 2010, combines the benefit of BASF's Distributed Matrix Structures (DMS) platform with BASF's Proximal Stable Matrix and Zeolite (Prox-SMZ) platform. This catalyst uses an integral Ni trap and separate non-RE based V trap.²⁻⁴

LITERATURE CITED

Available online at HydrocarbonProcessing.com.

YVES-ALAIN JOLLIEN is a process engineer for Tamoil S.A., Raffinerie de Collombey. With over six years of experience, he is the FCC unit process engineer. Mr. Jollien holds an MEng degree from the Swiss Federal Institute of Technology Lausanne; later, he studied for one year at the IFP School near Paris.

CARL KEELEY is the marketing manager, refining catalysts for Europe, Middle East and Africa, BASF Corp. He earned his MEng (Hons) in chemical engineering and applied chemistry from Aston University, UK. Mr. Keeley is a professional engineer (CEng). He has over 12 years of experience. Previously, he worked with UOP, BP and Dow.

JEREMY MAYOL is Tamoil's technical account manager, BASF Corp. With over 15 years of experience in the hydrocarbon processing industry, he is a recognized technical specialist in FCC unit operation. He has worked for BASF for four years. Prior to this, Mr. Mayol spent 12 years working for INEOS and BP.

STEFANO RIVA is the technical service manager, refining catalysts for Europe, Middle East and Africa, BASF Corp. With over 20 years FCC experience: 10 years with Engelhard and BASF in technical sales and technical service; two years with Tamoil and eight years working in the technical support group at ExxonMobil.

DR. VASILEIOS KOMVOKIS is the technology manager, refining catalysts for Europe, Middle East and Africa, BASF Corp. He holds BS and MS degrees in chemistry, and a PhD in chemical engineering from Aristotle University. He was a researcher at CPERI Institute of Thessaloniki and a research professor at the University of South Carolina.

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