Summary

The objectives for this project were developed after an in-depth analysis of the local and world situation of the refining opportunities for diesel production, and of the existing catalyst technologies in the market. The project’s team considered the following objectives:

1. Develop an FCC catalyst to increase the LCO (light cycle oil) yield by 3 vol.%
2. Increase the Cetane Index (CI) of the LCO by 4 numbers
3. Maximum gasoline loss of 2 vol.%, while maintaining the Octane number.

All of these results were required at constant coke when compared to a base catalyst of adequate zeolite and matrix surface areas. The catalyst results in one of the commercial FCC units of Ecopetrol in the Barrancabermeja refinery were:

- Increase of 2.3 vol.% in the LCO yield
- Increase of 3 numbers in the CI
- Decrease of 1.5 vol.% in gasoline yield, while maintaining octane number.

Introduction

The largest company in Colombia, Ecopetrol, and the world leader of FCC catalysts, Grace, joined their efforts, talents and resources in a technology innovation project to mitigate the deficit of diesel fuel in Colombia. Local and global market trends showed that the growth in the demand for diesel is greater than for gasoline. Several factors were key in developing the project’s objective to maximize LCO production, such as:

1. The conversion capacity of Ecopetro’s refineries, based upon FCC technology;
2. An increase in crude oil slates that are steadily richer in heavy oils;
3. The absence of specific catalyst solutions to meet the diesel objectives;
4. LCO is an important component in the streams being sent to diesel hydrotreating units.
This article presents the following stages of this joint development project:

1. The experimental design to obtain the best formulations for the catalysts
2. Laboratory testing
3. Development of the deactivation and simulation procedures for equilibrium catalyst (Ecat)
4. Evaluation in the DCR Circulating Riser pilot plant and the scale-up using a simulation model
5. Commercial evaluation in an FCC unit at Ecopetrol’s refinery in Barrancabermeja.

In the catalysts design phase, the following factors were considered: the impact of the type and quantity of the zeolite and matrix; the concentration of Rare Earths (RE₂O₃); as well as the catalyst stability and selectivity in a high contaminant metals’ environment (>10,000 ppm of Ni+V). The best formulations evaluated in the ACE reactors showed increases of 4.0 wt.% in LCO yield and nearly 4 numbers of CI. The evaluation of catalysts in the DCR pilot plant showed an incremental LCO yield of 3.0 wt.% with an improvement in CI of 3 numbers. Recognizing that in resid cracking the coke selectivity of the catalyst is one of the most important properties, great efforts were made for its optimization. The industrial plant scale-up allowed us to corroborate the excellent coke selectivity of the developed catalyst, and the simulations performed confirmed the incremental LCO yields and quality derived from the best formulation. The most important stage of a catalyst development project is its evaluation in the real world of a commercial plant. A commercial trial was started in April 2013 maintaining an average of 25% of resid in the feed throughout the test. The main goal for both companies was to corroborate the lab and pilot plant results in Ecopetrol’s commercial unit, as well as to reach the objectives programmed for the project. These were confirmed. Improved coke selectivity was also evident in the commercial FCC unit, which provided a better heat balance and increased operational flexibility.

**Experimental Design**

The first step of this project was to identify the catalyst’s parameters that affect LCO selectivity (distillation range 221-370°C [430-700°F]) while minimizing any gasoline yield loss. These were:

1. High surface area matrix with good bottoms cracking selectivity¹.
2. Moderate activity to improve LCO conversion while avoiding excessive LCO cracking.
3. Good coke and gas selectivity in resid cracking (fraction 550°C+ [1022°F+]).

Figure 1 shows a diagram of the experimental design for this project.

To select the matrix, 8 different commercial catalysts were evaluated in a fluidized bed micro-reactor (ACE) unit². The ACE unit was run at the following conditions: RxT: 505°C [941°F]; C/O ratios of 4, 6 and 8; reaction time 30 sec. The variables that will be optimized are: zeolite content, RE₂O₃ concentration in the catalyst, and matrix level. Twenty different catalyst formulations were prepared. To deactivate fresh catalysts and simulate the Ecat, two methods were used; Grace CPS-¹¹ method and a method developed for this project by ICP (called IDM)⁴⁻⁵. To develop this IDM method, an Ecat sample that contained the selected matrix was taken from a commercial unit. Then, in the lab, the effect of operating variables such as residence time, deactivation temperature and steam flow were determined, until the optimal conditions were defined that would simulate the physical-chemical properties, the activity and the selectivity of this Ecat. After the catalyst deactivation by the IDM method at 12,000 ppm of Ni+V equivalent, the pilot plant (DCR) studies were run. These studies were performed at the Colombian Petroleum Institute (ICP) [Instituto Colombiano de Petróleo] in isothermal conditions⁵, at RxT of 525°C [977°F] and C/O ratio between 4 and 17. For coke optimization it was necessary to optimize the proportion and the type of V and Ni traps. With the results obtained from the DCR unit, a scale-up was performed to a commercial unit, using a commercial model for simulation and optimization. Finally, the commercial trial was performed in an FCC Orthoflow Unit at the

**FIGURE 1: Experimental Methodology**
Ecopetrol refinery in Barrancabermeja. The feed used by the laboratory for the entire project is a blend of 70 vol.% VGO (vacuum gasoil) and 30 vol.% DMO (demetalized oil, obtained in the DEMEX unit of the Barrancabermeja refinery). This blend has the following properties: 18.5°API Gravity, 2.5 wt.% sulphur, 2.3 wt.% CCR (Conradson Carbon Residue) and 10 ppm of Ni+V.

Results and Discussion

Shown in Figure 2 are the results of the ACE tests (LCO yield as a function of the conversion) to select the catalyst’s matrix. These eight (8) catalysts were previously deactivated by the CPS-1 method. This chart shows that catalyst 2 presents higher LCO performance within a reasonable operational range for an FCC unit. In addition, it showed the best bottoms conversion and a good coke selectivity in metals-free testing.

Based on these results, this matrix platform was selected as the most appropriate to meet the project objectives, and then the other catalyst variables were optimized. Shown in Figure 3 is the experimental design of this phase of the project, where the aforementioned variables were evaluated in the following ranges: zeolite content (5-30 wt.%), $\text{RE}_2\text{O}_3$ concentration (0-6 wt.%) and the matrix level (20-40 wt.%). In this three-dimensional chart we observe that the maximum LCO performance is in the range of 30-33 wt.% matrix. Based on the different formulations that were studied, the best catalysts were selected for later studies.

The two best formulations, among the 20 prepared, were used to study coke selectivity in a high metals environment, where it was necessary to optimize the V and Ni traps. We also needed to investigate the effect of the deactivation mode on the coke selectivity of the FCC catalysts in order to handle resid feedstocks. We did this because it was observed that the deactivation methods used had been developed for catalyst technologies designed for gasoline mode operations. Therefore, ICP developed the IDM deactivation method to simulate the properties of this type of catalyst technology to maximize LCO.

Table I shows the activity and coke selectivity results for the two best catalysts comparing the two different deactivation procedures, ICP (IDM method) and Grace (CPS method) at constant conversion (50 wt.%). These results allow us to conclude that the IDM method, at similar metals levels (Ni+V), completely changed the relative activity and coke selectivity of the two deactivated catalysts. The catalyst deactivated by the IDM method required lower C/O ratio to reach the same conversion level with lower coke production. That is, after the hydrothermal deactivation, these catalysts were more active with better coke selectivity, since the IDM method produced a better matrix deactivation (higher Z/M ratio), hence minimizing the catalytic coke produced in the matrix structure. The higher activity (lower C/O) is related to the higher zeolite surface area. The better coke selectivity is related to the lower matrix area and the higher zeolite area, which means higher zeolite/matrix ratio, as is shown in Table I. This important result shows once more that all investigations can benefit from developing its own methods and analytical techniques that allow for correctly evaluating and studying new catalyst technologies. In this case, it can be concluded that the IDM method better simulated the catalyst technologies containing high levels of an active matrix that is designed to increase bottoms conversion to LCO.

The results obtained in the DCR pilot plant were used to perform the scale-up to the commercial plant using a proprietary model of ICP, which is tuned with the commercial plant data. This scale-up allows us, through information from the pilot plant, to calculate kinetic parameters that are associated with the catalyst of origin. Once obtained, these parameters are fed to the simulator to proceed under optimization mode to find the optimal operational conditions for the commercial unit. The FCC process model from
the scale-up of pilot plant data allows us to perform the heat balance of the commercial unit for each evaluated catalyst. Additionally we are able to perform optimizations toward specific products based upon the needs of the refinery, taking into consideration the operational restrictions of the unit.

Table II shows the scaled-up results. There are two base cases shown, reflecting that during the project timeline, the base catalyst was changed as well as the FCC unit where the commercial trial was performed. The original base case was used to define the project’s objectives, while the second base case was established from the FCC unit where the newly developed catalyst was tested. In these simulations there is a recycle effect, since it was considered that recycling heavy cycle oil (HCO) was a good practice for maximizing LCO production. The operating conditions allow us to conclude that the developed catalyst (ICP-4C) is more coke selective, since it produces a drop between 7-8°C [12.6-14.4°F] in the regenerator temperature at constant operating conditions. The yields reported with ICP-4C allow us to conclude that there is an increase of 4.3 vol.% in LCO yield compared to the first base case, and of 2.3 vol.% compared to the second base case, with an increase in the cetane index of 2.8 numbers. On the other hand, the decrease in gasoline yield was 1.1 vol.%. These results allowed us to meet the project objectives and to start preparations for the commercial trial.

The commercial trial in one of the FCC units of Barrancabermeja refinery started on April 23, 2013. In Table III, we present the main results from that trial, where the new catalyst (ICP-4C) had an 80% turnover in the Ecat inventory. The feed during the trial was 77 vol.% of VGO and 23 vol.% of DMO, which was 8% more resid (DMO) than the respective base case; so it was a slightly heavier, more refractory feedstock. The obtained yields, compared to the second base case, allowed us to corroborate that the developed catalyst maintained the main operating conditions while processing a slightly heavier feedstock. It was observed that ICP-4C provided
a significant decrease in the dry gas production. LCO production was increased by 2.3 vol.% while the cetane index increased by 3 numbers. The decrease in gasoline yield was only 1.5 wt.%. According to the economic evaluation, the ICP-4C catalyst operation achieved an economic benefit for the refinery of 0.34 USD/bbl. The most important conclusion of this project was that the successful strategic alliance of Ecopetrol and Grace to develop a catalyst provided valuable benefits for both companies, while achieving the objectives initially set for the project.

### References


