

B. ARAMBURU and E. PÉREZ, CEPESA,
Madrid, Spain, M. MIRANDA and M. C. MASTRY,
BASF, Sevilla, Spain

FCC catalyst deactivation studies to mimic refinery conditions for high-propylene applications

The fluid catalytic cracking unit (FCCU) is a conversion unit located at the heart of many refineries. Its main purpose is to crack crude oil-derived feedstocks into valuable liquid products, primarily LPGs (propylene and butylenes), and gasoline and light-cycle oil (LCO) precursors. The process uses a fluidizable catalyst, comprising an alumina-silica framework and tailored for each refinery to meet its specific needs. Often, the changing of a catalyst includes catalyst testing evaluations, employed by about 50% of the FCCUs in the world. The testing process is cumbersome, in which multiple methods are available to refineries.

The first step to a laboratory catalyst evaluation is the deactivation step. In this step, laboratory scientists aim to mimic what happens in a refinery over the course of several weeks or months within just hours in the laboratory. It becomes more complicated when a test aims to replicate the effect of contaminant metals that come into the FCCU via crude oil processing and deposit onto FCC catalyst particles. Multiple deactivation methods are available, with the most common methods being:

- Only steam
- Cyclic propylene steaming (CPS), which involves metals impregnation using a solvent and subsequent redox cycle
- Cyclic metals deposition unit (CMDU), which employs a cracking method.

After deactivation, refiners have the choice to test on a bench-scale unit or on a larger unit (e.g., a circulating pilot plant). This article is a study in which a circulating pilot plant was employed, and multiple deactivation methods were examined.

Catalyst evaluation at CEPESA La Rábida refinery. CEPESA provides transportation fuels and petrochemical feedstocks to domestic and international markets. It operates three refineries in Spain, with two refineries operating FCCUs (La Rábida in Huelva and Gibraltar San Roque in Cádiz). The FCCU at the La Rábida refinery was originally designed to produce a wide range of FCC products. One of the more important products for the La Rábida refinery is propylene ($C_3=$), which allows the refinery to be highly competitive in a challenging market. Future expectations for the petrochemicals market and historical FCC data (equilibrium catalyst trends and refinery requests statistics) both strongly suggest that the demand for propylene has been strong and will continue to be strong in the near term.

For this reason, the La Rábida refinery decided, based on laboratory testing and an FCCU trial, to use a maximum propylene catalyst technology—a technology that is aimed at processing challenging and changing feeds, while maximizing propylene production through both high-conversion and high-propylene selectivity.

To support this historical change, CEPESA's research center, located in Madrid, Spain, was tasked with catalyst evaluation.¹ The CEPESA organization follows a robust testing evaluation process for the implementation of catalyst changes. This involves receiving potential catalyst samples and testing these samples in a circulating pilot plant. The research center has undertaken multiple projects to increase technical expertise in the space of FCC catalyst deactivation and testing to prepare for future catalyst evaluation exercises.

Catalyst deactivation study. This FCC catalyst study focused on evaluating the effect of multiple deactivation variables in catalyst evaluation. These included:

TABLE 1. Deactivation conditions for multiple samples

Sample	Base catalyst deactivation	ZSM-5 deactivation
Ecat	N/A	N/A
Dcat B	CPS with 1/3 Ecat metals	15 hr, steam only
Dcat C	5 hr, steam only	5 hr, steam only
Dcat D	5 hr, steam only	15 hr, steam only
Dcat E	5 hr, steam only	30 hr, steam only
Dcat F	5 hr, steam only	75 hr, steam only
Dcat G	5 hr, steam only	100 hr, steam only

TABLE 2. Deactivated catalyst properties compared against Ecat sample

Sample	TSA, m ² /g	ZSA, m ² /g	Ni, ppm	V, ppm
Ecat	204	147	800	2,500
Dcat B	178	125	253	851
Dcat C	165	121	0	0
Dcat D	165	118	0	0
Dcat G	163	113	0	0

1. Steaming only vs. metals impregnation
2. Time dependence of ZSM-5 steam deactivation.

Previous CEPSA studies conducted with high ZSM-5 content (e.g., 5%–10% or more) have deactivated pre-mixed catalyst and ZSM-5, as well as catalyst separately from the ZSM-5. This part of the study represented an optimization for CEPSA's testing protocol. CEPSA is in a unique position to conduct this study because of the high ZSM-5 content, but also the transparency between supplier and operating company with respect to ZSM-5 loading. The loading is agreed upon by CEPSA and the supplier through unit optimization exercises.

In CEPSA's case, when a base catalyst and ZSM-5, in high quantities, are deactivated together, the ZSM-5 activity can be

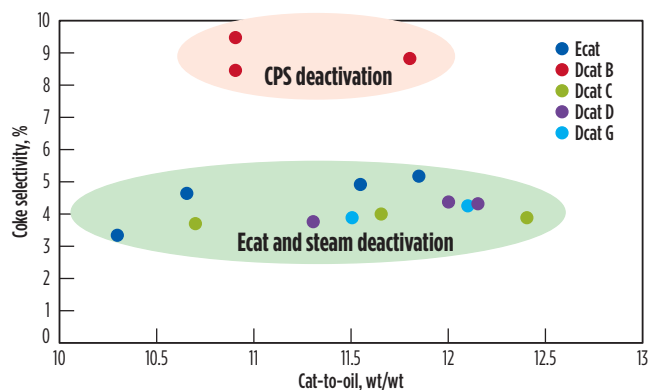


FIG. 1. Coke selectivity vs. catalyst-to-oil ratio comparing CPS and steam deactivation methods.

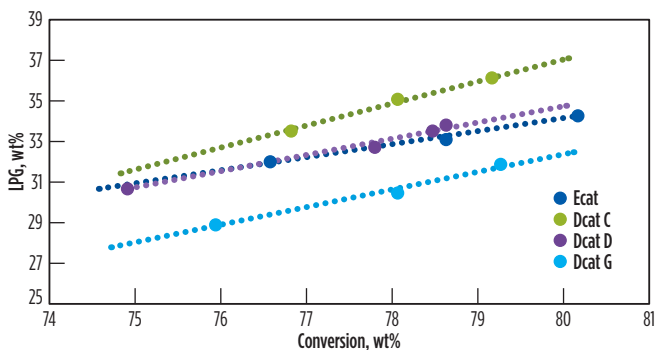


FIG. 2. LPG selectivity of Ecat vs. three Dcat samples.

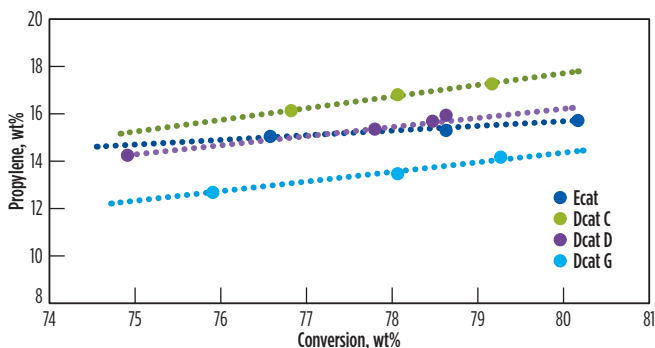


FIG. 3. Propylene selectivity of Ecat vs. three Dcat samples.

too high. For this reason, in CEPSA's high ZSM-5 loading cases, the deactivation of ZSM-5 requires either a higher steam temperature or longer steaming times. Because CEPSA's very high ZSM-5 case is so different than most refineries, the CEPSA research and development (R&D) center prefers to receive base catalyst and ZSM-5 additive separately (i.e., not in the same particle).

To ensure the most accurate comparison of the laboratory evaluation with refinery conditions, the benchmark chosen was an equilibrium catalyst (Ecat) from the La Rábida refinery. The following deactivation conditions were chosen for this:

1. A comparison of pure steam deactivation and metals impregnation via CPS. In the latter case, because the CPS method is known to exaggerate metals activity,² leading to higher hydrogen and coke than Ecat, the level of metals chosen in this study was one-third that of the Ecat.
2. A ZSM-5 deactivation duration study was also conducted. For the separate ZSM-5 additive deactivation ladder, a time ladder was chosen between 5 hr–100 hr. The final evaluation of

TABLE 3. Feed properties used in cracking study

Property	Unit	Value
Refractive index, 67°C		1.48
Density, 15°C	g/cc	0.896
Aniline point	°C	98.6
MCRT	%	0.1
Asphaltene content	%	0.05
Total N	ppm	885
S	%	0.39
Na	ppm	< 1
Cu	ppm	< 0.1
Fe	ppm	0.1
Ni	ppm	0.2
V	ppm	< 0.1
Ca	ppm	< 0.1
Mg	ppm	< 0.1
Boiling point, ASTM 1160		
5%	°C	378.4
10%	°C	394.2
30%	°C	421.3
50%	°C	441.9
70%	°C	472.2
90%	°C	525.9
UOP K		12.19
Molecular weight	g/mol	446.4
Aromatics	%	14.97
Napthenics	%	21.18
Paraffins	%	63.85

this deactivation study is to weigh both the deactivation/testing outcome and the practicality of running a long test.

The conditions implemented in this study are shown in TABLE 1. In all cases, the ZSM-5 additive content in the catalyst was set at 17%. The base catalyst was the same for each deactivation, being deactivated either by CPS or only steam. The deactivation catalyst (Dcat) is the deactivated fresh catalyst + deactivated ZSM-5 additive.

Due to the objectives of this study, results from Dcat B are used to study the CPS effect, and results from Dcats C, D, and G were used to study the steaming time effect. The deactivated catalyst properties were compared against the Ecat sample (TABLE 2).

Results and discussion. The Ecat and Dcat samples were evaluated in a circulating riser pilot plant located at the CEPESA R&D center in Madrid, Spain. Each sample was tested at 3-4 catalyst-to-oil ratios. In each cracking evaluation, the riser temperature was maintained constant at 530°C/986°F.

To ensure the most representative yield slate for the cracking evaluation, feed from the La Rábida refinery was used in the cracking evaluation. The feed properties are shown in TABLE 3. Because the 15-hr deactivation for ZSM-5 was found to best match Ecat performance, only the results for 5 hr, 15 hr and 100 hr are summarized in TABLE 3 for conciseness.

Coke selectivity was examined first to compare the two deactivation methods: CPS with metals and steaming only. In FIG. 1, the Ecat and all steam Dcats (C–G) gave similar coke selectivities (3%–5%). Conversely, the coke selectivities given after CPS deactivation (Dcat B) were double that of Ecat (e.g., 8.5–9.5%). This mismatch indicates that, even at one-third the metals seen on the Ecat, the metals effect from this CPS deactivation was not representative of the refinery operations. For instance, the CPS deactivated metals distribution is not the same. It was seen that CPS deactivation gives a homogenous distribution of contaminant nickel (Ni)—whereas, in a refinery and on Ecat samples, it is well known that Ni is not homogeneously distributed, but rather concentrated on the outer portion of the catalyst particles.² Furthermore, the redox cycles in CPS are often not enough to condition the metals sufficiently.

Because of these two effects, namely maldistribution and insufficient metal deactivation through conditioning, the effect of metals is often exaggerated even when loaded at lower than Ecat levels. When coke selectivity does not match the refinery operation, this affects all other yield slates in a testing exercise. For example, higher coke selectivity often means higher hydrogen selectivity. If both coke and hydrogen are disproportionately represented, so will the liquid product yield slate. Therefore, steam deactivation protocols were deemed more representative of refinery operations. The rest of the study will focus on the results of this process.

Focusing on the steam deactivation protocols, the next evaluation compared the yield selectivities of Dcats C, D and G. Since total LPG and propylene are the La Rábida refinery's focus for liquid products, these were examined first. The total LPG yield of Ecat and Dcat D (with ZSM-5 deactivated for 15 hr) best matched one another (FIG. 2). Shorter ZSM-5 deactivation gave LPG yields far exceeding the Ecat. Conversely,

the 100-hr deactivation time (Dcat G) gave much lower LPG.

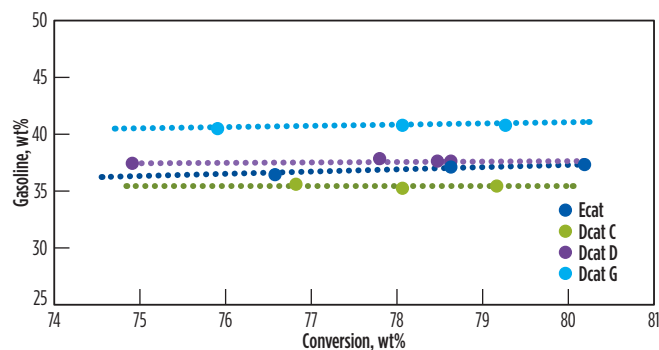


FIG. 4. Gasoline selectivity of Ecat vs. three Dcat samples.

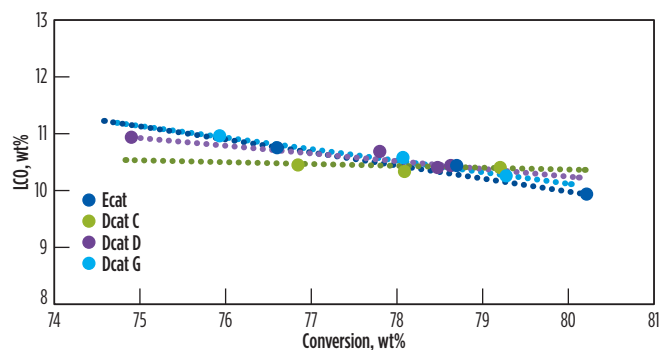


FIG. 5. LCO selectivity of Ecat vs. three Dcat samples.

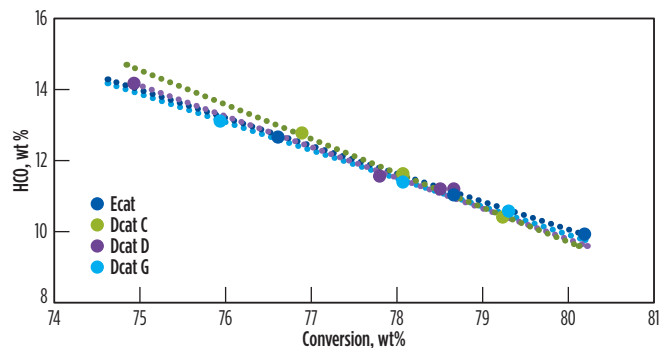


FIG. 6. HCO selectivity of Ecat vs. three Dcat samples.

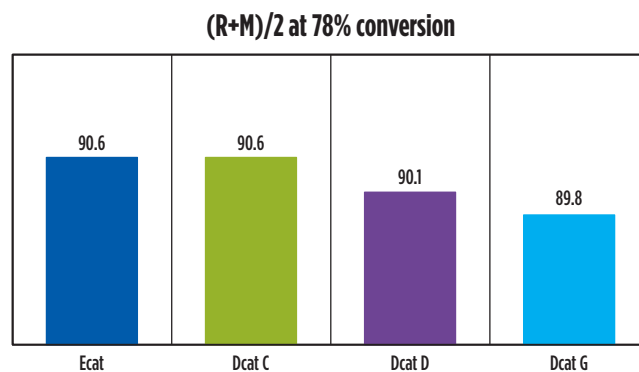


FIG. 7. Octane of Ecat vs. three Dcat samples.

The same results were seen when looking at propylene yield (FIG. 3), with Ecat results matching best with Dcat D.

The same conclusion can be drawn when examining gasoline yield (FIG. 4). These results are expected, since the effect being studied is a ZSM-5 deactivation effect, which will give gasoline and LPG split differences, while largely leaving other yields unaffected.

The heavier product yields are as expected, with no effect seen between the deactivation protocols on LCO and HCO yields—as shown in FIG. 5 and FIG. 6, respectively.

Finally, when looking at octane $[(RON + MON)/2]$ in FIG. 7, Dcat C was found to match that of Ecat, while the value of Dcat D (15-hr ZSM-5 deactivation time) was also found to closely match, although it was lower by half a number.

Takeaways. This comprehensive study of deactivation variables provides valuable insights into best practices for catalyst evaluation. The CPS deactivation study demonstrated that, even for a refinery running approximately 3,400 ppm Ni and V, steam deactivation is the protocol that best matches refinery Ecat. Using CPS deactivation would exaggerate the coke selectivity. If an evaluation is conducted at iso-coke, an exaggerated coke selectivity response can lead to non-representative conclusions. One solution to this could be to lower the metals even further (e.g., 15%–20% that of Ecat), or to employ a cracking deactivation method (e.g., CMDU), in which metals are appropriately distributed and conditioned, or to move to a steam-only deactivation campaign, as was done in

this exercise.

The second conclusion from this study was that the optimal steaming time for a ZSM-5 additive was 15 hr. After examining yields from a range of ZSM-5 additive steaming times, this case best matched all major product yields and closely matched gasoline octane. As expected, heavy products, such as LCO and HCO, were unchanged by this deactivation ladder, and still matched the yields of Ecat.

Finally, an important learning was uncovered when looking at Dcat properties vs. Ecat properties. It was determined that the physical parameters were not indicative of performance. This study showed that the Dcat sample that most closely matched Ecat physical parameters was the least representative sample in terms of product performance. This learning emphasizes the importance of focusing on performance testing vs. trying to match a set of physical parameters in the deactivation procedure design phase.

A robust laboratory facility, and a close partnership with the catalyst provider, led to this comprehensive study in which learnings can be applied to future studies. Studies like this are the enabler to continued value generation from the CEPESA R&D center for its partner refineries. **HP**

LITERATURE CITED

- ¹ Llanes, J. M., et al., “New catalyst increases FCC olefin yields,” *Hydrocarbon Processing*, April 2014.
- ² Xiao, F. S. and X. Meng, *Zeolites in Sustainable Chemistry*, Springer Berlin Heidelberg, Berlin, Germany, 2016.

Electronic permissions to BASF SE from *Hydrocarbon Processing*
November © 2019 Gulf Publishing Company



refining-catalysts@basf.com
www.catalysts.basf.com/refining