

A. SHACKLEFORD, BASF, Detroit, Michigan;
A. TAN and B. EREN, BASF, Houston, Texas

Driving FCCU value through fresh and flushing catalyst activity modeling

Refiners are continually challenged to maximize economic gain in the face of cost pressures and plant operating constraints. The fluidized catalytic cracking unit (FCCU) plays an integral role in the optimization of the facility. FCC catalyst is often one of the largest budget items in the refinery. Therefore, the balance between FCCU performance and catalyst costs has a significant impact on refinery profitability.

Frequently, an FCCU will set the catalyst addition rate by targeting equilibrium catalyst (Ecat) activity or the levels of Ecat metals. Given regular changes in feed quality and refinery operating objectives, it can be difficult to predict what catalyst addition is needed, especially if flushing catalyst (which is also known as “purchased Ecat” because it is often purchased from another unit) is used. Some refiners use process models or empirical “rules of thumb” for fine-tuning addition rates, thereby enabling improved value capture. However, even the best process models are limited in their ability to accurately predict catalyst activity during transient periods, as they are designed to give steady-state results.

This article highlights a theoretical model basis for predicting catalyst activity, reflecting transients and non-steady-state conditions due to feed quality and both fresh and flushing catalyst addition rates. This model achieves better activity control for improved profitability. Taking this a step further develops the fresh vs. flushing catalyst profile to provide a guideline on the ratio of flushing catalyst needed to replace 1 ton (t) of fresh catalyst, based on metals and activity difference.

To better optimize the catalyst addition rate of an FCCU, an activity model has been developed to calculate and predict catalyst activity based on the simplified catalyst decay function, considering the metals effect in deactivation modeling and catalyst age distribution. This activity model is a benefit to refiners because the model helps refiners quickly optimize the catalyst addition rate by targeting a desired Ecat activity with the available forecasted feed rate and quality. This model relies on consistent Ecat sampling and testing for accurate usage, coupled with a good feed forecast; refiners can operate at a constant Ecat activity and reduce variance introduced by the feed. Maintaining steady Ecat activity is essential for refiners to operate profitably. Financial losses can amount to \$0.13/bbl per 1 wt% fluidized activity test (FACT) lost, depending on unit economics and median Ecat activity.

Another benefit of the activity model is the capability to include flushing catalyst into the model. Flushing catalysts are

sourced from spent catalyst withdrawn from low-metals gasoil FCCUs and are often used to flush metals in residue (resid) FCCUs. Low-metals gasoil FCCUs or vacuum gasoil (VGO) units can be defined through a combined nickel (Ni) and vanadium (V) level of less than 2,000 parts per million (ppm); however, refinery requirements may vary. In many cases, flushing catalysts can allow fresh catalyst additions to be reduced, offering an opportunity to reduce operating expenses—flushing Ecat quality has variations like a single unit’s Ecat or greater if composited from multiple refineries compared to well-controlled fresh catalyst properties. This adds another element of variability in maintaining Ecat activity. Very little information has been published with methods for calculating the effect of flushing catalyst on Ecat activity and the fresh catalyst addition rate. Therefore, it is very difficult for engineers to predict the impact of flushing catalysts.

A heuristic method commonly encountered in industry is to replace 1 t of fresh catalyst additions for every 2 t of flushing catalyst additions. As detailed in this article, the commonly used rule of thumb is often optimistic for estimating the reduction of fresh catalyst additions at constant activity, and the effect of flushing Ecat on fresh catalyst requirements can vary widely. Refineries must balance operational costs and profit maximization opportunities by maintaining a consistent yield selectivity profile. After accounting for catalyst cost, refineries can materialize up to \$0.08/bbl in yield capture alone.

In this article, the development of an activity model capable of including flushing catalysts is described, along with a refinery case study in which the activity model was successfully applied to optimize the catalyst addition rate.

Catalyst deactivation model basic theory. The simplified catalyst decay function commonly used in industry^{1,2,3} is shown in Eq. 1:

$$-\frac{da}{dt} = \theta \times a^d \quad (1)$$

where:

a = Ecat activity (second order)

t = catalyst age in the unit, days (d)

d = order of deactivation

θ = specific decay constant, d^{-1} .

The decay constant (θ) represents the combination of various mechanisms that cause the catalyst activity to decline over

time, such as hydrothermal deactivation of matrix and zeolite, pore mouth plugging, etc. The decay constant and the order of deactivation are constants that can be adjusted to fit the calculated model activity to a set of measured activity values.

First-order deactivation ($d = 1$) and second-order deactivation models ($d = 2$) are commonly used in industry, often because the calculations can be simplified when using the integrated forms. A multiple of different reactions occur within the riser of an FCCU. Experimentation has shown that a pseudo-first-order deactivation ($d = 1$) is a good approximation of the reaction kinetics. However, as the reactants become increasingly diluted with cracked products, and as coke builds up on the catalyst, the extent of the reaction is diminished. Several values—from 1.6 to 4—have been reported in literature, but, most commonly, a value around 2 is used ($d = 2$).^{3,4}

The decay function in Eq. 1 assumes that the activity of the catalyst will eventually decay to zero. Including a steady-state activity in deactivation modeling allows a more consistent fit of deactivation data and could partly explain the reported range of deactivation order. The steady-state activity is the non-zero activity reached after very long aging. We can include the steady-state activity (a_s) into the simplified decay function, as shown in Eq. 2:

$$-\frac{da}{dt} = \theta \times (a - a_s)^d \quad (2)$$

Steady-state activity can be assumed between 20%–30% of conversion, since it is a good representation of asymptotic activity after a very long steaming. The simplified decay function lends itself to easy implementation in a spreadsheet model, where the circulating catalyst inventory age distribution can be calculated, along with the activity of each age fraction represented by a function closely approximating the integral of Eq. 2:

$$a_{(t+1)} = a_{(t)} - \theta \times (a_t - a_s)^d \quad (3)$$

To obtain an activity for each fraction of the age distribution, a starting point is needed. The activity at $t = 0$ is the fresh activity. In practice, true fresh activity is never measured, as the catalyst activity is simply too high to be measured by laboratory equipment. Often, fresh catalyst will be steamed at a standard set of conditions—such as for 5 hr at 1,450°F (788°C) in 100% steam—to deactivate the catalyst to an activity level that is easier to measure. It is a common mistake to use this freshly steamed conversion in deactivation calculations.

Freshly steamed catalyst will typically have a FACT conversion in the region of 75%–80%, and a second-order activity of 3–4 [activity = conversion/(100 – conversion)]. FACT is measured by using an advanced cracking evaluation (ACE) unit. Historically, catalyst conversion was measured with a fixed-bed unit and referred to as microactivity (MAT). At present, MAT is used interchangeably with FACT.

The true fresh conversion—if it were measured directly—would typically be a value in the region of 85%–92%; thus, activity would be in the range of 5.5–9. A fresh conversion of around 88%–89% is suggested as a good starting point and can be adjusted later to see if the model fit is improved.

Fresh catalyst activity can also be estimated by steaming the fresh catalyst at a variety of steaming times and then extrapolating the results. Such effort is not necessary in most cases, par-

ticularly for developing a deactivation model for a single fresh catalyst. The model is not highly sensitive to small changes in the fresh activity, provided that the starting value is reasonable.

In addition to calculating the activity of catalyst as it ages in the unit, the age of distribution is needed. The age distribution of the E_{cat} can be calculated, as shown in Eq. 4:

$$I_t = e^{\frac{1-t}{\tau}} - e^{\frac{-t}{\tau}} \quad (4)$$

where:

$I_{(t)}$ = fraction of the catalyst inventory that has been in the unit for t days (d)

τ = average catalyst age in the unit, d

e = catalyst inventory/(total catalyst addition rate \times retention factor).

It is also possible to maintain an approximate calculation of daily age distribution in a spreadsheet model by simple mass balance calculations to obtain $I_{(t)}$. Combining these calculations, the equilibrium activity, \bar{a} , of the catalyst in the unit can be defined (Eq. 5):

$$\bar{a} = \int_0^{\infty} a(t) \times I(t) dt \quad (5)$$

In the deactivation model, a good fit to commercial E_{cat} activity data is achieved by maintaining a calculation of age distribution out to 300 d and by calculating the equilibrium activity shown in Eq. 5 by numerical integration. For units that have extremely low turnover, the age distribution will need to be greater than 300 d.

Metals effects in deactivation modeling. The deactivation of catalyst by contaminant metals is calculated separately to the simplified decay function. Several contaminant metals found in FCCU feeds cause a loss of catalyst activity, with V and sodium (Na) typically being the most important metals to consider. Na and V are both found to be mobile, with significant inter-particle migration of metals indicated by sink-float skeletal separation of E_{cat} into age fractions.⁵

It is reported⁶ that the activity of catalyst with increasing V is reduced by the fraction $e^{(-V/V37)}$, where V37 is the V level required to reduce the activity to 37% of the zero V activity. This expression suggests that the length of time the contaminant metal is present on the catalyst is unimportant. This is consistent with trends generally observed in industry.

Na has been found to be about equally destructive toward zeolite as V, and the effects of these metals are synergistic.⁷ The mechanisms of these metals on the deactivation of catalysts are complex, and the effect of metals on activity will vary from unit to unit. It is proposed that Na directly attacks zeolite by the formation of sodium hydroxide (NaOH), and the role of V is to catalyze and facilitate the formation of NaOH. This mechanism requires oxidation of V to a +5 oxidation state, along with the presence of steam, without which partial ionization is not possible.

V and Na effects vary widely. As a broad rule of thumb, these metals will reduce FACT or MAT activity by 0 wt%/1,000 ppm –4 wt%/1,000 ppm, with higher activity loss occurring under more oxidizing conditions—such as full carbon monoxide (CO) combustion regeneration—at higher regenerator temperatures and at higher steam partial pressures in the regenera-

tor. In many units, such as that shown in **FIG. 1**, the destruction of zeolite by metals is observed as the predominant mechanism for deactivation. Other units may show much less correlation between activity and metals.

Adding the expression for metals deactivation to Eq. 5 to include a first-order deactivation mechanism for metals on the equilibrium activity results in Eq. 6:

$$\bar{a} = \int_0^{\infty} a(t) \times I(t) dt \times e^{(-k_{M1}M1 - k_{M2}M2 - k_{M3}M3 - \dots - k_{Mn}Mn)} \quad (6)$$

where $M1, M2$, etc., are the ppm concentrations of any contaminant metals on Ecat that are selected for inclusion in the deactivation model.

The deactivation constants (k_{M1} , etc.) are best estimated by fitting the deactivation calculation to a set of historical data. In practice, it is found that modeling only Na and V is often enough, although other metals that could potentially be considered include iron (added), calcium (added) and potassium. In the examples studied for this article, no statistical indication of catalyst deactivation by Ni was observed. **Note:** Some assume a deactivation effect for Ni to be at one-quarter that for V.

Activity calculation of blends of fresh catalyst and flushing Ecat. Some assumptions are needed to estimate the Ecat catalyst activity when using a combination of fresh catalyst and flushing catalyst. It may be assumed that the hydrothermal deactivation constant and metals deactivation constant for flushing catalyst are the same as the fresh catalyst. In practice, these assumptions have been found to yield reasonable estimates when predicting flushing catalyst effects. For those knowledgeable in catalyst formulation, it is reasonable to estimate a relative deactivation coefficient by comparing properties such as rare earth and zeolite content. Since the modeled Ecat conversion reduces approximately linearly with metals, Ecat activity can be calculated based on added metals, with the assumption that metals already present in the flushing Ecat are already accounted for in the initial activity.

The model integrates the catalyst activity over an age distribution out to 300 d. For flushing catalyst, one approach could be to treat the initial Ecat activity as a starting fresh activity and to start the clock for the age distribution when the flushing catalyst is first used in the second unit. The problem with this approach is that the decay function is based on the average activity, and the model will result in a stability of activity for the flushing catalyst that is lower than actual. This results in transient errors in the calculated Ecat activity in the unit when the addition rate of flushing catalyst is changed.

A more successful approach is to make some reasonable assumptions about the age distribution and activity distribution of the flushing catalyst, and to model the particle activity. The average age of the flushing catalyst may be known or can be estimated using typical values for a gasoil FCCU. An average gasoil FCCU will have a circulating catalyst inventory of 250 t and a daily effective fresh catalyst addition rate of around 3.5 tpd, giving an average catalyst age of approximately 71 d.

Eq. 4 can be used to generate an age distribution of the flushing Ecat (I_p) from the estimated average catalyst age. Once the flushing Ecat is reused, it will obtain a new age distribution—referred to as “aged flushing catalyst.” In setting up this model, the

initial age distribution can be established in the model for the aged flushing catalyst portion of the unit inventory, using Eq. 7.

$$I_F(t) = \sum_{n=1}^t I_P(n) \times I_E(t-n) \quad (7)$$

where:

$I_F(t)$ = fraction of the aged flushing catalyst portion of the inventory, with an age of t days

$I_E(t)$ = fraction of the fresh catalyst portion of the inventory, with an age of t days

$I_P(t)$ = assumed or known fraction of fresh flushing Ecat, with an age of t days.

A comparison of the age distributions of flushing Ecat and the aged flushing catalyst portion of the unit catalyst inventory is shown in **FIG. 2**.

Refinery case study. This refinery has a relatively small catalyst inventory of 60 t, along with fresh and flushing catalyst addition rates of 5 tpd and 2 tpd, respectively. As a result, turnover is very quick, with an average catalyst age of less than 9 d. Hence, the ability to forecast and control the catalyst activity helps a great deal in unit optimization.

The activity model was first calibrated for the refinery, using the historical catalyst addition rates and Ecat catalyst analysis data. Calibration is required to adjust the metal factors (k_{M1} and k_{M2}) and deactivation constant (θ) for each specific refinery. An excellent fit of the theoretical model in predicting the catalyst activity was achieved as shown in the trend of the activity modeling results (measured vs. model) in **FIG. 3**.

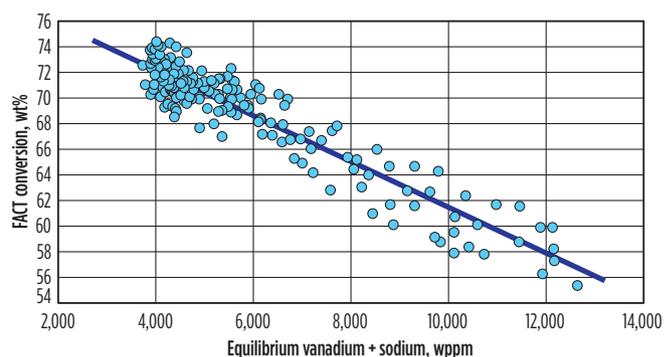


FIG. 1. Benchmarking of global FCCUs exhibiting the compounding effects of metals on deactivation of the catalyst.

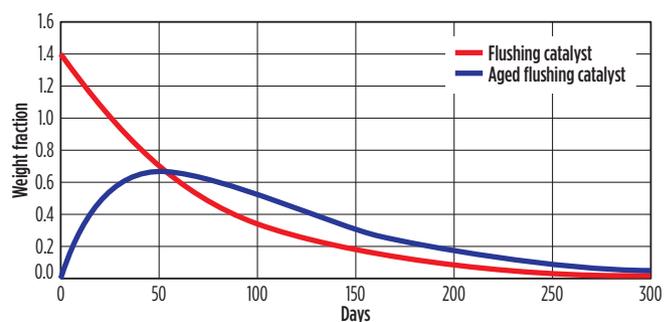


FIG. 2. Comparison of the age distributions of the fresh flushing Ecat and aged, secondary flushing catalyst.

With the calibration completed, the activity model is used to calculate the required catalyst addition rate for achieving a target Ecat activity by inputting the forecast feed rate and metals. With the activity model, the refinery was able to operate at the target catalyst activity consistently without any loss opportunities, even with frequent changes in feed quality.

The tested Ecat catalyst activity received several days later was used as feedback to compare against the predicted activity from the model for validation and to ensure that the model remains sound and good for further predictions. The proactive control of activity and getting the activity one number closer to the target resulted in up to \$15,000/wk over waiting for vendor Ecat results and responding reactively.

Flushing catalyst study. With flushing catalyst being built into the activity model, the impact of flushing catalyst on catalyst activity is easily studied by comparing the eventual catalyst activity at various addition rates of fresh catalyst and flushing catalyst. At the same Ecat activity, the amount of flushing catalyst that is required to replace 1 t of fresh catalyst is summarized in FIG. 4, considering the difference in activity and metals levels of the flushing catalyst. As detailed in FIG. 4, for a flushing catalyst that is 8 wt% higher in activity and 7,000 ppm lower in total Na + V compared to the unit's Ecat, 2 t–2.5 t of flushing catalyst will be required to replace 1 t of fresh catalyst to achieve

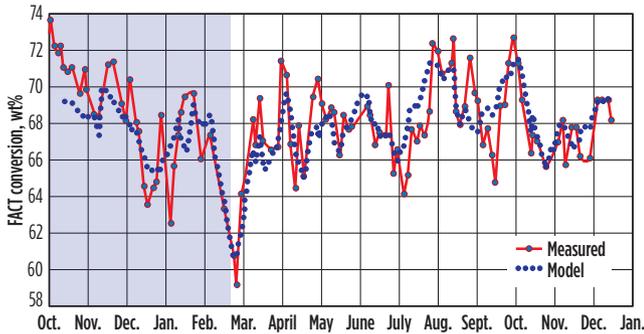


FIG. 3. Activity modeling results (measured vs. model). The period in blue was used for calibration of the model. The period in white shows the improved control of catalyst activity that the refiner was able to achieve by implementing the catalyst addition rates predicted by the model.

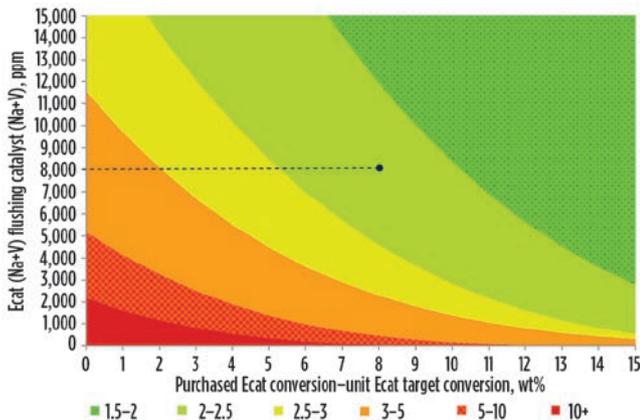


FIG. 4. The legend shows the amount of flushing catalyst required to replace 1 tpd of fresh catalyst to maintain constant Ecat activity.

constant Ecat activity. FIG. 4 provides a quick reference for refiners to optimize the addition rates of flushing and fresh catalysts.

Commercial FCCU flushing catalyst validation. A unit processing resid went from using fresh plus flushing catalyst to using exclusively fresh catalyst. The unit wanted to maintain an Ecat activity of 71 FACT. Key details are shown in TABLE 1. The difference between the flushing catalyst and the final Ecat metals when the flushing catalyst was removed (Na + V) was 2,850 ppm, with an activity difference of eight numbers. Using FIG. 4, this puts the unit in the yellow range requiring 2.5:1–3:1 ratios of flushing catalyst to fresh catalyst. To maintain an Ecat activity of 71, the unit ultimately replaced 4 tpd of Ecat with 1.5 tpd of fresh catalyst for a ratio of 2.7:1 to maintain activity. This is in the predicted range of 2.5:1–3:1 and verifies the usefulness of FIG. 4. In addition, despite the higher metals on Ecat, there was no change in hydrogen or coke selectivity due to the flushing catalyst not containing metals passivation technology.

Furthermore, utilizing FIG. 4 allows for a quick visualization of fresh-to-flushing catalyst cost ratios and how metals trapping can influence the usage of flushing Ecat. For this example, if fresh-to-Ecat costs are greater than the 3:1 ratio, Ecat can be a cost-effective solution for this unit. However, if the fresh-to-flushing catalyst ratio is less than 2.5:1, then the unit might not see the cost benefits of using flushing Ecat. FIG. 4, when applied appropriately, highlights cost ratio thresholds for varying metals levels and activity deltas when the unit is considering using flushing Ecat.

Takeaways. The activity model is proven capable as a proactive (feed-forward) approach to achieving a targeted activity without the rigorous inputs of proprietary process simulation software modeling, which often fails to address transient periods. This allows refiners to adjust the catalyst addition rate to changing feed quality, thus preventing lost revenue due to unoptimized activity. Modeling is then taken a step further to incorporate the usage of flushing catalyst for activity impact. This develops the fresh vs. flushing catalyst profile (FIG. 4), allowing effective management of Ecat activity. FIG. 4 provides quick guidance on how much flushing catalyst is needed to replace 1 t of fresh catalyst, based on the metals and activity difference.

TABLE 1. Commercial unit example where flushing catalyst was removed

	With flushing catalyst	Flushing catalyst properties	Without flushing catalyst
FACT, wt%	71	77	71
Ni, ppm	7,400	100	8,900
V, ppm	2,600	350	2,700
Na, wt%	0.2	0.16	0.21
Na + V, ppm	4,900	1,950	4,800
Delta iron, wt%	0.23	0	0.3
Antimony, ppm	2,000	0	2,300
Fresh catalyst addition, tpd	6.5	—	8
Flushing catalyst additions, tpd	4	—	0

In the first case study, due to distance, the refinery has a significant delay in receiving Ecat catalyst activity results from when the sample is taken. A model was built using historical Ecat samples and unit feed rates, as well as feed metals and fresh and catalyst addition rates, to develop an accurate model fit of Ecat catalyst activity. By establishing confidence with the model, the refinery can more confidently optimize feed slates and minimize Ecat activity fluctuations. Even waiting half a week for Ecat results can result in a \$0.06/bbl loss in revenue when the Ecat activity is one number off.

The second case study shows the impacts of displacing fresh and flushing catalyst, which validates the mathematical model proposed. Flushing catalyst can be an economical solution for refiners processing resid feeds and facing operational expense pressures. The model is distilled to use a simple approach considering the difference in metals and activity between the flushing and Ecat catalyst to understand replacement ratios. In both case studies, complex decisions around catalyst management were reduced to straightforward exercises when coupled with the data-driven tools used in this article. With this framework, refiners can effectively balance value capture and catalyst costs. **HP**

LITERATURE CITED

- ¹ Wooyoung, L., "Dynamic optimization of catalyst makeup rate for catalytic cracking systems," *Industrial Engineering Chemistry and Process Design and Development*, January 1970.
- ² Weekman, V., et al., "Kinetics of catalytic cracking selectivity in fixed, moving and

fluid-bed reactors," *AIChE Journal*, May 1970.

- ³ Blanding, F. H., "Reaction rates in catalytic cracking of petroleum," *Industrial and Engineering Chemistry*, June 1953.
- ⁴ Corella, J. and E. Frances, "On the kinetic equation of deactivation of commercial cracking (FCC) catalysts with commercial feedstocks," *Catalyst Deactivation*, 1991.
- ⁵ Zhao, C., "Deactivation and testing of hydrocarbon processing catalysts," ACS Symposium Series, American Chemical Society, 1996.
- ⁶ Leuenerger, E. L., "Method predicts activity of vanadium-contaminated FCC catalysts," *Oil & Gas Journal*, 1985.
- ⁷ Xu, M., et al., "Pathways for Y zeolite destruction: The role of sodium and vanadium," *Journal of Catalysis*, 2002.

ALEXIS SHACKLEFORD is an Executive Account Manager for BASF, based in Detroit, Michigan. She provides technical and commercial support for FCCUs around the area. She joined BASF's refining catalyst division in 2009, and has held a variety of roles, including technology specialist, marketing specialist and technical service engineer. She has authored several articles for many oil and gas publications. Prior to BASF, Ms. Shackleford worked at Shell Oil Co.'s Deer Park, Texas, refinery. She earned a BS degree in chemical engineering, with a minor in biomedical engineering from Michigan State University.

ALVIN TAN is the Regional Technical Service Manager for BASF's refining catalyst business in Asia Pacific. He has more than 12 yr of experience in FCC operations and process engineering. Prior to joining BASF, Mr. Tan was the lead FCC engineer at Singapore Refining Co. As a member of the BASF Global Technical Service Team, Mr. Tan is a key player in providing quality technical service support to meet customers' needs. He earned an honors degree in chemical engineering from the National University of Singapore.

BAHA EREN is a Technical Service Engineer for BASF's refining catalyst business, and is based in Houston, Texas. In addition to providing technical service for North American accounts, he utilizes his experience in FCC kinetic modeling and statistical analysis to support the broader technical service teams. Mr. Eren earned a BS degree in chemical engineering from the University of Texas.

Electronic permissions to BASF from *Gas Processing*
September © 2020 Gulf Publishing Company



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