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FCC catalyst and additive evaluation—A case study

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ABSTRACT

Fluid catalytic cracking (FCC) unit has significant impact on refinery economics producing valuable products like gasoline and light olefins. Mandatory environmental regulations have imposed stringent quality limits on refinery products, especially on gasoline and diesel fuels. Through selection and effective utilization of catalyst and additives, refiners have been successful in achieving value additions as well as in meeting product quality norms. FCC catalyst market is competitive and it is often difficult to select catalyst based on vendor's claims. It is important to match the plant performance closely to understand unit constraints and exploit the new catalyst capabilities to full extent. Authors, using state-of-the-art facilities for catalyst characterization, evaluation and simulation tools selected superior catalysts and additives for their commercial units. The paper elaborates the laboratory evaluation methodology adopted; modeling techniques used for making yield predictions and presents case studies of successful catalyst and additive selection and use in a commercial FCC unit.

1. Introduction

Fluid catalytic cracking (FCC) unit is a major secondary catalytic process in the refinery, converting low value vacuum gas oil (VGO) feeds to high value streams like gasoline and light olefins. The value addition from this unit is over US$200 per ton of feed processed. Continuous attempts are being made to improve this margin through process optimization, selection and use of improved catalysts and additives as well as hardware modifications [1,2]. Refiners often face challenging task of judiciously selecting and switching to improved catalysts and additives for maximizing profits without violating hardware constraints. Some of these constraints that need to be considered during selection of optimal catalysts for an operating FCC unit are wet gas compressor and regenerator air blower capacities, riser and regenerator temperatures, catalyst circulation rate, cyclone limitations, vapor traffic in the fractionation column, etc. The continuous demand by refiners for improved catalysts and additives drives the catalyst vendors to improve their products making the catalyst market extremely competitive.

The selection of suitable catalysts and additives by the refiners involve both technical and commercial aspects. Some of these are benchmarking performance of the existing catalyst, developing performance targets for new procurement, obtaining catalyst and additive samples from vendors, evaluation of catalyst or additive through pilot plant/micro-reactor studies and prediction of performance on the commercial scale, economic evaluation and finalizing new catalyst, procurement and plant scale trial with the selected catalyst and benefit assessment. Selection of suitable catalysts and additives is thus an involved work and assumes critical significance due to catalyst performance aspects, profitability and trouble free operation of the FCC unit.

Fresh catalyst undergoes continuous deactivation in the FCC unit. As a result, the performance of the fresh FCC catalyst is not representative of the performance of the circulating catalyst inventory or equilibrated catalyst (e-cat) in FCC unit. Fresh catalyst gives high conversion, coke and gas yields as compared to e-cat. Surface area of the e-cat is typically about 50–60% of the fresh catalyst and the catalyst activity is typically ten units lower compared to fresh catalyst. Fresh catalyst undergoes the following changes when added to the circulating catalyst inventory (e-cat) in the FCC unit:

(a) Catalyst picks up metals like nickel (Ni) and vanadium (V) from the feed in the riser section of the FCC. Due to this metal build up on the catalyst, the coke and gas selectivity of the catalyst gets altered.
(b) Catalyst is exposed to steam in riser, stripper and regenerator at varying severity levels of temperature and steam partial pressures, as a result of which it undergoes hydrothermal deactivation leading to a gradual surface area and activity loss.
(c) Catalyst is exposed to oxidizing environment in the regenerator and reducing environment in the riser section and the

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catalyst undergoes several hundred cycles of reaction and regeneration every day.

(d) In the regenerator, catalyst is exposed to highest temperatures, i.e. about 700 °C or more, along with steam in an oxidizing environment. The deactivation due to zeolite destruction is more pronounced, especially if the catalyst contains high levels of vanadium.

(e) In partial combustion units, the regenerated catalyst retains significant amount of coke leading to reduced activity.

In order to maintain catalyst activity, fresh catalyst is added continuously to the e-cat inventory and some portion of the spent e-cat is purged from the unit. Due to this, catalyst inventory in the unit is a mixture of particles of different ages. On an average, the catalyst residence time in the unit is several days depending on the catalyst addition rate and circulating catalyst inventory.

Thus, in order to determine the potential performance of a catalyst in the commercial scale FCC unit, it is necessary to first lab deactivate the fresh catalyst to simulate plant e-cat and then perform activity studies with the lab deactivated catalyst to determine the yield pattern. The lab deactivation protocol adopted should be capable of mimicking the changes (a–e) in the catalyst caused by the commercial FCC unit-operating environment as closely as possible.

In addition to the main catalyst, to meet specific objectives, operating FCC unit may be using additives like gasoline sulphur reduction (GSR), octane booster, etc. These additives tend to deactivate faster comparatively. Therefore it is important to recognize this aspect and device deactivation protocol appropriately.

Different evaluation methodologies are followed by different laboratories [3] involving lab deactivation of catalysts and additives. In the following sections, evaluation methodology adopted by the authors and commercial performance of the selected catalysts and additives in an operating FCC unit is discussed.

2. Experimental

2.1. Lab deactivation of catalysts

In-use refinery fresh catalyst is treated as base catalyst. It is subjected to lab deactivation involving metal doping, reduction and hydrothermal deactivation to simulate plant equilibrated catalyst (e-cat) in lab. Metals are loaded on the base catalyst over several cycles of cracking using a concentrated metal-doped VGO feed followed by catalyst regeneration at conditions similar to those encountered in the commercial FCC unit. Twenty cycles of reaction and regeneration were adopted for loading the metals in a cyclic manner.

Subsequently, the metal-doped catalyst is subjected to reduction with a reducing gas mixture of 5% hydrogen in nitrogen to achieve better match with plant e-cat for coke and gas yields. The catalyst is then subjected to accelerated hydrothermal deactivation by steaming at 816 °C using 80% steam:20% nitrogen mixture. Catalyst samples are drawn at different time intervals during steaming and their activity and surface properties are measured (Fig. 1). The time at which a close match is obtained with e-cat is fixed as the steaming duration for the catalyst deactivation protocol. The lab deactivation protocol thus finalized with the base catalyst is employed for fresh vendor catalyst samples received against a commercial tender for catalyst supply. In the catalyst evaluation case presented in this work a match with e-cat was obtained after 18 h of steaming.

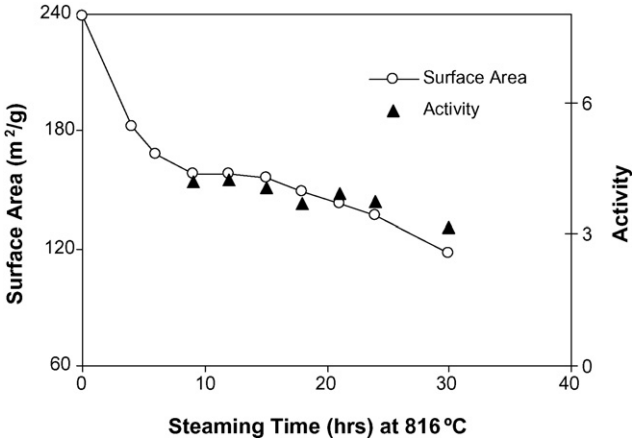

Fig. 1. Typical fresh catalyst deactivation profile.

Age distribution of particles in the catalyst inventory becomes important for catalysts having high initial activity and poor hydrothermal stability. In this work, the deactivation protocol adopted did not include age distribution effects. Instead, to rule out bias against such catalysts, additional activity studies were carried out with catalyst samples generated by subjecting them to lower and higher severity of deactivation and the ranking was compared with that obtained using the finalized deactivation protocol. In general, it was observed that the ranking remained same.

2.2. Activity studies

Catalyst activity studies were performed in a bench scale FCC unit, ACE—Model R+, supplied by M/s Kayser Technology Inc., USA. Gas products are analyzed using online refinery gas analyzer (M/s AC Analyticals). Liquid product was analyzed for boiling point distribution using a SIMDIS gas chromatograph (M/s AC Analyticals). Coke deposited on the catalyst was burnt in a catalyst regeneration step and measured using an online CO_2 analyzer. Activity studies spanning a wide range of conversion were carried out with e-cat and lab deactivated base and vendor catalysts for estimating reaction kinetics.

For evaluation of GSR additives, activity study was carried out with fresh and lab deactivated additives at 25% concentration of the additive in a mixture with e-cat. Gasoline sulphur content was measured using a gas chromatograph (PerkinElmer Arnel Clarus 500 model) equipped with sulphur chemiluminescence detector (Sievers 355 model). High sulphur vacuum gas oil feed containing 2 wt% sulphur was used in the study. E-cat was used in this study as it did not contain GSR additive.

2.3. Catalyst characterization

Lab deactivated catalysts and plant e-cat were analyzed for their surface properties i.e. total surface area (ASTM D3663-99), matrix/zeolite surface areas and pore volume (ASTM 4365-95). Unit cell parameter of the zeolite was determined as per ASTM D3942-97. Attrition loss of the catalyst was determined as per ASTM D5757. Attrition test is crucial as it gives an idea of the possible catalyst losses from the FCC unit.

3. Modeling and simulation

The overall modeling philosophy adopted is represented in Fig. 2 and involves a bench scale unit model for estimating catalyst kinetics and a FCC plant model for predicting commercial yields.

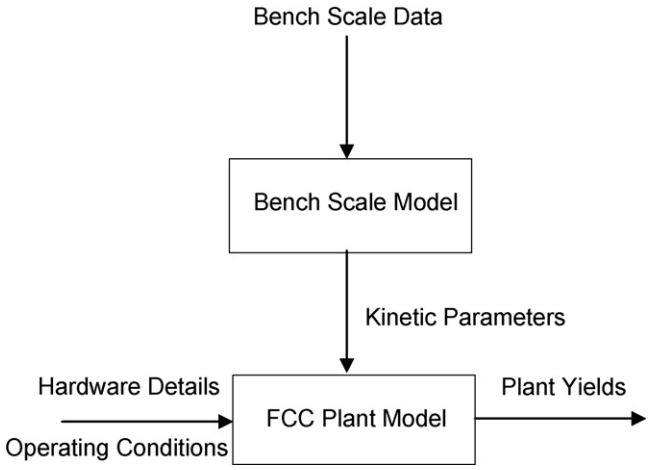

Fig. 2. Overall modeling philosophy.

3.1. Modeling of the bench scale unit

A four lump kinetic model was used to describe the complex cracking reactions of an FCC unit. These lumps are VGO (370+ °C), total cycle oils (187–370 °C), gasoline (C_5-186 °C) and coke. The coke lump consisted of coke, gas and liquefied petroleum gas (LPG). Correlations were developed based on experimental data for coke and gas yields. Using these correlations the gas and coke yields were estimated in the model. The deactivation due to coke lay down was accounted through a model described in the literature [4]. According to this model the kinetic constants will be deactivated in a non-selective manner. The laboratory fluidized bed reactor is modeled as an unsteady state reactor, where in the feed enters as a small pulse for a short time period and is subsequently stripped with nitrogen gas to remove the accumulated hydrocarbons. Cracking of feed occurs till the hydrocarbons are completely stripped out from the catalyst. To simulate this time dependent behavior it is important to model and integrate the governing equations for the entire time period. The catalyst in the fluidized bed reactor is assumed to be completely mixed, where as the gas flows in a plug flow manner. The gas flow is described by three equal volume stirred tanks in series. Differential equations for species balance were written around each cell. The equations were integrated over time from injection time till the end of stripping time to compute the reactor yields. Model parameters are pre-exponential factors and activation energies of kinetic constants, deactivation model parameters, coke and gas yield parameters. These were estimated by minimizing the deviation between the model predicted yields and the experimental values.

3.2. Modeling of the commercial FCC unit

Feed was assumed to vaporize instantaneously at the riser inlet. Catalyst slip velocities were used to estimate catalyst density in the riser. Volume expansion due to cracking reactions and hence changes in axial catalyst density were considered in the model along with reduction in catalyst activity due to coke deposition, and reduction in temperature along the riser length due to endothermic cracking reactions. Feed physical properties such as heat of vaporization, liquid and gas specific heat, enthalpies, etc. were estimated using Aspen Plus while for the catalyst the measured values or literature correlations were used. FCC riser and termination sections were modeled as mixed tanks in series. For modeling the regenerator the model suggested by Arbel et al. [5] was used. Details of model can be found in recent publication of Ravi Kumar et al. [6].

3.3. Model predictions with lab deactivated catalysts

Plant yields and temperature profiles were closely matched through simulations using kinetic parameters for the lab deactivated base catalyst (Table 1). Kinetic parameters with lab deactivated vendor catalysts were used in the plant model to predict commercial yields. To carry out relative evaluation, catalyst circulation rate was maximized without violating air blower and wet gas compressor limitation, while maintaining the riser outlet temperature. Feed preheat was adjusted to keep the riser outlet temperature constant.

4. Results and discussions

Results from two case studies viz. FCC catalyst evaluation and selection of GSR additive are discussed below.

4.1. Case A: FCC catalyst evaluation

Evaluation study involving four vendor catalysts and one base catalyst was carried out. Activity studies with lab deactivated catalysts ‘alpha’, ‘beta’, ‘gamma’, ‘delta’ and ‘base’ indicated that catalyst ‘gamma’ gave the highest conversions at all reaction conditions (Fig. 3a and b). However, this catalyst also gave the highest coke yield. In comparison, catalyst ‘alpha’ gave improved gasoline and LPG yields and reduced coke and dry gas make.

Table 1
Comparison of model prediction with plant data

	Plant test run data	Model prediction	
		Plant e-cat	Lab deactivated catalyst
Yield pattern (wt%)			
Gas	1.1	1.0	1.1
LPG	15.8	15.9	16.0
Gasoline	42.1	42.4	42.3
Total cycle Oils	30.7	33.4	33.3
Unconverted VGO	5.2	2.2	2.2
Coke	5.1	5.1	5.1
Conversion (186 °C)	64.1	64.4	64.5
Total feed rate, TPD	2709	2709	2709
Feed pre-heat temperature (°C)	338.4	338.4	338.4
C/O ratio	6.2	6.86	6.86
Riser temperature (°C)	493	491	493
Dense phase temperature (°C)	640	634	635
Dilute phase temperature (°C)	670	664	667
Air flow rate (mole/min)	33.5	33.5	33.5

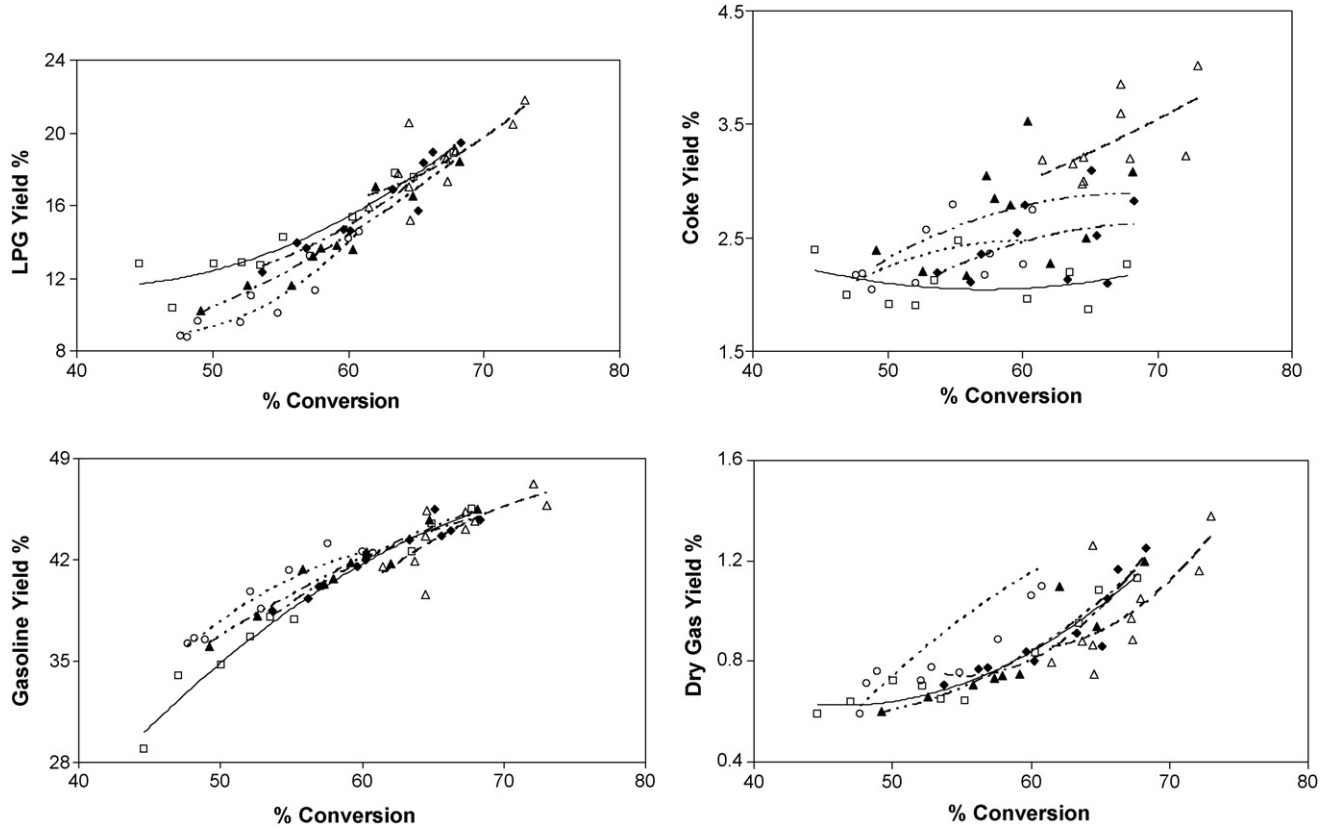

Fig. 3. (a) LPG and gasoline yields with different lab deactivated catalysts. (b) Coke and dry gas yields with different lab deactivated catalysts. Alpha (◆), beta (□), gamma (△), delta (○), base (▲).

Table 2
Predicted yields at optimum operating conditions with different catalysts

	Base	Alpha	Beta	Gamma	Delta
Yield pattern (wt%)					
Gas	1.4	1.5	1.4	1.3	1.5
LPG	13.6	15.4	16.0	16.7	11.3
Gasoline	41.3	42.7	41.5	41.7	40.5
Total cycle oils	34.3	32.4	31.8	29.5	34.6
Unconverted VGO	4.7	3.4	4.9	5.9	7.5
Coke	4.7	4.6	4.4	4.9	4.6
Conversion (186 °C)	61.0	64.2	63.3	64.6	57.9
Feed rate, TPD	2800	2800	2800	2800	2800
Feed preheat temperature (°C)	360	365	370	370	350
C/O ratio	6.5	6.0	7.2	7.2	7.2
Riser top temperature (°C)	496	494	494	496	496
Regenerator dense phase temperature (°C)	633	639	614	622	618
Regenerator dilute phase temperature (°C)	653	665	651	630	649
Air flow rate (kmol/min)	35.0	35.0	35.0	35.0	35.0
Wet gas compressor flow rate (kN m^3/h)	11.1	12.5	12.9	13.3	9.4
Profit/loss over base catalyst (million US$/year)	0	+2	+0.5	−0.5	−3.3

Model predictions were made under optimal operating conditions with each catalyst for maximizing their value addition and compared with the base catalyst (Table 2). The FCC unit air blower capacity was completely utilized by all catalysts. Catalyst 'alpha' did not violate any other operating limits. This catalyst was also coke selective and hence there existed a scope for processing refractory feeds with this catalyst. The value addition with this catalyst was highest among all catalysts (US $2 million per annum) and hence it was recommended for procurement. Commercial FCC unit yields matched closely with lab predicted yields (Table 3) for selected catalyst validating the evaluation methodology adopted.

Table 3
Comparison of plant performance with yield predictions for selected catalyst

	Lab predictions	Plant yields
Feed throughput, TPD	3500	3500
Product yields (wt%)		
Gas	2.5	2.0
LPG	16.6	16.3
Gasoline	44.8 (up to 180 °C)	47.1 (up to 220 °C)
Total cycle oils	23.5	23.5
Unconverted VGO	8.4	7.1
Coke	4.2	4.0

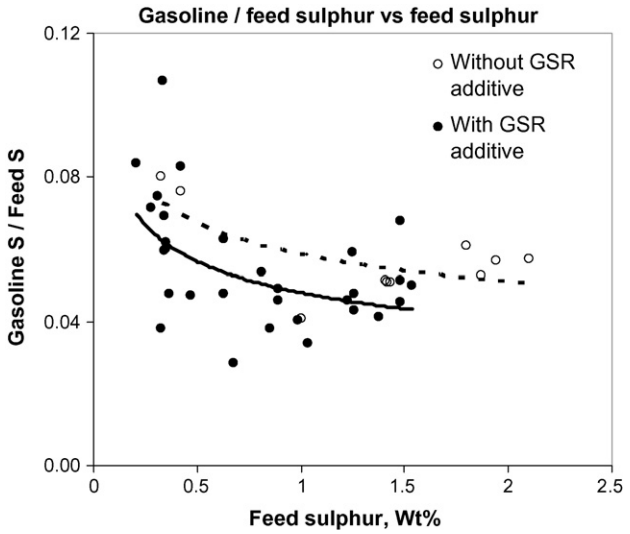

Fig. 4. Commercial plant performance of the selected gasoline sulphur reduction (GSR) additive.

4.2. Case B: selection of gasoline sulphur reduction additive

Two GSR additives 'alpha' and 'beta' were evaluated. Additive 'beta' was selected owing to its better sulphur reduction performance and superior attrition resistance. Lab results indicated a gasoline sulphur reduction of 29% with fresh 'beta' additive and 8% with lab deactivated 'beta' additive. Plant trial with this additive resulted in a gasoline sulphur reduction of 25% with high sulphur VGO feeds and 18% reduction with low sulphur VGO feeds at 15% concentration of the additive in the inventory (Fig. 4). Due to the use of the additive, refinery was able to process 5% more high sulphur crudes without violating gasoline sulphur specifications.

5. Conclusion

A methodology for evaluation and selection of optimum catalyst and additives for operating FCC units has been presented. For proper evaluation, deactivation methodology adopted should be capable of mimicking changes occurring in the catalyst in the FCC unit very closely. While making the choice of optimum catalyst or additive careful consideration needs to be given to the quality of feeds likely to be processed, the FCC hardware utilization with the catalyst for typical operating throughput scenarios and feeds processed as well as product yields and quality. Selection and use of optimum catalyst and additives helps the refiner to achieve their objectives quickly.

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