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Challenges, catalyst technology and catalytic solutions in resid FCC

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Abstract

The concurrent evolution of resid fluid catalytic cracking (RFCC) processes and catalyst technology over the years is discussed. Resid FCC catalysts today are designed making use of the following features: (a) High activity, selectivity and metals resistant zeolites; (b) Highly accessible catalyst architecture for optimal site utilization, bottoms cracking, Conradson carbon residue (CCR) conversion and easy stripping; and (c) Specially designed metal-support interaction systems to reduce the detrimental effects of metal contaminants. The future will require even more robust RFCC catalyst systems. These catalyst systems should be very accessible and effective in cracking large hydrocarbon molecules and should have the capability to handle contaminants such as metal-, sulfur-, and nitrogen-compounds. Conversion of CCR to non-coke components will be crucial in order to reduce the delta coke and hence improve the processability of heavier resids. Processability here is meant not only in terms of coke and heat balance considerations, but also involves avoiding fouling of the unit hardware by unconverted heavy hydrocarbons and coke precursors. Last, but not the least, present and future catalyst technology must be formulated and adapted to the specific commercial process unit needs and constraints, thus leading to the most cost effective solution for the refiner. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction: Conventional vs. resid FCC

Catalytic cracking in the early days (1940's), consisted mainly of gas oil and vacuum gas oil (VGO) fluid catalytic cracking (FCC), aimed at the maximization of gasoline production. While, in hydroprocessing VGO is considered to be a resid, traditionally the cracking of low metal resids has always been referred to as 'conventional' VGO FCC.

If arbitrarily, we define resid in terms of Conradson carbon residue (CCR) levels of higher than 2%wt, then we can derive the following marketshares for Akzo Nobel in the VGO and resid market segments (see Table 1).

2. History and evolution of resid FCC catalysts

2.1. The first round

The first round of resid FCC (RFCC) started [1], when metal contaminated feedstocks such as, heavier vacuum gas oils, so called 'dirty' wash oils, and deeper flashed or deasphalted resid streams were often routed to a conventional VGO FCC unit. The contamination of feed with metals (V, Ni, Fe and Na) began to play a role in terms of selectivity (coke, gas)

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Table 1
Resid vs. VGO applications in FCC (1996)

	% Feed	% FCC catalyst consumption	Akzo nobel market position
VGO	72	64	No. 2
Resid	28	36	No. 1

and activity (deactivation by coke, higher temperatures in the regenerator) of the catalyst. Examples of this are the early (1950) studies by Mills [2] on the effect of iron in clay-based catalysts, which indicated that, if the iron is removed coke and gas make can be reduced.

Rothrock and Connor [3,4] investigated the laydown and deactivation of metals on FCC catalysts and elucidated the activity of the metals (Ni, V, Fe, etc.) as dehydrogenation catalysts. As in hydroprocessing, the importance of the degree of dispersion and metals penetration into the catalyst pores were recognized. Grane and Cimbalo [5,6] investigated the aging and deactivation kinetics of metals on FCC catalysts as a function of the number of oxidation and reduction cycles.

While in most of the laboratory deactivation protocols the number of redox cycles is rather limited for practical purposes (in the 10–100 range), the number of cycles in commercial FCC units is significantly higher. Typical regenerator cycle data for commercial FCC units are shown in Table 2.

As is illustrated in Fig. 1, during the early cycles of deactivation the age of the metals is extremely important, but after having gone through many cycles of oxidation and reduction the effect of age becomes minor. In terms of fighting the detrimental dehydrogenation activity of metals, the ability of a cracking catalyst to rapidly deactivate the metals deposited becomes a critical characteristic.

Table 2
Reactor–regenerator redox cycles in commercial FCC

Estimated number of cycles		
Time	Small catalyst inventory, high addition	High catalyst inventory, low addition
1 h	12	4
1 day	300	100
1 week	2100	700
Average catalyst age	10.000	30.000

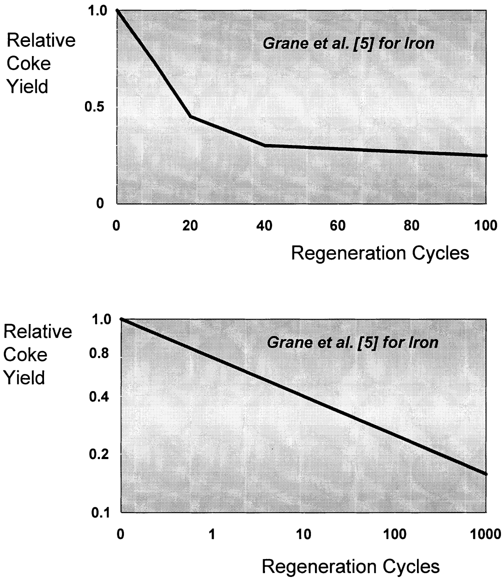

Fig. 1. (A) Metal dehydrogenation activity vs. number of regeneration cycles, showing fast initial rate of deactivation of metals activity. (B) Log–Log scale relation.

Cimbalo et al. [6] demonstrated that, metals deactivate at different rates for different catalysts. A mechanism of deactivating metals was proposed, being that metals are encapsulated or become inaccessible due to collapse of the amorphous silica–alumina structure.

2.2. Zeolites incorporation into FCC catalysts

The introduction of high activity and stability metal (rare earth)-exchanged zeolites revolutionized FCC operations and enabled the introduction of shorter contact time plug-flow riser-type FCC designs.

Initially the zeolites were either incorporated into the 'amorphous' silica–alumina gel catalyst types in the case of the existing synthetic microsphere based FCC manufacturing processes, or crystallized in situ as in the classic treated clay-based catalysts such as, the first Filtrol catalysts and Houdry, now Engelhard FCC, catalysts. A recent review of these processes has been given by Woltermann et al. [7].

Plank and Rosinski [8] found that zeolites should be dispersed in a relatively inactive matrix in order to prevent overcracking. Elliott [9] developed a catalyst with zeolite incorporated into a silica sol and clay based binder for this purpose. These 'full' zeolite catalysts were commercialized with a minimum of non-zeolitic 'matrix' activity, aiming for the optimum in activity and coke selectivity.

With regards to RFCC operations and catalyst design philosophy [10] two schools of thinking seem to emerge:

- The minimum delta coke approach: Usually applied in coke-limited units, making use of a full zeolite catalyst; and
- The maximum bottoms cracking approach: Non coke-limited FCC units (sometimes with dedicated heat removal systems), with a moderate zeolite and a significant non-zeolitic larger pore type activity.

Filtrol catalyst technology, because of the special nature of the catalyst binder system and resulting pore architecture, produced the first dedicated resid catalysts of this second school. Alafandi and Stamires [11] in 1977 emphasized the need for an optimization of encapsulation of the zeolite into the catalyst particle vs. the degree of porosity and permeability required for effective cracking. The Filtrol catalyst technology is the one, where the particle permeability and hence effective use of the active zeolite component is particularly optimized.

2.3. *The octane or ultra stable Y (USY) zeolite era*

Activity and selectivity of zeolites can be reasonably correlated with the unit cell size (UCS) of the zeolite, which is a measure of the silica to alumina ratio in the zeolite structure. Zeolites, which have not been fully exchanged with rare-earth, so-called hydrogen Y (HY) or partially rare earth exchanged (RE-HY) zeolites, equilibrate at a lower UCS. These zeolites exhibit a lower tendency towards hydrogen transfer reactions resulting in higher octane gasoline and lower delta coke. The thermal stability of these zeolites is however inferior to fully rare-earth exchanged Y zeolites (REY).

Consequently, hydrothermally stabilized or so called ultrastable Y (USY) zeolites were developed. USY zeolites maintain their structural stability at temperatures above 1000°C. Today USY or partially rare earth exchanged RE-USY zeolites are still the key active components of many low delta coke RFCC catalysts.

Low UCS, USY zeolites unfortunately are not very active. Often upto twice the quantity of zeolite is required in order to reach the same conversion level, as compared to REY and/or RE-HY based catalysts. The zeolite crystallinity retention after vanadium deactivation of USY is at least as good as for RE-HY zeolites; the activity retention however is far less.

It has been [1,10] suggested and observed that the zeolite is not simply destroyed, but that at least part of the deactivation is due to the fact that the limited number of available acid sites in USY zeolites are easily 'neutralized' by contaminants. Therefore, zeolites which combine the activity stability of USY types and the activity of RE-HY types obviously would be a more appropriate solution in these applications (see section on High Activity and Stability Zeolite Technology).

2.4. *The arrival of metal traps and metal scavengers*

Protection of zeolites by metal scavengers then became an important field in RFCC catalyst development. Dedicated metal traps, scavengers and/or additives (solid catalyst and/or feed additives as Sb, Bi, Sn, etc.) were developed and commercialized in order to combat the negative effect of metals, mainly vanadium (V) and nickel (Ni). The effectiveness of these separate particle metal scavenging systems was far from optimal [1], and the question of how to realistically deactivate and retest the catalyst became an important issue.

The concept was revived as pioneered by Rothrock and Connor [3,4] of realistic cyclic aging and deactivation of metals on catalyst instead of pore volume impregnation followed by steaming. While in the 'old days', cyclic deactivation of a catalyst was a very difficult and time consuming exercise, nowadays modern, reliable and automated laboratory equipments are now available to do this task [1,12].

For commercially realistic cases, metals deposition, dispersion and mobility on a catalyst are very different compared to the often used traditional laboratory deactivation techniques [12,13]. A consequence is that in the case of metal traps, the accessibility of the

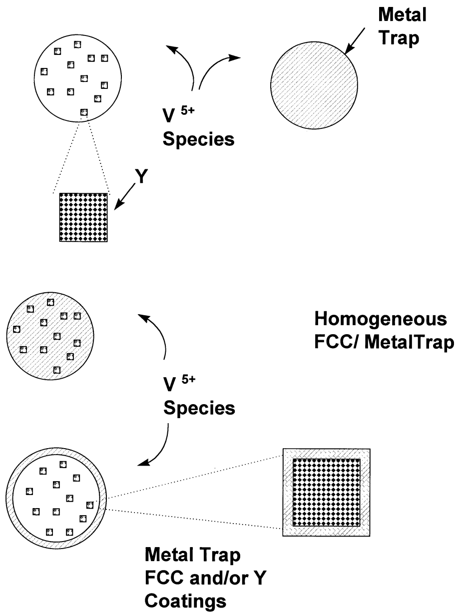

Fig. 2. (A) Concepts of metal protection: Metal trap additive concept. (B) Concepts of metal protection: Homogeneous and/or coating.

metal-scavenging component appears to be very critical [10,14], dictating that the strategy to protect catalysts needs to change.

2.5. *Accessible catalytic surface for metal-support reactions*

As discussed in the foregoing section, the effectiveness of a separate metal trap particle will be far from optimal. Improved catalyst concepts to address this, such as, coating the FCC particle or the component which needs to be protected (e.g. zeolite), have been proposed by several researchers. A comparison of these two concepts is shown in Fig. 2. A recent example is described by Wielers et al. [15].

Ideally, the catalyst support system itself should be able to deactivate the metals. The Filtrol catalysts with their special, very accessible catalyst support, indeed excel in protecting the zeolite against vanadium [14].

2.6. *High activity and stability zeolite technology*

The disadvantages of USY zeolites are the low activity and the selectivity side-effects caused by the formation of non-framework aluminum. These drawbacks can be partially addressed by the use of chemically dealuminated (DAY) and/or chemically substituted (LZ-210) zeolites. While with these zeolites coke selectivities improve, activity and activity retention after deactivation with vanadium deteriorate even further [16].

Table 3
Alternative high modulus zeolites

TCC catalyst, testing of beads

Zeolite type	Conversion, %wt	Coke, %wt
REY	40.9	4.2
RE-USY	44.5	3.7
RE-LZ-210	45.7	4.3
RE-HMY[a]	50.8	3.5

[a] HMY: High modulus Y.

Direct synthesis of lower aluminum per unit cell (or higher SiO_2/Al_2O_3 ratio) zeolites, as illustrated by Levinbuk [17], is an elegant alternative which results in improved activity as well as coke selectivity. Structural defects and non-framework aluminum are avoided by this route. Unfortunately, the crystallization times required to produce these zeolites without the use of costly templates are presumably commercially prohibitive. Data for these high modulus (SiO_2/Al_2O_3 ratio) zeolites are shown below in Table 3.

In 1986, Akzo Nobel introduced a new technology to manufacture high activity and high stability Y-type zeolites. These 'ADZ' zeolites are very suitable for resid as well as non-resid applications. ADZ zeolites as described by Humphries et al. [16] exhibit the activity of RE-HY zeolites combined with a better stability than USY zeolites. They also show a significant improvement in structural stability as well as activity retention towards vanadium and sodium. Examples of the hydrothermal stability and metal (V) resistance of the ADZ zeolites incorporated into FCC catalysts are given in Table 4 and Table 5.

2.7. *Mass transfer limitations and accessibility*

In conventional FCC, it is often claimed that cracking reactions are not diffusion limited for vapor phase gas oil cracking because of the small size of the catalyst particle. While we even question this assumption for VGO cracking, in RFCC we know that this is

Table 4
Hydrothermal stability of ADZ zeolites

Surface area retention, %		
(After steaming)	5 h at 760°C	5 h at 790°C
HY	65	50
USY	80	74
ADZ	90	84

Table 5
Vanadium resistance stability of ADZ zeolites

Relative activity vs. deactivation		
	ADZ-50	RE-USY
Base	100	100
Cyclic deactivation with 5000 ppm vanadium		
Low severity	98	95
Medium severity	92	84
High severity	90	75

certainly not the case. There are observable diffusion restrictions within a zeolite or a loss of activity for moderate size molecules [14,18].

Mann et al. [19], using a special technique to study the mass transfer into a catalyst particle by SEM, have illustrated the fact that the accessibility of a typical catalyst is far from perfect. Under average riser conditions, we can envision that the larger hydrocarbons will only penetrate into the outer shell of the catalyst particle and hence, will only have access to a limited number of active sites. Coke formation and pore mouth blocking will further aggravate the situation. Fig. 3 illustrates a shell-core model for FCC catalysts [14].

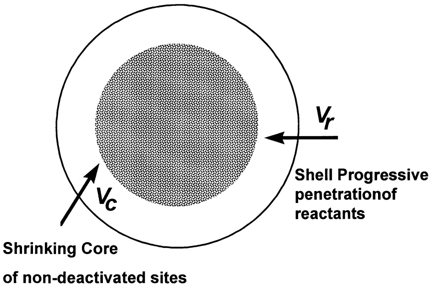

Fig. 3. Shell-core model in FCC: Supply and demand model (14). Note that the front velocity will be a function of compounds.

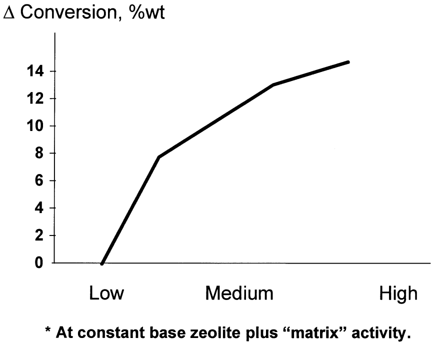

Fig. 4. Catalyst activity by accessibility improvements.* *At constant base zeolite plus "Matrix" activity, in SCT pulse VGO testing.

Falabella et al. [18] applied the cracking of 1,3,5 tri-isopropyl-benzene (TIPB) as a test reaction to study the activity and accessibility of zeolites. Zeolite acidity, as well as accessibility, controlled the rate of reaction, while conversion deteriorated according to the loss in accessibility when incorporated in a traditional FCC catalyst system.

To illustrate this for VGO molecules (see Fig. 4), short contact time (SCT) laboratory testing has been performed with VGO on catalysts, with approximately the same number of active sites, although the catalyst architecture has been adapted in order to vary the catalyst accessibility. Accessibility of the catalysts was measured using a proprietary test [14].

Activity, selectivity and pore architecture of the non-zeolite ('matrix') components of RFCC catalysts have always been important factors for optimal performance. Catalyst accessibility and non-zeolite activity becomes, even of greater importance in the case of SCT cracking of larger resid type molecules. In the following figure (Fig. 5) results are given of a laboratory study comparing various resid catalysts in a modified classical microactivity test (MAT), known as a microsimulation test (MST), vs. a newly developed SCT fluid bed type test for heavy resids.

As shown in Fig. 5, the net bottoms cracking (Defined as NBC $=100 - \text{Coke} - \text{Bottoms}$, in %wt) potential of catalysts with a high accessibility and mesopore activity becomes much more pronounced at short contact times, while the delta coke penalty which is normally observed in long contact time test units is strongly reduced.

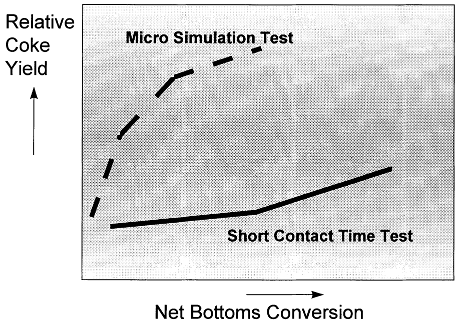

Fig. 5. Short contact time resid testing using medium hydrotreated resid feedstock (4% CCR).

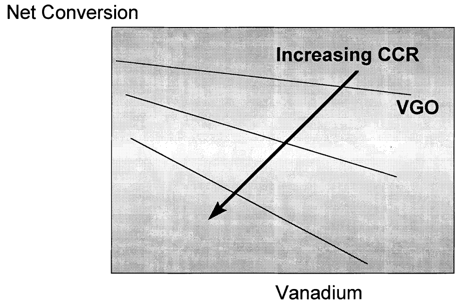

Fig. 7. The real challenge in resid FCC is active site accessibility. Data taken from Khouw et al. [21].

This new laboratory bench scale unit is based on the concept of simulating the temperature and time history of a small catalyst package moving through a commercial riser [20]. The test clearly deviates in design from classic fluid bed tests and is able to produce 'MAT-like' accuracy and productivity with high CCR content feedstocks at short catalyst and oil contact times. An illustration of this new test concept is shown in Fig. 6.

Catalyst deactivation by metals will also have an impact as illustrated in Fig. 7, which represents the data of Khouw et al. [21]. Vanadium contaminated equilibrium catalyst from an RFCC unit was tested in a short contact time riser. Although for VGO cracking hardly an activity loss is noted, with higher CCR feedstock, conversion drops dramatically. From this we can conclude that the accessibility of acid sites rather than the destruction of the sites (e.g. zeolite) seems to be the most important problem. Similar results have been reported by us [14,22]. To explain this effect, a model is proposed wherein both the large molecules as well as the deactivating agents (vanadium, sodium, nitrogen) are competing for the same limited number of accessible sites.

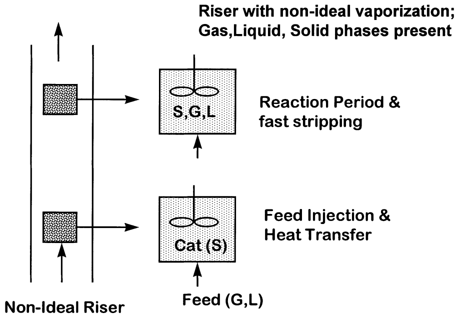

Fig. 6. New short contact time test: 'Package in time concept'.

Zhao [23] studied the deactivation by sodium in commercial operations and found that in the case of commercial sodium deactivation of FCC catalysts the matrix surface area is more strongly affected than the zeolite. This illustrates again that, for RFCC catalysts the emphasis for improvement should probably be more on the non-zeolite porous 'matrix' and catalyst accessibility and less so on the zeolite.

3. Recent and future trends

3.1. *Designed metal support interactions*

Catalyst support systems have been designed, which are able to more effectively encapsulate and deactivate the active metals within the RFCC catalyst. These very accessible multipurpose (activity + metals deactivation) systems form an integral part of recent state-of-the-art RFCC catalyst grades. These systems can of course be combined with high stability zeolites and applied in high vanadium and nickel RFCC operations. Examples of results obtained with various combinations of these catalyst and support systems are shown below in Table 6.

As addressed in a previous publication [13], the simulation of a catalyst deactivated by metals is not a simple task. In the case of vanadium for instance, the

Table 6
Improvements in nickel resistance

Catalyst		Coke at constant conversion	Bottoms at constant conversion
Zeolite	Support		
USY	Standard	3.0	20.0
RE-USY	Standard	2.7	16.4
ADZ	Advanced-1	2.5	15.5
ADZ	Advanced-2	2.3	14.9
ADZ-R	Advanced-3	2.1	14.0

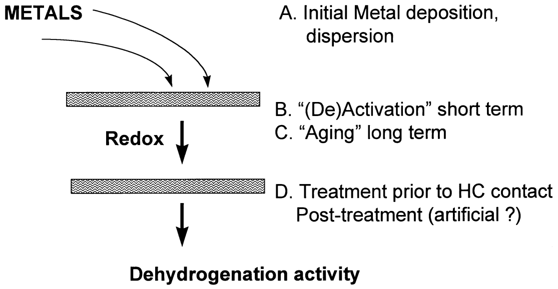

Fig. 8. Metals–catalyst support interactions.

oxidation state of the metal during and at the end of the deactivation will have an important impact on catalyst activity as well as selectivity. Table 7 indicates, estimates for the vanadium reactivity as well as mobility as a function of deactivation conditions. Studying equilibrium catalysts from many resid operations, we observed that the activity and/or mobility of metallic vanadium (V or V^0) is far less than in the fully oxidized state (V^{+5}). Table 7 demonstrates that, by adding a reduction step it is always possible to correct the dehydrogenation activity of the metals.

An important question is whether the fast high temperature (fully oxidized vanadium) redox aging of the catalyst followed by a full reduction does not mask differences in metals–catalyst support interactions (see Fig. 8), which may occur in real commercial deactivation. For a proper evaluation of catalysts, we may need to simulate the interaction between the catalyst support and the metals better.

To address this, modifications in the existing cyclic deactivation (CD) procedures will be proposed [24], based on recent results including a study of redox kinetics of metals in FCC. The separate steps of this modified process are shown in Fig. 9. Basically, the modified procedure will consist of a first stage of cyclic impregnating of the catalyst with metals under very mild conditions of 550–650°C, whereby the coke can be burned off without oxidizing the vanadium and without steam, followed by a second stage of cyclic oxidation and reduction steps at more severe isothermal conditions (for instance 750–800°C), whereby the oxidation state of the vanadium is controlled in the regenerator step at the level of the equilibrium catalyst (E-cat) to be simulated.

3.2. *Delta coke: CCR coke conversion*

The newest generation of resid catalysts is not only less sensitive to metals but can also handle CCR in a

Table 7
Vanadium activity vs. deactivation conditions

	Dehydrogenation activity	Mobility	Reducibility
'Free' metals	?	140	100
Mitchell impregnation[a]	100	100	100
Cyclic deactivation			
50 cycles	50	50	
100 cycles	40		
50 cycles+reduction	25		
Mitchell+cyclic redox			
30 cyclic redox	65		68
30 cyclic redox+reduction	30		
Equilibrium catalyst	20	20	25

[a] Mitchell method set at 100% as base.

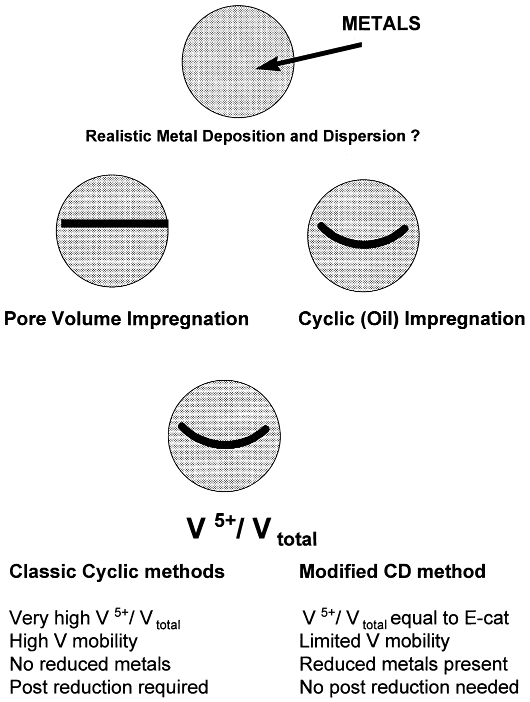

Fig. 9. (A) Conceptual picture of realistic cyclic deactivation. Step one: Metals deposition. (B) Conceptual picture of realistic cyclic deactivation. Step two: Metals 'aging'.

Table 8
Progress in the conversion of CCR

Catalyst		
Zeolite	Support	Max CCR[a], %wt
REY	Standard	0.9
REUSY	Standard	1.4
ADZ50	Advanced-1	2.0
ADZ50	Advanced-2	3.5
ADZ50R	Advanced-3	4.5

[a] Typical commercial data on maximum allowable CCR in feed, set by delta coke limitations.

better way, meaning that a larger fraction of the CCR can be converted to non-coke components. Examples of data obtained with these new resid catalysts are shown below in Table 8.

Aside of the importance of CCR conversion for delta coke reduction, also the impact of unconverted coke precursors on coking and fouling of FCC or RFCC unit hardware is of great importance. Breevoord and Wilcox [25] indicated the importance of catalyst accessibility also in this respect.

3.3. *Delta coke: reaction, dehydrogenation, CCR and stripping*

Investigating coke selectivity and coking on a laboratory scale has not been easy. Brevoord et al. [26] conclude that, for a good evaluation of the coke selectivity of resid catalysts, all contributions to coke need to be determined properly:

- Reaction or catalytic coke;
- Dehydrogenation or metal coke;
- Conradson carbon coke; and
- Soft coke (incomplete stripping, entrained hydrocarbons).

In order to do so, several testing techniques have been developed enabling short contact time testing of heavy resids (up to 10% wt CCR) and high metal contents at both bench scale as well as pilot-scale levels.

4. Looking into the future

The future will ask for even more robust RFCC catalyst systems. These catalyst systems should be very accessible and effective in cracking large hydrocarbon molecules and should have the capability to handle the contaminants like metal-, sulfur-, and nitrogen-compounds.

Conversion of CCR to non-coke components will be even more crucial in order to reduce the delta coke.

Last, but not the least, present and future catalyst technology must be adapted to the specific commercial process unit needs and constraints, thus leading to the most cost effective solution for the refiner.

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