The coke selectivity of an FCC catalyst underpins the unit's operability and profitability with wide ranging impacts to catalyst circulation rates, product yields, and regenerator combustion kinetics. In the 1987 *Catalagram* article "Coke Selectivity Fundamentals," Charles Wear explains coke selectivity in plain terms and touches on how it can have profound effects on the unit's heat balance, operating window, and overall product yield slate. Wear's write up also emphasizes that a "one-size-fits-all" approach to catalyst design is destined to fall flat.

These insights from the late 1980s continue to ring true today. A refiner's ability to work with industry partners to optimize FCC operation, feedstock and catalyst selection will be imperative to successfully navigate shifts in product demand and refined product margins. Grace's collaborative relationships with customers enable our technical experts to design catalysts that maximize operational flexibility and product value. For example, latest innovations offering improved coke selectivity, including FUSION® and PARAGON™ technologies, incorporate novel metals trapping functionality and to help optimize customer operation.

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Coke Selectivity Fundamentals

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Coke selectivity is a term that often means different things to different people. So to lead off our discussion, let's focus on a definition: Coke selectivity is the relative coke-making tendency of any given cracking catalyst. In the vernacular, a catalyst that has "good coke selectivity" means it produces lower coke compared to some reference catalyst. This is usually considered a favorable characteristic, since liquid yields are preferred.

That seems fairly straightforward, but the often misunderstood part is just what the phrase "coke-making tendency" really means. Many times it is confused with coke yield as expressed in say, weight percent of fresh feed. However, the coking tendency of a catalyst in the context of "coke selectivity" is actually its tendency to produce delta coke.

The Concept of Delta Coke

The concept of delta coke is neither novel nor complicated. It is simply the difference between coke on spent catalyst (at stripper outlet) and coke on regenerated catalyst, expressed as a weight percent of catalyst.

More correctly, delta coke can be thought of as the amount of coke formed on the catalyst for a single pass of the catalyst through the reactor which, in the continuous steady-state operation of a commercial FCCU, is also equal to the amount of coke burned off the catalyst in the regenerator.

Delta coke also has kinetic significance, especially on the reactor side of the process where it formed. The coke on catalyst per pass is a combusfunction of many variables, including but not limited to: feed quality and dispersion at the nozzle, reactor temperature and pressure, catalyst activity and contact time, and last but not least, catalyst coke selectivity.

Therefore, when all other variables affecting delta coke are more or less constant, a catalyst that possesses "coke selectivity" will exhibit lower delta coke at any given activity.

A "coke balance" around the regenerator results in a useful expression for delta coke. The coke yield must equal the difference in coke entering and leaving the regenerator. Therefore, note that

Coke Yield = C/O (CSC-CRC)
or
$$\frac{CSC\text{-}CRC = Coke\ Yield}{C/O} = Delta\ Coke$$

where:
Coke Yield is wt.% Feed
C/O is Cat Circulation,
   lb. Cat/lb. Feed
CRC is Coke on Spent Catalyst,
   wt.% Catalyst
CRC is Coke on Regenerated Catalyst,
   wt.% Catalyst

coke yield and cat/oil must be expressed on the same feed basis, fresh or fresh plus recycle, to yield a meaningful number.

Since coke yield and cat/oil are related to delta coke in the above mentioned manner, it follows that a coke "selective" catalyst can decrease coke "yield", but not necessarily. For instance, in many cases, coke selective catalysts will operate with higher cat/oil ratios with little or no change in coke yield. An understanding of this requires examination of the FCCU heat balance and the interaction of process operating variables.

Heat Balance Effects

A commercial unit, like all steady state processes, must be in energy balance. This means that the total energy coming into the process must equal the energy leaving the process, as shown in Figure 1. The energy to heat the fresh feed, recycle feed and stripping steam to reactor outlet temperature, to heat the air to flue gas temperature, to supply the endothermic heat of reaction and any losses to the atmosphere—all of this must come from the coke's heat of combustion. A portion of the feedstock is therefore "consumed" to supply the energy requirements of the process.

One consequence is that the coke yield as weight percent feed is determined by the sum of these energy requirements, not by the catalyst coke selectivity (or feed coking tendency for that matter). This is the key concept that distinguishes delta coke, which is catalyst and feed related, to coke yield, which is not. We will return to this concept in a moment.
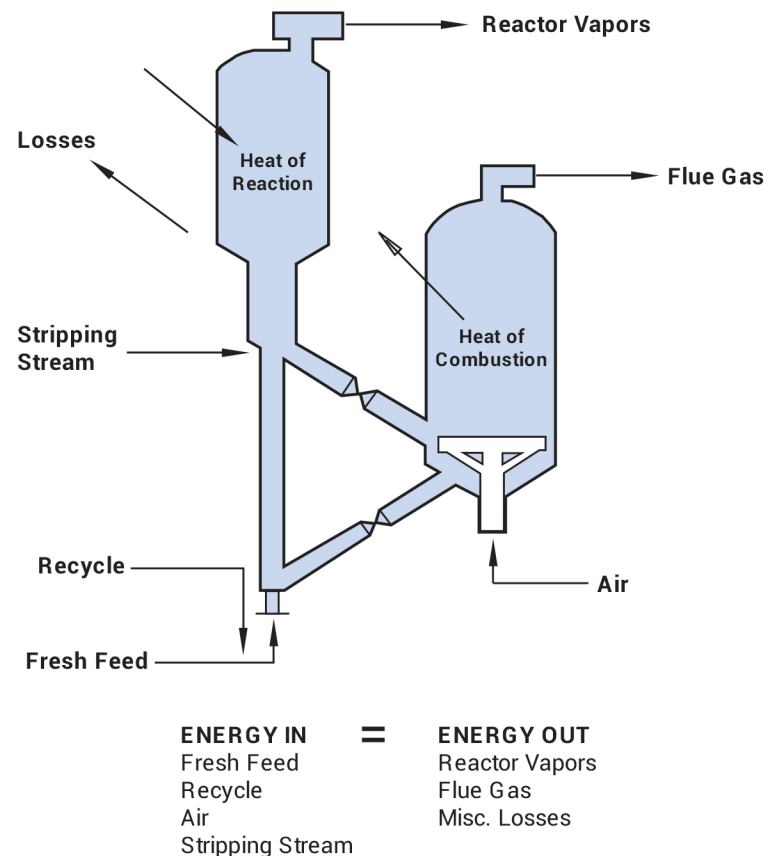

ENERGY IN   **=**   **ENERGY OUT**
Fresh Feed   Reactor Vapors
Recycle   Flue Gas
Air   Misc. Losses
Stripping Stream

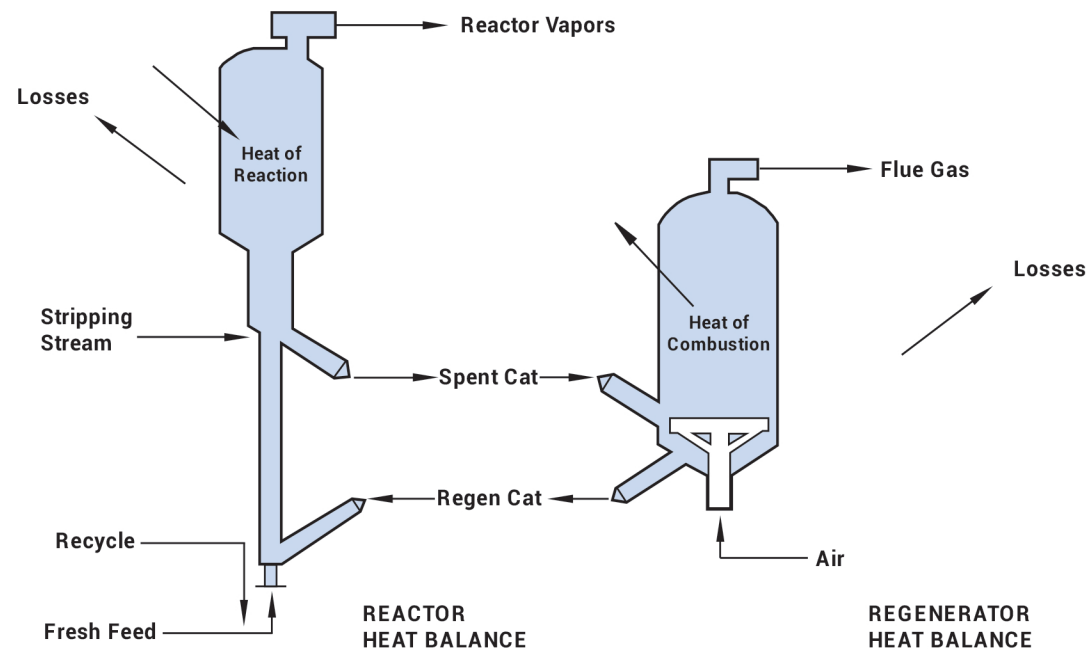**Figure 1.** Simplified Overall Energy Balance

Figure 2. Energy Balance of Reactor and Regenerator Involves Catalyst Circulation Rate

The principle of energy balance holds for the individual reactor and regenerator as well as the overall process, as shown in Figure 2. Table 1 lists the simplified components to balance each vessel. By equating the regenerator heat production to the heat transferred by catalyst, a useful relationship can be derived:

Heat of Coke Combustion + Other Terms
= Heat Transferred by Catalyst

Coke Yield (ΔHc)
    $\cong$ C/O Cp^{Cat} ($T_{Regen} - T_{Rx}$)

Delta Coke =
$$\frac{Coke\ Yield}{C/O} \cong \frac{Cp^{Cat}}{\Delta Hc}\ (T_{Regen} - T_{Rx})$$

Noting that the catalyst heat capacity (Cp^{Cat}) is constant for any particular case, along with the coke's specific heat of combustion (Hc) when hydrogen in coke and degree of CO combustion are constant, the following proportionality holds:

Delta Coke $\propto$ ($T_{Regen} - T_{Rx}$)

Reactor Heat Requirements	Regen Heat Production	Heat Transferred by Catalyst
+ Heat of Reaction	+ Heat of Coke Combustion	
+ Heat Up Feed	- Heat Up Air	
+ Heat Up Recycle	- Heat Up Coke	
+ Heat Up Strip Stream	- Heat Up Rx Entrainments	(C/O) Cp ^{cat} (T_{Regen}-T_{RX})
+ Account for Losses	- Account for Losses	
- Heat from Regen Entrainments		

Table 1. Energy Balance Relationship

This implies that a coke selective catalyst will, for a constant reactor temperature, reduce regenerator temperature. This is exactly what is observed commercially. Consider the unit in full combustion that has changed to a catalyst with different coke selectivity. Depending on the shift in delta coke, the changes shown in Figure 3 occur.

Of course, unit response to coke selective catalysts is not limited to regenerator temperature reductions. Consider the

unit in partial CO combustion, where a drop in regenerator temperature could possibly result in a undesirable increase in regenerated catalyst carbon level. For this case, it would be wise for the operator to intervene—via increased promoter additions and/or air rate-to burn more CO to CO_2 and thus return the dense bed to original temperature.

In this example, these "external stimuli" from the operator directly affect the overall heat balance by increasing the
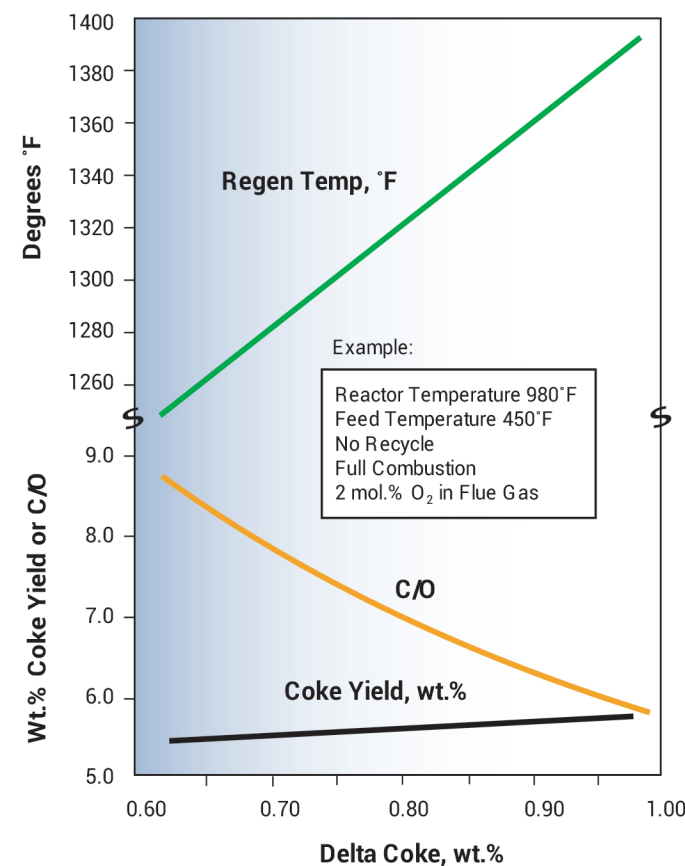
Figure 3. Typical Effect of Delta Coke on FCC Operation

heat release per pound of coke burned (higher CO_2/CO). It therefore takes the combustion of less coke to satisfy the energy demand of the process. So, for this partial combustion case, coke yield will drop at the same or nearly the same reactor/regenerator temperatures (and therefore cat/oil). It has to, because the catalyst caused a reduction in the delta coke, and by definition coke yield must be lower if delta coke drops at constant cat/oil!

Remember earlier in this discussion it was stated that catalyst (and feed quality) have a direct effect on delta coke, but that the unit heat balance determines coke yield. As the preceding example showed, sometimes it's difficult to separate what changes were caused directly by catalyst (or feed) as opposed to heat balance changes made by the operator.

In reality, the difference is not very important in many cases. The important point is that coke selective catalysts will, in more cases than not, allow an operator to have more flexibility in running his plant. Here are some of the ways we have seen operators use Davison coke selective catalysts to their fullest extent, and thus alleviate operating constraints and improve refinery profitability:

- Increase reactor temperature to produce maximum gasoline octane.
- Increase cat circulation for increased conversion.
- Increase resid content for additional bottoms destruction.
- Increase feed rate to satisfy increased product demand.
- Increase CO_2/CO for lower coke yield.

As with many things in life, "more" catalyst coke selectivity in all cases does not necessarily mean "better". A thorough review of the base operation, including goals and constraints, should be performed before any catalyst change is considered. For example, some operations are precluded from the use of incremental catalyst coke selectivity. Consider the unit in full combustion, at maximum catalyst circulation and feed temperature, that cannot "heavy-up" the feed nor accept a lower reactor temperature. This obviously is not a unit that would profit from catalyst coke selectivity. It is a unit, however, which could greatly benefit by removing these limitations, and many have done exactly that via revamps.

A Check on Data Consistency

The fact that delta coke can be measured directly by comparing the difference in coke levels between spent and regenerated catalyst samples was discussed earlier. Delta coke determined in this manner, versus the calculations of delta coke from the unit heat balance, can be a useful tool to check data consistency.

Most process engineers will calculate coke yield using air rate and flue gas composition, and then calculate catalyst circulation rate by heat balance. These coke yield and cat/oil results can then be used to calculate a delta coke. If this "heat balance method" to obtain delta coke differs substantially from the direct sampling method, it could mean one or more of the following:

- Incorrect flue gas analysis or air rate (the most common problem).
- Nonrepresentative catalyst samples (also a common problem).
- Error in heat balance method, data or assumptions.
- Excessive entrainment of interstitial hydrocarbons through the stripper.

Types of Delta Coke

It is convenient to define components of delta coke as to source, and several proposed breakdowns have been published. A sampling is listed in Table 2. The three components of delta coke defined here can be influenced by proper catalyst design:

1. Catalytic-the coke deposit formed when hydrocarbon is cracked via acid site catalysis.

Unit	A		B	
Catalyst	Zeolite-Low Metals		Zeolite-High Metals	
Feed Type	Gas Oil		Resid	
Delta Coke Types	Wt% Cat	% Total	Wt% Cat	% Total
Catalytic	0.52	65	0.40	29
Cat/Oil	0.12	15	0.10	14
Contaminant	0.12	5	0.40	29
Feed/Nondistillable	0.04	15	0.50	28
Total	**0.80**	**100**	**1.40**	**100**

Table 2. Typical Delta Coke Breakdowns [1, 2]

2. Cat/Oil-adsorbed/unstripped hydrocarbons entrained by catalyst flowing through the stripper.

3. Contaminant-coke produced as byproduct of contaminant metal (V, Ni, Cu, Fe) dehydrogenation activity.

Catalytic Delta Coke

Most cracking catalysts have two sources of acid sites, and therefore two types of activity-zeolite and matrix. Zeolite is crystalline silica/alumina with a specific structure. In the usual case it is where most of the overall catalyst activity resides.

The balance of the catalyst particle is defined as the matrix. It may be similar to the zeolite in composition (silica/alumina), but does not have the particular crystalline structure unique to zeolites. Many of today's matrices resemble the amorphous catalysts of the 1950's and 60's.†

The activity associated with the zeolite and the matrix have very different selectivity patterns, especially in regard to coke. This is illustrated in Figure 4. As matrix activity relative to zeolite is minimized, delta coke at constant activity decreases—the catalyst becomes more "coke selective".

Differences in zeolite type also affect coke selectivity. The key issue is the chemical composition (Si/Al ratio) of the equilibrated zeolite, which is measured by X-ray as the unit cell size. Zeolites that equilibrate with high Si/Al ratios (low cell sizes) exhibit retarded hydrogen transfer rates which, among other things (such as increasing gasoline octane), reduce catalytic coke make. Davison's experience with these zeolites, generically referred to as "ultrastable" or USY types, is unmatched in the industry. The premium form of USY, patented by Davison as "Z-14US", is the core technology behind Davison's current octane catalyst product line. The coke selective properties of these octane
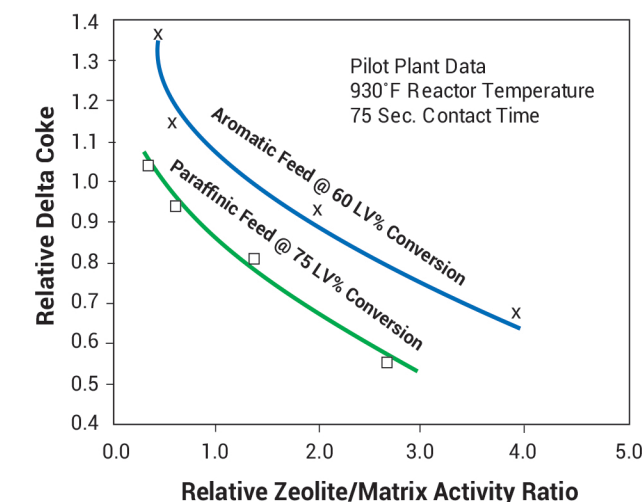
Figure 4. Effect of Zeolite/Matrix Activity on Catalyst Coke Selectivity

catalysts have been thoroughly treated in earlier *Catalagram* magazines (Numbers 73 and 74).

Cat/Oil Coke

Cat/oil coke is perhaps the most insidious component of delta coke because[1] it is totally independent of any beneficial chemical reaction taking place, such as making gasoline, and[2] it has the highest heat of combustion (highest hydrogen content) which leads to high intraparticle temperatures during regeneration.

A properly designed and operated catalyst stripper will minimize the amount of hydrocarbons that flow into the regenerator along with the circulating spent catalyst. Stripping steam rates of at least two lb. per 1000 lb. of catalyst circulated are typically recommended. Increasing catalyst level (residence time) in the stripper can also be effective in minimizing carry-over. The common commercial practice is to increase steam rate and/or stripper level until no further reduction in regenerator temperature is observed, providing, of course, reactor-side catalyst losses do not increase.

Steam injection displaces hydrocarbon vapor between catalyst particles – it is not very effective in reversing surface adsorption or pore condensation. In some cases, higher reactor (stripper) temperatures have been found to reduce cat/oil coke. The mechanism may involve volatizing and/or further cracking of desorbed material.[3]

Cat/oil coke is also influenced by catalyst matrix pore size and surface area. Catalyst "strippability" can be measured in the lab by subjecting an inert porous material to heavy oil, followed by nitrogen stripping at typical reactor operating conditions. The results is shown in Table 3 as a function of stripping time and temperature.

† In the 1980's most high matrix catalysts were neither selective nor metals tolerant. Today's high MSA MIDAS® catalysts have been known to improve coke selectivity by eliminating and cracking coke precursors.

Surface Area, M²/g	439	389	105
Pore Volume, cc/g	0.89	1.8	1.14
Volume Avg. Pore Diameter, A	72	184	436
Stripping Temperature	Unstripped Coke (Wt% FF) After 1 Minute		
900°F	17.3	17.7	6.4
990°F	2.0	1.7	1.3
Stripping Temperature	Unstripped Coke (Wt% FF) After 15 Minutes		
900°F	1.5	1.3	1.1
990°F	1.7	0.9	0.8

Conditions: MAT REACTOR: 5 gm. Charge, 16 WHSV, 3 C/O, WEST COAST FEED, N_2 STRIPPING AT 30 SCCM,

Volume Avg. Pore Diameter: $\dfrac{40{,}000 \text{ (pore Volume)}}{\text{Surface Area}}$

Table 3. Effect of Surface Area on Hydrocarbon Stripping

Catalyst	500 ppm Ni (Impregnated After Steam Deactivation[1])		500 ppm Ni + Sb
	Fresh	Aged[2]	Aged[2]
Super-D (50 m²/gm)[3]			
MA, V%	68.5	69.5	69.0
H₂, Wt%	0.21	0.08	0.075
Coke, Wt%	2.6	2.5	2.45
Competitor B (115 m²/gm)[3]			
MA, V%	70.0	68.0	69.5
H₂, Wt%	0.42	0.38	0.145
Coke, Wt%	4.15	4.2	2.8
Competitor A (220 m²/gm)[3]			
MA, V%	79.0	78.0	77.0
H₂, Wt%	0.45	0.35	0.14
Coke, Wt%	4.0	3.9	3.8

[1]Deactivation Conditions: 1350°F, 100% Steam, 15 psig, 8 Hrs.

[2]Aged 13 Cycles in Cyclic Fixed-Fluid Bed Pilot Units; 40 WHSV, 3 c/o, 1000°F Reaction/1100°F Regeneration

[3]Typical Matrix Surface Area

Table 4. Metal Aging Study Results[10]

High intraparticle temperatures associated with adsorbed hydrocarbon have been the subject of several studies,[4,5] which showed that high surface area (hence, more adsorptive) catalyst particles are prone to deactivate rapidly when regenerated. Particle temperatures several hundred degrees higher than average regenerator bed temperatures were calculated.

To summarize, catalysts designed to minimize the cat/oil component of delta coke should have low surface area, large average pore diameter matrices to discourage hydrocarbon adsorption and enhance "strippability".

Contaminant Delta Coke

The hydrogen-producing effect of feed metals-particularly that of nickel, copper, and vanadium-deposited on the cracking catalyst is well known. Coke is a companion product of dehydrogenation, and from Table 2 it is clear that contaminant coke can be a substantial percentage of the overall delta coke for metals-laden catalysts.

The passivation of nickel by antimony (licensed by Phillips Petroleum Co.) and of vanadium by tin additives is being practiced commercially. ƒ Claims of a 50% reduction in hydrogen and coke produced by contaminant metals have been published. [6,7,8,9]

We have found that the level of hydrogen and coke production due to contaminant metals is also a function of catalyst matrix composition. Matrices with low alumina content and low surface areas are more effective in minimizing contaminant metal dispersion and dehydrogenation activity√ (Table 4).

Coke Selective Catalyst Properties

As can be seen from the preceding discussion, catalyst design has a direct bearing on the formation of various components of the overall "delta coke". Certain catalyst properties, associated with the true "coke selective" catalyst system, act to minimize delta coke for any given activity level. The essential ingredients are[1] a zeolite that will equilibrate at low unit cell size, while retaining the appropriate activity level to dominate that of the matrix and[2] a matrix of controlled surface area with large pores to maximize strippability and control dispersion and dehydrogenation activity of contaminant metals.

Davison has used these principles for years to design a wide range of catalysts. Current examples are members of the Octacat, GXO, and Nova families that have led the industry in coke selectivity, as well as octane enhancement. Davison R&D is focused on a continuous program of improving these products, as well as on the design of new coke selective grades such as the DXB family.

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ƒ Tin passivation is no longer practiced in the industry. Integral vanadium traps, such as those in IMPACT, are much more effective for selectivity preservation in high metals operations.