CATALYST DESIGN FOR THE MAXIMIZATION OF VALUABLE PRODUCTS IN THE FCC UNIT

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1. Synopsis

Fluid Catalytic Cracking is one of the most important processes in the petroleum refinery operations because it produces more valuable products per barrel of feed than other refinery processes. The FCC unit can process any type of crude oil fraction, from light to heavy molecular weight hydrocarbons, with different concentrations of contaminants: S, N, Na, Ni, V, Fe, Mg, K, Ca, resins, and asphalthenes. The yields and quality of the major products depend upon the chemical composition of the feedstock thus influencing the entire refinery economics.

To design the FCC catalyst for each type of FCC feedstock composition based upon varying unit operating conditions and constraints is a very difficult issue. The main objective is to achieve the maximum potential valuable products in the commercial unit, which depends on the optimal interaction of feedstock composition and catalyst design. Three major parameters of the catalyst have to be considered in the catalyst design: activity, stability and selectivity.

The catalyst activity is related with the amount of active components present in the catalyst formulation: zeolite type and concentration, matrix active components and Re_2O_3. Catalyst stability is related to the catalyst's capacity to resist the unit deactivation severity especially in the regenerator, while selectivity is the capacity of the catalyst to maximize the valuables products yields while achieving the FCC unit objectives. To optimize catalyst selectivity it is important to consider the zeolite type and amount, the acid site concentration including site distribution and strength, the zeolite and matrix pore size distributions, the matrix type and activity, the amount of Re_2O_3 and the presence of additives.

This paper describes the effect of the major catalyst components on the activity and selectivity for the most valuable products yields ($C_4^=$, LPG, gasoline and coke). At the same time, the analysis considers the maximum feed potential yields and the correlation with the equilibrium catalyst (Ecat) performance. The Ecat performance of different catalysts was studied in the ACE unit at standard conditions, where the maximum feed potential yields are taken as the target for each Ecat sample. To select the best catalyst for the commercial unit it is necessary to include the catalyst stability and the coke selectivity concept, which means the effect of the catalyst in the heat balance. All of these concepts are considered in this paper.

2. Introduction

FCC catalysts are generally comprised of zeolite Y, a functional matrix, binder, and kaolin clay. The main cracking activity comes from the zeolite Y, a highly crystalline aluminosilicate with a three dimensional pore structure. All the FCC catalysts contain different concentration of zeolite Y, which in most catalysts has been partially exchanged with a mixture of rare earth cations (Re^{3+}), with the

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objective to increase its activity and to improve its stability in the highly severe hydrothermal deactivation environment of the FCC regenerator[1].

One of the most important properties of the zeolite used in the FCC catalyst is the unit cell size (UCS), which identifies the amount of Al and Si atoms in the structure of the zeolite. There are a total of 192 tetrahedral atoms in each unit cell of the Zeolite Y[1]. The UCS of fresh commercial FCC catalyst is in the range 24.50 to 24.65°A. After the hydrothermal deactivation in the FCC regenerator, the zeolites Y is dealuminated and for that reason the UCS of the Ecat (catalyst circulating in the commercial unit), decreases to a range of 24.24 to 24.40 °A. The effect of the UCS on selectivity of cracking has been well documented[2, 3]. Several pilot plant studies with different catalysts deactivated in the laboratory, allow concluding that the gasoline yields increase as the UCS increase from 24.25 to about 24.31°A[1]. However, if the UCS increases to a value higher than 24.31°A, the gasoline yield decreases.

The coke and the LPG are very important products for the FCC unit. If the UCS increases from 24.25 to 24.31°A, these two products decrease to a minimum around 24.31°A. Gasoline and Research Octane Number (RON) move in the opposite directions. The RON and MON decrease as the UCS increase. These changes in the activity and selectivity of the zeolite with the UCS are mainly related to the cracking and hydrogen transfer reactions. It is not the objective of this paper to study these reactions, however, it is important to understand that these reactions are related to the operating objectives of each FCC unit and they are dependent on the catalyst design. The catalyst activity, selectivity, and stability, and product quality (RON in case of Gasoline) are dependent on the following parameters: type of Zeolite, which is identified by the UCS, the Zeolite concentration, which affects the catalyst activity, and the Rare Earth (Re_2O_3) Zeolite content, which affect its UCS. If the Re_2O_3 Zeolite content increases, the UCS increases that would cause the gasoline to increase, but the LPG and the RON to decrease.

The other major FCC catalyst component is the matrix, which can be defined as everything that it is not active zeolite. This includes the binder, the clay, and active and modifies alumina, and other functional components. The matrix components are responsible for: bottoms conversion, contaminant metals resistance (Ni, V, Na, and Fe), catalyst density, and pore volume and pore size distribution for faster diffusion of the heavy molecules from the feed into the active catalytic sides inside the catalyst particle. One of the most important roles of the matrix active components is to increase the matrix surface area, and matrix acidity necessary to pre-crack the larger and heavier molecules in the feedstock into smaller ones that can enter to the active sites present in the zeolite pores. During the very severe hydrothermal deactivation in the FCC unit, around 50% of the initial zeolite present in the fresh catalyst is destroyed and becomes part of the matrix[1].

One very important and useful property of the FCC catalyst is the Z/M ratio (zeolite/matrix). This ratio is defined as the zeolite surface area/matrix surface area. Considering that this ratio depends on the Zeolite and matrix stability, it is recommended to evaluate this ratio in the laboratory deactivated and Ecat catalysts. Catalysts with a high Z/M ratio are mainly designed for gasoline and those with low Z/M are for bottoms conversion in order to increase LCO production.

Fresh FCC catalysts are too active to study directly in the laboratory and for that reason it is necessary to deactivate them at different operating conditions (temperature, time, steam partial pressure and metals). Techniques of catalyst pretreatment include steam deactivation at very high temperatures (between 750-815°C), different steam concentration (20-100%), different processes for metallation (Ni+V), and finally different age distribution methods. The objective to deactivate the catalyst is to simulate the Ecat activity and selectivity, and the Ecat physical properties, the metals content (Ni and V) and metals activity, which mainly affect the coke and gas yield. The deactivated catalyst performance depends on how well it was deactivated to simulate the Ecat properties and for that reason

the catalyst deactivation and Ecat simulation process is very important during the FCC catalyst selection procedure.

3. Results and discussion

3.1 Fresh and Deactivated catalyst properties

For this study seven different commercial catalysts were selected. Table 1 shows the main physicochemical properties. These catalysts have different type and amount of zeolite with different concentrations of Re_2O_3 (0% to 4.0 wt %), different levels of alumina, and varying pore volumes (PV). The catalyst 1 contains the lowest amount of Zeolite while catalyst 5 is the one with highest Zeolite content but without any Re_2O_3. Catalyst 6 and catalyst 7 have very active Zeolite.

Table 1. Fresh catalyst Properties

	Cat. 1	Cat.2	Cat.3	Cat. 4	Cat.5	Cat.6	Cat.7
Surface Area, m^2/g	282	384	312	336	393	341	286
PV, cm^3/g	0.36	0.48	0.44	0.42	0.41	0.43	0.43
RE_2O_3, %wt	3.0	1.9	3.7	3.9	0.15	2.5	1.6
Al_2O_3, %wt	45.2	43.5	49.2	46.1	42.2	46.8	45.4

To study the FCC catalyst in the laboratory, it is necessary to deactivate them hydrothermally. Table 2 shows the properties of the seven catalysts deactivated hydrothermally at 815°C (1500°F) for 4 hr using 100% steam without metals. The FCC fresh catalysts deactivated without metals may have some Ni and V content up to maximum of 50 ppm and 75 ppm, respectively. These traces of metals in the catalyst are coming from raw materials. If a higher concentration of Ni and V is present in any fresh catalyst the sample could be contaminated with a small amount of Ecat.

Table 2. Properties of the deactivated catalyst without metals

Deactivation conditions: 4 hrs., 1500°F, 100% steam

Properties	Cat. 1	Cat.2	Cat.3	Cat. 4	Cat.5	Cat.6	Cat. 7
Total Surface Area, m^2/g	162	225	187	185	236	209	191
UCS, °A	24.33	24.26	24.30	24.33	24.24	24.29	24.29
RE_2O_3, wt%	3.0	1.8	3.6	3.9	0.15	2.5	1.7
Al_2O_3, wt%	45.4	42.2	48.3	44.5	41.1	47.7	45.1
Ni, ppm	20	24	14	19	15	36	26
V, ppm	70	50	40	70	40	45	60
Total area retention; %	57	59	60	55	60	61	67
Z/M	3.2	4.4	3.9	4.2	4.2	3.9	3.3

According to table 2, if the amount of Re_2O_3 goes up, the UCS increases. The catalysts stability is expressed as a function of the total surface area retention, where for this deactivation conditions the total retention varies from 55% to 67%, the Zeolite surface area retention varies from 55% to 60% (not reported), and the matrix surface area retention varies from 60% to 80%. These results allow conclusion that these catalysts have a good hydrothermal stability at very high deactivation temperature (815°C).

The Z/M ratio of these deactivated catalyst are from 3.2 to 4.4, which means these catalysts are designed mainly for gasoline production.

Table 3. Deactivated catalyst properties with metals							
Deactivations conditions: 1000 Ni, 2000 V - CPS-1 @1450F							
Properties	**Cat. 1**	**Cat.2**	**Cat.3**	**Cat. 4**	**Cat.5**	**Cat.6**	**Cat.7**
Total Surface Area, m^2/g	151	215	189	188	239	209	179
UCS, °A	24.31	24.27	24.29	24.29	24.24	24.29	24.28
RE_2O_3, wt%	2.9	1.9	3.8	3.9	0.1	2.5	1.7
Al_2O_3, wt%	45.4	42.2	48.3	44.5	41.1	47.7	45.3
Ni, ppm	1056	1070	1065	1021	1022	1050	1023
V, ppm	2110	2100	2170	2150	2100	2130	2160
Total area retention; %	54	56	61	56	61	61	63
Z/M	3.2	4.4	3.9	4.2	4.2	3.9	3.5

In the FCC catalyst evaluation process it is very important to deactivated catalysts simulating the corresponding Ecat properties. With this objective, Grace developed many years ago, the CPS (Cyclic Propylene Steam) protocol[4]. In this case the seven catalysts were deactivated using CPS-1 protocol at 788°C (1450 °F) and approximately 3000 ppm of Ni+V.

Table 3 shows the main properties of the seven deactivated catalyst using this different protocol. Comparing catalysts properties from table 3 with properties of the catalysts deactivated just hydrothermally without metals in table 2, reveals that the hydrothermal deactivation conditions at 815°C and using 100% steam are more severe than the CPS-1 with metals. For this conclusion it is important to keep in mind that the vanadium at high temperature and high steam partial pressure is very mobile and destroys the zeolite structure[5].

The total surface areas of the catalyst deactivated with 3000 ppm of metals are quite close to most of the seven catalysts deactivated without metals (table 2). At the same time, both deactivation protocols produce a very close UCS, if we realize that the XRD analytical method for UCS has a repeatability of 0.02°A. The total area retention of both deactivation methods is also very close, which confirm the good catalyst stability. These results allow conclusion that for catalyst deactivation with metals it is important to reduce the deactivation temperature and increase the deactivation time. The CPS-1 protocol use 30 cycles and 50% steam, where the total time of deactivations is 20 hours.

3.2 Activity and selectivity of the Hydrothermal deactivated catalyst

The deactivated catalysts using both methods were evaluated in the ACE unit at 980°F (527°C) reactor temperature, three C/O ratios (4, 6 and 8), and with standard VGO, which properties are reported in table 4. Using those measured properties, the following feed characteristics were calculated[6]: the hydrogen content: 12.5 wt%, correlation index: 38.5 and the amount of saturates 62.5 wt%.

The calculated and the physicochemical properties from the table 4, allows us to classify the VGO used in this study as a paraffinic feed. At the same time, it is possible to calculate and predict the maximum potential yields of the most important FCC products[6, 7]: maximum potential gasoline yield (MPGY): 55.6

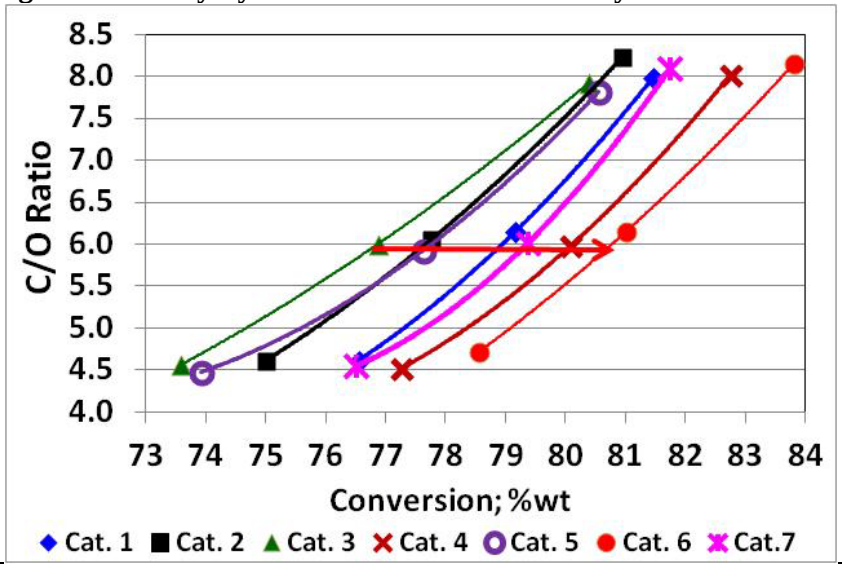
Table 4. Feed Properties	
Specific Gravity; g/cc	0.9010
API; °API	25.5
Sulfur content; %wt	0.369
Total Nitrogen, %wt	0.12
Basic Nitrogen; %wt	0.05
Conradson carbon, %wt	0.68
Aromatics carbon; %	18.9
Naphtenic carbon; %	17.4
Parafinic carbon; %	63.6
Destillation; °C	
IBP	153
5%	267
10%	319
30%	393
50%	437
70%	484
90%	557
95%	595
FBP	681
Refractive Index	1.5030
K Factor	11.94
Average Molecular Weight	406
Aniline Point, °C	91.1
Sodium; ppm	1.2
Nickel, ppm	0.4
Vanadium; ppm	0.2

wt%, LPG: 19.5 wt%, Dry gas: 1.73 wt%, LCO: 18.0 wt% and a maximum conversion (Grace Crackability factor): 79.8 wt%. The RON and MON numbers at the maximum gasoline point are[4]: 90.5 and 79.9, respectively. Also the delta coke is 0.29, which is very low and confirms the paraffinic composition of this VGO. The MPGY is a very important tool used as a reference for the gasoline yields during the catalyst selection process, especially in those cases where maximize gasoline is one of the most important objectives for the FCC unit operations.

Figure 1 shows the conversion (activity) at different C/O ratios for the seven catalysts. These plots show that the seven catalysts are quite active, considering that at typical C/O ratio of 6.0, the conversion varies from 76.5 wt% to 81 wt%. However, Cat.6 is the most active catalyst (highest conversion at constant C/O ratio) and the Cat.3, Cat.2 and Cat.5 are very similar in activity. Although Cat.1 contains the lowest amount of zeolite, this catalyst is more active than Cat. 3, Cat. 2, and Cat. 5 despite having more zeolite. As was mention before, this performance is related to the zeolite concentration, the zeolite type in the catalysts formulations, the type and amount of matrix components, and the R_2O_3 concentration in the zeolite. The ranking in terms of activity will be then: Cat.6>Cat.4>Cat.7>Cat.1>Cat.2=Ca.5>Cat. 3.

ACE results also allow studying the catalysts selectivity. Figure 2 shows the gasoline yields as a function of conversion. These plots allow comparing the experimental MPGY for this VGO, with the predicted calculated MPGY. As was mention before, this VGO has a potential MPGY of 55.6 wt% and the experimental values for four of the seven catalysts are higher than 54 wt%.

Figure 1. Activity-hydrothermal deactivated catalyst

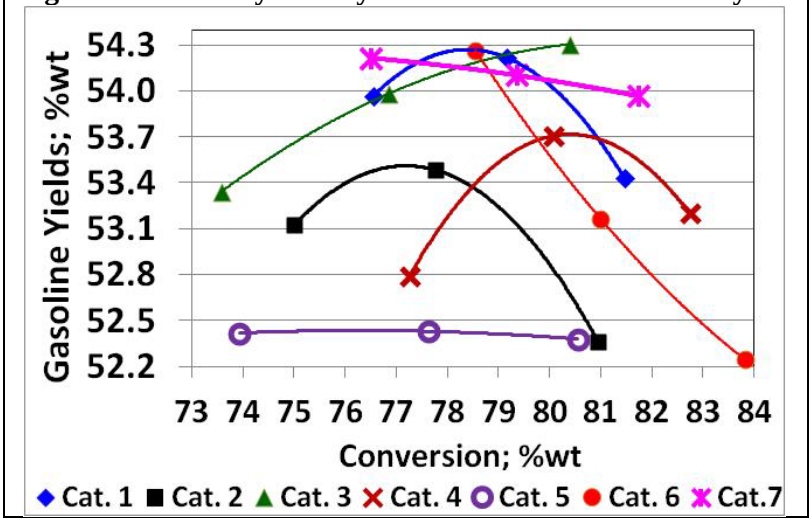


This is a very good agreement if we take into account the ACE repeatability of ±1 wt%, and also considering that the comparison is between calculated values with experimental results. These results allow to confirm that Cat.6 and Cat.7 are too active, since the gasoline yield is in the over-cracking zone, very high conversions (>76 wt%) at C/O ratio of 4.5. To analyze these catalysts and to get the MPGY experimentally it is necessary to operate at lower C/O ratio and/or to deactivate them at higher severity (higher time).

It is interesting to see that Cat. 3 which is not the most active catalyst have very good gasoline selectivity (gasoline yields/conversion). The Cat.3 has a high Re_2O_3 content, part of this amount functions as a vanadium trap. This catalyst needs more cracking reaction severity to get the MPGY (higher C/O). In the other hand, the catalyst with no Re_2O_3 and lowest UCS (Cat.5) had the lowest gasoline yields, while the catalysts with a UCS from 24.29°A to 24.33°A produce the highest gasoline yields.

Figure 3 shows the ACE results for the total $C_4^{=}$´s. In this case, the catalyst without Re_2O_3 and the lowest UCS (Cat.5) produces the highest C_4 olefins, while the catalysts with the highest Re_2O_3 and the highest UCS produce the least $C_4^{=}$´s (Cat.1, Cat.4 Cat.6 and Cat.7). These results allow concluding that Cat.5 has the lowest hydrogen transfer reaction rates. This reaction is a bimolecular reaction, between one olefin and one naphthene and therefore needs two acid sites (two Al^- sites in the zeolite structure) in neighborhood position, which means two very close Al^- in the zeolite structure. If we consider that the bond Al-O (1.74°A) is longer than the bond Si-O (1.61°A), then for the zeolite with the lowest UCS there is lower probability of two Al atoms in the structure in neighborhood position and for that reason the rate of hydrogen transfer reactions is the lowest one, in other words this catalysts doesn´t consume the olefins produced and the concentration of light olefins (C3+C4) and the LPG should be much higher. This performance is also valid with the olefins in the gasoline range and the RON number for Cat. 5 should be the highest one (higher olefins in the gasoline means higher RON number).

Figure 2. Gasoline yields Hydrothermal deactivated catalysts



One of the most important variables to study during the catalyst selection process is the delta coke, defined as the amount of carbon in the spent catalyst produced in the ACE unit during the feed and catalyst interactions at 527°C reaction temperature. This carbon is equivalent to the amount burned in the regenerator to produce the heat required for the FCC unit.

Figure 4 shows the results of delta coke for the seven catalysts. These results are very interesting and have to be correlated with the feedstock quality for each specific FCC unit. As it was mentioned, the

calculated delta coke of the VGO used in this study was 0.29, which means that the differences between the results in Figure 4 are related to the amount of coke produced on each catalyst during the reactions with the feed.

Figure 3. C_4 Olefins – Hydrothermal deactivated catalysts

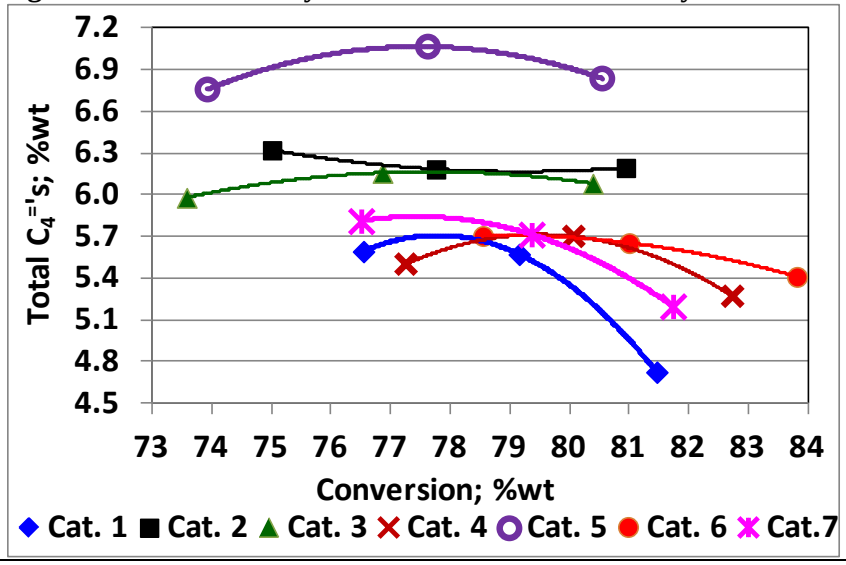
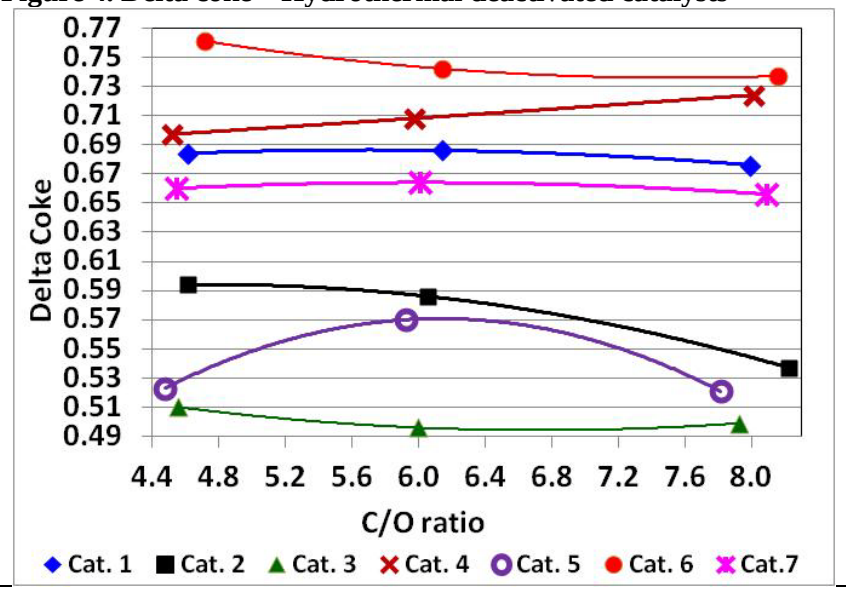


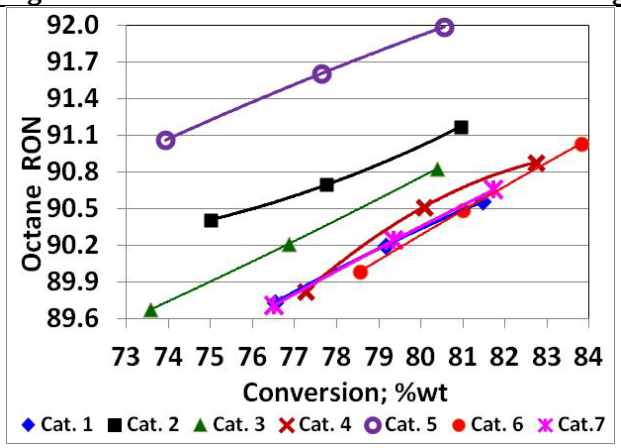
Figure 4. Delta coke – Hydrothermal deactivated catalysts



If the feed for the commercial unit is paraffinic and/or hydrotreated feed, the best catalyst should be selected between Cat.6, Cat.4, Cat.1 and Cat.7, because the unit needs activity and coke to stay in heat balance. However, if the feed has residue (heavy material, high metals) then the contaminant coke and the additive coke (coke related to the heavy material from the feed) will increase, so the catalytic coke have to be optimized, therefore Cat.3 and Cat.2, could be the best option. Cat.5 should not be considered, because to the contaminant metals (V) will increase and this catalyst doesn´t have Re_2O_3. Lower coke in the reactor translates to lower regenerator temperature and higher catalyst circulation rate, therefore higher C/O, higher cracking severity, and more conversion. In other words, it is possible to obtain higher conversion in the unit with a more coke selective catalyst, less active catalyst, such as Cat. 3, based on the results in Figures 1 and 4.

Figure 4 shows that Cat.1, Cat.4, Cat.6 and Cat.7, produce the highest delta coke and these catalysts also have the highest rate of hydrogen transfer reactions, but less C4 olefins (Fig. 3), so it can be concluded that the hydrogen transfer reactions are also involve in the coke formation.

Figure 5. RON octane and Olefins content in the gasoline



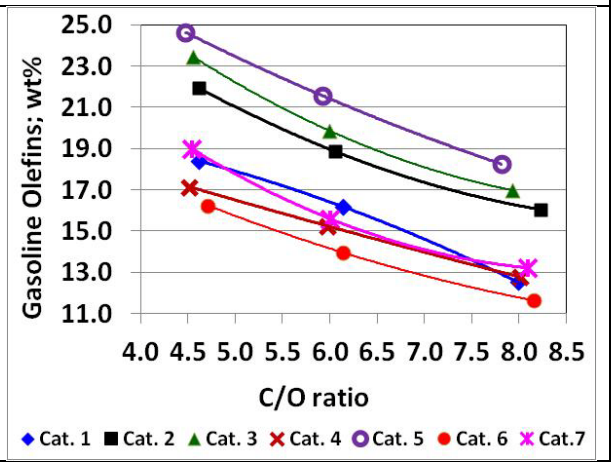


Figure 5 shows the RON and the amount of olefins in the gasoline. This figure confirm that Cat.5 has lower hydrogen transfers reactions rate and for that reason the highest RON is produced, due to the highest concentration of olefins in the gasoline. Cat.1, Cat.4, Cat. 6 and Cat.7 have the highest hydrogen transfer reactions rate, therefore there is lower RON and lower olefins content in gasoline.

3.3 Activity and selectivity of the deactivated catalyst with metals

The seven catalysts deactivated by CPS-1 at 788°C (1450°F) and with 3000 ppm of Ni+V were evaluated in the ACE unit with the same standard VGO (table 4). Figure 6 shows the activity of the catalysts. The ranking in terms of activity will be: Cat. 6>Cat.4>Cat.1>Cat.7=Cat2=Cat.3=Cat.5. The performance in terms of activity is quite similar to the catalysts deactivated without metals (Figure 2); however the conversions obtained for the CPS-1 deactivated catalysts are lower than those catalysts without metals. After CPS deactivation and 3000 ppm of (Ni+V) the conversions at constant C/O vary from 73 wt% to 78 wt%, at least 3 wt% loss in conversion, which is mainly related to the effect of the metals deactivation at those conditions, where the V destroys the zeolite and the V and Ni destroy the matrix components.

Figure 7 shows the gasoline yields. In this case Cat.6 is still in the over-cracking range; however the difference is smaller, assuming the MPGY is around 54.7 wt%, which is very close to the calculated MPGY of this feed (55.6 wt%). Cat.4 and Cat.3 are also good catalysts for gasoline production with 0.5 wt% lower yield than Cat.6. These three catalysts are very stable and have excellent gasoline selectivity, considering their gasoline yields are close to the hydrothermally deactivated catalysts without metals, and the MPGY of the feed used is achievable with these three catalysts. The other four catalysts (Cat.1, Cat. 2, Cat.5 and Cat.7) are more affected by the vanadium, since the reduction in gasoline yields is higher. Cat.5 is not recommended if the unit works at metals concentrations (Ni+V) higher than 2000 ppm, because the gasoline yields will be severely affected in the commercial unit.

It is important to analyze how the CPS deactivation protocol with metals changes the ranking of the catalyst in terms of gasoline selectivity. The deactivated catalysts without metals (Figure 2) have the following ranking: Cat.6>Cat.1=Cat.3=Cat.7>Cat. 4>Cat. 2>Cat.5, while the ranking of the seven CPS-1 deactivated catalysts with metals is as follows: Cat.6>Cat.3=Cat.4>Cat.2=Cat1>Cat.7>Cat.5, for this

reason it is mandatory to evaluate and select the FCC catalyst, after deactivation with the same amount of metals as the Ecat.

Figure 6. Activity of the deactivated catalyst with metals

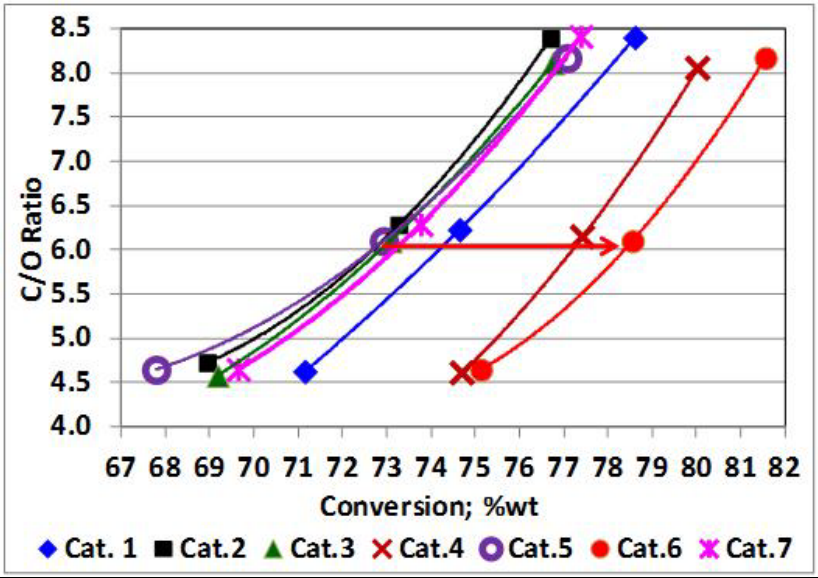
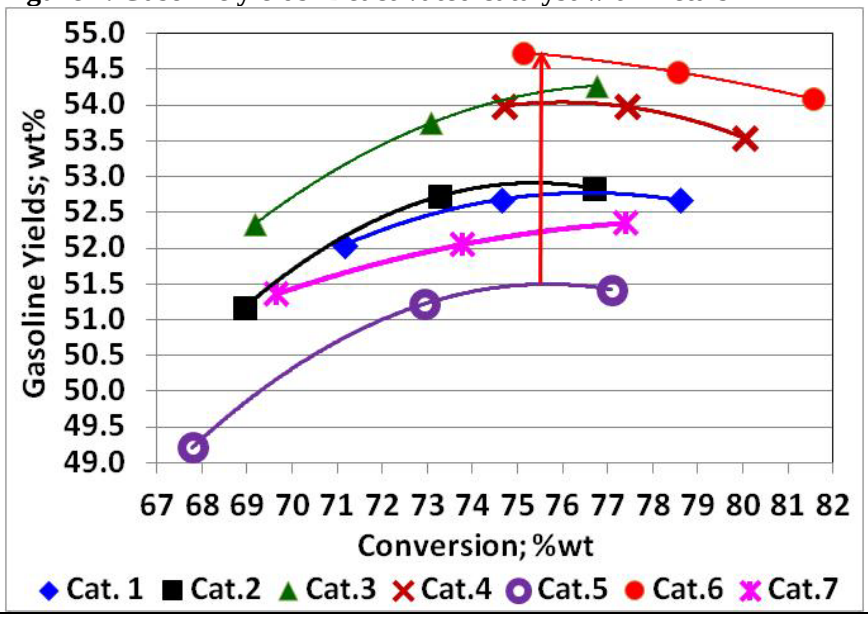


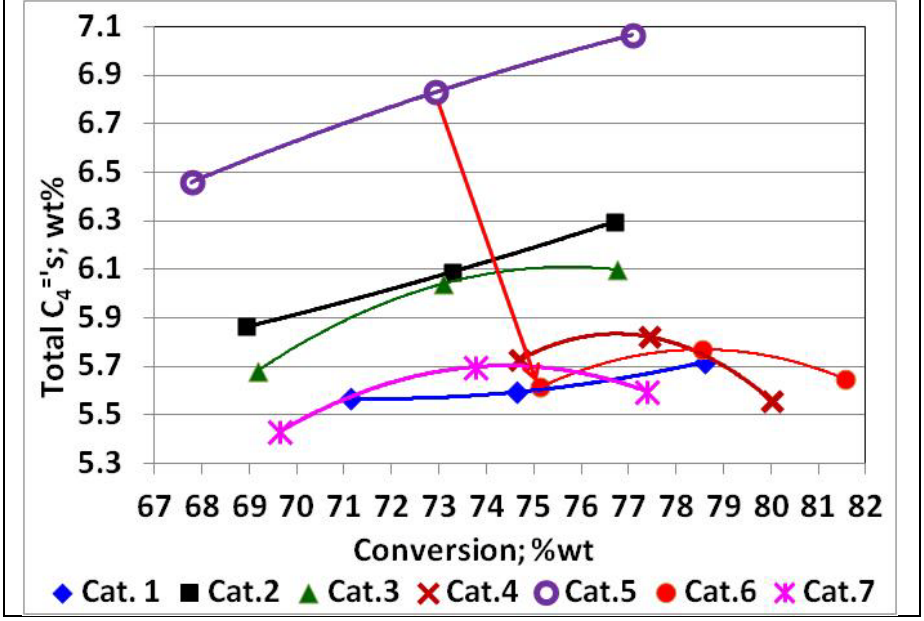
Figure 7. Gasoline yields- Deactivated catalyst with metals



For a refiner it is very important to understand how resistant and stable is the selected catalyst in the presence of the same amount metals as the Ecat. The catalyst stability concept is very important for the refiner, considering its relationship with the fresh catalyst addition rate. More stable catalyst could reduce the fresh catalyst addition rate to achieve the same conversion in the commercial unit.

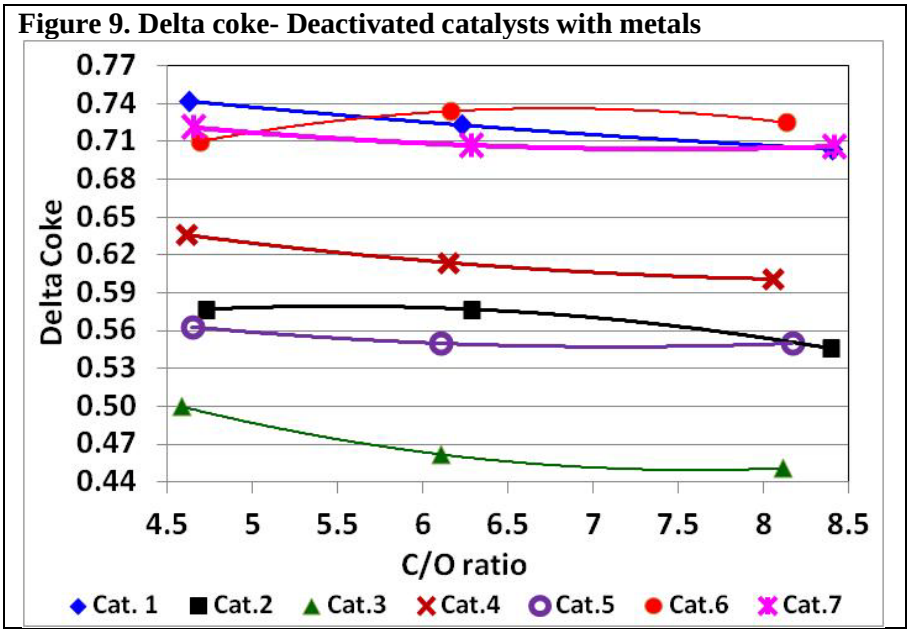
The ranking for the total C_4 olefins production will be: Cat.5>>Cat.2=Cat.3>Cat.4=Cat. 6=Cat.1=Cat.7 (Figure 8), which is similar to the ranking of deactivated catalyst without metals (Figure 3).

Figure 8. Total $C_4^{=}$'s yields – CPS Deactivated catalyst with metals



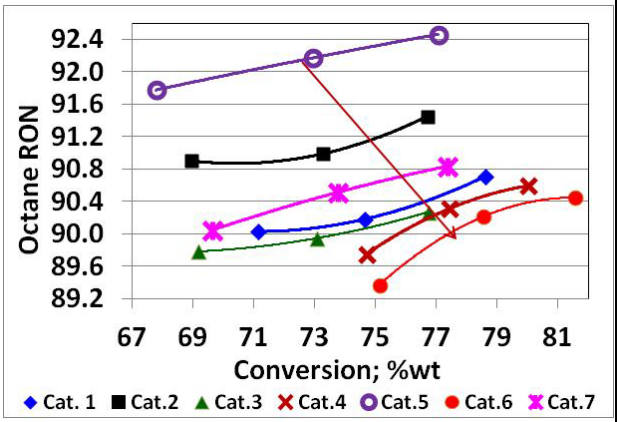
As it was mentioned, during the FCC catalyst selection process it is necessary to understand the effect of the new selected catalyst in the heat balance, in other words the effect of the new catalyst for the regenerator temperature and for the cat/oil ratio, defined as the amount of the catalyst active sites in the reactor per unit feed rate. Figure 9 shows the delta coke of the seven catalysts deactivated CPS-1 with 3000 ppm of metals. Based on these results the ranking of catalysts in terms delta coke is: Cat.3<Cat.5<Cat.2<Cat.4<Cat.7=Cat1<Cat.6. Each catalyst has to be selected according to the FCC unit objectives and feed quality.

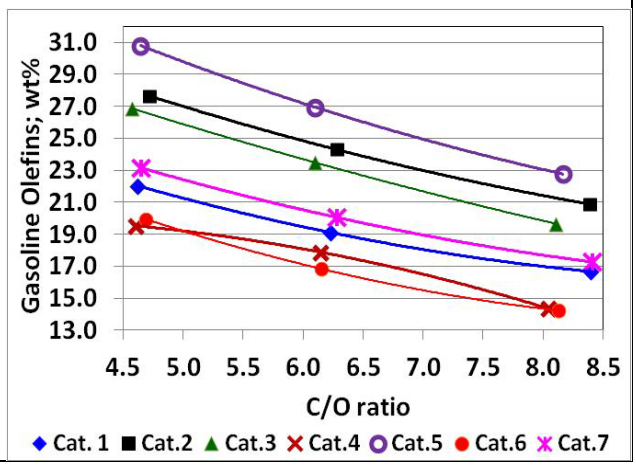
Figure 9. Delta coke- Deactivated catalysts with metals



The figure 10, confirm that the catalyst with the lowest hydrogen transfer reactions is the Cat. 5 and the catalyst with the highest one is Cat.6, for these reasons Cat.5 makes the highest octane number, while Cat.6 produces the lowest one.

Figure 10. RON octane and Olefins content in the gasoline-CPS with metals





To select the catalyst for one FCC unit it is mandatory to have the complete yields at constant conversion, constant C/O ratio, and constant coke, where each sets of yields give very important information to translate the results to the commercial FCC unit conditions. Table 5, shows the yields and gasoline PIONA analysis of the seven CPS-1 deactivated catalysts with metals at constant conversion.

Table 5. ACE yields - Deactivated catalysts CPS-1 with 3000 ppm of metals

	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5	Cat. 6	Cat. 7
Conversion; %wt	75.0	75.0	75.0	75.0	75.0	75.0	75.0
C/O ratio	6.3	7.3	7.1	4.8	7.1	4.6	7.0
$H_{2;\ \%wt}$	0.38	0.35	0.15	0.12	0.29	0.16	0.46
Dry Gas; %wt	1.94	1.95	1.69	1.57	1.95	1.54	2.10
C3=; %wt	4.45	4.63	4.50	4.55	5.21	4.41	4.42
C3; %wt	0.84	0.77	0.78	0.89	0.85	0.77	0.85
Total C3's; %wt	5.29	5.40	5.28	5.43	6.05	5.18	5.28
Total C4=s; %wt	5.63	6.19	6.05	5.78	6.94	5.65	5.61
iC4; %wt	3.99	3.80	3.85	4.28	3.98	3.87	3.92
n-C4; %wt	0.86	0.77	0.81	0.93	0.80	0.82	0.86
Total C4s; %wt	10.54	10.79	10.76	11.00	11.76	10.35	10.44
LPG Wt%	15.83	16.20	16.03	16.44	17.81	15.53	15.71
Gasoline; %wt	52.71	52.90	54.12	54.01	51.48	54.74	52.18
LCO; %wt	19.27	19.67	19.52	19.08	19.48	19.41	19.79
Bottoms; %wt	5.61	5.38	5.43	5.93	5.54	5.58	5.16
Coke; %wt	4.57	4.08	3.24	3.01	3.91	3.29	4.94
Delta Coke	0.72	0.56	0.46	0.63	0.55	0.71	0.71
Paraffins + Isoparaffins; %wt	36.34	33.89	35.70	36.94	32.40	36.55	35.53
Olefins (gasoline); %wt	19.00	22.43	21.32	19.64	24.65	20.15	18.98
Naphthenes+Aromatics; %wt	44.66	43.69	42.98	43.43	42.95	43.31	45.30
RON	90.32	91.25	90.13	89.84	92.31	89.43	90.61
MON	79.87	80.04	79.45	79.51	80.58	79.14	80.01

With all this information it is possible the draw the following conclusions:

1. Cat.6 is the most active catalyst because it needs the lowest C/O ratio to achieve the same conversion.
2. Cat.6, Cat.4 and Cat.3 are the most gasoline selective catalysts. It is important to remember that Cat.6 with metals is in the over-cracking zone.
3. Cat.5 (without Re_2O_3) is the most $C_4^=$ and LPG selective catalysts, due to the lowest hydrogen transfer reactions. This catalyst shows the highest RON and MON number and the highest olefins concentrations in the gasoline.
4. Cat.3 is the most coke selective catalyst because it has the lowest coke yield and lowest delta coke. Cat.4 and Cat.6 at constant conversion have low coke yields but it is at a very low C/O ratio, which means low catalyst circulation rate. This could be a real problem if the unit is limited in catalyst circulation. For this reason it is very important to have the same sets of yield results but at a constant coke.
5. The final catalyst selection depends on the feed quality. If the feed is paraffinic and/or hydrotreated feed (low delta coke and low metals content in the Ecat), Cat.6, will be the best option. It has the highest activity (low C/O ratio) and the highest delta coke. Cat.1 and Cat.7 will be also good options, depending on the feed variability and unit limitations. These catalysts will help the unit with the heat balance. It will increase the regenerator temperature to burn the carbon on the Ecat and to produce the energy required to keep the unit in a good heat balance given flexibility in the operating condition.
6. Cat.3 and Cat.4 will be the best option for those units operating with residue and heavy material (high metals and high concarbon residue). These catalysts have the best coke selectivity with the lowest hydrogen production (gas selectivity). Units running with residue and heavy material usually have very high metals content on the Ecats, so these catalysts have Ni and V traps in order to reduce metals activity and the contaminant coke but to increase the catalytic coke, which means higher conversion. The reduction of the contaminant coke will help the heat balance and the temperature of the regenerator while maintaining good catalyst circulation rate.
7. Cat.5 will be a good option for those units running with VGO where the main objectives are RON and MON, LPG, and total C_4 olefins.
8. Depending on the feed quality, the main unit objectives and unit limitations it is possible to make blends of these catalysts, optimizing the FCC unit operating conditions and the economical benefits.

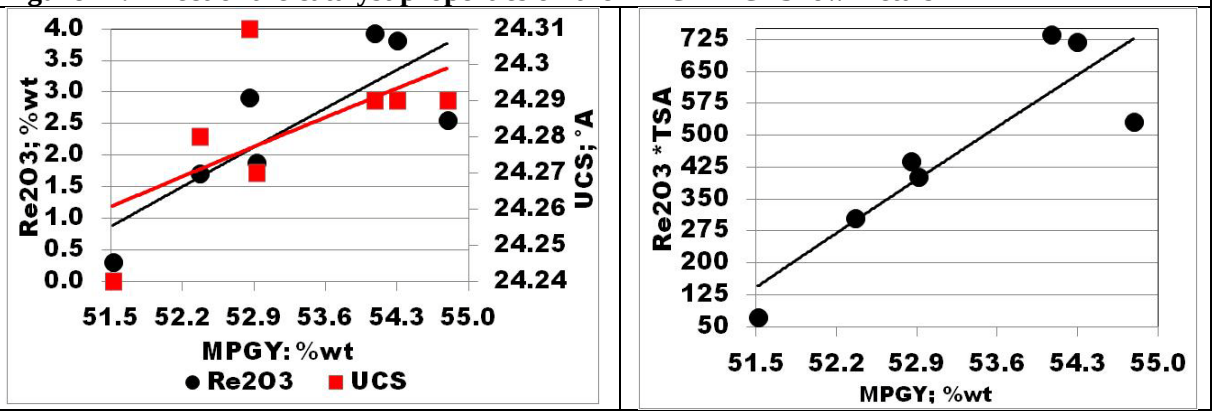
4. Effect of the catalyst design in the Ecat performance

One very important objective of this study is to use the feed maximum potential yield as a target to analyze the Ecat performance. Grace, as a part of the technical service, receives more than 4000 Ecat samples per month. These samples are characterized in more than 30 physicochemical properties and are evaluated in the ACE unit at standard conditions; TRx: 980°F (527°C), C/O ratio of 6.0, 30 sec reaction time, and a 9 gr of catalyst sample. The feed used for the evaluation of all the Ecat samples in the ACE unit, has 23.1°API, 1.5 wt% of concarbon residue, a hydrogen content 12.2 wt%, and a Correlation Index 43.4. For these properties the following maximum potential yields were predicted: the MPGY: 53.8 wt%, the LPG: 18.2 wt%, the coke yields 3.6 wt%, and the crackability factor 76.7 wt%. At the same time this feed was tested in the ACE unit with three different Grace commercial catalyst and the experimental maximum gasoline yields with the three catalysts show an average of 54.1±0.2 wt%. Based on this result we can assume that the MPGY of feed used in the ACE Ecat catalyst evaluation is 54 wt%.

To interpret correctly the ACE Ecat's results, it is necessary to define the most important catalyst properties that affect the MPGY. Figure 11 shows the effect of the Re_2O_3, the UCS, and the product Re_2O_3*TSA (Total Surface Area) on the MPGY obtained in the ACE unit with the seven catalysts. As it was mention before the feed used for this study with the seven catalysts have a MPGY of 55.6 wt%. According to the results in the Figure 11 and the MPGY of the feed used, it is possible to conclude that

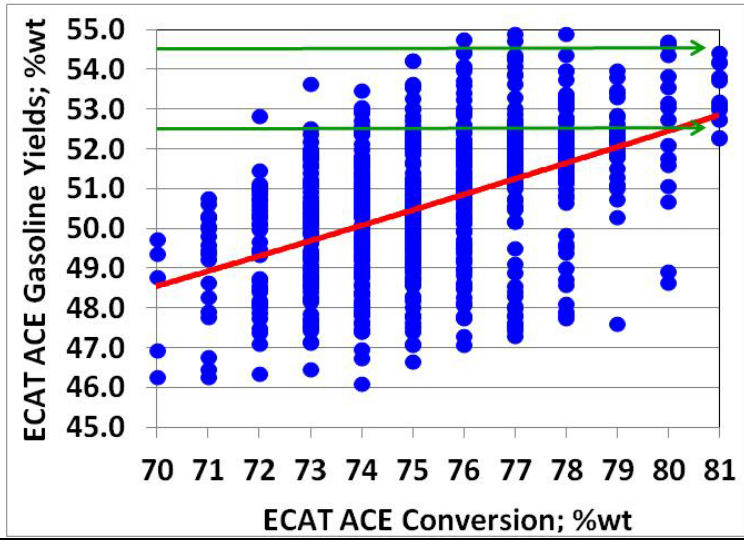
the catalysts with a Re_2O_3 content higher than 2.5 wt%, an UCS higher than 24.28°A, and a TSA around 200 m^2/g, which means having the product Re_2O_3*TSA higher than 500, will be quite close to the MPGY for this feed. In order to have a TSA around 200 m^2/g of the deactivated catalyst with low metals it is recommended to have high Zeolite concentration in the catalyst formulation. These parameters: Re_2O_3 content, UCS, the amount of Zeolite, and TSA are the most important properties considered in this study to get the MPGY of any feed. However, depending on the type of feed and unit main objectives, it is also important to have in the catalyst formulations metals traps, matrix activity and stability, and catalyst pore volume, among others.

Figure 11. Effect of the catalyst properties on the MPGY – CPS low metals



To analyze the catalyst design on the Ecat catalyst performance, more than 700 Ecat samples from 12 FCC units from different countries were selected. The selected Ecats were from those FCC units with an ACE activity (conversion) higher than 70 wt%. The reason for this assumption is that an Ecat with an ACE activity higher than 70 wt% is designed mainly for gasoline production and it also should have an adequate fresh catalyst addition rate to produce acceptable yields in the commercial unit.

Figure 12. ACE gasoline yields as a function of ACE conversion



The figure 12 shows an obvious correlation between ACE conversion and gasoline yields; where the ACE gasoline yield at standard conditions (one single point) increases when the conversion increases. We can see that for any particular ACE conversion point there is a range of gasoline yields, which is

correlated with the amount of metals, fresh catalyst addition rate, the Re_2O_3 content, the UCS, the presence of ZSM-5 (P2O5), the zeolite and matrix content, the commercial unit deactivation severity (partial o full combustion), etc. However, the point we want to emphasize is that the feed used in the ACE Ecat analysis has a MPGY of 54 wt% and considering the ACE repeatability of ±1 wt%, we can assume that a good gasoline ACE results are those in the range of 52.5-54.5 wt%, which means, it is necessary to have an ACE conversion minimum of 74 wt%. In this analysis it is also important to consider that at a very high ACE conversion the gasoline yields could be in the over-cracking point and in this case the gasoline yields will be lower than the range considered. So the question is: which are the catalyst design parameters that make possible to achieve the Ecat maximum gasoline yields in the ACE at standard conditions?

Figure 13. Re_2O_3 and UCS effect in the Ecat ACE gasoline yields

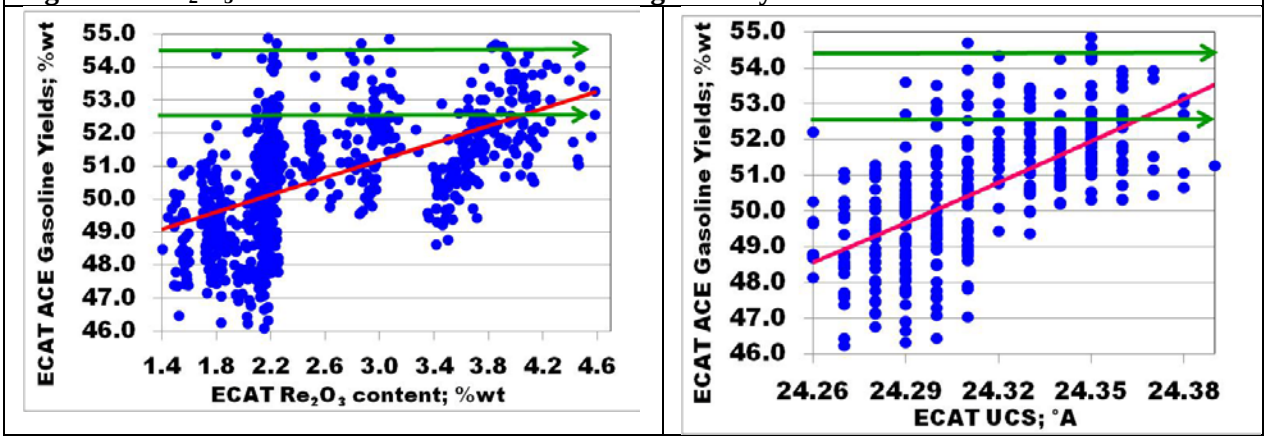


Figure 14. Re_2O_3, TSA and Matrix surface area effect in the gasoline yields

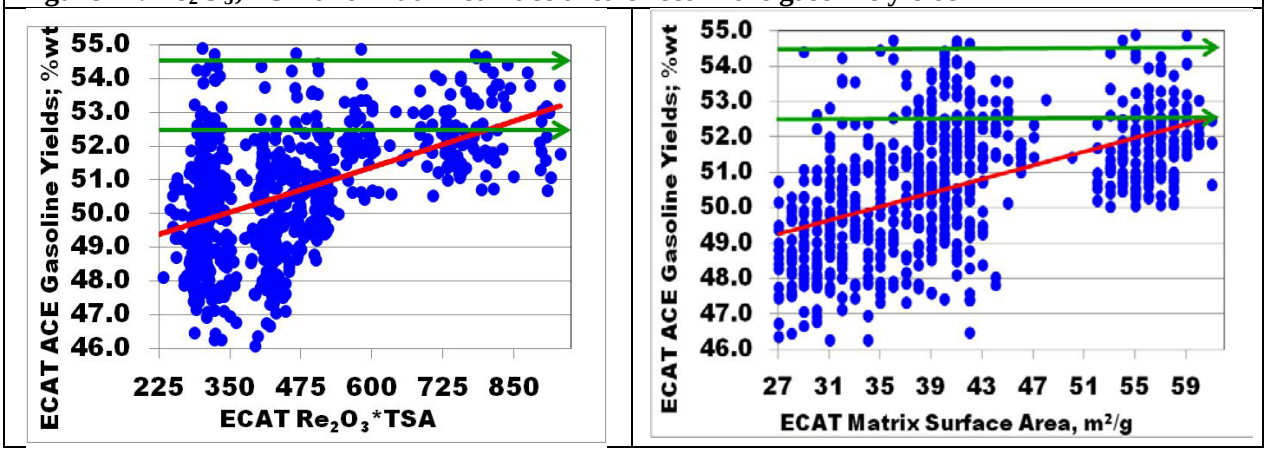


Figure 13 confirms that the Re_2O_3 and the UCS are two important properties for catalyst designed for gasoline production to achieve the MPGY of the feed. In according to these Ecat results, a minimum of 2.2 wt% of Re_2O_3 and UCS of 24.29°A are needed to get the MPGY. On the other hand, figure 14 confirms that the product Re_2O_3*TSA is also an important property of the Ecat, where values higher than 475 are required to get the MPGY. It is interesting to see how the Ecat matrix surface area plays an important role, where minimum value of 35 m^2/g is required. In the TSA, the UCS and the matrix surface area are included into the concept of catalyst stability and catalyst metals resistance. Finally, figure 15 shows the Ecat metals (Ni+V) effect on the ACE gasoline yields. If the Ni+V increase the ACE gasoline yield decreases. It is well known that the V is very mobile in the FCC environment and destroys the zeolite structure, this mobility is affected by the unit combustion mode, where in the partial

combustion units, and the V is less mobile due to the presence of CO in the regenerator. At the same time, the Ni+V destroy the matrix components, these are the mains reason why the Ni+V concentration on the Ecat affect the ACE and the unit gasoline yields.

Figure 15. Ecat Ni+V effect on the gasoline yield and ACE coke yield

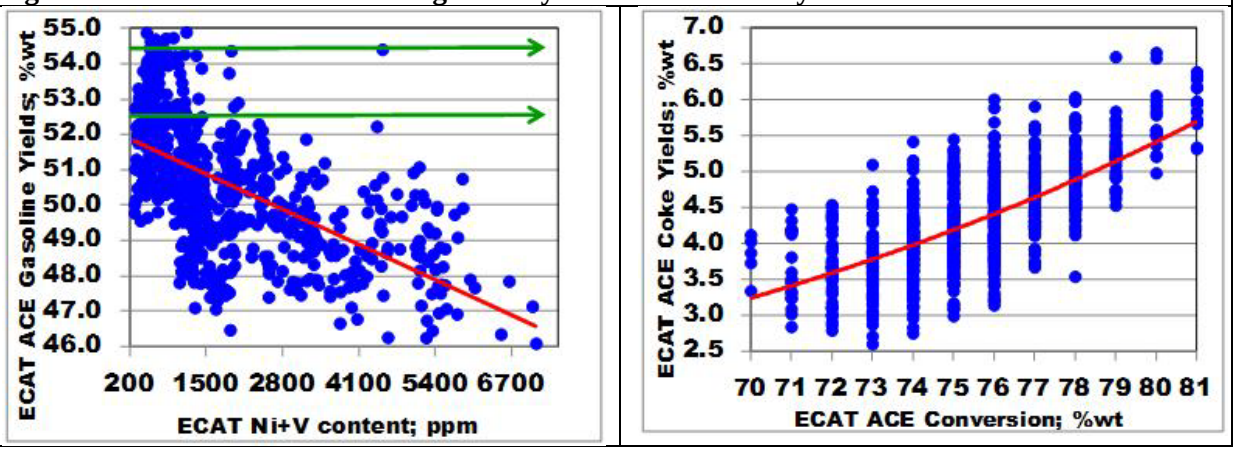


Figure 15, also shows that to be close to the maximum gasoline yield in the ACE unit the Ni+V concentration have to be lower than 2000 ppm, where each 1300 ppm of Ni+V can decrease the gasoline yields approximately by 1 wt%. For this reason it is necessary to keep proper fresh catalyst addition rate to maintain good Ecat quality. On the other hand, figure 15 also shows that if the Ecat activity increases (higher ACE conversion) the coke yield increases. To keep the commercial unit in a good heat balance it is important to take care of the Ecat activity and the catalyst coke selectivity, which is affected by the Re_2O_3 concentration, the matrix activity, the contaminant metals concentration, and catalyst metals activity. The control of the hydrogen transfer reaction is the objective in catalyst coke selectivity.

The main conclusions of this study is that to design a commercial catalyst for one specific FCC unit it is a very complicated issue, there are so many variables and properties that are necessary to consider. To evaluate and to select an FCC catalyst for a particular unit it is also very complicated issue, the feed is perhaps the most important variable with the major impact on the catalyst performance.

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6. Resume

Uriel Navarro Uribe, Chemist, Ph. D. more than 30 years of experience in the petroleum industry, 24 years at Ecopetrol, Barrancabermeja Refinery and (Colombia Petroleum Institute, 9 years in Grace as Technical Service Manager in Latin America.