Operation of FCC with mixtures of regenerated and deactivated catalyst

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Abstract

The operation of FCC with mixtures of coked and regenerated catalyst was studied with a riser simulator reactor on two equilibrium catalysts at 550°C. The coked catalysts maintain an activity level that enables them to be used in the mixtures. The catalytic performances of the regenerated catalysts were used as references against which the behaviors of 25:75 and 50:50 (coked:regenerated) mixtures were compared. It was observed that overall catoil has to be increased to maintain conversion. While the yields of gases, gasoline and LCO showed to be independent of the operative mode, changes were observed in the selectivity to light olefins C4–C6 that are mainly due to changes in the yields of the isoparaffins in the groups. In turn, these changes could be the consequence of the resulting density of paired acid sites in the zeolite components on hydrogen transfer reactions, due to the contributions by the coked and regenerated portions of catalysts. Coke yields in mixtures of coked and regenerated catalysts are not higher, which would allow increasing catalyst circulation without impacting on heat balance. The particularities of this new operation of FCC are very dependent on catalyst properties. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: FCC; Deactivated catalyst; Catalyst recycling; Selectivity; Delta coke

1. Introduction

The catalytic cracking of hydrocarbons, FCC, plays a key role in modern refining, since it is one of the major fuels and raw materials producers [1]. In present days, its technology is based on the utilization of transport, diluted fluidized bed reactors with a very short residence time (riser cracking). The standard configurations put regenerated catalyst from the regenerator into contact with the feedstock in a single injection point at the base of the riser; then the mixture of hydrocarbons and catalyst particles travel together upwards the riser, while cracking reactions take place, until they are disengaged, catalyst being sent to the regenerator where coke is burnt off to reinitiate its operative cycle. During its history of about 50 years, the technology of FCC (catalyst, additives, hardware, process parameters and operation, etc.), has always been subjected to continuous improvements and changes, the present days driving forces for new developments being the necessity to process increasingly heavier feedstocks [2], to obey environmental regulations [3], and to increase profit by gains in yields and product quality. Among the new ways of operating commercial FCC units, the very short contact times units [4], the split feed injections [5] and the recycling of deactivated catalyst mixed with regenerated catalyst [6] can be mentioned.

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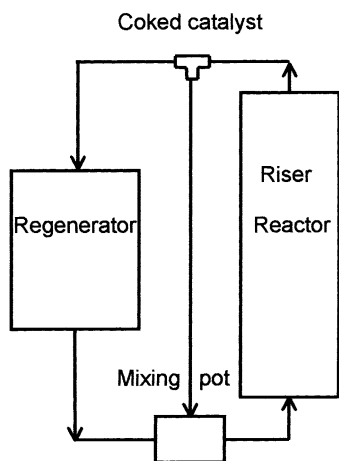*E-mail address:* usedran@fiqus.unl.edu.ar (U. Sedran).

Fig. 1. Schematic representation of the recycle of coked catalyst.

The technology that recycles deactivated catalyst and mixes it with regenerated catalyst has been named "RxCat" (formerly "X-design") by UOP [7]. A very simple scheme is presented in Fig. 1. Its claimed most positive characteristic is that it is possible to increase total catalyst circulation without an impact on heat balance, since coke yield would not be increased [6]. One of the basic points is that the coked, spent catalyst is still active, and its mixture with regenerated catalyst, feasible. An expected benefit, based on a lower reactor temperature and a higher circulation rate of catalyst contacting the feed, is an enhancement of catalytic cracking against thermal cracking, thus, reducing dry gas yield and increasing gasoline yield. It is necessary that the delta coke produced in the standard operation by the catalyst to be used be low, say under 0.7%. However, there is no publication in the open scientific literature describing this new operation of FCC, and a number of questions can be

raised like, for example, the impact on product selectivity, or the true characteristics of the "effective" new catalyst facing the reactant hydrocarbons, since the overall properties of the mixture are different from those of the individual components.

It is the objective of this paper to study in the laboratory, with commercial catalysts and feedstocks and a riser simulator reactor, the catalytic performances of mixtures of spent and regenerated catalysts in the FCC operation, as well as the consequences that the approach would produce on product yields, selectivities, and coke formation issues.

2. Experimental

Two equilibrium commercial FCC catalysts sampled from running refineries were used (catalyst A, BR1160, Engelhard, UK, and catalyst B, Vision 418, FCC, SA, Brazil); their main properties are shown in Table 1. Catalyst A is a conventional, high unit cell size catalyst, while catalyst B is an octane catalyst, with low unit cell size. The feedstock used was virtually metal-free, commercial vacuum gas oil (Petrobrás, Brazil) and its properties are also presented in Table 1.

The experiments were performed in an internal recirculation, fluidized bed laboratory unit, the riser simulator reactor [8,9], which was specifically designed for FCC studies. An impeller rotating at very high speed on top of the chamber that keeps the catalyst between two metal porous plates, induces the internal circulation of the reacting mixture in an upwards direction through the chamber, thus, fluidizing the catalyst. When the reactor is at the desired experimental condition the reactant is fed through an injection port, and immediately after the reaction time is attained, products are evacuated and analyzed

Table 1
Properties of catalysts A and B and feedstock

BET specific surface area ($m^2\,g^{-1}$)		Unit cell size (Å)		Zeolite content (%)		Rare earth oxide content (%)		Feedstock			
A	B	A	B	A	B	A	B	Distillation[a] (°C)	Density ($g\,cm^{-3}$)	Sulfur (%)	Aniline point (°C)
175	139	24.31	24.23	9.1	16.9	1.31	1.26	399 (10%) 470 (50%) 544 (90%)	0.924	0.57	96.4

[a] The value in parenthesis indicate yields of various temperature.

by gas chromatography. The unit has been extensively and successfully used for catalyst evaluation [10,11], assessment of kinetic, diffusion and adsorption parameters [12–14], and studies about reaction mechanism [15]; additional descriptive details of the reactor can be found in these publications. The unit allows for the reproduction of commercial conditions in the laboratory, such as temperature, catoil ratios, fluidization and, particularly, very short contact times.

Two types of experiments were done with both catalysts. The first ones were reference experiments performed under the standard operation with regenerated catalysts, so as to establish a comparison basis; the experimental conditions in the isothermal regime were temperature: 550°C, catoil ratio: 4.93 (catalyst A) and 4.00 (catalyst B), contact times: 3, 6, 9, 12 and 15 s. The experiments at 15 s contact time were repeated many times to produce coked catalyst to be mixed with regenerated catalyst. The coked samples were also tested alone. In the second type of experiments, the mixtures were used with the ratios 50:50 and 25:75 (coked:regenerated), under different overall catoil ratios. In all the cases, coke was determined by means of a temperature-programmed oxidation and further methanation procedure [16]. Conversions were defined as the sum of the total yields of gases, gasoline, LCO and coke. The end cut points for gasoline and LCO were n-C12 (boiling point, 216°C) and n-C20 (boiling point, 344°C), respectively.

3. Results and discussion

Although, the residence time in riser reactors in modern FCC units is very short, typically under 10 s [4], the catalyst particles become severely deactivated after converting the VGO feedstock, and they are sent to the regenerator unit where coke is burnt off, an important amount of heat being transported by the catalyst back to the reactor. With coke loads that change as a function of catalyst and feedstock properties and operative conditions, but that usually range from 0.7 to 1.5 wt.%, the catalyst should still maintain activity if it is to be mixed with regenerated catalyst from the regenerator and recycled to the riser. There are not many publications in the open literature about the activity remaining on coked FCC catalysts. It has been shown that three different regenerated catalysts
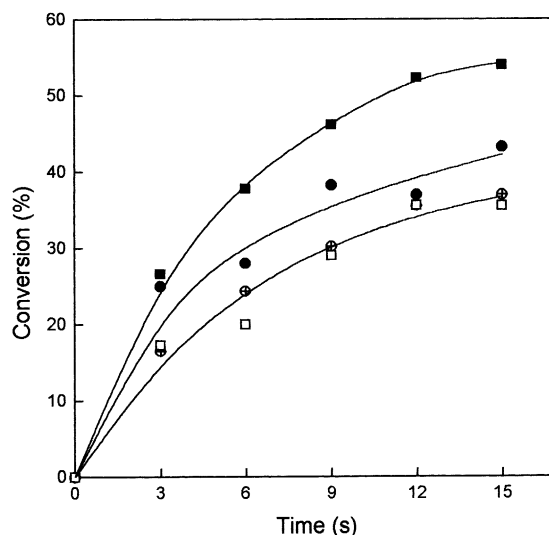

Fig. 2. Catalyst A: conversion as a function of contact time. Catoil 4.93. Symbols: standard operation, (■) regenerated and (⊕) coked catalyst; operation with mixtures, (●) 25:75, (□) 50:50 (deactivated:regenerated) catalyst.

that have MAT activities of 69, 73 and 74, have spent catalyst MAT activities of 58, 63 and 62, with coke loadings of 0.75, 0.70 and 0.78 wt.%, respectively [6]. In the average, these changes represent losses of approximately 15% referred to the regenerated catalyst. These results are close to those observed by Forissier et al. [17], who also used the MAT technique with equilibrium catalysts that had been previously coked in a wider range (up to 1.4%), and two feedstocks; for 0.75 wt.% coke, the drops in MAT activity were about 19%. Turlier et al. [18] showed that coke deposition along the riser is very fast, and that after about 10% of total length, coke increases very slowly; MAT activities after this position keep stable at about 68.

As an example for this work, the activities at 550°C of both regenerated and coked catalyst A are shown in Fig. 2. The experiments with the coked catalyst were performed on samples that had been previously contacted during 15 s at the same temperature, with a coke load of 0.59%. As expected, the regenerated catalyst shows a higher activity than the spent catalyst (conversions are higher during the whole range of contact times). The retention of activity was assessed in two different ways: conversions at a given contact time like, e.g. 15 s, were 54.0% for the regenerated catalyst

and 37.0% for the coked samples, while the values of the kinetic constants for overall VGO conversion, leading to gasoline and gases plus coke, from the classic three-lump model, regressed from the whole set of experiments with different contact times and with concentrations expressed as mass fractions, were 0.139 and 0.076 s^{-1} for the regenerated and coked samples, respectively. If compared with the previously mentioned references, these figures could be understood as suggesting a higher loss of activity. However, it should be considered that the contact regimes between catalyst and reactants are very different in MAT units and the riser simulator reactor; in effect, the latter reactor ensures a more realistic representation of the FCC reacting environment.

The activity profiles of the mixtures with ratios of 50:50 and 25:75 (coked:regenerated) for the case of catalyst A with the same total catoil of 4.93 can be observed in Fig. 2 as a function of contact time. As expected, the activity of the mixtures of regenerated and coked catalysts is between those of the individual fractions (refer to Fig. 2, mixture 25:75), although, the mixture 50:50 and the deactivated catalyst behave closely. In that sense, it has to be considered that the properties of the mixtures are not the result of the direct addition of the properties of the fractions, and that under reaction conditions, the two components would produce coke, and consequently deactivate, at different rates. If the performance of the catalysts is measured through a given index, it is to be expected that the higher the content of coked catalyst in the mixtures, the closer the behavior of the mixtures and the deactivated catalysts, probably following an asymptote, as suggested by these results.

However, if total catoil is increased, it can be seen in Table 2 that activity increases, approaching that of the regenerated catalyst. This issue clearly points to

Table 2
Catalyst A: cracking activity of mixtures 50:50 (coked:regenerated) as a function of catoil[a]

Catoil ratio	Conversion (%)
4.93	35.5
6.80	42.9
8.63	49.9
4.93[b]	54.0[b]

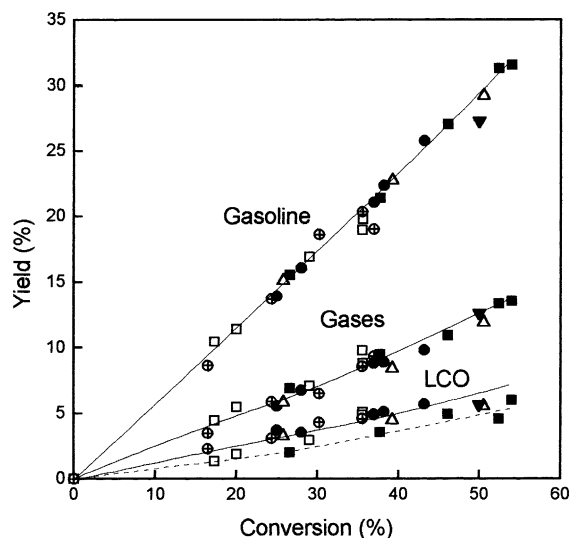[a] Temperature 550°C, contact time 15 s.
[b] Standard operation.

Fig. 3. Catalyst A: yields of gases, gasoline and LCO as a function of conversion for various operative modes. Symbols as in Fig. 2. Mixtures 50:50 (deactivated:regenerated) castalyst: (△) catoil 6.80 and (▼) catoil 8.63.

the fact that, in order to maintain activity under the operation with recycled catalyst, circulation in commercial risers has to be increased.

It may be more interesting to observe changes in yields and selectivities due to the operation with mixed catalysts. As shown in Fig. 3, when mixtures are used, the yields of gasoline do not depart significantly from that obtained under the standard operation, selectivity being 56.9%. The yield curves of gases, also included in Fig. 3, are again essentially the same for the standard and the mixed catalyst operations and the selectivity is 23.3%. This only trend for gasoline and gases yields is also followed by the results from the operation with mixtures at higher catoil ratios, and even with the deactivated catalyst alone. A small difference is observed in LCO, since the operation with mixtures yields slightly higher amounts of LCO, due to the lower activity of the mixtures; selectivity is approximately 13.0%, whereas for the standard operation it is 9.7%. According to the shape of the yield curves, the values of the selectivity for each of the hydrocarbon lumps are essentially constant in the conversion range studied, all the operations showing about the same selectivity to gases and gasoline, and slightly higher selectivity to LCO in the case of mixtures.
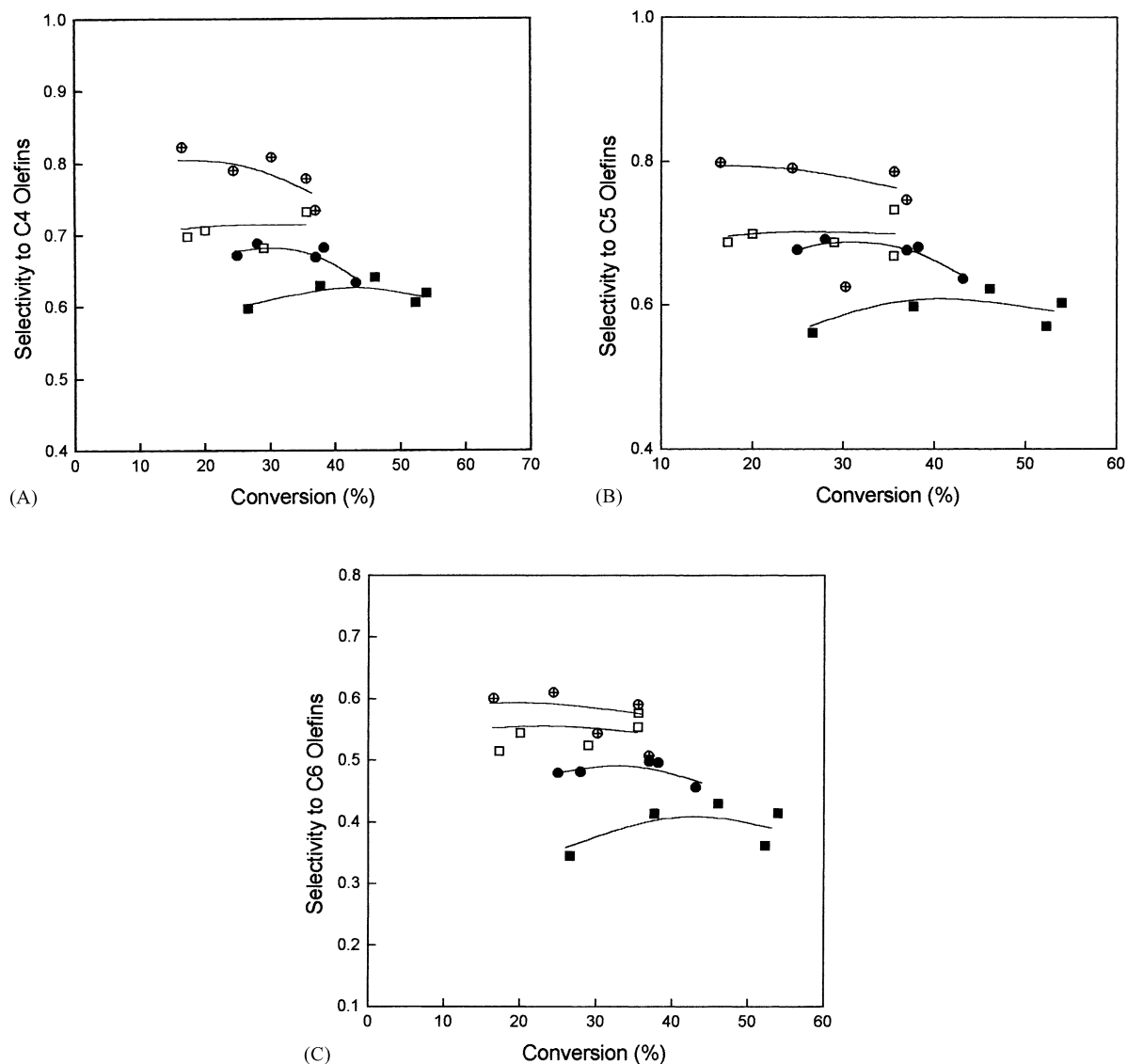
Fig. 4. Catalyst A: selectivity to C4–C6 olefins as a function of conversion for various operative modes. (A) C4=/C4; (B) C5=/C5; (C) C6=/C6. Symbols as in Fig. 2.

The most important changes in selectivity for catalyst A are observed in the light olefin fractions. In effect, the olefinicities of the C4–C6 cuts are shown in Fig. 4, where it can be seen that in all the cases the curves are stable and then show a slight decrease as a function of conversion, at higher conversions, that could be assigned to the higher incidence of secondary hydrogen transfer reactions. Moreover, the olefin selectivities are the highest when only the deactivated catalyst is used, particularly in the C5 and C6 hydrocarbon groups; the fact that in these coked catalysts the density of paired acid sites in the zeolite, which is the most important factor controlling hydrogen transfer in FCC catalysts [13] is very much reduced, can account for these variations. This suggestion is based on the well known negative influence of the loss of

Table 3
Catalyst A: effect of catoil on the selectivities to olefins with mixtures 50:50 (deactivated:regenerated)[a]

Catoil	Selectivities		
	$C4{=}/C4_{total}$	$C5{=}/C5_{total}$	$C6{=}/C6_{total}$
4.93	0.732	0.733	0.576
6.80	0.625	0.613	0.442
8.63	0.578	0.566	0.395
4.93[b]	0.629[b]	0.597[b]	0.414[b]

[a] Temperature 550°C.
[b] Standard operation.

active sites due to zeolite dealumination on hydrogen transfer reactions, which is controversial [19], since it has been explained as the consequence of either the reduced capacity for olefin adsorption (e.g. [20]) or the decreased density of paired acid sites (e.g. [13,21,22]).

When the mixtures 50:50 and 25:75 are used at the same catoil as the standard operation, it is clear that at the same conversion level there is a net gain in the relative amount of olefins in the C4–C6 groups. Consistently with the highest selectivity observed in experiments with only coked catalysts, this benefit in olefin selectivity is more important when the ratio between deactivated and regenerated catalyst increases. For a given mixture, however, as total catoil is increased over that used in the standard operation, in order to increase conversion, the benefit in olefin selectivity decreases, and it could also be lower than the values observed in the standard operation (refer to Table 3, where conversion was about 40%). This evidence could be rationalized considering that for a given ratio between coked and regenerated catalysts in the mixtures, higher overall catoils imply in fact that the amount of regenerated catalyst facing the feedstock approaches that of the standard operation: for example, catoils of 6.80 and 8.63 in the 50:50 mixtures imply catoils of 3.40 and 4.32 based only on the regenerated catalyst, that are increasingly closer to the reference catoil of 4.93, used with the regenerated catalyst. As a consequence, the density of zeolite paired acid sites, and its impact on selectivity in these groups, will be similar in both cases.

Indeed, these changes in selectivity are the result of the lower yield of isoparaffins in the corresponding group, while olefins are produced at the same rate as a function of conversion, independently of the
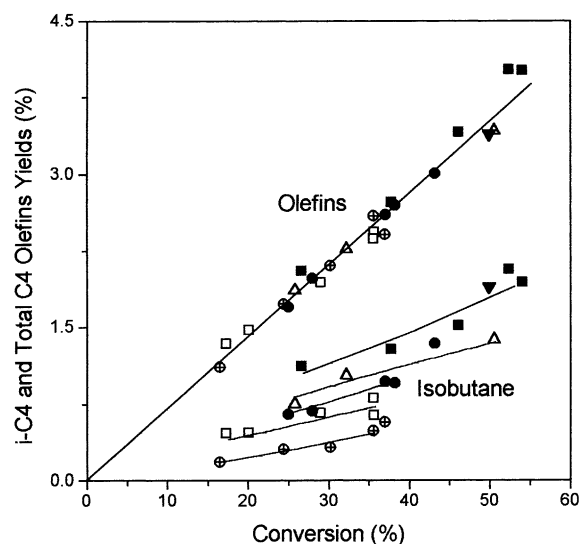

Fig. 5. Catalyst A: yields of total C4 olefins and isobutane as a function of conversion for various operative modes. Symbols as in Fig. 3.

operative mode. For example, in the particular case of C4 compounds, it can be seen in Fig. 5 that the yield of isobutane decreases significantly as soon as part of the catalyst used is previously coked, the yield being minimum in the case of using only the deactivated catalyst; moreover, when the total catoil is increased for a given mixture, isobutane yields approach the one observed in the regenerated catalyst. It has to be considered that isobutane, which is one of the most representative products of catalytic cracking [23], needs a final hydride transfer step to desorb from an adsorbed carbenium isobutyl cation. As stated [9,19], this type of bimolecular reaction would be particularly affected by coke deposition; on the other hand, olefin desorption from a carbenium ion can be produced via monomolecular proton transfer to the catalytic surface [24]. Concerning the C5 group, the same behavior was observed with total olefins and isopentane.

The yields of coke deserve special consideration, because this is one of the main issues associated to this new operation of FCC units. In an overall view, the yield curves are qualitatively similar in all the cases, showing a fast increase and then a stabilization trend. As shown in Fig. 6 for catalyst A, coke yields in the mixtures 50:50 and 25:75 with the same catoil as the standard are about the same, and smaller than that
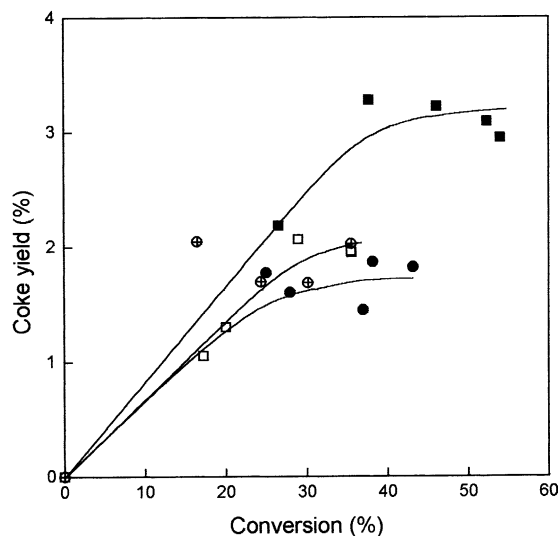
Fig. 6. Catalyst A: yield of coke as a function of conversion. Symbols as in Fig. 2.

formed in the standard operation. However, when the catoil was increased from 4.93 to 6.80, coke yields increased in about 25% over the standard (data not shown). All these observations also reflected in terms of delta coke on catalyst. These results are consistent with a general equation relating coke yield, catalyst recycling ratio, delta coke and catoil, that can be derived from coke mass balances performed in different locations of a unit operating with mixtures of deactivated and regenerated catalysts under the scheme of Fig. 1. These results are also in accordance with results from commercial comparative studies [7].

Another set of similar experiments was performed on catalyst B, which is a low unit cell size catalyst. Considering that the mixtures 50:50 in the case of catalyst A required strong variations in the total catoil so as to approximate to the conversions of the standard operation, the catalytic performance of catalyst B was studied with mixtures 25:75. The experiments confirmed the main observations produced on catalyst A. The activity of catalyst B under the standard operation at catoil 4.00 is shown in Fig. 7, showing to be more active than catalyst A, even though its unit cell size is smaller, due to its higher load of zeolite in the catalyst. Mixtures 25:75 tested at the same catoil are less active, but then it was possible to reproduce the activity profile of the regenerated catalyst by
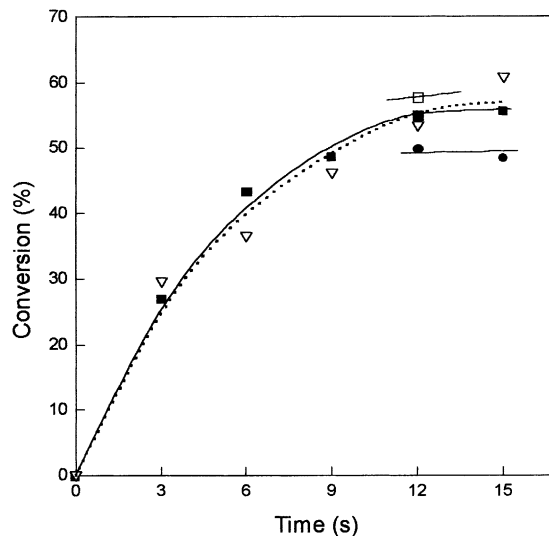

Fig. 7. Catalyst B: conversion as a function of contact time. Symbols: (■) standard operation with regenerated catalyst, catoil 4.00; operation with mixtures 25:75 (deactivated:regenerated) catalyst, catoils: (●) 4.00, (▽) 4.93 and (□) 5.55.

increasing the catoil in the mixture from 4.00 to 4.93. The yield curves of gases, gasoline and LCO are shown in Fig. 8, where it can be seen that they follow the same pattern under the two operations
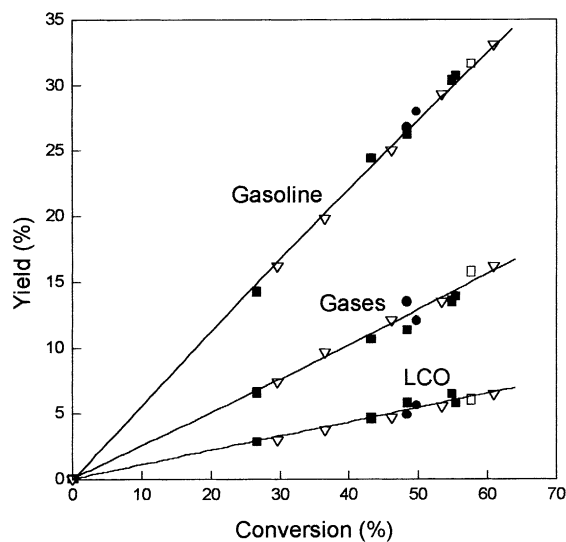

Fig. 8. Catalyst B: yields of gases, gasoline and LCO as a function of conversion for various operative modes. Symbols as in Fig. 7.
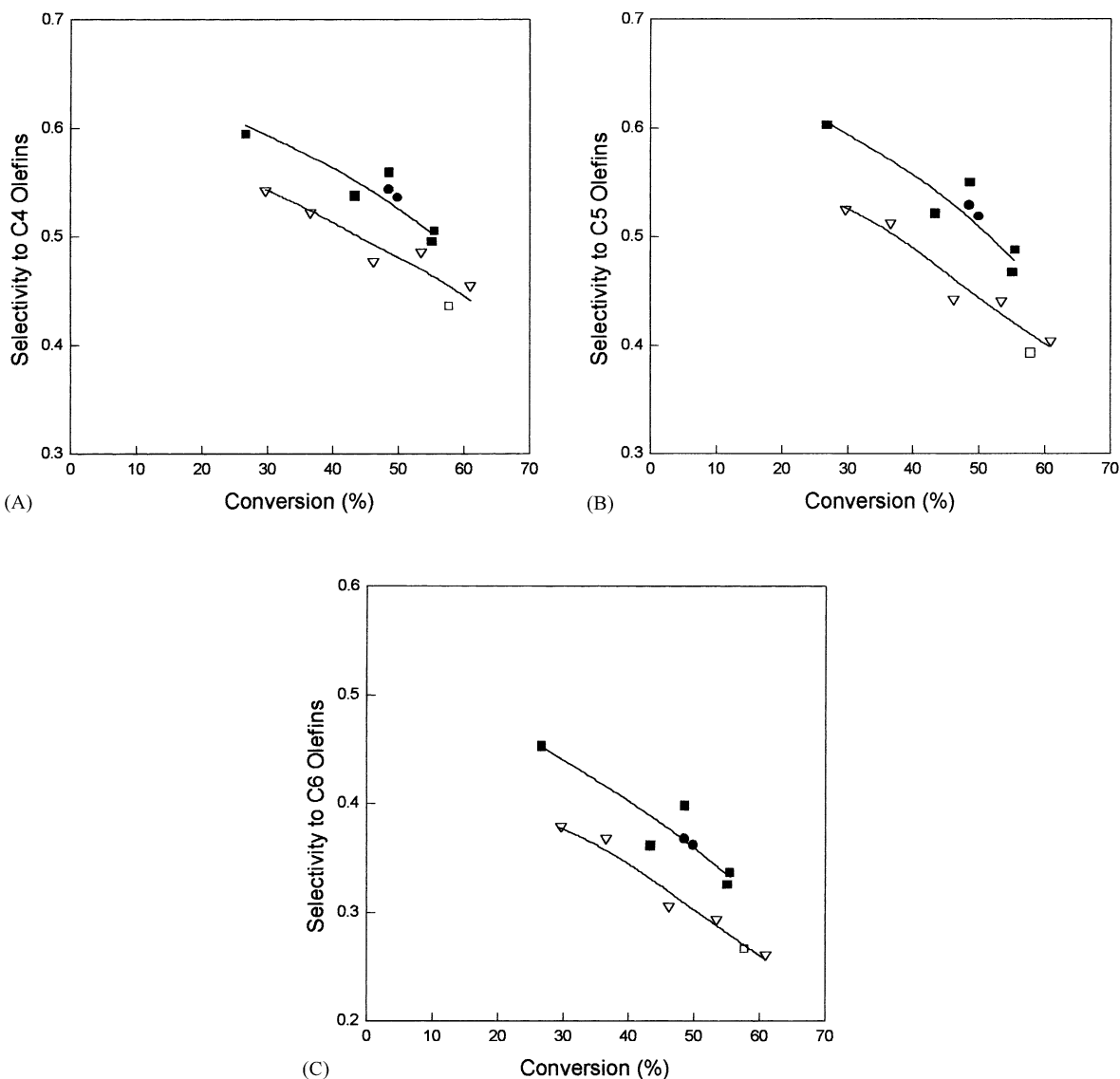
Fig. 9. Catalyst B: selectivity to C4–C6 olefins as a function of conversion for various operative modes. (A) C4=/C4; (B) C5=/C5; (C) C6=/C6. Symbols as in Fig. 7.

and the various catoils; in this case, no differences are observed in LCO. Consequently, selectivities for gases (25.9%), gasoline (53.7%) and LCO (10.6%) are constant in the range of conversions studied.

In the case of catalyst B the selectivities to light olefins as a function of conversion (refer to Fig. 9) show to be decreasing for all the C4–C6 groups in the conversion range studied; as already stated, it is

believed a consequence of the increasing incidence of hydrogen transfer reactions as conversion increases. The changes in olefin selectivity when operating with mixtures 25:75, as compared to the standard operation, confirm the previous reasoning on catalyst A. In effect, while using mixtures 25:75 with the same catoil as the standard operation produces very similar results in light olefin selectivity, the higher overall catoil

leading to the same conversion profile as the regenerated catalyst makes olefin selectivity to be lower than the one observed in the standard operation. In that sense, it should be considered that the overall catoils of 4.93 and 5.55 used for this particular case of mixtures of coked and regenerated catalyst B, imply catoils based only on the amount of regenerated catalyst of 3.69 and 4.15, respectively, that are close or even higher than the reference value of 4.00. Furthermore, as it was previously shown for catalyst A, the yields of the isoparaffins in the groups and their relationship with hydrogen transfer govern changes (data not shown), because the yield of olefins is not affected by the operative mode, while the isoparaffins are sensitive to it. As a consequence, the yields of isobutane and isopentane are higher when operating with mixtures at the standard or higher catoils.

As it is shown in Fig. 10, coke yields in catalyst B are about the same in the operation with mixtures and the standard, independently of the catoil used. Again there exists consistency with coke mass balances in FCC units operating with recycling of coked catalyst.

The comparison of results between the two catalysts allows defining similarities and differences in relation to the operation with mixtures of coked and regenerated catalysts. It was observed for both catalysts that coked samples maintained activity and that the mixtures with coked catalysts, that are less active, required that overall catoil be increased in order to recover at least the same activity as the standard. In that case, the yields of the main hydrocarbon groups do not change significantly, but depend essentially on conversion. The need for a higher catoil, the balance on the density of paired acid sites in the zeolite component resulting from the adoption of different masses of coked and regenerated catalysts in the mixtures, and their relationship with hydrogen transfer, induce changes in the selectivity to light olefins on both cata
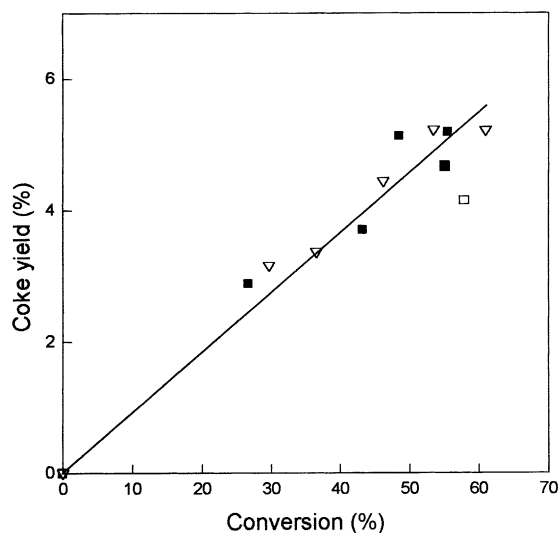

Fig. 10. Catalyst B: yield of coke as a function of conversion. Symbols as in Fig. 7.

lysts, that are the direct consequence of the variations in the yield of the isoparaffins in the corresponding groups.

The assessment of gasoline octanes (RON) was performed by applying the Anderson's method [25] on the gasoline fraction of the products in each experiment. Results are presented in Table 4, where it can be seen that average octane numbers reflect the characteristics of each catalyst; in effect, catalyst A is conventional, while catalyst B is an octane catalyst. Concerning the influence of the operative mode, it can be seen that mixtures at the same catoil as the standard tend to produce lower RONs in the gasoline (see case of catalyst A), but as catoil is increased, gasoline RONs increase (see case of catalyst B). These changes could be associated to those in the yields of aromatics in gasoline, which have the same trend (data not shown), since this

Table 4
Average gasoline octane numbers (RON, [22])

Catalyst A			Catalyst B		
Operative mode	Catoil	Average RON	Operative mode	Catoil	Average RON
Standard	4.93	87.8	Standard	4.00	89.0
Mixture 25:75	4.93	85.7	Mixture 25:75	4.00	89.5
Mixture 50:50	4.93	86.1	Mixture 25:75	4.93	90.0
Deactivated	4.93	85.0	Mixture 25:75	5.55	92.0

hydrocarbon group is very important in determining the RON.

It was verified on both catalysts that coke yields in the operation with mixtures are not higher than the standard; this is an important fact that would allow decoupling catalyst circulation from heat balance in commercial units.

It has to be considered that these experiments were performed under the isothermal regime. It can be expected in commercial units that, if delta coke is not too high, the increase due to the operation with mixtures can be admitted and then, even though temperatures in the regenerator would be higher, the combination of the two catalyst streams (high temperature from the regenerator and low temperature from the reactor exit) would yield a catalyst flow back to the riser with a lower temperature. This fact, along with a higher catalyst circulation rate would improve the relationship between catalytic and thermal cracking reactions, and lower dry gas yields are expected [6]. Moreover, the mixing device could be used in fact as a high temperature stripper. The higher delta coke observed in this new operative mode could also help to improve the situation in units where delta coke is too low.

4. Conclusions

FCC catalysts maintain a considerable level of activity after being coked in cracking a VGO feedstock. This characteristic makes it possible to recycle deactivated catalyst and mix it with regenerated catalyst in order to establish a new operative way of FCC riser reactors. However, since mixtures are less active than regenerated catalyst, it is necessary to increase overall catoil in order to recover previous conversions and yields. While yields of the main hydrocarbons groups gases, gasoline and LCO show to be a function of conversion only, changes are observed in selectivity to light olefins C4–C6. Benefits or penalties in light olefin selectivity are due, in fact, to changes in the yields of isoparaffins (isobutane, isopentane) in those groups, that can be associated to the actual balance of paired acid sites in the zeolite component, in turn changing as catoil is modified for a given ratio between coked and regenerated catalyst.

The yields of coke with mixtures are not higher than in the standard operation. Then, when delta coke in the standard operation is not significant, it would be possible to accept the increase in coke on catalyst derived from the operation with mixtures and, thus, heat balance could be decoupled from catalyst circulation in commercial units. Although, the experiments were performed isothermally, it is predictable that the temperature in the mixture formed by the two streams (regenerated and coked catalysts) will be lower, and consequently reactor temperature can be also decreased; this may impact positively on gasoline and dry gas selectivities. Even the mixing pot could act as a high temperature catalyst stripper. However, it was shown that the particular results of the operation with recycled coked catalysts strongly depend on catalyst properties.

The riser simulator reactor is a proper laboratory tool for studying new operative ways of the FCC process.

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