Comparison between MAT Flow Fixed Bed and Batch Fluidized Bed Reactors in the Evaluation of FCC Catalysts. 2. Naphtha Composition

Francisco J. Passamonti, Gabriela de la Puente, and Ulises Sedran*

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ, UNL - CONICET),
Santiago del Estero 2654, (3000) Santa Fe, Argentina

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A comparison was performed between the performances of a MAT type reactor (flow fixed bed) and a CREC riser simulator reactor (batch fluidized bed) in the conversion of two VGO feedstocks (aromatic and paraffinic types) over three commercial equilibrium FCC catalysts, under similar conditions. In both units the reaction temperatures were 500 and 550 °C. The catalyst-to-oil relationships were from 2.3 to 6.2 (cumulative) and 6.2, and the times were from 15 to 40 s (time on stream) and from 5 to 30 s (reaction time) in the MAT reactor and the CREC riser simulator reactor, respectively. Results were compared in terms of the composition of the naphtha, in view of its contribution to the gasoline pool. Advantages were observed with data from the CREC riser simulator reactor, mainly derived from the fact that naphtha yields were, in general, closer to commercial values and showed a stable primary product behavior. Thus, they are easier to analyze as naphtha selectivities did not depend on the conversion reached. On the contrary, naphtha yields in the MAT reactor showed a maximum as a function of conversion. The comparison of the product distributions observed in the naphthas from each unit at the same conversion level showed that they can be very different; the naphtha obtained in the CREC riser simulator reactor was more paraffinic and less aromatic than the one obtained with the MAT reactor, and the proportions were similar to commercial values. Ranks of catalysts based on the various hydrocarbon fractions observed in the naphtha from each setup also differed in most of the cases. The differences in the results could be the consequence of notoriously different contact between reactants and catalyst and operative modes in each reactor, then impacting on the complex set of reactions occurring in FCC.

Introduction

The catalytic cracking of hydrocarbons (FCC) is the main process in hydrocarbon conversion to gasoline and light olefins in the petroleum refining industry.[1] Its main characteristic is the conversion of low value, high molecular weight hydrocarbons into valuable products, with a high operative flexibility. Recent trends are inducing changes in the operation of FCC units, such as the need to process heavier feedstocks, to increase integration with petrochemistry (mainly concerning propylene yield[2,3]) and to intensify environmental care. Moreover, emerging economies are increasing substantially their demands for middle distillates[1,4] (diesel fuels, where FCC contributes with a poor quality cut). In this way the hardware, the operative modes, and the commercial catalysts are changing continuously and opening to new challenges and knowledge demands. One of the most perceptible trends is the use of increasingly heavier residual feedstocks, with more contaminant metals and higher Conradson carbon residue (CCR), promoted by the decline in the quality of crudes.

Catalyst selection procedures, as well as catalyts and process developments, call for a proper laboratory tool to help produce evaluations as close to reality as possible. Most of the evaluation procedures and also process developments have been performed on MicroActivity Test-type fixed bed reactors (MAT[5]). Similar methodologies can be applied to flow reactors with confined fluidized beds (FFB), that in the last times became very common in laboratories related to FCC. An alternative view can be built based on the CREC riser simulator laboratory reactor.[6] The unit has a bed fluidized in a chamber and mimics, in ideal terms, the riser reactor in commercial units, following the analogy between position in the riser and reaction or residence time in the laboratory unit. It was shown in a previous paper[7] that, in comparison to MAT-type reactors, the CREC riser simulator reactor allows the defining of catalyst rankings that are more sensitive to various test parameters and that some hydrocarbon group yields are overall closer to commercial values. Particularly, differences between reactors are notorious in the coke yields, which are very important from the operative standpoint, with much higher yields observed in MAT units. The most significant differences in the performances of the two reactors were explained as the consequence of the very different flow models, that is, the contact between reactants and catalysts.

Even though a shift in fuel demands can be observed worldwide,[1,8] gasoline has been, and many times is, the issue to maximize in FCC processing. As a consequence, FCC

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* To whom correspondence should be addressed. E-mail: usedran@fiq.unl.edu.ar.

(1) O'Connor, P. *Stud. Surf. Sci. Catal.* **2007**, *166*, 227–251.

(2) Jun, L.; Wei, L.; Zhonghong, Q.; Huiping, T.; Yuxia, Z. *Stud. Surf. Sci. Catal.* **2007**, *166*, 55–66.

(3) Corma, A.; Melo, F. V.; Sauvanaud, L.; Ortega, F. *Catal. Today* **2005**, *107−108*, 59–61.

(4) Corma, A.; Sauvanaud, L. *Stud. Surf. Sci. Catal.* **2007**, *166*, 41–54.

(5) ASTM D-3907/03.

(6) de Lasa, H. I.; US Patent 5,102,628, 1992.

(7) Passamonti, F. J.; de la Puente, G.; Sedran, U. *Energy Fuel* **2009**, DOI: 10.1021/ef8008103.

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Table 1. Properties of the Feedstocks Used

	VGO-B	VGO-M
density 20/4 °C (gr cm^{-3})	0.9240	0.9162
deg. API	21.0	22.3
distillation (°C)		
10% v	399	361
30% v	441	408
50% v	470	432
70% v	498	456
90% v	544	494
Conradson carbon (% wt)	0.55	0.11
vanadium (ppm)	<0.1	0.73
nickel (ppm)	0.41	0.10
sulfur (% wt)	0.57	2.03
total nitrogen (ppm)	2800	1441
character	aromatic	paraffinic

Table 2. Properties of the Catalysts Used

catalyst	E-Cat M	E-Cat O	E-Cat P
unit-cell size[a] (nm)	2.426	2.424	2.429
rare-earth oxide (% wt)	1.19	0.00	3.06
zeolite load[b] (% wt)	18.0	15.9	14.0
BET surface area[c] (m^2 g^{-1})	158.0	151.0	137.0
acidity[d] (mmol NH_3 g^{-1})	0.036	0.015	0.011
Fe (% wt)	0.35	n.a.	0.40
Ni (% wt)	0.06	n.a.	0.06
V (% wt)	n.a.	n.a.	0.15
type	octane-barrel	octane	gasoline

[a] ASTM standard test method D-3942−85. [b] Johnson's method[32] with N_2 adsorption. [c] BET method, using N_2 adsorption. [d] NH_3 temperature-programmed desorption.

naphtha, which is the most important contributor to the gasoline pool, is usually the most important hydrocarbon group in FCC. There exist catalysts that are specially formulated to maximize gasoline,[9] and the FCC units can be operated in the "gasoline mode",[10] with their combination leading to the highest naphtha yields. In the selection of a maximum gasoline catalyst, usually, naphtha yields at a given conversion or coke yields[11] are considered. However, regarding the increasingly severe regulations about gasoline, the composition of the FCC naphtha is not a minor issue.

It is the objective of this manuscript to compare the different compositions observed in the naphthas obtained in the conversion of commercial vacuum gas oil feedstocks over commercial equilibrium FCC catalysts under similar experimental conditions in a MAT fixed bed reactor and in a fluidized bed CREC riser simulator reactor.

Experimental Section

Two commercial vacuum gas oils (VGO) were used, that were named VGO-B and VGO-M. VGO-B has aromatic character, and VGO-M is paraffinic. Feedstock characterization is presented in Table 1. The catalysts used were equilibrium samples from refineries that were supplied by different catalyst producers (E-Cat M, E-Cat O and E-Cat P), their properties being shown in Table 2.

The CREC riser simulator reactor is a batch, confined fluidized bed laboratory reactor that was designed specifically to address FCC studies.[6] Additional descriptive details can be found in, for example, refs 7, 12, and 13. Experiments were conducted at 500 and 550 °C, with a catalyst-to-oil relationship (C/O) of 6.2 and reaction times from 5 to 30 s. Mass balances closed to more than about 94% in all the cases.

A continuous flow fixed bed reactor based on the one defined by the ASTM D-3907/03 standard was used for a comparative set of experiments under the same temperatures. Differences from the standard reactor were in the condenser−collector design, where a precondenser was added, and in the use of a second stripping flow after the collection of the gas sample, which helped to remove products and unconverted feedstock from the reactor. The mass of catalyst was 4 g, and the mass flow rate of VGO was 2.6 g min^{-1}. The C/O relationship was changed by varying the operation time (time on stream) from 15 to 40 s, thus defining cumulative C/O relationships from 2.3 to 6.2. Mass balances closed to more than about 95% in experiments with time on stream longer than 25 s.

Product analysis and coke assessment were performed in the same way in both sets of experiments. Reaction products were analyzed by means of conventional capillary gas chromatography, with online sampling and injection in the CREC riser simulator and off-line injections in the MAT reactor. Coke was determined by means of a temperature-programmed oxidation procedure; carbon oxides from the combustion were transformed into methane and quantified with the help of a FID detector. Conversion was defined as the addition of the yields of dry gas (C_1-C_2), LPG (C_3-C_4), gasoline or naphtha (C_5 − 216 °C), LCO (216−344 °C), and coke. Selectivities were assessed as the relationships between product yields and conversion.

The research octane number (RON) of the naphtha cut was assessed by means of a modified Anderson's method.[14]

Results and Discussion

To avoid uncertainties derived from equilibration in the laboratory, equilibrium catalyst samples taken from refineries were used. The comparison of the performances of these two different laboratory devices in the conversion of commercial FCC feedstocks over equilibrium catalysts under similar conditions, in terms of both conversion and yields of the main hydrocarbon groups, was developed in a previous paper.[7] It is not possible to compare directly some of the parameters in the operation of these units, such as C/O relationships or reaction and operation times, because they have a different meaning as the result of the completely different flow models, that is, the contact between reactants and catalysts in each setup.

In the CREC riser simulator reactor the catalyst is fluidized by the recirculating gas mixture composed by reactants and products. Consequently, the catalyst particles always meet the same reacting mixture during the entire reaction time, whereas reactions take place, similarly to an ideal commercial riser reactor, and conversion increases steadily as a function of time. The flow model is that of a stirred reactor, a fact verified by Pekediz et al.[15] In the MAT reactor, the fresh feed always contacts a fixed catalyst bed that is suffering deactivation from coke deposits, and that also develops activity profiles along it that change as a function of time; then, instant and average conversion drop as time on stream increases.

However, if VGO conversion is considered an indication of catalyst activity, then E-Cat M was the one showing the highest activity in both setups. In general, the ranking of catalyst activity for given feedstock and reaction temperature was the same in both reactors.[7] It was observed that the higher the acidity (refer to Table 2) the higher the activity, but this property is the result of many different factors in the formulation of a FCC catalyst.

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(8) Gilbert, W. R.; Baptista, C. A.; Pinho, A. R. *Stud. Surf. Sci. Catal.* **2007**, *166*, 31–39.

(9) Marcilly, C. *J. Catal.* **2003**, *216*, 47–62.

(10) King, D. *NATO-ASI Ser. E* **1992**, *225*, 17–50.

(11) Ng, S. H.; Wang, J.; Fairbridge, C.; Zhu, Y.; Yang, L.; Ding, F.; Yui, S. *Energy Fuels* **2004**, *18*, 160–171.

(12) Passamonti, F. J.; de la Puente, G.; Sedran, U. *Ind. Eng. Chem. Res.* **2004**, *43*, 1405–1410.

(13) Al-Khattaf, S. *Ind. Eng. Chem. Res.* **2007**, *46*, 59–69.

(14) Anderson, P. C.; Sharkey, J. M.; Walsh, R. P. *J. Inst. Petrol.* **1972**, *58*, 83–94.

(15) Pekediz, A.; Kraemer, D. W.; Chabot, J.; de Lasa, H. *NATO-ASI Ser. E:* **1992**, *225*, 133–146.

Among the most significant facts, it was shown that the direct comparison of product yields is not possible based on the achievement of the same conversion in both units and that a given set of catalyst, feedstock, and reaction conditions may lead to different catalyst ranks.

Naphtha Yields. The naphtha yield curves have different shapes according to the results observed in each reactor. Figure 1 shows the yield curves in the experiments at 500 and 550 °C, where it can be seen that they were linear in the whole range of conversions in the experiments with the CREC riser simulator but had or insinuated a maximum as a function of the conversion in the case of the MAT reactor. These maxima have been associated to the setting up of an overcracking regime.[11,16,17] However, at conversions lower than 50% the yield curves in each reactor tend to similar values and behaviors. According to these observations, naphtha could be considered a stable primary product in the first case and an unstable primary product in the second case. At conversions over 70%, that is, close to commercial values, the naphtha yields observed in the MAT reactor are all lower than the ones corresponding to the CREC riser simulator reactor, that in turn are similar to commercial values.[18−21]

Reaction temperature has an important impact on the yield of naphtha, which reveals more manifestly with both reactants and all the catalysts in the results gathered in the CREC riser simulator reactor (see Figure 1, panels a and b, VGO-M). The naphtha yields are clearly lower at higher temperatures in the CREC riser simulator, in agreement with well-known FCC facts.[10,22] On the contrary, the naphtha yields decrease less sensitively with reaction temperature in the MAT reactor.[7]

An advantage from the set of results obtained in the CREC riser simulator reactor is that the comparison of the naphtha forming trends from each feedstock can be achieved more easily. In effect, it is clear from Figures 1b and 1c that for a given catalyst the paraffinic VGO-M yields approximately 10% more naphtha than the aromatic VGO-B in the whole range of conversions. The conversion of both feedstocks was discussed in detail in Passamonti et al.[7]

Even though the naphtha yields are very similar with all the catalysts, it is evident from the results in the CREC riser simulator reactor (both feedstocks, both temperatures) that catalyst E-Cat P is the best naphtha producer. This is consistent with its formulation showing high unit cell size and high content of rare earths. It was not possible to define a similar classification with results from the MAT reactor, because naphtha yields and selectivities depend very much on the conversion level, and consequently they may complicate the evaluation procedure.

Composition of the Naphtha Cuts. A very important issue in FCC processing is the resulting quality of the naphtha cut, which depends on its composition, in turn a function of a large number of parameters such as feedstock composition, operative conditions, and catalyst formulation.[22−24] In a trend that is

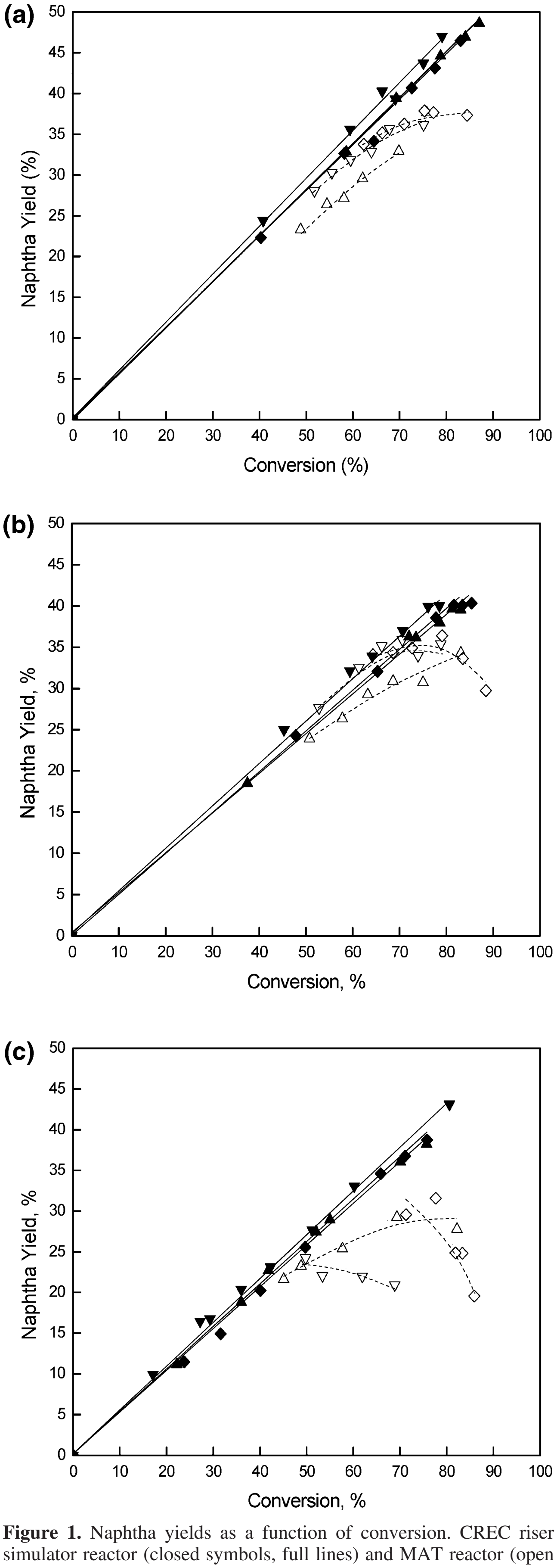

Figure 1. Naphtha yields as a function of conversion. CREC riser simulator reactor (closed symbols, full lines) and MAT reactor (open symbols, dashed lines). (a) VGO-M, temperature: 500 °C; (b) VGO-M, temperature: 550 °C; (c) VGO-B, temperature: 550 °C. Symbols: E-Cat M (◆), E-Cat O (▲), E-Cat P (▼).

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(16) Biswas, J.; Maxwell, I. E. *Appl. Catal. A: General* **1990**, *58*, 19–27.

(17) Myrstrad, T.; Engan, H. *Appl. Catal. A: General* **1998**, *171*, 161–165.

(18) Mandal, S.; Bhattacharyya, D.; Shende, V. B.; Das, A. K. Ghosh, S. *ACS Symp. Ser.*; ACS, Washington, DC, 1994, *571*,335−348.

(19) Nalbandian, L.; Vasalos, I. A., Dimaratos, I.; Vassilakis, K. *ACS Symp. Ser.* ACS, Washington, DC, 1994, *571*, 43−62.

(20) Casali, L. A.; Rocha, S. D.; Passos, M. L.; Bastiani, R.; Pimenta, R. D.; Cerqueira, H. S. *Stud. Surf. Sci. Catal.* **2007**, *166*, 148–162.

(21) Ravichander, N.; Chiranjeevi, T.; Gokak, D. T.; Voolapalli, R. K.; Choudary, N. V. *Catal. Today* **2008**, doi: 10.1016/j.cattod.2008.04.022, in press.

(22) Stokes, G. M.; Wear, C. C.; Suarez, W.; Woung, G. W. *Oil & Gas J.* **1990**, 58–63, July 2.

observed worldwide, most recent regulations on the composition of commercial gasoline follow the guidelines imposed after the amendment of the Clean Air Act in the USA,[25] leading, overall, to a substantial reduction in the permissible amounts of aromatics and olefins and a decrease in vapor pressure, as well as the banning of lead components. The FCC naphtha is highly aromatic and olefinic, and these factors, which are positive from the point of view of octanes, need to be balanced in the gasoline pool to comply with specifications. Sulfur content is another main issue about gasoline composition; since FCC is by far the major sulfur contributor to the gasoline pool,[10] various options to cut sulfur in FCC naphtha were developed. If additives for sulfur reduction in naphtha are added to the equilibrium catalyst, its impact could be evaluated in both laboratory units and compared.

An approximation of the fuel quality of the FCC naphtha can be done based on its octane index. It can be calculated with a chromatographic method based on Anderson's approach,[14] which considers the octane contributions of 31 hydrocarbon groups, some of them pure compounds. Further discussion is provided below.

Paraffins. The fraction of paraffins in the FCC naphtha obtained from a given feedstock is different according to the reactor used. As it is shown in Figure 2, for a given catalyst, in most of the experiments with each of the two feedstocks at both temperatures, the naphtha obtained in the CREC riser simulator reactor showed more paraffins than the one obtained in the MAT reactor. The relative amount of paraffins is esentially stable with conversion in all the cases in the CREC riser simulator reactor.

By contrast, a definite trend is not observed in the MAT reactor, where the paraffinic fraction in some cases increases with conversion, with the curve being steeper at high conversions over 80% (e.g., E-Cat M, Figure 2c), whereas in other cases it decreases slightly (e.g., E-Cat P, Figure 2, panels b and c). This behavior results from the fact that the yield of naphtha has or insinuates a maximum with conversion and then declines, whereas the yield of paraffins generally increases steadily (results not shown). At high conversions (low times of operation and extremely active catalyst), the olefins formed initially by cracking are quickly consumed and transformed into paraffins due to the different reactions that proceed on the surface carbenium ions derived from them.

It was observed with the two feedstocks over both setups that the most important yields of paraffins in the naphtha are those of the C_5 and C_6 groups, which amount to approximately 50−80% of the paraffins in the cut.

It can be seen in the results from the CREC riser simulator reactor that the effect of temperature is to decrease paraffins in naphtha as temperature increases. However, the same consequence can not be observed neatly in the results for the MAT.

The impact of the composition of the feedstock can be observed clearly in the results gathered in the CREC riser simulator reactor. In effect, for each catalyst, the naphtha obtained with the aromatic VGO-B has less paraffins than that from the paraffinic VGO-M. The results with the MAT reactor were less sensitive to the different feedstocks' composition.

It is to be noted that the rank of the catalysts following the proportion of paraffins in naphtha is not the same for both reactors (see Figure 2). In the results from the CREC riser

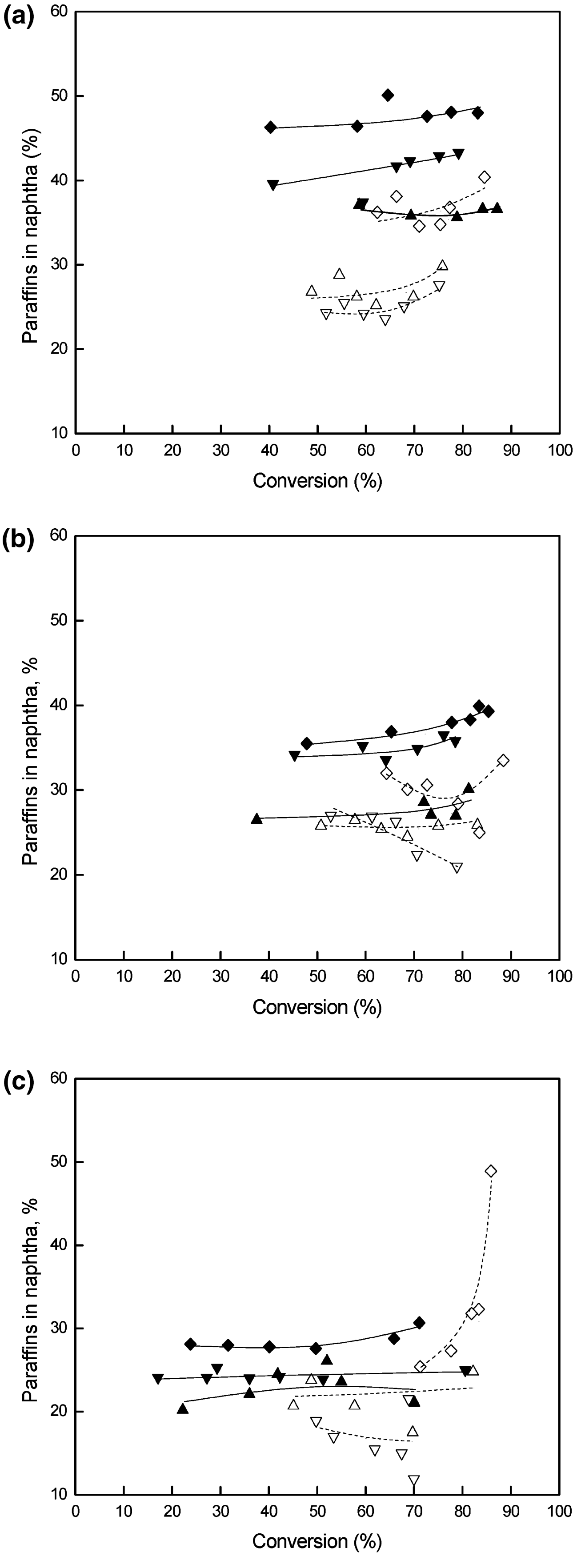

Figure 2. Paraffins in naphtha as a function of conversion. CREC riser simulator (closed symbols, full lines) and MAT (open symbols, dashed lines). (a) VGO-M, temperature: 500 °C; (b) VGO-M, temperature: 550 °C; (c) VGO-B, temperature: 550 °C. Symbols: E-Cat M (◆), E-Cat O (▲), E-Cat P (▼).

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(23) Upson, L. L.; Hemler, C. L.; Lomas, D. A. *Stud. Surf. Sci. Catal.* **1993**, *76*, 385–440.

(24) Lappas, A. A.; Iatridis, D. K.; Vasalos, I. A. *Catal. Today* **1999**, *50*, 73–85.

(25) US Environmental Protection Agency. URL: http://www.epa.gov/air/caa/.

simulator reactor, the rank is neat and independent from the conversion adopted for the evaluation, whereas in the MAT reactor it may depend on this selection.

Olefins. The proportion of olefins in naphtha observed in both reactors at 550 °C, which are shown in Figure 3, panels b and c, seems to be governed by similar overall trends as a function of conversion; in effect, when conversion is higher than approximately 50% for both feedstocks, the relative amounts of olefins decrease. The fractions of olefins in naphtha vary from minimum values of about 10% to maximum values of about 25−30%, depending on the catalyst and the feedstock.

However, different explanations could be considered for each setup. In the case of the CREC riser simulator reactor, the consumption of olefins by the secondary hydrogen transfer reactions, which is more perceptible at higher conversions, reflects more faithfully the overall reaction progress. This is apparent even under conditions with a certain degree of coke deposition on the catalyst surface that impact negatively on the concentration of paired acid sites and consequently on hydrogen transfer reactions.[26,27] On the contrary, the lower proportions of olefins at high conversions observed in the MAT reactor indeed correspond to the instants of highest catalyst activity, in the very early moments of the experiments, when a high concentration of active sites exists in the catalytic surface; these sites adsorb olefins as carbocations and consume them immediately in the very complex set of reactions of the FCC system.

The particular responses of hydrogen transfer and cracking reactions to different thermal levels had somewhat dissimilar impacts on the product distributions observed in both reactors. The positive effect of temperature on the naphtha olefinicity is observed when using the CREC riser simulator reactor with both feeds over all catalysts; the increase was between 20 and 40%, depending on the type of catalyst, when the reaction temperature was changed from 500 to 550 °C (see Figure 3, panels a and b). The increase in olefins at higher temperature is due to the higher activation energy of cracking reactions as compared to hydrogen transfer reactions and to consequent olefins conservation. This fact is not as clear when the MAT reactor is used since, at a given value of conversion, the olefinicity of naphtha virtually did not change with temperature.

The catalyst properties that impact on hydrogen transfer, such as the density of acid sites, should reflect on the amount of olefins in naphtha. For example, the addition of rare earths on the zeolite component of FCC catalysts is supposed to increase acidity and consequently activity.[28] However, when rare earths oxides are loaded over about 3%, its effect could be detrimental due to the generation of OH bridges between rare earth cations that decrease the amount of acid sites.[29] Considering the catalyst properties shown in Table 2, it is expected that the conservation of olefins be the highest with E-Cat O (octane catalyst, no rare earths), followed by E-Cat P and E-Cat M, for given feedstocks and conditions. The catalysts' rank in terms of hydrogen transfer capability can be observed clearly in the results gathered in the CREC riser simulator reactor for both feedstocks, but not in the results from the MAT reactor.

Aromatics. The fractions of aromatics in naphtha observed in the CREC riser simulator reactor are between 28−44%

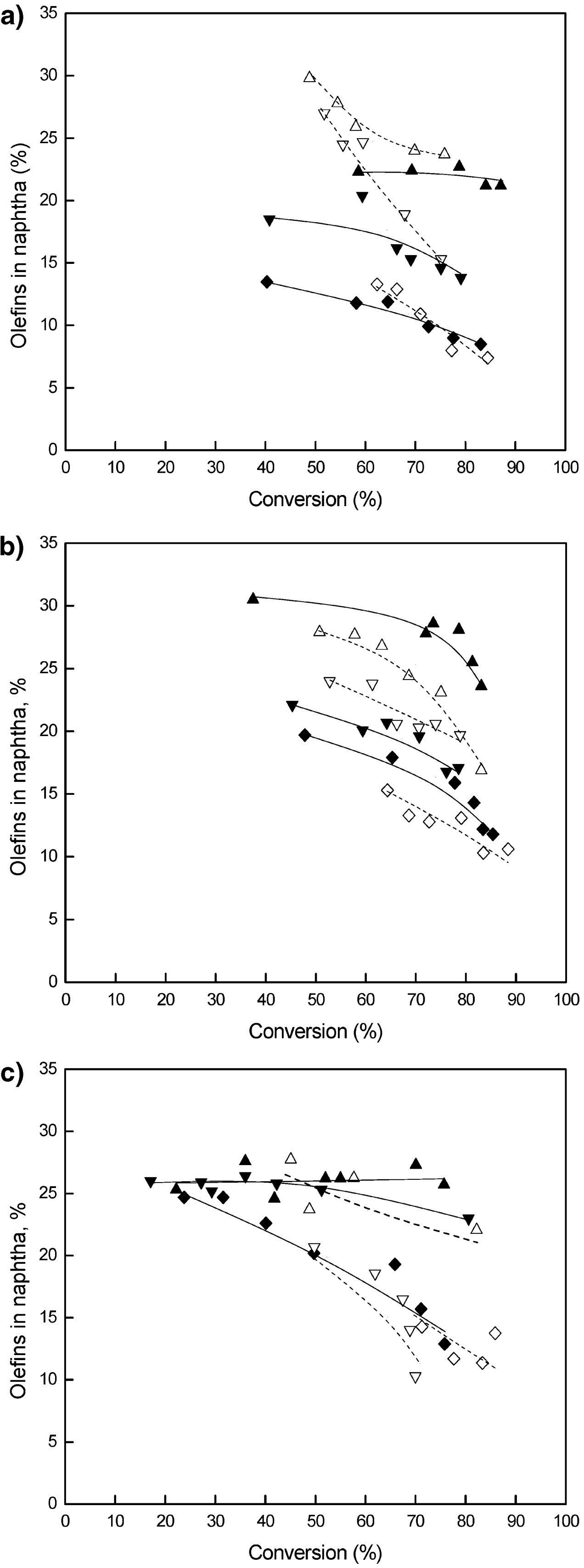

Figure 3. Olefins in naphtha as a function of conversion. CREC riser simulator (closed symbols, full lines) and MAT (open symbols, dashed lines). (a) VGO-M, temperature: 500 °C; (b) VGO-M, temperature: 550 °C; (c) VGO-B, temperature: 550 °C. Símbolos: E-Cat M (◆), E-Cat O (▲) y E-Cat P (▼).

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(26) Spretz, R.; Sedran, U. *Appl. Catal. A: General* **2001**, *215*, 199–209.

(27) Corma, A.; Melo, F. V.; Sauvanaud, L.; Ortega, F. J. *Appl. Catal. A: General* **2004**, *265*, 195–206.

(28) Falabella Sousa Aguiar, E. *FCC Rev.* **2001**, *26*, 3–11.

(29) Lemos, F.; Ramoa Ribeiro, F.; Kern, M.; Giannetto, G.; Guisnet, M. *Appl. Catal.* **1988**, *39*, 227–237.

(VGO-M, Figure 4.a y 4.b) and 32−45% (VGO-B, Figure 4c), approximately. These concentrations follow a similar behavior for all the catalysts, increasing slightly as a function of conversion. Usual commercial values vary from 20 to 33%.[30]

These proportions are significantly higher in the results from the MAT reactor. This could be the consequence of hydrogen transfer and oligomerization/cyclization reactions being favored at high conversion, that is, at short operation times in this unit, when there is a high concentration of active sites. Particularly when the feedstock was the aromatic VGO-B, the relative amount of aromatics was as high as 72% (E-Cat P, 550 °C). In general, two main sources may account for the initial formation of aromatics in the range of gasoline: cracking (dealkylation) and hydrogen transfer reactions. Dealkylation reactions would be prevailing if the feedstock is more aromatic and the catalyst very active; this could be exemplified with catalyst E-Cat P and VGO-B at short operation time (high conversion), as observed in Figure 4c. Ng et al.[31] reported concentrations close to 65% in the cracking of deasphalted VGOs from bitumen over a commercial equilibrium catalyst at 510 °C in a MAT reactor.

The higher reaction temperature has a mild impact on the content of aromatic compounds in naphtha, increasing it slightly. This characteristic can be observed in the results from both setups in Figure 4, panels a and b.

As expected, the more aromatic the feed, the more aromatic the naphtha (refer to Figure 4, panels b and c, for VGO-M and VGO-B, respectively, at 550 °C).[24] This characteristic was noticed in both reactors.

A catalyst rank in terms of concentration of aromatics in naphtha can be defined in the case of the CREC riser simulator reactor to be E-Cat M > E-Cat P > E-Cat O, that is coincident with the properties of hydrogen transfer of the catalysts. The rank is the same for the two feedstocks and temperatures.

It was not possible to define a catalyst rank for aromatics in naphtha in the case of the MAT reactor when using the paraffinic VGO-M feedstock, with catalysts showing approximately the same behavior besides their different properties (see Figure 4, panels a and b). Moreover, when using the aromatic VGO-B, the catalyst order (E-Cat P > E-Cat O > E-Cat M) was different from that of the fluidized bed reactor.

Octane Index. The RON values of the different naphthas obtained that are shown in Table 3 can be considered an indication of their quality as a fuel. Since the index did not change substantiantilly as a function of conversion for the ranges observed, average values are presented. Even though the values obtained in the laboratory look somewhat higher than those from actual refineries,[10,22] surely due to the different methods used (motor in refineries, chromatographic restrained to the C_5-C_{12} hydrocarbon cut in this work), it can be seen that the values from the CREC riser simulator and MAT reactors are similar for given catalyst, feedstock, and conditions. Slightly higher values in the MAT may be the consequence of the higher proportion of aromatics in naphthas obtained in that reactor. However, it must be noticed that these similar RON values do not correspond to similar product distributions in the cut but are the consequence of the actual composition of the naphthas, which are indeed different, as shown above.

The positive effect of increased reaction temperatures can also be observed in both sets of results; this is the result of increased cracking as a consequence of the higher activation

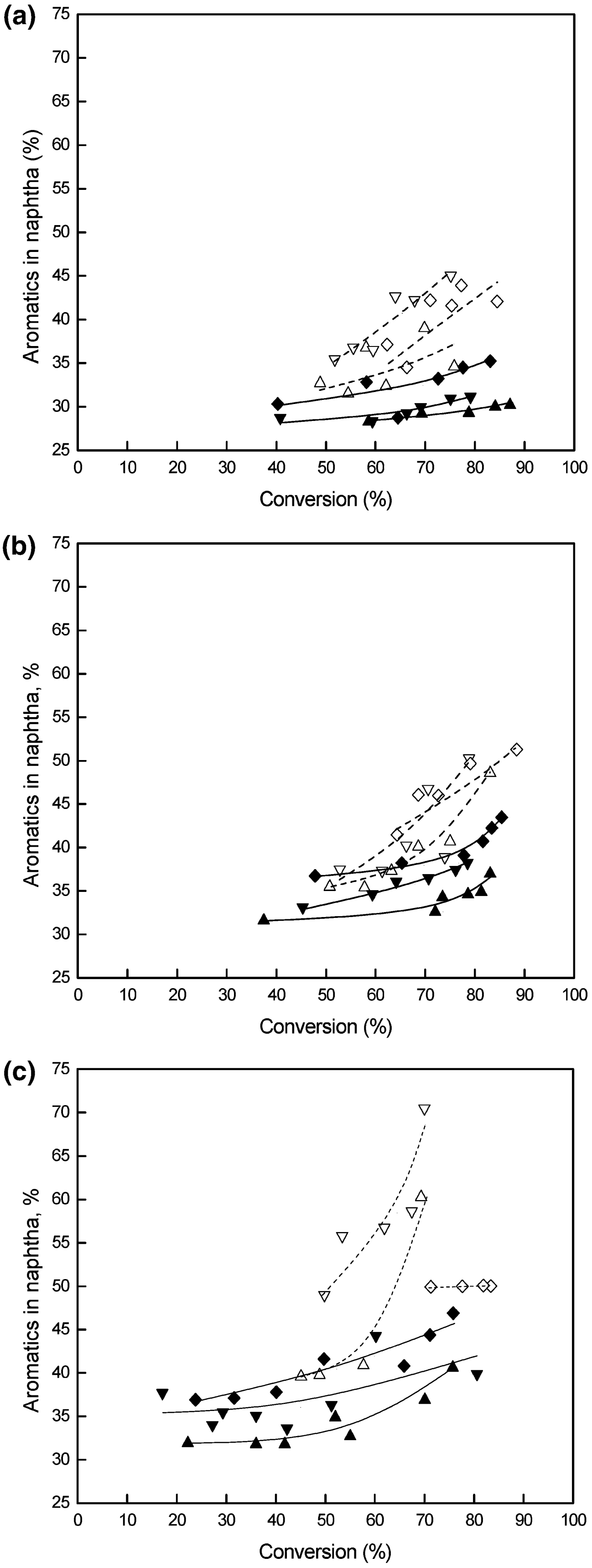

Figure 4. Aromatics in naphtha as a function of conversion. CREC riser simulator (closed symbols, full lines) and MAT (open symbols, dashed lines). (a) VGO-M, temperature: 500 °C; (b) VGO-M, temperature: 550 °C; (c) VGO-B, temperature: 550 °C. Símbolos: E-Cat M (◆), E-Cat O (▲) y E-Cat P (▼).

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(30) Schipper, P. H.; Sapre, A. V.; Le, Q. N. *NATO-ASI Ser. E:* **1992**, *225*, 147–182.

(31) Ng, S. H.; Wang, J.; Fairbridge, C.; Zhu, Y.; Yang, L.; Ding, F.; Yui, S. *Energy Fuels* **2004**, *18*, 172–187.

(32) Johnson, M. F. L. *J. Catal.* **1978**, *52*, 425–431.

Table 3. Average Research Octane Number (RON)

feedstock	VGO-B				VGO-M			
temperature (°C)	500		550		500		550	
reactor	RS[a]	MAT	RS	MAT	RS	MAT	RS	MAT
E-Cat M	94.7	95.0	97.1	96.6	93.3	93.8	96.3	96.0
E-Cat O	95.0		97.5	97.4	94.7	96.6	97.5	97.3
E-Cat P	94.0		96.5	98.2	93.3	94.7	95.9	96.3

[a] RS: CREC riser simulator.

energy of the reaction, as compared to hydrogen transfer, leading to a conservation of olefins that increase RON. This was noticed particularly in the results from the CREC riser simulator reactor (see section Olefins). It can be seen that the catalyst specifically formulated to produce gasoline with the highest octane numbers (E-Cat O) shows this attribute in all the cases in the CREC riser simulator reactor, thus assigning confidence to the operation of this unit.

In the results from the MAT reactor the reason for increased RONs at higher temperature seems to be the higher yield of aromatics (see Figure 4, panels a and b). With feedstock VGO-B, for example, the highest RON was observed in catalyst E-Cat P, due to the high yield of aromatics in naphtha.

The incidence of the feedstocks' characteristics can also be observed. Aromatic VGO-B showed higher RON values in both reactors, as expected, due to the higher proportions of aromatic compounds in the naphtha derived from it.

Conclusions

The results obtained in the conversion of two VGOs over three equilibrium FCC catalysts, using two different (flow fixed bed and batch fluidized bed) laboratory setups, and observed from the standpoint of naphtha composition, were clearly dissimilar. However, advantages can be observed with data from the CREC riser simulator reactor, mainly derived from the fact that naphtha yields showed a stable primary product behavior and that results were close to commercial values. In this way, naphtha selectivity did not depend on the conversion reached, and a catalyst rank can be stated more easily. On the contrary, naphtha yields in the well-known MAT reactor showed a maximum as a function of conversion.

The comparison of the product distributions observed in the naphthas from each unit at the same conversion level showed that they are very different; the composition of the naphthas obtained in the CREC riser simulator reactor was similar to those in commercial units, and more paraffinic and less aromatic than the one obtained with the MAT reactor. Ranks of catalysts based on the various hydrocarbon fractions observed in each setup also differed in most of the cases. In the fluidized bed reactor, these ranks reported results that were independent of the conversion level adopted for the analysis. The differences in the results could be the consequence of notoriously different contact between reactants and catalyst and operative modes in each reactor, that impact on the complex set of reactions of FCC. Also the high yield of coke at the beginning of the experiments in the fixed bed reactor could contribute to masking the results.

Together with evidence from previous works, for example, refs 7, 33, and 34, it was shown that the CREC riser simulator reactor is a proper tool for the evaluation of commercial FCC catalysts and feedstocks, and it is concluded that the evaluation of the catalytic performance of proposed equilibrium catalysts must be performed in an overall view, that is, including not only the catalyst and the feedstock but also the particular operative conditions.

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(33) Devard, A.; de la Puente, G.; Passamonti, F.; Sedran, U. *Appl. Catal. A: General*, **2008**, DOI: 10.1016/j.apcata.2008.10.036.

(34) Passamonti, F. J.; de la Puente, G.; Sedran, U. *Ind. Eng. Chem. Res.* **2007**, *46*, 9269–9273.