Comparison between MAT Flow Fixed Bed and Batch Fluidized Bed Reactors in the Evaluation of FCC Catalysts. 1. Conversion and Yields of the Main Hydrocarbon Groups

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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. A comparison of the product yield structure in each unit at the same conversion showed that they were very different due to the significant differences in the contact between reactants and catalyst and operative modes. Results were compared in terms of VGO conversion and the yields of the most important hydrocarbon groups LPG, gasoline, and coke. Some advantages were observed with data from the CREC Riser Simulator reactor, derived from the fact that yields are in general closer to commercial values, mainly concerning gasoline and coke. The yields of the main hydrocarbon groups also followed linear behaviors in this reactor, thus being easier to analyze, as selectivities did not depend on the conversion reached. On the contrary, yields showed a strong dependency on conversion in the MAT reactor, particularly in the case of gasoline and coke. The high coke yield in the first moments of the experiments in the MAT reactor could lead to modifications in the selectivities to certain reactions and products.

Introduction

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 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, operative modes, and commercial catalysts are changing continuously and opening new challenges and knowledge demands, even a discussion about the maturity and possible obsolescence of the process.[1] One of the most perceptible trends is the use of increasingly heavier residual feedstocks with more contaminant metals and higher Conradson carbon residue CCR fueled by the very high cost of oil. As a consequence of all these issues, a strong stimulation on the development of new commercial catalysts can be observed.[5]

Besides the standard requisite of finding the best choice among various options in the process of commercial catalyst selection, catalysts and process developments also call for a proper laboratory tool to help in an evaluation as close to reality as possible. The high complexity and extreme magnitude of the commercial process make it very difficult to be reproduced faithfully in the laboratory,[6] and most of the evaluation procedures and process developments have been performed on MicroActivity Test (MAT[7])-type fixed bed reactors. Obvious advantages are ease of construction and operation, but the setup configuration and characteristics, obviously differing from the commercial units, bring problems to closely mimic FCC; among others, very different contact between catalyst and reactants, long time of operation, development of activity profiles along the bed, collection of time-averaged reaction effluents, etc., all lead to complex result analysis.[8] Undoubtedly, MAT-type reactors have been the standard in FCC-related laboratories,[9] but in order to overcome some of the inconveniences mentioned, a large number of reactor configurations and operative approaches have been used.[10−12] Similar methodologies can be applied to flow reactors with a confined fluidized bed (FFB), which has become very familiar in FCC laboratories. Other devices, such as circulating pilot plants, certainly reproduce more

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Table 1. Properties of the Feedstocks Used

	VGO-B	VGO-M
density 20/4 °C (g cm^{-3})	0.9240	0.9162
°API	21.0	22.3
distillation (°C)		
10% vol.	399	361
30% vol.	441	408
50% vol.	470	432
70% vol.	498	456
90% vol.	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 oxides (% 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
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[42] with N_2 adsorption [c] BET method using N_2 adsorption.

closely the specific environment of FCC, but they are very expensive and consume large amounts of catalyst and reactants, and their operation is relatively complicated.[6]

An alternative view for FCC catalyst and feedstock evaluation, and for some issues in process development, can be built based on the CREC Riser Simulator laboratory reactor.[13] The unit was designed specifically to address FCC studies, has a bed fluidized in a chamber, and ideally mimics the riser reactor in commercial units, following the analogy between position in the riser and reaction or residence time in the laboratory unit. Even though the unit has been used in many FCC-related works, such as kinetics, diffusion, and adsorption modeling,[14,15] testing of new operative modes,[16−18] and assessment of particular product yields,[19] a direct comparison with the fixed bed reactors is necessary to validate it.

It is the objective of this manuscript to compare results obtained in the conversion of commercial vacuum gas oil feedstocks over equilibrium commercial FCC catalysts under similar experimental conditions in a MAT reactor and in a CREC Riser Simulator reactor in terms of conversions and various product yields.

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 are supplied by various catalyst producers (E-Cat M, E-Cat O, and E-Cat P), their properties being shown in Table 2.

The CREC Riser Simulator reactor[13] has a turbine on top of a chamber that holds the catalyst bed between porous metal plates. The turbine rotates at 7500 rpm, thus inducing a low-pressure area in the upper central zone in the reactor that makes gases recirculate in the upward direction through the chamber, thus fluidizing the catalyst bed. When the reactor is at the desired experimental conditions the reactant is fed with a syringe through an injection port and vaporizes instantly, thus setting the initial time. After the desired reaction time is reached, the gaseous mixture is evacuated immediately and products can be sent to analysis. Additional descriptive details can be found in, e.g., refs 20 and 21. Experiments were produced 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 were close to more than about 94% in all cases.

A continuous flow fixed bed reactor based on the one defined by ASTM D-3907/03 was used for the 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 collection of the gas sample that 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 in MAT reactors can be varied in different ways, e.g., changing the mass of catalyst at constant time on stream and oil flow rate[22] or changing the oil flow rate at constant time on stream and catalyst mass.[23] In this work the operation time (time on stream) was varied from 15 to 40 s, thus defining cumulative C/O relationships from 2.3 to 6.2. Mass balances were close to more than about 95% in experiments with time on stream being longer than 25 s.

Product analysis and coke assessment were performed in the same way in both sets of experiments. Reaction products were analyzed in a HP6890 Plus gas chromatograph with online sampling and injections in the CREC Riser Simulator and with off-line injections in the MAT reactor. A 30 m length, 0.25 mm i.d., and 0.25 μm phase HP-1 column was used with FID detection. 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 addition of the yields of dry gas (C_1-C_2), LPG (C_3-C_4), gasoline (C_5−216 °C), LCO (216−344 °C), and coke. Selectivities were assessed as the relationships between product yields and conversion.

Results and Discussion

It is not possible to compare directly some of the parameters in the operation of these two laboratory units, such as C/O relationships or reaction and operation times, because they have a different meaning as a result of the different contact between reactants and catalyst bed. However, it is the objective of this comparison to discuss similarities and differences in the performances of these setups for given feedstocks and equilibrium catalysts under similar conditions. Then, since it is well known that the simulation of the process of equilibration of fresh catalyst samples in the laboratory in order to obtain equilibrium catalysts is virtually impossible and imposes a factor of uncertainty,[6,24] equilibrium catalyst samples taken from refineries, instead of fresh catalyst samples deactivated in the laboratory, were used.

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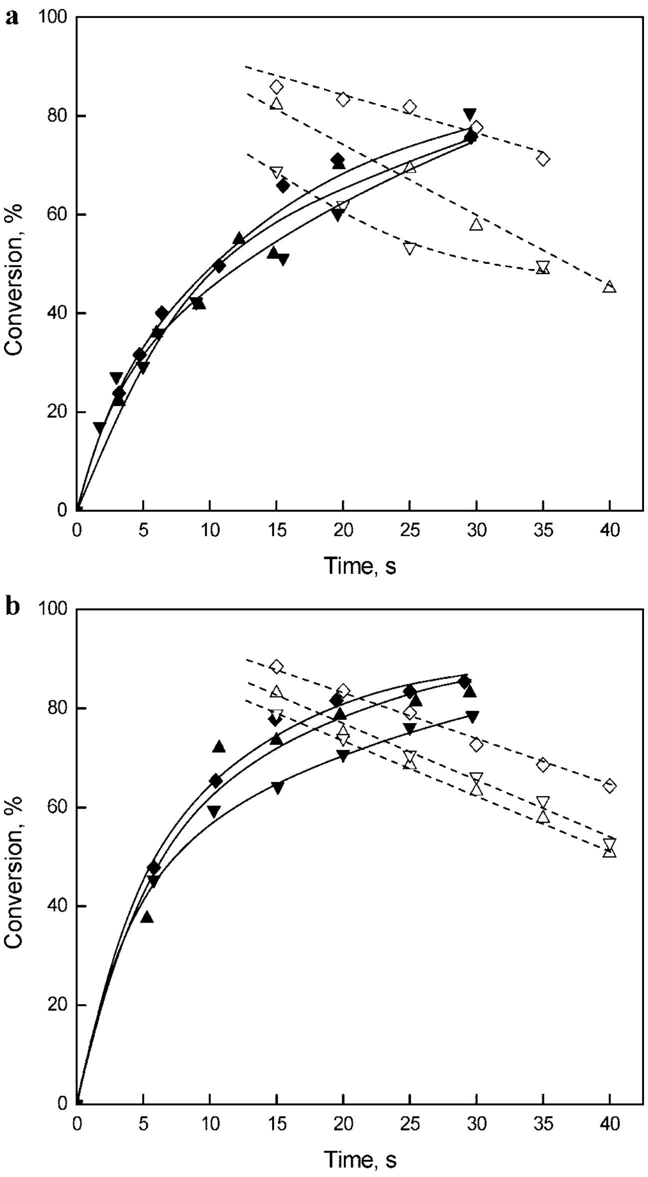

Figure 1. Conversion as a function of reaction time (CREC Riser Simulator reactor, closed symbols, full lines) and time on stream (MAT reactor, open symbols, dashed lines): (a) VGO-B and (b) VGO-M. Temperature: 550 °C. Symbols: E-Cat M (◆), E-Cat O (▲), E-Cat P (▼).

It is recognized for MAT reactors that it is difficult to attain good mass balances in the experiments with short time on stream or low oil flow rates,[25] and statistical analysis might need data reconciliation.[26] Inclusion of a second stripping stream after collecting the gas fraction in the operation of the MAT reactor helped to improve the mass balances in short time on stream experiments, that is, less than 25 s, that became usually over 90%.

Catalyst Activity. VGO conversion was considered an indication of catalyst activity. The conversions observed as a function of reaction time (CREC Riser Simulator) and time on stream (MAT) for the three catalysts and the two feedstocks at 550 °C are shown in Figure 1. In the case of the CREC Riser Simulator, which is a batch, closed reactor, conversion increased steadily as a function of reaction time with a decreasing rate.

The continuous flow MAT reactor, on the contrary, showed decreasing conversion profiles in all cases. It is obvious then that the rate of change of conversion in one case is opposed to the other. In the CREC Riser Simulator 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 whole reaction time while reactions take place, similar to an ideal commercial riser reactor, where a plug flow model could be assumed. The flow model is that of a stirred reactor, a fact verified by Pekediz et al.[27] In the MAT reactor, the fresh feed always contacts a fixed catalyst bed that is suffering deactivation from coke deposits and also develops activity profiles along it that change as a function of time; then conversion drops as time on stream increases.

Table 3. Conversion (%) at 500 °C and 20 s Reaction Time (CREC Riser Simulator reactor) or Operation Time (MAT reactor)

	VGO-B		VGO-M	
reactor	RS[a]	MAT	RS[a]	MAT
E-Cat M	63.0	79.1	72.6	80.2
E-Cat O	50.2	n.a.	70.1	69.8
E-Cat P	62.5	n.a.	69.1	67.9

[a] RS: CREC Riser Simulator.

It is to be expected that the catalyst activity levels are all in the commercial range of interest, as shown by the results at times close to 20−30 s in Figure 1, since the commercial catalysts used came from conversion units. Catalyst E-Cat M is the one showing the highest activity. In general, the ranking of catalyst activity for a given feedstock and reaction temperature is the same in both reactors (E-Cat M > E-Cat O > E-Cat P). Differences among catalysts are higher in the case of the MAT reactor, although such differences surely exceed those that could be observed in commercial units for the same catalysts and feedstocks. The activities observed for the various catalysts are very similar in the CREC Riser Simulator. As expected, conversions at 500 °C are somewhat lower than those at 550 °C (refer to Table 3), but the time evolutions in each setup are qualitatively similar.

However, the reactivity of the feedstocks, as revealed by the results in each reactor, is not the same (refer to Figure 1a and 1b). In effect, in general terms it is to be expected that for a given catalyst conversion of the paraffinic feedstock VGO-M is higher than that of the aromatic VGO-B,[28] as observed with the experiments in the CREC Riser Simulator. Conversely, the MAT reactor showed similar values of conversion for the two feedstocks on catalyst E-Cat O, but conversion for the aromatic feedstock VGO-B was somewhat higher on catalyst E-Cat M, besides its expectedly more refractory character and higher content of basic nitrogen (refer to Table 1), leading to lower conversions.[29] This unexpected behavior could be due to the fact that if VGO-B has long alkyl-substituting chains in the aromatic rings they could be subjected to a very intense dealkylation when the catalyst is fresh, which would translate into high conversions and, in certain way, mask the refractoriness of the feedstock.

Yields and Selectivities: Analysis of Hydrocarbon Groups. It can be seen in Figure 1 that the conversion profiles observed in the two setups for a given set of catalyst, feedstock, and temperature intersect. This point of identical conversions, which

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Table 4. Yields of Hydrocarbon Groups (%) Obtained at the Same Conversion in the CREC Riser Simulator and MAT Reactors

feedstock, reaction temp (°C)	catalyst	*t* (s)	conv. (%)	C/O		gasoline		LPG		coke	
				RS[a]	MAT	RS[a]	MAT	RS[a]	MAT	RS[a]	MAT
VGO-B, 500 °C	E-Cat M	31	72	6.1	3.0	41	36	14	8	6	16
VGO-B, 550 °C	E-Cat M	30	78	6.1	3.1	40	25	19	16	7	20
	E-Cat O	23	68	6.1	4.0	34	28	16	15	6	12
	E-Cat P	19	61	6.1	4.9	33	22	12	8	4	15
VGO-M, 500 °C	E-Cat M	24	68	6.1	3.9	39	35	14	11	6	10
	E-Cat O	19	69	6.1	4.9	37	33	14	15	5	6
	E-Cat P	19	69	6.1	4.9	41	35	12	10	3	8
VGO-M, 550 °C	E-Cat M	21	81	6.1	4.4	40	34	21	17	7	12
	E-Cat O	19	78	6.1	4.9	38	35	18	16	7	12
	E-Cat P	23	72	6.1	4.0	37	35	17	13	4	8

[a] RS: CREC Riser Simulator.

can be assessed by interpolation, however, shows a very different yield structure in each reactor. Table 4 shows the intersection points, where it can be seen that besides equal times (time on stream for the MAT reactor; reaction time for the CREC Riser Simulator reactor) and conversions, yields differ strongly, according to the reactor used. The differences are more significant in the case of gasoline and coke yields. These observations reaffirm the different meaning of time over each setup and preclude the possibility of single-point, equal conversion analysis.

LPG. The yield curves of LPG for all catalysts and feedstocks are shown in Figure 2. It can be seen that in the experiments with the CREC Riser Simulator LPG had a clear primary character as a stable product of VGO conversion; in all cases linear behavior could be observed with the only exception of catalyst E-Cat M at high conversions. This behavior is consistent with the essentially nil gasoline overcracking in this reactor that is described in the following section.

On the contrary, in experiments with the MAT reactor the LPG group showed a stable primary plus secondary behavior. This could be due to the gasoline cracking to lighter products at high conversion values, corresponding to high activity in the catalyst in experiments with short time on stream.[22]

In comparison to commercial LPG yields, those observed in the MAT reactor are lower. They also were lower than those in the CREC Riser Simulator reactor. For example, at 80% conversion yields in this work ranged from about 10% to 20% depending on the catalyst, feedstock, and reaction temperature used. At approximately the same conversion and temperatures other authors using MAT-type reactors reported yields of 12.1% at 510 °C[30] and from 15% to 20% at 500−520 °C.[31] The CREC Riser Simulator produced LPG yields that are closer to those in refineries at about the same conversion levels,[32] although commercial LPG yields strongly depend on the operation mode. For example, overall, it changes from 8% to 17% in the middle distillates mode (480 °C) to 18% to 26% in the gasoline mode (530 °C) to 37% in the light olefin mode (550 °C).[33] For both reactors, however, for given catalyst, feedstock, and conversion LPG yields increase at higher temperatures as a consequence of the overall increase in cracking reactions (results not shown).

If a catalyst ranking considering the LPG yields is desired, the analysis has to be performed carefully. Results in the CREC Riser Simulator reactor showed that for VGO-M at both reaction temperatures and for VGO-B at 550 °C (VGO-B was not used with all the catalyst at 500 °C) the LPG yields from each catalyst can be ordered E-Cat M > E-Cat O > E-Cat P. In contrast, the MAT reactor showed that the ranking at 550 °C was E-Cat O > E-Cat M > E-Cat P for the aromatic feedstock VGO-B. In the case of the paraffinic feedstock VGO-M, E-Cat O had a much larger yield than the other catalysts, which had similar yields. Then, the comparison of catalyst performances in terms of the LPG yields was strongly influenced by the reactor type used.

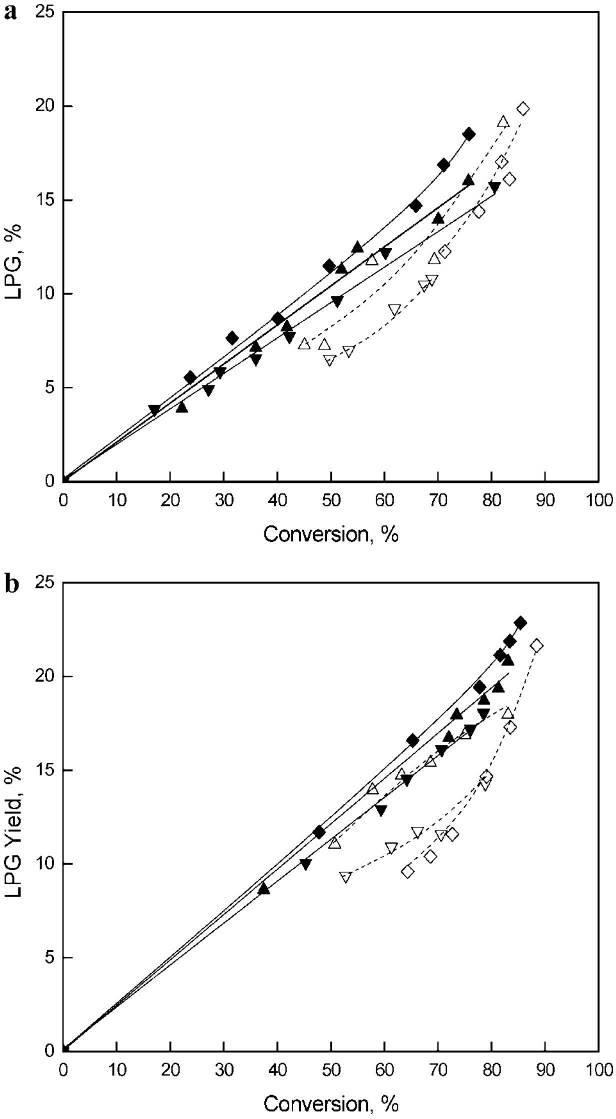

Figure 2. LPG yield as a function of conversion. CREC Riser Simulator reactor (closed symbols, full lines) and MAT reactor (open symbols, dashed lines): (a) VGO-B and (b) VGO-M. Temperature: 550 °C. Symbols: E-Cat M (◆), E-Cat O (▲), E-Cat P (98).

Gasoline. FCC naphtha is usually the most important hydrocarbon group in the process and the most important contributor to the gasoline pool. For a long time it has been, and many times is, an issue to maximize in FCC processing. Figure 3 for the experiments at 550 °C shows that evolution of the gasoline yield curves was different in each reactor. They were linear in the whole range of conversions in the experiments with the CREC Riser Simulator, typical of stable primary products. In the experiments in the MAT a maximum as a function of the conversion appeared or was insinuated. This is coincident with other observations in MAT reactors from, e.g.,

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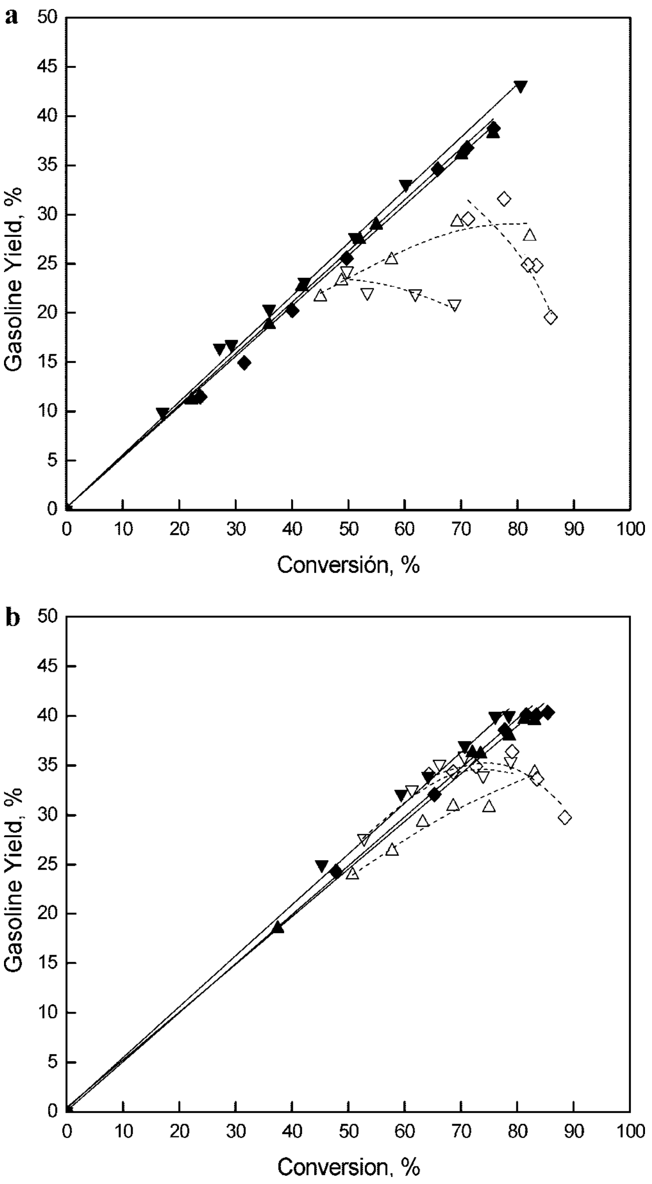

Figure 3. Gasoline yield as a function of conversion. CREC Riser Simulator reactor (closed symbols, full lines) and MAT reactor (open symbols, dashed lines): (a) VGO-B and (b) VGO-M. Temperature: 550 °C. Symbols: E-Cat M (◆), E-Cat O (▲), E-Cat P (▼).

Table 5. Yields of Gasoline at 70% Conversion: Feedstock VGO-M

	RS[a]		MAT	
reaction temperature (°C)	500	550	500	550
E-Cat M	39.5	34.5	36.0	35.0
E-Cat O	39.5	35.0	33.0	31.0
E-Cat P	41.5	36.0	35.0	33.5

[a] RS: CREC Riser Simulator.

Table 6. Average Research Octane Number (RON)

	VGO-B				VGO-M			
	500		550		500		550	
reactor	RS[a]	MAT	RS[a]	MAT	RS[a]	MAT	RS[a]	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	n.a.	97.5	97.4	94.7	96.6	97.5	97.3
E-Cat P	94.0	n.a.	96.5	98.2	93.3	94.7	95.9	96.3

[a] RS: CREC Riser Simulator.

ref 31 and 34. Biswas and Maxwell[35] associated this behavior (gasoline secondary cracking) to the setting of an overcracking regime. It is more perceptible with VGO-M (refer to Figure 3b) that the trends are similar in both reactors for conversions lower than 50%. At higher conversions the gasoline yields and selectivities observed in the MAT reactor are all lower than the ones corresponding to the CREC Riser Simulator, that in turn are similar to commercial values.[24,32,36,37]

The effect of reaction temperature on the yield of gasoline is important, and it is more manifest in the CREC Riser Simulator reactor than in the MAT reactor with both feedstocks and for all catalysts as shown in Table 5 for the example of VGO-M; this characteristic was essentially independent of conversion in the case of the MAT reactor. These lower gasoline yields at higher temperatures are consistent with well-known FCC facts.[33,38]

Even though the yields from each catalyst are very similar, it is possible to define directly a ranking based on the results obtained in the CREC Riser Simulator, showing that for both feedstocks and reaction temperatures E-cat P is the best gasoline producer. It is not possible to define such a ranking with results from the MAT reactor because gasoline yields and selectivities depend very much on the conversion level and consequently may complicate the evaluation procedure. From that point of view, then, results from the CREC Riser Simulator reactor are more suitable.

Gasoline Quality. Assessment of gasoline fuel quality is a very important issue in FCC catalyst evaluation that depends on a large number of parameters such as feedstock composition, operative conditions, and catalyst formulation.[28,38,39] An approximation on this point can be done based on the octane index of the naphtha obtained in each reactor system, calculated with a modified Anderson's approach.[40] The values from the CREC Riser Simulator and MAT reactors were similar (see Table 6), even though the compositions of the corresponding naphtha cuts were different. While the RON values from the MAT reactor are slightly higher in most of cases, both setups allow observing the positive impact of temperature on RON.

It was shown that the values obtained in the laboratory are somewhat higher than those from actual refineries,[33,38] but it must be considered that the methods used (motor in refineries, chromatographic in this work) are different.

Coke. Coke yields differ very much according to the reactor used. It can be seen in Figure 4 that the values assessed in the MAT experiments are coincident with previous reports.[25,31,34,41] These yields, that range from 13% to 20% in the case of VGO-B, and from 8% to 10% in the case of VGO-M, at 550 °C, and that are even more elevated in some cases, are significantly above those in the commercial operation. Again, this characteristic depends on the operation mode but fluctuates from about 3.5% in the middle distillates mode to about 5% in the gasoline mode.[32] The very high coke yield observed with feedstock

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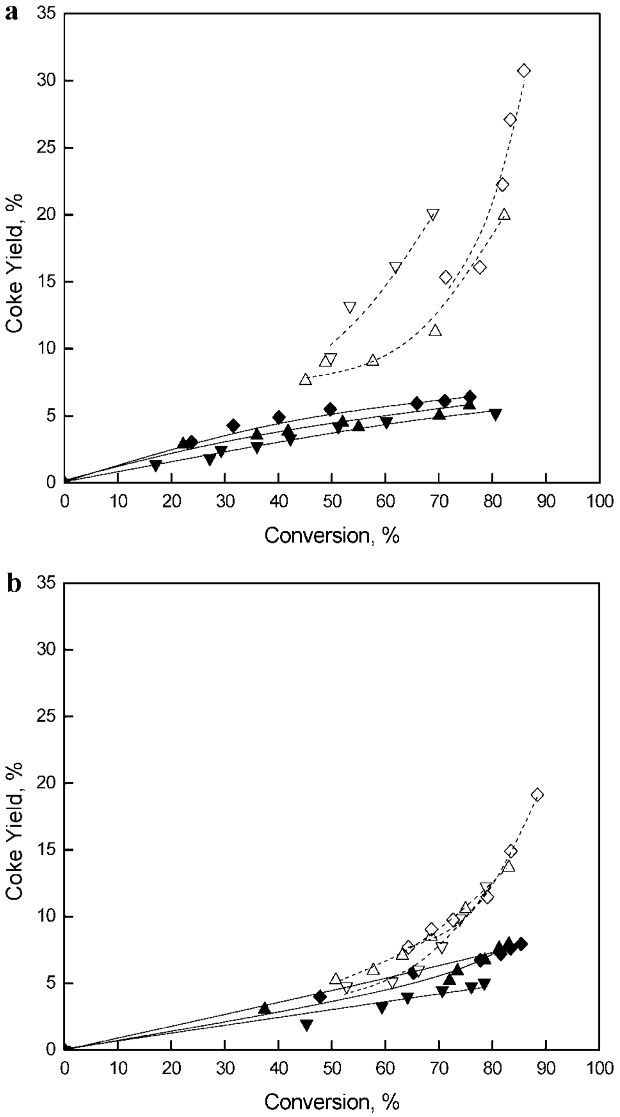

Figure 4. Coke yield as a function of conversion. CREC Riser Simulator reactor (closed symbols, full lines) and MAT reactor (open symbols, dashed lines): (a) VGO-B and (b) VGO-M. Temperature: 550 °C. Symbols: E-Cat M (◆), E-Cat O (▲), and E-Cat P (▼).

VGO-B (see Figure 4a) in the MAT reactor could be due to the possibility that it has long alkyl-substituting chains in the aromatic rings. These molecules could undergo very intense dealkylation when the catalyst is fresh and produce a high coke yield by aromatic ring condensation; this is consistent with the corresponding lower naphtha yields (refer to Figure 3a). It is clear that the coke yields in the CREC Riser Simulator reactor are much closer to commercial values.

The coke forming trend of the two feedstocks can be differentiated in the results obtained with both reactors; in effect, VGO-B (aromatic) yields more coke than VGO-M (paraffinic). However, the coke yield in each catalyst is different in each set up. For example, at 550 °C, using both feedstocks in the CREC Riser Simulator reactor, the catalyst ranking is E-Cat M > E-Cat O > E-Cat P; this ranking is the same in the MAT with VGO-M but changes to E-Cat *P* > E-Cat M ≈ E-Cat O with VGO-B. Different ranks of coke yields for various catalysts were also observed by Andersson and Myrstad[41] in the comparison of the conversion of residues in MAT and pilot-plant reactors.

Conclusions

Analysis of the results gathered in comparative experiments in a flow, fixed bed MAT reactor and a batch fluidized bed CREC Riser Simulator reactor showed that the last one is a proper tool for the laboratory evaluation of commercial FCC feedstocks and catalysts. The product yield structures of the main hydrocarbon groups in each unit at the same conversion were very different, and most of the differences observed between reactors can be justified based on the different reactants−catalyst contact and operative modes of the units. Some advantages were observed in the analysis of data obtained with the CREC Riser Simulator reactor, derived from the facts that yields are in general closer to commercial values, mainly concerning gasoline and coke; the yields also followed linear behaviors in this reactor, thus being easier to analyze, since selectivities did not depend on the conversion reached. On the contrary, yields showed a strong dependency on conversion in the MAT reactor, particularly in the case of gasoline and coke. The coke yield in the first moments of the experiments in the MAT reactor is so high that it could lead to modifications in the selectivities to certain reactions and products.

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