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Comparison between fixed fluidized bed (FFB) and batch fluidized bed reactors in the evaluation of FCC catalysts

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ABSTRACT

The laboratory reactors ACE fixed fluidized bed FFB and batch fluidized bed CREC Riser Simulator were compared in the conversion of two commercial vacuum gas oil feedstocks (paraffinic and aromatic types) over two equilibrium commercial FCC catalysts (octane-barrel and resid types) under similar conditions. Reaction temperatures were 510 and 540 °C and the catalyst to oil mass ratios were from 4 to 9 in the FFB unit, with time on stream varying from 112 to 50 s, and 6.35 in the CREC Riser Simulator, with reaction times ranging from 5 to 25 s. The results were contrasted in some cases to those of a DCR circulating pilot plant unit at 540 °C.

When the different product yields were considered, the same catalyst ranking was observed in both laboratory reactors on the whole, differences between catalysts and particularly between feedstocks being more perceptible in the FFB reactor. The CREC Riser Simulator reactor showed a linear yield curve for gasoline, which facilitated the analysis and comparisons; in this case, an overcracking regime was not shown, like in the case of the FFB reactor. The LCO yield curves were more defined and differences between catalysts developed more clearly in the FFB reactor. Coke yields were very high in the FFB reactor, typical of confined beds with continuous feed of the reactants, while in the CREC Riser Simulator reactor they were in the range of those observed in the pilot plant and commercial units.

The two laboratory reactors showed complementing potential in the laboratory evaluation of commercial catalysts and feedstocks for the FCC process.

1. Introduction

FCC is the major conversion process in many refineries, converting the VGO range (350–550 °C) portion of the crude oil, which represents about one third of the total refinery capacity, mostly to high value C3–C10 hydrocarbons which constitute the majority of the motor gasoline fuel produced and a variety of intermediate feedstocks for the petrochemical industry and for other high grade fuel production processes (e.g. isomerization, alkylation and MTBE synthesis) [1].

The need of continuous replacement of old by new catalysts particles, in order to maintain activity, provides an opportunity for substantial change in the FCC yield profile by the relatively simple change of the catalyst system, without having to wait for the end of the unit turnaround. This may be used by the refiner to adjust to changes in the fuel market or to changes in feedstock quality in a short time frame, thereby capturing differences in prices and improving the overall business profitability. Catalyst manufacturers have been introducing new technologies over the years and special emphasis is given to the fine tuning of the catalyst systems according to the characteristics of the particular FCC unit.

The strong impact of the catalyst on the global performance of the FCC unit and its profitability justifies the effort to guarantee the use of the best formulation available, and creates a demand for proper catalyst testing methodologies. Then, the procedure for the selection and evaluation of the FCC catalysts is critical [2]. Moreover, catalyst and process developments also call for a suitable laboratory tool to help in an evaluation as close to reality as possible. The high complexity and extreme magnitude of the commercial process severely complicate its faithful reproduction in the laboratory [3]. It is widely accepted that pilot circulating riser units reproduce more closely the specific environment of FCC commercial units [4], but they require both high investment and operating costs and their operation is quite complicated [5,6]. DCR Davison Circulating Riser units [7] are an example of these setups. Thus, laboratory tests are still the most commonly used methods to characterize the performance of FCC catalysts.

Most of the laboratory tests are performed on MicroActivity Test (MAT, ASTM D-3907/03)-type fixed bed reactors, for which neat

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advantages (e.g., ease of construction and operation) and disadvantages (e.g., operation mode and reactant–catalyst contact) are apparent. Undoubtedly, MAT-type reactors have been the standard in FCC-related laboratories [8], with a large number of different configurations and operative approaches being used [9–11]. A similar test methodology can be applied to flow reactors where a fluidized bed is confined (FFB [12]). In this case the bed nature is closer to that of commercial units, but the catalyst particles, which deactivate continuously by coke deposition, similarly to the case of MAT fixed bed reactors, see always a non changing, fresh feedstock. FFB reactors have become very familiar in FCC laboratories and tend to be the new standard setup [13].

The CREC Riser Simulator laboratory reactor [14] is the basis for the construction of an alternative approach for FCC catalyst and feedstock evaluation, as well as for some issues in process development. The reactor, with a fluidized bed of catalyst, ideally mimics the riser reactor in commercial units, following the analogy between position in the riser and reaction or contact time in the laboratory unit. It has been used extensively in FCC-related research, such as the modelling of kinetics, diffusion, and adsorption [15,16], the testing of new operative modes [17–19] and the assessment of particular product yields [20].

The performance of MAT units has been compared to that of pilot plant units, showing that for the same catalysts and feedstocks, many differences can be established in observed catalyst rankings and selectivities, depending on the catalyst type and deactivation procedures; most important differences were that, at constant conversion, a DCR pilot plant unit produced more olefins (both in gasoline and light gas) than the MAT unit, and that gasoline yields were lower and coke and LCO yields were higher in the MAT for active matrix catalysts [7]. Wallenstein et al. [21] demonstrated that by modifying the MAT technique it is possible to eliminate the ranking reversals identified in the comparison of catalyst selectivities observed in the ASTM-MAT and riser pilot units.

The comparison between the performances of a MAT reactor and the CREC Riser Simulator reactor in the evaluation of two commercial VGOs using three equilibrium catalysts showed that product yield structures were very different [22]. The yield curves of the main hydrocarbon groups as a function of conversion followed linear behaviors in the fluidized bed reactor, while a non-linear dependence on conversion was observed for the yields in the MAT reactor, particularly in the cases of gasoline and coke. Moreover, the consequences on product quality derived from the use of so different devices and contact modes were that, for example, the naphtha obtained in the CREC Riser Simulator reactor was more paraffinic and less aromatic than the one obtained with the MAT reactor; ranks of catalysts based on the various hydrocarbon fractions observed in the naphtha from each setup also differed in most of the cases [23].

It is the objective of this manuscript to compare the results obtained in the conversion of two commercial vacuum gas oil feedstocks over two equilibrium commercial FCC catalysts under similar conditions in laboratory FFB and CREC Riser Simulator reactors, in terms of conversions and various product yields. In order to validate overall results, the observations in the laboratory reactors were also compared to those from a DCR Davison circulating pilot plant unit.

2. Materials and methods

Two equilibrium commercial FCC catalysts were used, their properties being shown in Table 1. For use in the CREC Riser Simulator, catalyst particles were sieved and the fraction larger than 100 μm was used; however, all the properties in Table 1 were essentially the same for both fractions.

Table 1
Properties of the catalysts.

Property	Units	Catalyst	
X-ray fluorescence composition		E-cat R	E-cat L
SiO_2	%	50.8	60.7
Al_2O_3	%	43.4	34.9
RE_2O_3	%	2.43	0.63
P_2O_5	%	1.46	1.58
Na_2O	%	0.53	0.47
Fe_2O_3	%	0.66	0.81
TiO_2	%	0.32	0.30
SO_4	%	0.11	0.13
Ni	ppm	1204	3520
V	ppm	894	174
Cu	ppm	28	9
Sb	ppm	46	19
Physical properties			
Apparent bulk density	g/mL	0.88	0.81
Y zeolite crystallinity (XRD)	%	26	27
Unit cell size, Ao (XRD)	nm	2.426	2.425
Accessibility (AAI)[a]	a.u.	15.0	4.5
BET SA	m^2/g	178	153
Micropore SA (*t*-plot)	m^2/g	120	126
External SA (*t*-plot)	m^2/g	59	27
Particle size distribution			
<149 μm	%	93	90
<105 μm	%	70	61
<80 μm	%	45	32
<40 μm	%	3	1
<20 μm	%	0	0

[a] The AAI (Akzo Accessibility Index) was assessed following the method by Hakuli et al. [47].

The properties of the feedstocks used, which were two commercial vacuum gas oils with different characteristics, are shown in Table 2; VGO-L (paraffinic) has high API density and concentration of saturated compounds, while VGO-R (aromatic) has low API density and high concentration of aromatic compounds.

The laboratory reactors used were the CREC Riser Simulator [14] and an ACE (Model R+, supplied by M/s Kayser Technology Inc., USA) fixed fluidized bed unit (FFB) [24].

Table 2
Properties of the feedstocks.

Property	Feedstock	
	VGO-L Paraffinic	VGO-R Aromatic
Density 20/4 (g/cm^3)	0.8984	0.9328
API (°)	25.3	19.6
Distillation (°C)		
0 v%	223.1	317.4
10 v%	369.8	392.4
30 v%	431.3	439.6
50 v%	477.4	469.6
70 v%	537.3	502.4
90 v%	701.8	543.0
Final	750.0	597.0
Total sulfur (%)	0.215	0.534
Basic nitrogen (ppm)	578	1014
Aniline point (°C)	107.6	83.6
Ramsbottom carbon residue, RCR (%)	1.71	0.43
Saturates (%)	60.9	47.4
Monoaromatics (%)	14.2	18.3
Diaromatics (%)	16.0	21.0
Triaromatics (%)	5.7	8.6
Polyaromatics (%)	3.1	4.8
Viscosity (cStk)		
60 °C	37.7	73.9
82.2 °C	16.7	27.2
100 °C	2.0	14.8