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Laboratory evaluation of FCC commercial catalysts Analysis of products of industrial importance

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Abstract

The results of the conversion of a VGO over six equilibrium commercial FCC catalysts with different formulations in a batch CREC Riser Simulator laboratory reactor at 500 and 550 °C, catalyst to oil ratio 6.1 and reaction times from 3 to 30 s, were analyzed. It was possible to define the main catalyst characteristics in terms of various evaluation items, such as activity, gasoline yield and quality, LPG yield and coke yield, or the yields of particular compounds like, e.g., isobutane. Important differences in activity between catalysts were not observed, but catalyst properties reflected clearly as significant differences in gasoline, LPG or coke selectivities. Particularly, catalyst's hydrogen transfer properties impacted on gasoline composition and isobutane yield. The results showed that the CREC Riser Simulator reactor is an important tool for the evaluation of both commercial catalysts and feedstocks and process conditions.

Keywords: FCC; CREC Riser Simulator reactor; Catalyst evaluation

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1. Introduction

The process of catalytic cracking of hydrocarbons (FCC) plays a key role in the modern refineries, generating liquid fuels (gasoline, kerosene and middle distillates), and raw materials for important associated processes (synthesis of MTBE, alkylation, isomerization, etc.) that produce cleaner fuels [1]. FCC feedstocks are made up of low value hydrocarbons, with high molecular weight, and they are converted into lighter and more valuable products during the cracking process. Its protagonism is reinforced by the effect of more severe legislation about environmental care, better integration with the petrochemical industry and the increasing needs to convert residual feedstocks [2]. In this sense, FCC is the most efficient route [3].

Even though the process technology can be considered established [4], it undergoes continuous innovations in the technological devices. This characteristic is also observed in the constant developments in FCC catalysts technology [5]. Since the FCC has notable versatility and processes very important volumes, small improvements in the conversions, the quality of the products or the best usage of resources, they all induce strong benefits. As a consequence, catalysts result very specific, or ''custom made'', to the requirements of the refinery. Since the impact of the catalyst on the global performance of the unit justifies the continuous effort to guarantee the use of the best formulation available, the procedure for the selection and evaluation of the FCC catalysts is critical [5]. Thus, for a suitable optimization of the selection methodology, it is necessary to have means of reliable evaluation in the laboratory.

The commercial feedstocks are usually vacuum gas oils. The operation is cyclical, with catalyst particles having an average size of 70 μm and circulating between a fluidized bed transport riser reactor, where they are deactivated by coke formation in the very short contact time (<10 s) with reactive hydrocarbons, and a regenerator where the coke is burnt off, under very severe conditions, with temperatures over 700 °C and water steam. The regenerated catalyst returns to the reactor to face the feedstock again and therefore to reset the cycle [5]. As a consequence, it undergoes strong changes in its properties, from its fresh state to that known as ''equilibrated''. Given the

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process characteristics, it is very difficult to reproduce it faithfully in the laboratory [6], and most of catalysts evaluation procedures are based on the MicroActivity Test (MAT, ASTM D 3907) [7]. The test is based on a fixed bed reactor, subjected to a number of design and operation problems, that require a complex interpretation of results [8].

An alternative methodology of evaluation is based on the use of the CREC Riser Simulator reactor, specifically designed for FCC studies [9]. The advantages of the CREC Riser Simulator have been discussed widely [10]. The information generated in each experience provides not only a complete analysis of the yield of the main groups of products (dry gas, LPG, gasoline, LCO and coke), but also the individual product yields. Nevertheless, it is not a common practice in catalyst evaluation procedures to focus the analysis on, for example, a particular compound yield.

It is the aim of this work to perform an overall analysis of the yields and selectivities of hydrocarbons (either groups or individual) obtained in the conversion of a commercial feedstock over different FCC catalysts by using a CREC Riser Simulator reactor under conditions of the commercial operation.

2. Experimental

Six equilibrium commercial FCC catalysts provided by different refining companies, that were used under different operation modes (olefins, gasoline, resid conversion), were selected. The main catalysts' properties are shown in Table 1. In general, the catalyst properties define their use. For example, Ecat-R is a catalyst used in a refinery where resid is added to the feedstock. Its properties are similar to those of Ecat-P, although it is a catalyst oriented to gasoline maximization. Ecat-W is a conventional catalyst, with high unit cell size and high rare earth content, while Ecat-O is an octane catalyst with low unit cell size, without rare earths. Ecat-D is probably an octane-barrel catalyst. The feedstocks used were commercial vacuum gas oils: VGO for most of the experiments, and VGO-P for some comparisons. The feedstocks' properties are shown in Table 2.

Table 2
Properties of the feedstocks used

	VGO	VGO-P
Distillation (°C)		
10%	384	389
50%	456	449
90%	528	510
Density (g/cm^3)	0.908	0.927
Sulfur (%)	0.69	1.57
Aniline point (°C)	81.4	80.5
Conradson carbon (%)	0.28	0.16

The conversion experiments were performed in a batch fluidized bed laboratory unit with internal recirculation, the CREC Riser Simulator reactor, whose operation has been described previously [10]. The experimental conditions were: reaction temperature of 500 and 550 °C, catalyst-to-oil ratio (CatOil) 6.2 and reaction times between 3 and 30 s. Reaction products were analyzed by standard capillary gas chromatography. Mass balance calculations showed agreements over 94% in all the cases. The conversion in each experiment was calculated as (100 − unreacted VGO). The gaseous and liquid products (with <20 carbon atoms per molecule) were quantified by means of an internal standard. Coke yields were assessed by means of a method including the temperature programmed oxidation of the carbonaceous deposits on the catalysts sample and further methanation of the carbon oxides evolved. The selectivities were calculated as the relationships between the yield of a certain product (or group of products) and the conversion.

The research octane number (RON) of the gasoline cut defined between the boiling points of 3-methyl-1-butene and *n*-dodecane, was assessed by means of a modified Anderson's method [11].

3. Results and discussion

The conversion of the VGO as a function of the reaction time, on all the catalysts, is shown in Fig. 1. For the sake of clarity, as an example, only the data corresponding to one reaction temperature (550 °C) were included. As expected, since the CREC Riser Simulator reactor is batch, the conversion increases steadily as a function of contact time. When the temperature of reaction was 500 °C the results were qualitatively similar, but with lower conversion values. It is observed in Fig. 1 that the catalysts present activities in a not

Table 1
Properties of the catalysts used

Catalyst	UCS[a] (nm)	BET[b] Sg (m^2/g)	Zeolite load[c] (wt.%)	V (ppm)	Ni (ppm)	REO[d] (wt.%)	MAT conversion (%)
Ecat-D	2.423	139	16.9	2675	3995	1.26	66
Ecat-M	2.426	158	18.0	1900	600	1.19	–
Ecat-O	2.424	151	15.9	n.a.	n.a.	0.00	–
Ecat-P	2.429	137	14.0	1550	675	3.05	68
Ecat-R	2.427	125	14.8	5845	5066	2.94	63
Ecat-W	2.431	124	14.3	3290	1032	3.50	–

[a] Unit cell size, ASTM D-3942-85.

[b] BET method, N_2 adsorption.

[c] Johnson's method [12] with N_2 adsorption.

[d] REO: rare earth oxides.

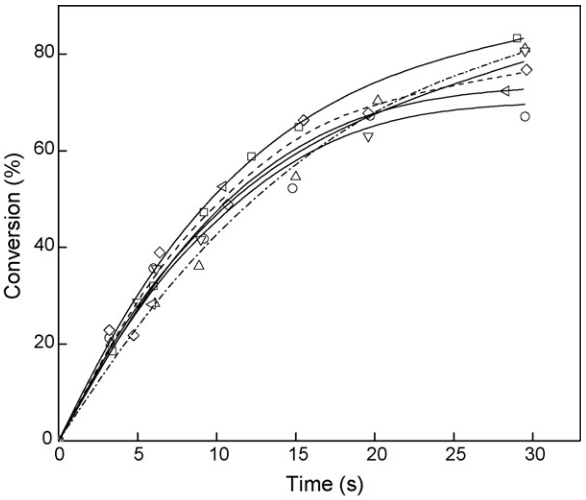

Fig. 1. VGO conversion as a function of reaction time over catalysts (□) Ecat-D, (○) Ecat-O, (△) Ecat-W, (+) Ecat-R, (▽) Ecat-P and (◇) Ecat-M. Temperature: 550 °C.

too wide range, in spite of their different properties. Since all the catalysts used are commercial, it is expected that their activities will be within a range of commercial interest, with differences that can be attributed to the different formulations. This particularity is also confirmed with the MAT evaluation data available, presented in Table 1.

For the various catalysts evaluated the gasoline yields present clear differences. In a refinery, due to the large volumes processed, even small positive variations in the gasoline yield might represent great benefits. Results corresponding to the experiments performed at 550 °C are shown in Table 3. Gasoline showed to be a primary product in all the cases. The values of gasoline selectivity can be considered typical (between 50 and 60%), and differences can be observed of up to seven percentage points in selectivity between catalysts at typical conversion of 70%. As expected, the catalysts that present the higher selectivities are those oriented to maximize gasoline, like Ecat-M, Ecat-P and Ecat-R. On the contrary, Ecat-D is clearly the one with lower gasoline yield. At 500 °C the same tendencies were observed but the gasoline yields are significantly higher, due to the conservation of this hydrocarbon group when the catalytic activity is lower.

It is also observed in Table 3 that, according to the RON values, the reaction temperature is an important parameter for the resulting gasoline quality. Hydrogen transfer reactions, that play a very important role in the process, can be represented in a descriptive approach consuming olefins and naphthenes to generate aromatic plus paraffins [13]. The fuel quality increases with the reaction temperature due to the more important impact of the temperature on the cracking reactions as opposed to those of hydrogen transfer. Usually, both cracking and hydrogen transfer reactions are not considered in particular but in general views, and in this way, it is possible to show that the energy of activation of hydrogen transfer is lower than that of cracking [14]. Then, at the highest reaction temperature hydrogen transfer is attenuated, olefins are preserved and, following a global balance on the gasoline composition, an increase in the RON values is observed. In general, the ranking of the gasoline RON for the various catalysts is the same at both temperatures.

Table 3
Average gasoline selectivities and octane numbers in the VGO conversion

Catalyst	Gasoline selectivity (%)		RON	
	550 °C	500 °C	550 °C	500 °C
Ecat-D	49.5	55.8	97.4	94.5
Ecat-M	53.3	59.0	97.0	94.7
Ecat-O	52.2	58.3	97.5	94.9
Ecat-P	56.7	62.2	96.3	93.8
Ecat-R	55.6	59.1	97.0	94.8
Ecat-W	52.0	57.0	96.5	94.2

Larger differences in the performances of the catalysts are observed if they are compared, for example, concerning the LPG and coke yields. It is always interesting to know the behavior of LPG yields, since there are some compounds in the cut that are of particular interest as petrochemical raw materials. For example, propylene, with very high and increasing demand; isobutylene, that is a raw material for the MTBE synthesis; or isobutane, that is a raw material for alkylation. In addition, in some countries with modest natural gas, the LPG constitutes an important gas fuel. It is observed in Fig. 2 that LPG is clearly a primary product of the VGO conversion. The values of LPG selectivities are from approximately 19 (Ecat-R) to 23% (Ecat-D or Ecat-M), thus defining significant differences if a selection is to be performed with that specific objective.

Among the components of the LPG fraction, isobutane (one of the products of particular interest) is considered as an index of the extension of catalytic cracking reactions occurring on acid sites [15]. Its production can be explained by means of the conventional β-scission cracking mechanism [16], where most stable tertiary carbocations formed on the catalytic surface desorb as branched products. Particularly in initiation steps, pentacoordinated carbonium ions that are also formed on the surface participate in cracking reactions, but linear, smaller

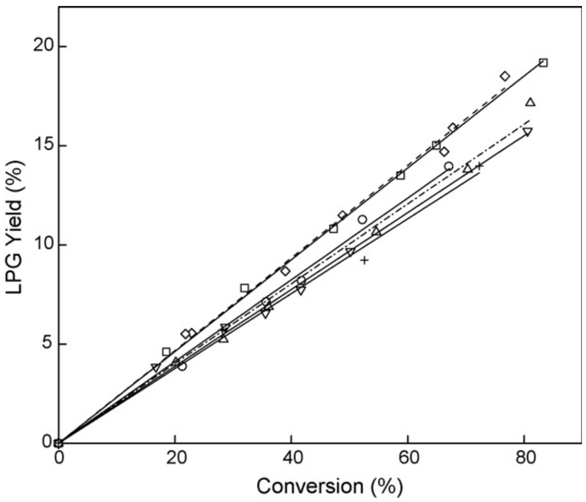

Fig. 2. LPG yields as a function of the VGO conversion. Temperature: 550 °C. Symbols as in Fig. 1.

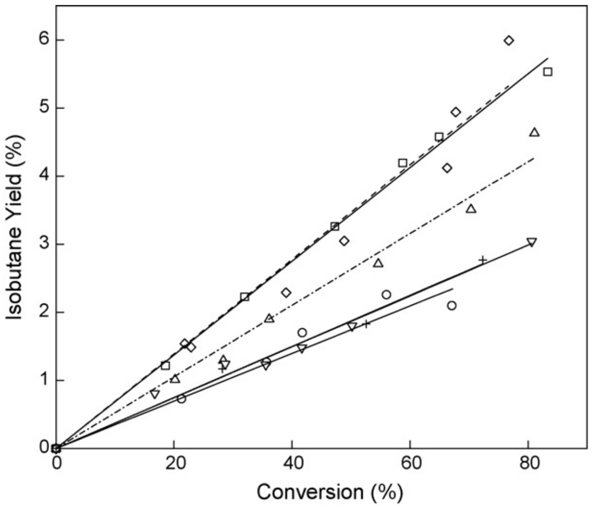

Fig. 3. Isobutane yields as a function of the VGO conversion. Temperature: 550 °C. Symbols as in Fig. 1.

molecules are favored [17]. Nevertheless, it can be noticed that although significant differences in the catalyst activities are not observed, there exist important differences in the isobutane yields, as it is shown in Fig. 3. Isobutane yields and selectivities can be ranked according to Ecat-D ≈ Ecat-M > Ecat-W > Ecat-R ≈ Ecat-P ≈ Ecat-O. This order is not the same as the one observed in activities.

According to this, the isobutane yields would depend not only on the level of conversion and the reaction temperature, but also on the catalyst properties. In this sense, it must be considered that the main source of isobutane is the hydrogen transfer to isobutylene or to adsorbed isobutyl carbocations [18]. Thus, the ranking of isobutane yields or selectivities observed could be linked to the hydrogen transfer properties of the catalysts. Based on the properties of each of them, Ecat-O, with low unit cell size and without rare earth oxides, is the one that presents the lowest hydrogen transfer ability and consequently the lowest selectivity to isobutane (refer to Fig. 3). The existence of rare earth oxides at intermediate loads (1.2–1.3%) in the cases of Ecat-D and Ecat-M could justify their higher selectivities, given the more intense hydrogen transfer activity originated by the hydrolysis of rare earth cations, in turn leading to new acid sites. On the other hand, in the remaining catalysts Ecat-P, Ecat-R and Ecat-W, the high load of rare earth oxides (about 3%) would negatively affect this quality [19], due to the generation of OH bridges between rare earth cations that decrease the amount of acid sites. In this group, the catalyst with larger unit cell size and therefore higher selectivity to isobutane, Ecat-W, stands out.

The comparative analysis of the performances of the different catalysts used with the same feedstock also allows to discuss more specific points like, for example, the olefinicity of the gasoline cut. This is an important issue in reference to the stability of the product, given the gum-forming trend of olefins (in particular, the conjugated diolefins [20]), to the attainment of the normative restrictions about gasoline composition, or to the gasoline fuel quality (octane numbers). Given the higher selectivity to gasoline, the proposed analysis is more sensitive at 500 °C, although the same observations are applicable to the information generated at 550 °C.

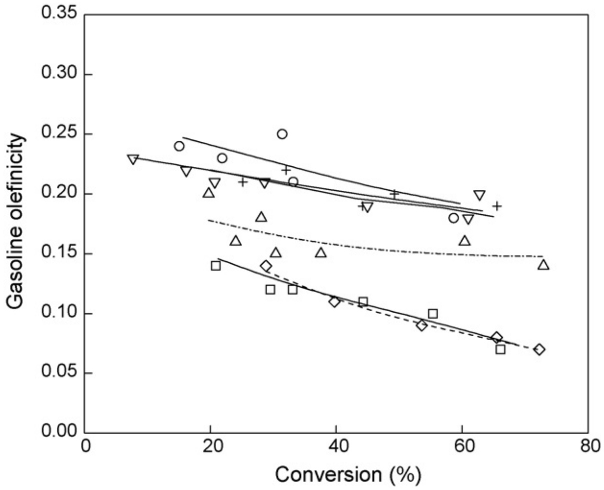

Fig. 4. Gasoline olefinicity obtained in the VGO conversion. Temperature: 500 °C. Symbols as in Fig. 1.

The olefinicity (the ratio of olefins yield to gasoline yield) of the gasoline cut produced by the various catalysts is shown in Fig. 4. Most important differences between the catalysts can be justified based on their hydrogen transfer properties, since these reactions, in a descriptive approach, can be represented consuming olefins and naphthenes and producing aromatic plus paraffins [13]. According to the previous description in respect to isobutane yields, Ecat-D and Ecat-M catalysts have higher ability to transfer hydrogen and produce consequently gasoline with lower olefinicity, as opposed to that produced, for example, by Ecat-O, that presents lower hydrogen transfer capacity.

The formation of coke has particular interest, since it controls the heat balance of the catalytic cracking unit: the heat generated during its combustion in the regenerator is used to sustain the endothermic cracking reactions. This point is critical in processing resid feedstocks, since excessively high coke yields can generate operative problems. The values of coke yields are presented in Table 4. Important differences between the yields can be observed; for example, Ecat-P is a catalyst with low coke selectivity, while others, such as Ecat-D or Ecat-W show significantly higher coke yields, that make them not appropriate for use in the conversion of feedstocks with high intrinsic tendency to coke formation.

Table 4
Coke yields in the VGO conversion

Catalyst	Coke yield (conv = 80%)
Ecat-D	10.5
Ecat-M	7.6
Ecat-O	7.3
Ecat-P	5.1
Ecat-R	7.4
Ecat-W	10.6

Temperature 550 °C.

Table 5
Comparison of group yields between laboratory results and commercial data

	Refinery	This work
Temperature (°C)	535	550
Conversion (%)[a]	69.3	70.5
Gas (%)	4.0	4.9
LPG (%)	16.6	15.7
Gasoline (%)	43.5	44.8
Coke (%)	5.2	5.1

Ecat-P catalyst.
[a] Conversion calculated as: 100 − VGO − LCO.

In order to establish an overall comparison between laboratory results and commercial data for a given catalyst, the same feedstock VGO-P used with Ecat-P in a refinery was used in the laboratory, results being shown in Table 5. It can be seen that, for the conditions used, the yields of the most important groups are very close, thus confirming that it is feasible to perform the evaluation of equilibrated commercial catalysts in the laboratory under conditions similar to those of the refinery, by using the CREC Riser Simulator reactor.

4. Conclusions

The overall analysis of the main groups yields, or individual hydrocarbons of particular interest in the conversion of standard FCC feedstocks, allowed to evaluate different equilibrated commercial catalysts comparatively.

The LPG, gasoline and coke yields and the gasoline quality (RON) were clearly differentiated according to the different formulations of the catalysts. The experimental detail of product distributions allowed to evaluate the yields and selectivities shown by the various catalysts to a particular product, like for example, isobutane, that are of interest in some units. In respect to the gasoline formed, the analysis of composition allowed to evaluate, for example, its tendency to gums formation, by considering gasoline olefinicity as an index.

The comparison between laboratory results and refinery data with a given catalyst showed very close performances, and confirmed that the experimental methodology proposed, based on the CREC Riser Simulator reactor, allows to predict the performance trends of a particular catalyst in a commercial unit.

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