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Laboratory evaluation of the impact of the addition of resid in FCC

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ABSTRACT

The conversion and product distributions from a mixture of 10% atmospheric tower bottom resid and a DO hydrocarbon cut similar to LCO that represented commercial feedstocks were assessed over two equilibrium commercial FCC catalysts in a laboratory CREC Riser Simulator reactor. The reaction temperature was 550 °C, the catalyst to oil ratio was 5.8 and the reaction times were up to 25 s. The conversion of the mixture as compared to the DO base feed was higher in the case of the most active, conventional catalyst, and remained very similar on the resid catalyst. Since the yields of the main hydrocarbon groups dry gas, LPG, gasoline and coke followed very similar trends when the two pure feedstocks were converted, the corresponding yields from the mixture also obeyed that behaviour, and were the consequence of the conversion reached. The impact of the different catalyst formulations was observed in, for example, the selectively different yields obtained from the conversion of the resid, and in the composition of the gasoline. Independently of the catalyst, the gasoline was more olefinic and less aromatic when the resid was present. It was shown that in order to evaluate properly a given combination of feeds, catalysts and conditions, they must be considered together.

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1. Introduction

Some current trends lead to important changes and new demands in the refinery process of catalytic cracking of hydrocarbons (FCC) [1]. Among them, the increasing restrictions about fuels composition (particularly the content of sulfur in fuels), the need to decrease the environmental impact of petroleum use and processing, and the own economy of refining have played a significant role. Also, the increasing interaction with petrochemistry is a clear tendency in refining that involves FCC [1].

The present extremely high and increasing cost of crude oil, as well as the worldwide sustained decrease in the consumption of fuel oil, cause a higher utilization of residual hydrocarbon cuts in refining and particularly in FCC units [2]. Although this addition of resids to conventional FCC feedstocks (vacuum gas oils, VGO), is a rather standard operative strategy founded on the

process' versatility and efficiency to transform low value hydrocarbons into useful products with high value, it is manifest that the use of resids is increasing steadily. An extreme option is the FCC technology able to operate with residual feedstocks only, using specific resid catalysts [3,4].

Residual cuts usually boil above 530 °C and, in comparison to VGOs, have more polynuclear aromatic hydrocarbons, sulfur and nitrogen species, and higher content of catalyst contaminant metals such as Ni, V, Na and Fe [2,5]. All these issues are not desirable because of their contribution to higher coke yields, to the emissions of SO_x and NO_x, and to the presence of sulfur among products. Moreover, the chemical structure of the components of a resid is extremely complex [6]. The higher coking potential of resids is shown in the large CCR Conradson Carbon index of these cuts, which is above 2.

The operation of FCC with some fraction of resid included in the feedstock calls for a close evaluation of catalysts and

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reactants and stimulates demands of fundamental knowledge, such as the specific reactivity of the residual cut in use. Usually higher temperatures are necessary to achieve convenient conversions, and the catalysts must have higher thermal and hydrothermal resistance and contaminant metals tolerance, as well as minimum coke yield and a good relationship between catalytic and thermal bottoms conversion. Good accessibility is also a requirement to minimize intraparticle mass transfer limitations [1]. All these conditions, together with the particular operative approaches used, lead to custom-made catalysts as the most profitable choice. Moreover, for a given refinery, it is usual to change the source of resid and its proportion into VGO, thus stressing the evaluation and selection processes, that become more complex [7]. Even though VGOs and resids differ considerably, it is not a regular practice to evaluate the conversion of resids on purpose, and there are few laboratory techniques published for the evaluation of residual feedstocks [8,9].

de la Puente et al. [10] developed a laboratory method that allowed assessing resid's conversion and product distribution on equilibrium FCC catalysts. In the method, that was based on the careful assessment of the masses of the reaction products, the resid is dissolved into toluene and methyl naphthalene at 15 and 25%, respectively, and converted at 550 °C, while the pure solvents are also converted under the same conditions to provide background information. However, it is necessary from the operative point of view to define the behavior of mixtures made up of actual hydrocarbon cuts and resids. It is the objective of this work to evaluate comparatively the performances of two different commercial equilibrium FCC catalysts, of the resid and conventional types, in the conversion of an atmospheric tower resid from a naphthenic crude mixed into a hydrocarbon cut close to a FCC light cycle oil (LCO) that can represent more complex hydrocarbon mixtures. Experimental conditions close to those in the refinery were used in a CREC Riser Simulator reactor [11].

2. Experimental

Two commercial FCC catalysts equilibrated in refineries were used; they were of the conventional type, identified as E-cat D, and of the resid type, identified as E-cat R. The catalysts' properties are shown in Table 1. The AAI index was assessed following the method by Hakuli et al [12]. The residual

Table 1 – Catalyst properties

Catalyst	UCS ^a (nm)	Specific surface area ^b (m ² /g)	Zeolite content ^c (wt.%)	REO ^d (wt.%)	AAI ^e
E-CatR	2.427	125	14.8	2.94	8.3
E-CatD	2.423	139	16.9	1.26	5.5

^a Unit cell size, ASTM D-3942-85.

^b BET method, N₂ adsorption.

^c [20]. N₂ adsorption.

^d Rare earth oxides.

^e Akzo Accessibility Index [12].

Table 2 – Properties of the feedstocks

		DO	Resid
Density (g/cm ³)		0.900	0.954
°API		25.5	16.2
Sulfur(%)		n.a.	1.4
CCR(%)		n.a.	8.11
Total nitrogen(ppm)		n.a.	1650
Iron(ppm)		n.a.	28
Nickel(ppm)		n.a.	13
Vanadium(ppm)		n.a.	30
Distillation (°C)			
Initial	162.8	Initial	294.8
10%	198.5	10%	411.7
30%	222.9	20%	448.8
50%	254.1	30%	473.1
70%	294.9	40%	500.2
90%	341.7	Final	513.9
Final	365.1	Yield(%)	45.6

feedstock was the bottom stream from an atmospheric distillation tower (ATR), obtained from a naphthenic crude. The base hydrocarbon cut, similar to a FCC light cycle oil was named Diesel Oil (DO). Both feeds were obtained from refineries in Argentina, and their characteristics are shown in Table 2. Runs were performed with the DO cut alone in order to gather background information, and mixed with 10 wt.% of resid, for each catalyst and every experimental condition. Some experiments were performed with the resid alone, using catalyst E-cat R, and the results were analyzed following the approach by de la Puente et al. [10].

The experiments were performed in a batch fluidized bed laboratory unit with internal recirculation, the CREC Riser Simulator reactor [11], that was specifically designed for FCC studies; additional descriptive details of this reactor can be found in, e.g., [13,14]. The reaction temperature was 550 °C, the reaction times ranged from 5 to 25 s and the overall catalyst to oil ratio was 5.8, achieved with a catalyst mass of 0.8 g. Mass balances in the experiments closed to approximately 95%.

Reaction products were analyzed on-line by conventional capillary gas chromatography and classified as the main hydrocarbon groups dry gas (C1-C2), LPG (C3-C4), gasoline (C5-216 °C), LCO (216–344 °C) and bottoms (compounds boiling over 344 °C). Coke was assessed by means of a temperature programmed oxidation method, in which carbonaceous materials are burnt off and later the carbon oxides formed are converted to methane and quantified by a FID detector. Conversion was defined as the sum of the yields of dry gas, LPG, gasoline and coke. Selectivities were calculated as the relationship between the corresponding yields and conversion.

3. Results and discussion

A hydrocarbon cut from a commercial FCC unit (DO) was selected to represent complex hydrocarbon mixtures to mimic resid-FCC feedstock mixtures. The DO was considered representative of commercial feedstocks, given that it is a very complex mixture of hydrocarbons, but its lower reactivity as

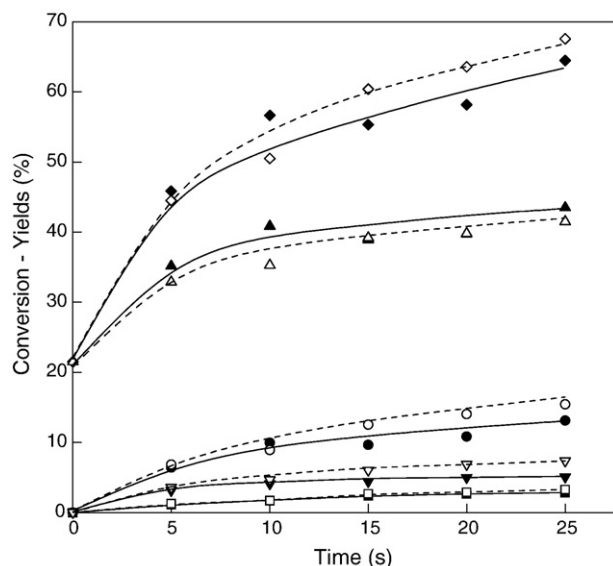


Fig. 1 – Conversion of DO and yields of the main hydrocarbon groups. Temperature: 550 °C. Symbols: catalyst E-cat D, open symbols, dotted lines; catalyst E-cat R, closed symbols, full lines; conversion (♦); dry gases (■); LPG (●); gasoline (▲); coke (▼).

compared to VGOs would allow discriminating the effects of the addition of resid on conversion and product selectivities. The DO was used pure to generate background information, and mixed with 10% of the bottom stream of an atmospheric distillation tower (resid). The amount of resid in the mixture was considered demonstrative of tests in refineries that are aimed at the reduction of the magnitude of residual streams, and that should not alter significantly the FCC operation. The DO showed the properties typical of these cuts, with boiling points between approximately 190 and 360 °C, and a high proportion of aromatic compounds.

The conversion of the pure DO and the yields corresponding to the main hydrocarbon groups obtained over the two catalysts are shown in Fig. 1. It can be seen that conversions, which expectedly increased as a function of reaction time in this closed system, were in a similar range over both catalysts, catalyst E-cat D being more active. These conversion levels are

Table 3 – Yields of the main hydrocarbon groups from the conversion of DO, the resid and their mixture

Catalyst	E-cat D			E-cat R		
	DO	Resid-DO	Resid ^a	DO	Resid-DO	Resid
Conversion (%)	60.2	63.9	85.2	56.7	55.5	83.4
LPG yield (%)	14.7	13.0	23.3	11.1	10.6	21.3
Gasoline yield (%)	39.7	40.9	45.4	41.5	38.0	47.7
Coke yield (%)	5.9	6.7	13.3	4.5	4.5	10.7
Gasoline selectivity (%)	65.9	64.0	53.3	73.2	68.5	57.2
Coke selectivity (%)	9.8	10.5	15.6	7.9	8.1	12.8

Temperature 550 °C. Reaction time: 15 s.

^a From Ref. [10].

lower than those obtained with usual FCC feedstocks (VGO) due to the aromatic character of the cut, which make it refractory. It is to be noted that initial conversions are not zero but include the content of gasoline in DO (about 21%, refer to Table 2). The higher activity of catalyst E-cat D can be observed in the higher coke and LPG yields; however, gasoline yields are somewhat higher with catalysts E-cat R.

Moderate changes in the yields are observed when the mixture 10% resid-DO is cracked over the two catalysts (refer to Table 3). However, each catalyst showed a distinctive behavior in terms of conversion of the mixture, because catalyst E-cat D increased it in approximately four to six percentage points while catalyst E-cat R did not change it significantly. The increase in conversion with catalyst E-cat D

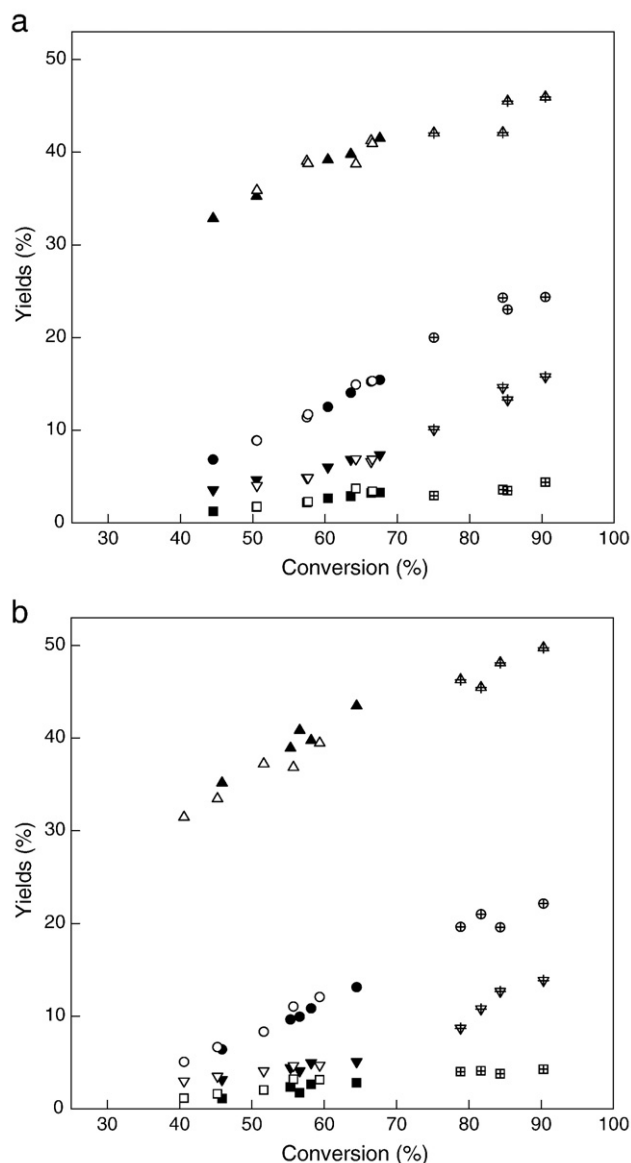


Fig. 2 – Conversion of DO, resid-DO mixture and resid. Yields as a function of conversion. Temperature: 550 °C. a) Catalyst E-cat D; b) Catalyst E-cat R. Symbols: closed (DO), open (resid-DO), + center (resid); dry gases (■); LPG (●); gasoline (▲); coke (▼).

could be due to the contribution of a higher reactivity of at least a fraction of the resid as compared to DO; some molecules in the resid, with high molecular weight, could have long aliphatic chains in the aromatic rings, that would behave in catalytic cracking in a way similar to a paraffinic, lighter feedstock [15,16]. On the contrary, the activity of the catalyst E-cat R would not be enough to exhibit this behavior with the mixture.

The slight effect of the presence of the resid in the feedstock on product yields can be observed more clearly in the comparison of the yield curves for the two feedstocks, and their mixture, on a given catalyst. The results for each catalyst are shown in Fig. 2, where it can be seen that the yield curves of the most important hydrocarbon groups as produced by the resid, the DO and their mixture follow a very similar trend as a function of conversion. Indeed, with this particular set of feeds, the yields seem to depend only on the conversion achieved. However, some differences in the yields can be observed between catalysts, based mainly in their differences in the conversion of the resid, as shown in Table 3. The method developed by de la Puente et al. [10] to determine the specific product slate from a resid when it is converted by a commercial equilibrium FCC catalyst showed that, in effect, under the same conditions, catalyst E-cat R yields more gasoline than catalyst E-cat D, that translate moderately into the conversion of the resid-DO mixture (refer to Fig. 2a and b and selectivities in Table 3). The resid catalyst E-cat R, then, would be convenient if the selectivity to gasoline is to be maximized in the refinery when this particular residual cut is to be processed added to a conventional feedstock.

As expected, the resid has a higher coking potential, and the more elevated coke yield expected when adding the resid to the base feedstock was noticed over both catalysts (refer to

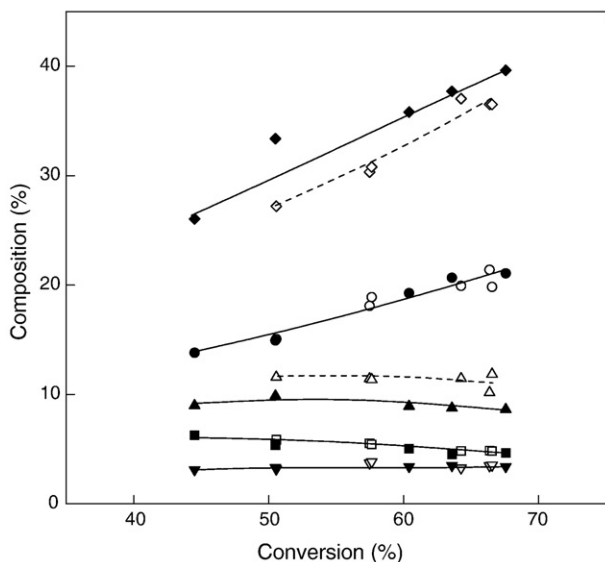


Fig. 3 – Gasoline composition as a function of conversion for DO (closed symbols, full lines) and resid-DO mixture (open symbols, dotted lines) feedstocks. Temperature: 550 °C. Symbols: aromatics (◆); i-paraffins (●); olefins (▲); n-paraffins (■); naphthenics (▼). Catalyst: E-cat D.

Table 4 – Overall and LPG isobutane selectivity and C4 group olefinicity in the conversion of DO, the resid and their mixture

Catalyst	E-cat D			E-cat R		
	DO	Resid-DO	Resid ^a	DO	Resid-DO	Resid
iC4 Selectivity (%)	6.6	7.0	7.6	4.5	4.7	6.2
iC4/LPG	0.32	0.31	0.28	0.26	0.25	0.24
C4=/C4total	0.31	0.31	0.42	0.43	0.43	0.47

Temperature 550 °C. Reaction time: 15 s.
^a From Ref. [10].

Table 3). However, the better coke selectivity of the resid catalyst E-cat R can be observed clearly.

Since the composition of the gasoline cut depends not only on process conditions and catalyst properties but also on feedstock structure, it is different if the DO alone or its mixture with the resid is converted. The changes observed are shown in Fig. 3 for the example of catalyst E-cat D. Main differences are observed in the content of olefins, that is higher, and to a lower extent in the content of C6–C9 aromatics, that is lower, when the resid is present in the feedstock. This reveals that, even though the proportion of resid in the mixture is small, it is possible to monitor the consequences that its addition to the feedstock has on gasoline; expectedly, the higher the proportion of resid, the more intense the changes. C10–C12 aromatics were not included in the figure because they are already present in high proportion in the DO cut.

The impact of the addition of the resid on the yield of particular hydrocarbons in FCC that are raw materials for downstream processes like, for example, isobutane for alkylation, or C3–C5 olefins for the same process, or for MTBE or TAME ethers synthesis, can be analyzed. As an example, yield, global selectivity to isobutane and some relationships observed for both catalysts with the DO, the resid and their mixture are shown in Table 4. In the case of isobutane, it is known that its yield and selectivity strongly depend on the activity and hydrogen transfer capacity of the catalyst and the characteristics of the feedstock [17]. Moreover, hydrogen transfer controls the relationship between isobutane and isobutene, since one of the main sources of isobutane in this catalytic system is the hydride transfer to adsorbed isobutyl carbocations that can be formed from isobutene [18]. Differences in the selectivities for each catalyst are remarkable and reflect their characteristics, both in the case of DO and the resid, that translate into the conversion of the mixture; resid catalyst E-cat R, that is less active in cracking conventional feedstocks and has lower hydrogen transfer ability than E-cat D due to the high content of rare earths in its formulation [19], shows in all the cases lower selectivity to isobutane and higher selectivity to olefins as compared to catalyst E-cat D.

4. Conclusions

The evaluation of the impact of the addition of residual cuts to FCC feedstocks was accomplished by using a hydrocarbon cut

with boiling range close to LCO, to represent complex hydrocarbon mixtures, to which 10% of an ATR resid was added. Two equilibrium commercial catalysts of different type were used under conditions close to commercial ones. The conversion of the mixture as compared to the base feed was different on each catalyst, since it increased in the case of the most active catalyst but did not change significantly in the case of the resid catalyst.

Results were consistent with background information about the hydrocarbon yields from the resid and the DO separately. In effect, for this particular combination of catalysts, reactants and conditions, the yields of the main hydrocarbon groups are very similar independently from the feedstock, thus reflecting in an addition-type response for the resid-DO mixture. The properties of the catalysts, and their corresponding different responses, were exposed in the analysis of some important yields, and in the composition of the gasoline fraction, that showed higher olefinicity when the resid is present in the reacting medium.

It was confirmed that the CREC Riser Simulator is a proper tool to evaluate conversions, group and particular hydrocarbon yields obtained under conditions similar to those of the commercial FCC process, even with heavy feedstocks. However, these results showed that this type of analysis should be performed considering simultaneously the complete set of elements (catalyst, operative conditions, base feedstock and resid).

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