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## Reactivity of the saturated, aromatic and resin fractions of ATR resids under FCC conditions



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#### HIGHLIGHTS

- SARA fractions from a naphthenic crude were converted on FCC catalysts.
- SARA fractions produce hydrocarbons in the same range as VGO feedstocks.
- Yields of the hydrocarbon groups from the various fractions reveal their nature.
- Yields from a resid are not the direct addition of the yields from the SARA fractions.
- CREC Riser Simulator reactor confirmed as a proper tool for FCC related studies.

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#### 1. Introduction

The bottom fractions of crude oils and other heavy hydrocarbon cuts in refineries are generically named resids; they are very complex mixtures of heavy molecular weight hydrocarbons which can be separated into two main groups, designated malthenes and asphaltenes plus carbenes. Asphaltenes are black or brownish polar compounds formed by macromolecules with multiple condensed aromatic rings with relatively high contents of hetero-atoms and contaminant metals. Maltenes in turn are brown

#### G R A P H I C A L A B S T R A C T



#### ABSTRACT

SARA (saturate, aromatic, resin and asphaltene) fractions composing an atmospheric tower resid from a naphthenic crude were separated using the ASTM 2007 method. Two commercial equilibrium catalysts, of the conventional and resid types, were used to convert the aromatic, resin and saturate fractions under conditions of the FCC process. The reaction experiments were performed in a CREC Riser Simulator reactor. Reaction temperature was 550 °C, reaction times were from 5 to 20 s, the catalyst mass was 0.8 g and the catalyst to oil relationship was 5.0. The various fractions were used dissolved in toluene at 20 wt.%. The hydrocarbon reaction products were grouped into dry gas, LPG, compounds in the gasoline and LCO boiling ranges and coke. All the fractions converted almost completely, but differences in the yields of the main hydrocarbon groups were observed which revealed the fractions' nature.

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or light brown compounds which are soluble in n-heptane, composed by three structurally different fractions such as saturates, aromatics and resins [1,2]. Resids have higher contents of contaminant metals, polynuclear aromatics, heteroatoms and complex macromolecular groups than standard hydrocarbon feedstocks [3] but their use in refineries has been increasing neatly in the last decade [4].

Among the various options to process residual feedstocks, hydrocracking, catalytic cracking (FCC), coking and deasphalting are proper choices that show relative advantages and disadvantages, defining FCC as one of the most efficient ones [5]. FCC plays a central role in refining, being the major conversion process in many refineries, where it converts the VGO fraction in crude oil



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(350–550 °C) into high value C3–C10 hydrocarbons which constitute the majority of the motor gasoline fuel produced and also a diversity of feedstocks for the petrochemical industry and for other fuel production processes such as isomerization, alkylation and ether synthesis [6]. At present, FCC technologies exist that can process even "pure" resids; in those cases the technology is conceptually equivalent to that in standard processes, differences being imposed by the singular characteristics of the residual feedstocks, such as metal content or CCR (Conradson Carbon Resid), which are, usually, atmospheric or vacuum towers [7].

The above mentioned characteristics define severe problems in processing resids in catalytic processes such as FCC, a fact which has not slowed down its utilization. Then, given this increasing use and consequent impact on refinery operation and profits, both fundamental and practical knowledge is demanded by refiners and process technologists. Among them, it is important to know the specific contributions from the various fractions composing resids, which would be expectedly different, in order to predict the impact of adding a given resid to VGO.

The method that is the most used to separate heavy hydrocarbon cuts into their constituting fractions is the SARA (saturate, aromatic, resin and asphaltene) method, which is based on the different solubilities of the fractions in various solvents [7–9]. Starting from Jewel et al. [10], other studies ended with the ASTM D 2007-93 method [11], which includes adsorption on a chromatographic clay/silica gel column. The method separates four fractions, that is, saturated, which are nonpolar compounds comprising linear, branched and cyclic hydrocarbons; aromatic, which comprise more polarizable compounds, containing one or more aromatic rings; resins, which are associated with the stabilization of the asphaltenes in the resid (the resin molecules are adsorbed on the surface of colloidal particles and act as asphaltene dispersant [8,12]), and asphaltenes. The asphaltene designation is a widely used term referring to a solubility class rather than a chemical class; it refers to a fraction precipitated by the addition of excess liquid paraffinic hydrocarbons, such as n-heptane or n-pentane [12].

It is to be noted that, so far, the conversion of the various fractions in resids were studied by means of thermal processes [13–15] and no publication exists about the catalytic cracking conversion of those separate fractions. It is the objective of this work to separate an atmospheric resid into its composing SARA fractions in order to study their corresponding intrinsic reactivities and product distributions on equilibrium, conventional and resid FCC catalysts. In this way, this article complements previous research on the effect of the addition of residues to standard FCC feedstocks, which was accomplished following an approach of increasing complexity, starting from the reactivity of the residue [16] to its mixtures with LCO [17] and VGO [18] The experiments were performed under typical conditions of the commercial process in a laboratory CREC Riser Simulator reactor [19], which mimics the commercial FCC units.

#### 2. Experimental section

The source resid was an atmospheric tower bottom stream (ATR) from a naphthenic crude, its main properties being shown in Table 1.

The ATR resid was fractionated by means of the ASTM D 2007-93 methods [11]. Asphaltenes were separated first by precipitation with n-pentane and the remaining mixture was fractionated chromatographically in a two column train with specific solvents. The first (top) column had an attapulgite clay bed which adsorbs polar or resin compounds (FR fraction) and the second one is filled with

Table	1
Table	

Property	Units		Value
Density	g/cm <sup>3</sup>		0.954
°API			16.2
Sulfur	%		1.4
CCR	%		8.11
Total nitrogen	ppm		1650
Iron	ppm		28
Nickel	ppm		13
Vanadium	ppm		30
Distillation	°C		
		Initial	294.8
		10%	411.7
		20%	448.8
		30%	473.1
		40%	500.2
		Final	513.9
Yield	%		45.6

silica gel which separates aromatics (which remain adsorbed, FA fraction) from saturated (FS fraction) compounds. The columns are rinsed with n-pentane and the effluents are passed through the columns again. Finally the columns are disconnected, the FA aromatic fraction being removed from the silica gel phase with toluene and the FR resin fraction from the attapulgite clay phase with a 50:50 volume mixture of acetone and toluene which is collected in a flask containing anhydrous CaCl<sub>2</sub> to remove the aqueous components.

The reactivity of the individual SARA fractions was studied over two commercial equilibrium catalysts, of the conventional (E-Cat D) and resid (E-Cat R) types, their properties being shown in Table 2. Catalyst acidity was assessed by means by pyridine temperature programmed desorption (TPD).

The reaction experiments were performed in a CREC Riser Simulator reactor, which is a batch, fluidized bed laboratory reactor which closely mimics the commercial FCC process conditions [19]. The unit has been described comprehensively elsewhere [21]. Reaction temperature was 550 °C, reaction times were from 5 to 20 s and the catalyst to oil relationship was 5.0, achieved with a catalyst mass of 0.8 g. In order to study the corresponding reactivities, the various fractions were dissolved in toluene at 20 wt.%, following a technique which allowed an easier handling of these viscous fractions. Identical experiments were performed with pure toluene (TOL), so as to generate comparative background information and discern the particular contributions to the product distribution exerted by the solvent and the corresponding fraction reactants [16]. This experimental approach was developed to facilitate the handling of very viscous or solid reactants in laboratory reactors, and has been successfully used to study, e.g., the conversion of recycled plastics [22] or residual hydrocarbon feedstocks [16] over FCC catalysts. Benzene or toluene are proper solvents which hardly convert on equilibrium FCC catalysts under process conditions and whose products can be mostly distinguished from those of the reactants themselves. The asphaltene fraction was not studied due to its extremely difficult separation and handling in the laboratory.

Reaction products were analyzed by on-line conventional capillary gas chromatography and coke yields were assessed by means of thermal programmed oxidation followed by conversion of the carbon oxides into methane and quantification with a FID detector. In the overall analysis, the hydrocarbon reaction products were grouped into dry gas (C1–C2), LPG (C3–C4), compounds in the gasoline (C5-216 °C) and LCO (216–344 °C) boiling ranges and coke. Conversion was defined as the addition of the yields of the various groups, including coke.

Table 2			
Properties	of the	catalysts	used.

- . . .

Catalyst	TCU <sup>a</sup> (nm)	Surface area <sup>b</sup> (m <sup>2</sup> /g)	Zeolite content <sup>c</sup> (wt.%)	REO <sup>d</sup> (wt.%)	AAI <sup>e</sup>	Acidity <sup>f</sup> (mmol/g)	Ni (wt.%)	V (wt.%)
E-Cat D	2.423	139	16.9	1.26	5.5	0.101	0.4	0.27
E-Cat R	2.427	125	14.8	2.94	8.3	0.042	0.51	0.58

<sup>a</sup> Unit cell size, ASTM D-3942-85.

<sup>b</sup> BET method,  $N_2$  adsorption.

<sup>c</sup> Johnson' method [20], N<sub>2</sub> adsorption. <sup>d</sup> Para Farth ovides

<sup>d</sup> Rare Earth oxides.

Albermale Accesibility Index.

<sup>f</sup> Pyridine TPD.

#### 3. Results and discussion

#### 3.1. Separation of fractions

Table 3 shows the yields of the various fractions after separation from the source resid. It can be seen that the FS saturated fraction is the most important one, in consistency with the characteristics of the source crude, which was of the naphthenic type. This fraction is composed by nonpolar compounds which include cyclic and normal and branched linear saturated hydrocarbons. The FA aromatic fraction includes hydrocarbons which are mainly compounds with benzenic rings, or naphthenic-aromatic. The FR resin fraction includes very polar compounds which are strongly adhesive, solid or semisolid with molecular weights in the 500-50,000 range and H/C relationships about 1.3-1.4. The FR resin fraction is associated to the stabilization of the asphaltene fraction, since its molecules can adsorb on the surface of asphaltene colloidal particles, thus acting as steric dispersant agents [2]. Different structures were proposed in relation to hydrocarbons in the resin fraction: poliaromatic compounds with a large number of aromatic rings, with substituting alkyl chains and heteroatoms, and groups of aromatic rings linked by alkyl chains [23].

# 3.2. Conversion of the fractions and yields of the main hydrocarbon groups

VGOs, which are the usual feedstocks in FCC, are very complex hydrocarbon mixtures covering a wide range of boiling points. Thus, conversion is usually defined in a more arbitrary way; particularly, for these experiments, reactants are considered to boil over 344 °C, which is the boiling point of the n-C20 paraffin, and products to boil at less than 344 °C. Coke is also a product.

The background experiments with pure toluene (TOL) showed that it converted to a certain extent at 550 °C, as shown in Table 4 for the example of 5 s reaction time on catalyst E-Cat D. The main products in the conversion of TOL were benzene and xylenes from the disproportionation reaction and very small amounts of hydro-carbons with six or less carbon atoms per molecule, aromatics with nine carbon atoms per molecule, and traces of naphthalene and methylnaphthalene. Concerning coke production, TOL showed a maximum yield of 1.79 wt.% at 20 s reaction time. Experiments performed without catalyst showed that the thermal cracking of toluene is negligible under these experimental conditions.

Table 3Yields (wt.%) of the various fractions in the ATR.

Fraction	Yield
FS	43.8
FR	31.3
FA	16.6
Asphaltenes	8.3

#### Table 4

Conversion (wt.%) and product yields (wt.%) over catalyst E-Cat D from pure toluene at 550 °C and 5 s reaction time [17].

Conversion	9.50
C6-	0.20
Benzene	3.00
Toluene	90.50
C8 Aromatics	4.60
C9 Aromatics	0.30
Coke	1.30

In order to analyze with more details the mass balances in the experiments and the yields of the various hydrocarbon groups from the conversion of the resid fractions, the corresponding masses of hydrocarbons can be calculated by subtracting from the total mass of a given group in the experiments with the solution of a fraction in TOL, the mass formed by the solvent alone, which is known from the yield curves in the experiments with pure TOL under the same conditions. Then, the hydrocarbon yields from the resid fractions, including coke, can be determined with the following Eq. (1) and (2), which imply the assessment of careful mass balances

$$y_i (\text{wt.\%}) = \frac{m_{i,Fraction}}{m_{Fraction}} \times 100$$
 (1)

$$m_{i,Fraction} = m_i - m_{i,TOL}$$
 (2)

 $m_{i,Fraction}$  is the mass of the group *i* produced by the conversion of a given resid fraction,  $m_i$  is the mass of the group produced by the TOL-Fraction solution and  $m_{i,TOL}$  is the mass produced by toluene, as known from experiments with the pure solvent and considering the 0.8 dilution factor.  $m_{Fraction}$  is the mass of resid fraction fed to the reactor and  $y_i$  is the yield of the group *i*.

In order to solve the mass balances, it is assumed that the resid fraction and the toluene solvent perform as reacting systems which do not interact to each other and that the actual differences in the yields in the experiments performed with the solution or the solvent alone (e.g., due to changes in true toluene partial pressure) are not significant. Moreover, the conversion of a given resid fraction into hydrocarbons can be calculated from the various yields according to

$$\begin{aligned} x (\text{wt.\%}) &= y_{\text{C1}-\text{C2}} (\text{wt.\%}) + y_{\text{C3}-\text{C4}} (\text{wt.\%}) + y_{\text{C5}-\text{216}^\circ\text{C}} (\text{wt.\%}) \\ &+ y_{\text{216}-344^\circ\text{C}} (\text{wt.\%}) + y_{\text{coke}} (\text{wt.\%}) \end{aligned}$$
(3)

Table 5 shows examples of mass balances in the experiments. Conversions of the various resid fractions over the two catalysts were very high (over 93%) and essentially constant in the experiments. In all the cases the conversions of the fractions were higher with catalyst E-Cat D than with catalyst E-Cat R, thus showing its higher activity, a characteristic that had been observed before in the evaluation of residual feedstocks [17,18].

The yields of the main hydrocarbon groups in the conversion of the various resid fractions are shown in Figs. 1 and 2 for catalysts

Table 5	
Examples of mass balances in the experiments. Reaction time, 10 s	. Masses in mg.

Catalyst	Fraction	m <sub>initial</sub>	<i>m</i> <sub>C1-C2</sub>	<i>m</i> <sub>C3-C4</sub>	m <sub>C5-216°C</sub>	<i>m</i> <sub>216-344°C</sub>	m <sub>coke</sub>	m <sub>products</sub>	x (%)
E-Cat D	Saturated Aromatic	29.73 28.57 21.72	0.97 0.69	8.06 5.50	17.44 18.00	1.00 1.11	2.26 3.02	29.73 28.33	100.0 99.2
E-Cat R	Resin Saturated Aromatic	31.72 33.95 28.30	0.84 1.01 0.96	3.05 5.95 4.37	23.72 24.00 18.72	0.75 1.19 1.11	3.30 0.58 1.44	31.66 32.73 26.59	99.8 96.4 93 9
	Resin	33.95	0.80	2.52	25.93	0.28	2.43	31.95	94.1



Fig. 1. Yields (wt.%) of the main hydrocarbon groups in the conversion of the resid fractions and ATR on catalyst E-Cat D. (a) Dry gas, (b) LPG, (c) C5-216 °C, (d) 216–344 °C, (e) Coke. Symbols: Fraction FS (▲), Fraction FA (■), Fraction FR (●), ATR (◊).



Fig. 2. Yields (wt.%) of the main hydrocarbon groups in the conversion of the resid fractions and ATR on catalyst E-Cat R. (a) Dry gas, (b) LPG, (c) C5-216 °C, (d) 216–344 °C, (e) Coke. Symbols: Fraction FS (▲), Fraction FA (■), Fraction FR (♦).

E-Cat D and E-Cat R, respectively. It can be seen in the comparison of the yields of the main groups over both catalysts that the FS saturated fraction is the one with the highest yields of dry gas and LPG, while the FR resin fraction shows the highest yield of gasoline and coke; concerning LCO, the FA aromatic and FS saturated fractions show the highest yields, which were very similar.

These results are consistent with the composition of the FS fraction, which is composed by naphthenic and paraffinic compounds. According to Xu et al. [24], who used deasphalted oil including saturates, aromatics and resin fractions, and based on the carbon-ion mechanism for FCC reactions, the main products expected from the cracking of saturated compounds in this range are gasoline, diesel and LPG, with low coke yield. Our results are coincident in the sense of low coke yields and high LPG and LCO yields. Moreover, the high dry gas yields observed with the FS fraction are consistent with the fact that these products are primarily the consequence of thermal cracking reactions, which are expected to impact more significantly on linear hydrocarbon chains or alkyl groups in naphthenic molecules [25].

The aromatic rings in the molecules composing the FA aromatic fraction cannot be opened easily under these conditions of catalytic cracking, although some of the substituting groups could

Table 6Overall and LPG isobutane selectivity and olefinicity in the C4 group in the conversionof the various fractions and the ATR. Reaction time, 15 s. Temperature 550 C.

Catalyst	E-Cat D				E-Cat R			
Feedstock	FS	FA	FR	ATR <sup>a</sup>	FS	FA	FR	ATR <sup>a</sup>
iC4 Selectivity (%) iC4/LPG C4=/C4 total	10.48 0.35 0.25	6.83 0.34 0.29	3.01 0.29 0.29	7.60 0.28 0.42	8.90 0.31 0.35	7.11 0.31 0.37	1.71 0.22 0.44	6.20 0.24 0.47

<sup>a</sup> From Ref. [19].

dealkylate and additional cracking reactions proceed on them in the same manner as for saturated compounds. In case of being two or three aromatic rings involved, the resulting products would be in the gasoline or LCO boiling ranges [24]; however, the aromatic rings could also follow other reaction routes, such as condensation into coke or alkylation with olefin molecules and dealkylation by cracking. These facts could explain the intermediate yields of dry gas, LPG and gasoline observed with this fraction. Observations from Xu et al. [24] showed that the higher the aromatic content in a mixture of fractions, the more favored the yields of gasoline and LCO, a fact observed in this work for LCO yield, particularly with E-Cat R (see Fig. 2d).

The FR resin fraction includes structures similar to those in the FA fraction, but with a higher concentration of molecules with a large number of aromatic nuclei [23] which may easily condensate to yield coke [24], thus justifying the highest coke yields observed with this fraction and also with the FA fraction (see, e.g., Fig. 1e). Moreover, the more significant gasoline yields observed with the FR fraction could be justified by the occurrence of dealkylation reaction on constituents of the group. The alkyl chains  $((-CH_2-)_n$  methylene groups) which bridge polyaromatic nuclei in those molecules may be subjected to cracking, thus leading to smaller aromatic structures, in turn subjected to dealkylation and producing aromatic hydrocarbons in the boiling point range of gasoline.

The different molecules present and the different resulting overall compositions in resids from diverse source crudes, as well as the interactions or competition between the components of the various fractions when fed together [17,18,24] can validate discrepancies noted in the comparisons of the selectivities to the various hydrocarbon cuts when using the "pure" fractions (this work) and deasphalted feedstocks [24].

It is important to notice that the LPG yields are larger in the conventional catalyst E-Cat D than in the resid catalyst E-Cat R (Figs. 1b and 2b). This is in harmony with the results observed in the conversion of the source ATR over the same catalysts [17,18], where LPG yields were also higher in catalyst E-Cat D. Moreover, the yields of LPG from the FS fraction are higher than those obtained with the ATR, (Figs. 1b and 2b), thus suggesting that interactions occur between the components of each fraction when they are taking part of the ATR and consequently influence the various yields. This is also reflected in the very dissimilar yields of the fractions, is reacted over both catalysts (see Table 6).

The selectivity to olefins in the C4 group observed in the cracking of the various resid fractions, which can be considered as an index of the intensity of the hydrogen transfer reactions ( $i_{HT}$ ), shows that they occur more intensively in catalyst E-Cat D than in catalyst E-Cat R, in consistency with previous observations [17,18,26]. That occurs in spite of the fact that E-Cat R shows higher rare earth content (see Table 2), which usually impacts on the rate of these reactions. Rare earths are considered crucial to improve hydrogen transfer properties, but if the load is above approximately 3%, like in the case of catalyst E-Cat R, rare earth ions may form OH bridges between them, leading to a decrease in the catalyst acidity below that expected from the hydrolysis of the individual cations [27,28]. Moreover, the total amount of acid sites as measured by pyridine TPD (see Table 2), shows that the acidity of catalyst E-Cat R is lower than that of catalyst E-Cat D. The hydrogen transfer indexes shown by the individual fractions are lower (that is, the hydrogen transfer reactions are more intense) than that of the ATR; asphaltenes present in the ATR, which adsorb strongly [29], may impact negatively on the density of paired acid sites, which control hydrogen transfer reactions [30], thus decreasing their intensity.

The gasoline yields obtained from the different fractions, which range from 50 to 80 wt.%, are individually higher than the yields from the ATR, which are not over 50 wt.%, as it can be observed in Figs. 1c and 2c.

In the conversion of toluene the yield of products which are not aromatic compounds in the boiling range of gasoline are negligible, and then those not aromatic hydrocarbons in the range observed in the conversion of the mixtures of the various fractions with toluene can be considered as produced by the resid fractions only. All the fractions yield branched paraffins in the C5–C9 range (mainly i-pentane and 2- and 3-methylpentane) and normal paraffins in the C5–C12 range (mainly n-pentane), as can be seen in Table 7. Both normal (mainly C5 and C6) and branched (mainly 2- and 3-methyl-1-butene, and 2-methyl-2-butene) olefins, and naphthenes (cyclopentane) occur in lower amounts in the range. The FS saturate fraction is the one with the highest yields of non aromatic compounds in gasoline over both catalysts.

It can be seen in Table 7 for all the fractions, but particularly for the FR resin fraction, that, by far, the most important hydrocarbon group in gasoline is that of aromatics, where the compounds with a single ring prevail, representing more than 90% of the aromatic group, a fact which could be supported by the possible cracking of the  $(-CH_2-)_n$  bridges which link aromatic nuclei or with one or two rings present in the FR resin fraction. Hydrogen transfer from naphthenic compounds and cyclization and further hydrogen transfer from paraffins may be the most important sources for aromatics in gasoline in the conversion of the FS saturate fraction. In the case of the FA aromatic fraction, dealkylation of the substituted aromatic compounds and cracking of naphthenic-aromatic hydrocarbons may be the main sources for aromatics in gasoline. This last type of reaction could also be contributing in the case of the FR resin fraction.

The composition of the LCO cut is in all the cases essentially aromatic, particularly comprising methyl and dimethylnaphthalene, as well as C3-naphthalene species. The yield of LCO from ATR is significantly larger than those from the individual fractions, a fact which can be considered as an evidence of interactions or competitions among fractions when they react together.

The yield of coke from the various fractions is compared against that of the source ATR in Figs. 1e and 2e. Particular yields are all higher in the case of catalyst E-Cat D, as expected considering its higher activity and the fact that the resid catalyst E-Cat R was specifically designed to have better coke selectivity. These facts were also observed in the conversion of the ATR alone [17] or mixed with a VGO [28]. It can be seen over both catalysts that the fraction producing more coke is the FR resin fraction, that the FA aromatic fraction shows intermediate yields and that the lowest yields are observed with the FS saturate fraction. This is an expected observa-

Table 7
Hydrocarbon group compositions of the C5-216 °C cuts (wt.%). Reaction time 10 s.

	E-Cat D			E-Cat R		
	FS	FA	FR	FS	FA	FR
Paraffins	29.5	20.3	6.4	20.8	16.8	5.9
Naphthenics	2.2	2.1	0.8	1.7	1.9	1.3
Olefins	8.5	7.3	2.1	6.2	6.5	2.8
Aromatics	59.8	69.9	90.3	69.3	74.5	89.8

tion, considering the particular compositions of the fractions. In the thermal cracking of the SARA fractions from crudes [14] or ATRs [15], asphaltenes were by far the highest coke producers, but the same rank as the one observed here was reported for the other fractions. It can be seen that it is not possible to predict the coke yield when the ATR is converted over these catalysts as the addition of the particular contributions from the fractions, affected by their concentration, thus suggesting that the fractions do not behave separately when taking part of the ATR.

#### 4. Conclusions

The dilution in toluene of the various SARA fractions composing an ATR from a naphthenic crude, which were separated by the ASTM 2007 method, allowed to determine in the laboratory their reactivities and product distributions when converted on conventional and resid equilibrium FCC catalysts, which were compared to the "pure" resid. All the fractions convert extensively, but the differences in the yields of the main hydrocarbon groups from the various fractions are noteworthy and reveal their nature. The highest LPG and gasoline yields were obtained with the FS saturate fraction and the FR resin fraction, respectively, while coke was formed more importantly by the FR resin fraction. In most of the cases the FA aromatic fraction showed intermediate yield profiles.

These results would allow estimating the impact of the addition of a resid of known composition to a typical VGO feedstock. However, it is not possible to assess the yields of given groups from the resid by the direct addition of the yields from the different fractions, due to interactions among the various fractions and the corresponding products when the resid is converted on these catalysts.

The characteristics of the catalysts' formulations, such as the higher activity of the conventional catalyst E-Cat D, and the better coke selectivity of the resid catalyst E-Cat R, among others, are evident in the experiments performed with the various fractions; the higher feedstock conversion and the lower coke yield which were observed for each catalyst under the same conditions, respectively, support this statement.

These results confirm the versatility of the CREC Riser Simulator to support FCC evaluation procedures and the need to perform them under a joint catalyst-feedstock-process conditions approach.

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#### References

 Gilbert W, Baptista C, Teixeira MA. Calculating atmospheric residue FCC product slate. PTQ 2000; Winter: 49–53.

- [2] <www.repsol.com/pe\_es/productos\_y\_servicios/productos/peasfaltos/ fisicoquimica/composicion/> (17.01.13).
- [3] Letzsch WS, Ashton AG. The effect of feedstock on yields and product quality. Stud Surf Sci Catal 1993;76:441–98.
- [4] Harding RH, Peters AW, Nee JRD. New developments in FCC catalyst technology. Appl Catal A 2001;221:389–96.
- [5] Phillips, G. Advances in residue upgrading technology. PTQ 2002; SPRING: 93– 99.
- [6] Jiménez-García G, Aguilar-López R, Maya-Yescas R. The fluidized-bed catalytic cracking unit building its future environment. Fuel 2011;90:3531–41.
- [7] Fan T, Buckley JS. Rapid and accurate SARA analysis of medium gravity crude oils. Energy Fuels 2002;16:1571–5.
- [8] Nalwaya V, Tantayakom V, Piumsomboon P, Fogler S. Studies on asphaltenes through analysis of polar fractions. Ind Eng Chem Res 1999;38:964–72.
- [9] Kharrat AM, Zacharia J, Cherian VJ, Anyatonwu A. Issues with comparing SARA methodologies. Energy Fuels 2007;21:3618–21.
- [10] Jewel DM, Weber JH, Bunger JW, Plancher H, Latham DR. Ion-exchange, coordination, and adsorption chromatographic separation of heavy-end petroleum distillates. Anal Chem 1972;44:1391–5.
- [11] ASTM. Standard test method for characteristic groups in rubber extender and processing oils by the clay-gel adsorption chromatographic method. D2007-91: ASTM international; 1993.
- [12] Pereira JC, López I, Salas R, Silva F, Fernández C, Urbina C, et al. Resins: The molecules responsible for the stability/instability phenomena of asphaltenes. Energy Fuels 2007;21:1317–21.
- [13] Ancheyta-Juárez J, López-Isunza F, Aguilar-Rodríguez E. Correlations for predicting the effect of feedstock properties on catalytic cracking kinetic parameters. Ind Eng Chem Res 1998;37:4637–40.
- [14] Karacan O, Kok MV. Pyrolysis analysis of crude oils and their fractions. Energy Fuels 1997;11:385-91.
- [15] Alvarez E, Marroquín G, Trejo F, Centeno G, Ancheyta J, Díaz JAI. Pyrolysis kinetics of atmospheric residue and its SARA fractions. Fuel 2011;90:3602–7.
- [16] de la Puente G, Devard A, Sedran U. Conversion of residual feedstocks in FCC. evaluation of feedstock reactivity and product distributions in the laboratory. Energy Fuels 2007;21:3090–4.
- [17] Devard A, de la Puente G, Sedran U. Laboratory evaluation of the impact of the addition of resid in FCC. Fuel Process Technol 2009;90:51–5.
- [18] Devard A, de la Puente G, Passamonti F, Sedran U. Processing of resid–VGO mixtures in FCC: Laboratory approach. Appl Catal A 2009;353:223–7.
- [19] de Lasa H.I. U.S. Pat. 5,102,628 1992.
- [20] Johnson MFL. Estimation of the zeolite content of a catalyst from nitrogen adsorption isotherms. J Catal 1978;52:425–31.
- [21] Passamonti F, de la Puente G, Morgado E, Gilbert W, Sedran U. Comparison between fixed fluidized bed (FFB) and batch fluidized bed reactors in the evaluation of FCC catalysts. Chem Eng J 2012;183:433–47.
- [22] de la Puente G, Klocker C, Sedran U. Conversion of waste plastics into fuels: Recycling polyethylene in FCC. Appl Catal B 2002;36:279–85.
- [23] Navarro L, Álvarez M, Grosso JL, Navarro U. Separación y caracterización de resinas y asfaltenos provenientes del crudo castilla. Evaluación de su interacción molecular. CT&F 2004;2:53–67.
- [24] Xu Ch, Gao J, Zhao S, Lin S. Correlation between feedstock SARA components and FCC product yields. Fuel 2005;84:669–74.
- [25] Schipper PH, Sapre AV, Le QN. Chemical aspects of clean fuels production. NATO-ASI Ser E 1992;225:147–82.
- [26] Devard A, Pujro R, de la Puente G, Sedran U. Hydrocarbon yield structure in the conversion of heavy model molecules (Quinolin-65) on fluidized catalytic cracking catalysts. Energy Fuels 2012;26:5015–9.
- [27] Lemos F, Ramoa Ribeiro F, Kern M, Giannetto G, Guisnet M. Influence of lanthanum content of La HY catalysts on their physico-chemical and catalytic properties. Appl Catal 1988;39:227–38.
- [28] Maugé F, Gallezot P, Courcelle J, Engelhard P, Grosmangin J. Hydrothermal aging of cracking catalysts. II. Effect of steam and sodium on the structure of LaHY zeolites. Zeolites 1986;6:261–6.
- [29] Nassar NN, Hassan A, Pereira-Almao P. Effect of surface acidity and basicity of aluminas on asphaltene adsorption and oxidation. J Colloid Interface Sci 2011;360:233–8.
- [30] de la Puente G, Sedran U. Evaluation of hydrogen transfer in FCC catalysts. A new approach for cyclohexene as a test reactant. Chem Eng Sci 2000;55:759–65.