

# Formation of Gum Precursors in FCC Naphthas

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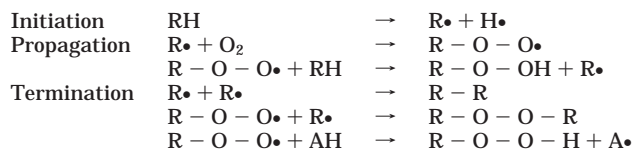
The trends to the formation of gum precursors in gasoline were studied through the yields and selectivities of C5 olefins in the conversion of both a VGO and nC16 over two equilibrium commercial FCC catalysts. The experiments were performed at 500 and 550 °C, catalyst-to-oil ratio of 6.1 and short contact times of up to 12 s in a Riser Simulator laboratory reactor. The behaviors of C5 olefins observed in the conversion of both reactants were similar: the yield of olefins (linear, branched, and cyclic) and dienes increased as a function of contact time and temperature, the amounts being different according to the characteristics of the catalysts. Gasoline composition was very sensitive to the formulation of the catalysts and their resulting hydrogen transfer capabilities. In the conversion of gas oil, maximum selectivities of about 59, 21, 31, and 3.3% were observed for total, linear, iso-, and cyclic olefins in the C5 group, respectively, and the maximum selectivity of dienes in the group was 3.9%. For the same hydrocarbons, the conversion of nC16 showed higher yields at the same conditions. It was verified that the reaction temperature is especially important to control the yield of diene compounds. A simple test methodology to predict the stability of FCC naphthas could be based on a reduced set of experiments with equilibrium catalysts, either with a commercial feedstock or test reactant nC16.

## Introduction

The formation of resinous, polymeric compounds with a very complex composition, that are usually named “gums”, is a factor that compromises the stability of gasolines. The most obvious consequences of this issue are that it may condition the feasibility of storing the gasoline for long periods of time, and even induce problems in the operation of internal combustion engines. The potential of gum formation in a given gasoline depends on its composition, in turn a function of the composition of the various hydrocarbon cuts that are blended in the gasoline pool in refineries. Those cuts come from different processes such as reforming, catalytic cracking (FCC), isomerization, oxygenates, straight run distillation, alkylation, or thermal processes, and, consequently, they differ in their contributions to the potential of gum formation. Isomerase and reformate streams have a low incidence, but FCC naphtha, or the cuts derived from thermal processes have a strong impact on this issue.<sup>1</sup>

The number of publications on this subject is very reduced. However, there exists agreement in considering that, in particular, cyclic and branched olefins are the main gum producers.<sup>2</sup> Also, very reactive, conjugated diene compounds are considered promoters of these reactions, and a synergistic effect with mono-olefins may result. The oxidation of the olefins in the gasoline by

means of the contact with air, which occurs through a mechanism of free radical reactions in series, is the primary reason for the formation of gums, although some other compounds such as mercaptans are also related to this issue. The first step is the hydroperoxidation of olefins, that is believed to be<sup>1</sup>



Then, it is to be expected that the operative parameters in the FCC process, which is also one of the main contributors to the gasoline pool, have an influence in gum formation. In that sense, feedstock composition, type of catalyst, incorporation of additive catalytic materials and reaction temperature are to be taken into account. In general terms, lighter feedstocks, more active catalysts and lower severity in the operation are known to be positively correlated with the decrease in the formation of gums.<sup>3</sup> The conditions that prevail in some areas of the FCC units, specially those that favor the occurrence of thermal reactions, may impact on the formation of dienes; then, gas–solid separation devices are potentially important in the generation of gum precursors.<sup>4</sup>

For a given feedstock, the specific incidence of the catalyst used as well as the operative conditions on the

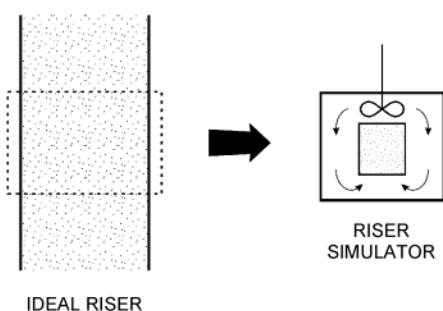
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**Figure 1.** Schematic representation of the Riser Simulator reactor.

**Table 1. Properties of the Catalysts Used**

catalyst	UCS (Å)	surface area (m <sup>2</sup> /g)	zeolite content <sup>17</sup> (%)	RE oxides (%)
E-cat D	24.23	139	16.9	1.26
E-cat O	24.24	151	15.9	

**Table 2. Properties of the VGO Used**

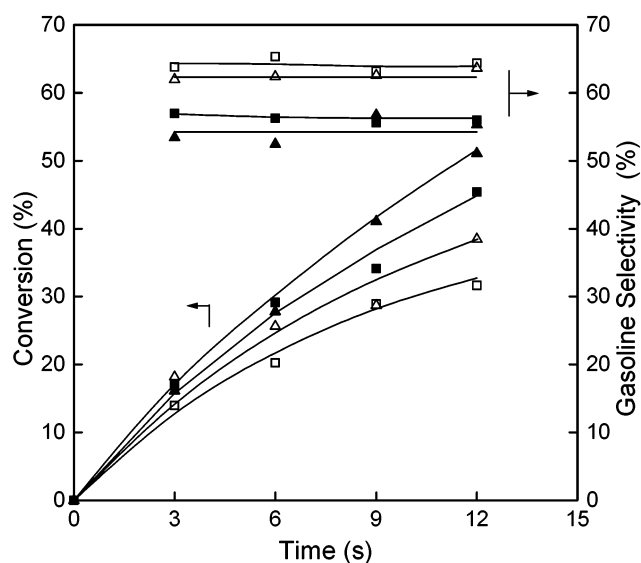
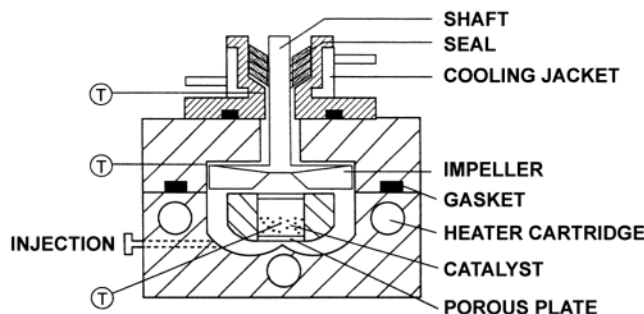
density (g/cm <sup>3</sup> )	0.924
distillation (°C)	
5%	380
20%	425
40%	457
60%	484
80%	521
95%	548
sulfur (%)	0.57
aniline point (°C)	96.4
Cu, Fe, Na, Ni, V (ppm)	<5

gum forming trends are not known in detail. In this work, the importance of such factors on the yield of compounds involved in the formation of gums (linear, branched and cyclic olefins, and dienes) are studied in the laboratory using a Riser Simulator reactor, a commercial feedstock, and a test reactant over commercial equilibrated catalysts at different thermal levels.

### Experimental Section

Two equilibrated commercial FCC catalysts produced by FCC S. A. (Brazil) were used, their most important properties being shown in Table 1. It is to be noted that their properties are similar, except that E-cat D has a standard content of rare earths. These two catalysts were sampled from running refineries; particularly, E-cat O was used in a refinery operated in the "light olefins mode", devoted to maximize their yields. The reactants were a commercial vacuum gas oil (properties shown in Table 2) and normal hexadecane (nC16, Fluka +99.0%), which was used as a test reactant.

The experiments were done in a batch fluidized bed reactor named Riser Simulator, that was designed specifically for tackling studies about FCC issues. Its basic design concept considers that a small slice of an ideal riser, carrying the mixture of catalyst particles and hydrocarbons that "see" each other while move along the riser after being put into contact, can be located into a batch reactor with internal recirculation. Thus, residence time and position along the ideal riser can be considered analogous to reaction time evolved in the Riser Simulator (refer to Figure 1). An impeller rotating at very high speed on top of the chamber that keeps the catalyst between two metal porous plates, induces the internal circulation of the reacting mixture in an upward direction through the chamber, thus fluidizing the catalyst. When the reactor is at the desired experimental condition the reactant is fed through an injection port, and immediately after the reaction time is attained, products are evacuated instantly and analyzed by



**Figure 2.** Conversion of VGO and selectivity to gasoline as a function of reaction time. Symbols: E-cat O (■), E-cat D (▲). Temperature 500 °C (open symbols) and 550 °C (closed symbols).

gas chromatography. Coke yields were determined by means of temperature-programmed oxidation. The reactor has been used in the evaluation of commercial catalysts,<sup>5</sup> the study of new operative modes,<sup>6,7</sup> the assessment of kinetic<sup>8</sup> or diffusion-adsorption<sup>9</sup> parameters and the study of reaction mechanisms.<sup>10</sup>

The reaction conditions were the following: temperatures 500 and 550 °C, catalyst-to-oil ratio of 6.1, and reaction times of 3, 6, 9, and 12 s. Reaction products were analyzed by on-line gas chromatography. Gasoline was defined to include from C5 to C12 hydrocarbons. Octanes (RON) in the gasoline cuts were calculated by means of a modified Anderson's method.<sup>11</sup>

### Results and Discussion

The overall performance of the two catalysts in the conversion of the VGO is shown in Figure 2 as a function of reaction time. It can be seen that catalyst E-cat D is more active than catalyst E-cat O, as shown by the higher conversion values obtained at every condition.

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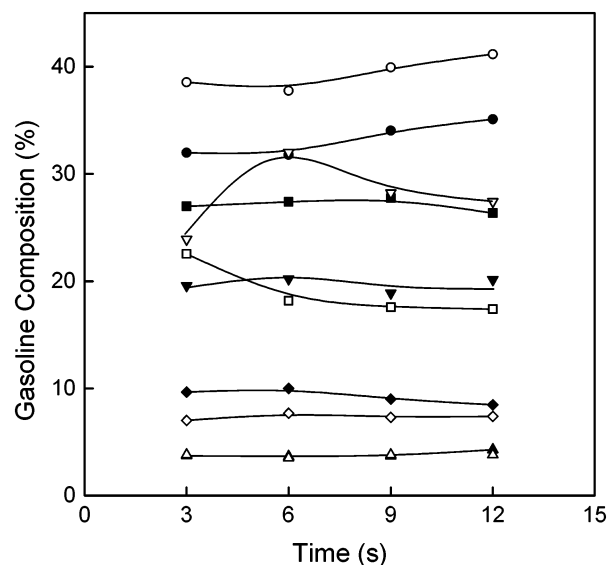
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**Figure 3.** Composition of gasoline as a function of reaction time in VGO cracking. Symbols: E-cat D (open symbols); E-cat O (closed symbols). Olefins (■), Aromatics (●), iso-paraffins (▼), *n*-paraffins (▲), naphthenics (◆). Temperature: 550 °C.

This fact could be associated with the slightly higher zeolite content of E-cat D and to the presence of rare earths in its formulation. It can be seen that the selectivity to gasoline is very similar in both catalysts (slightly higher in E-cat O, which is less active), approximately 62% at 500 °C and 55% at 550 °C. When the reactant was *n*-hexadecane, the same qualitative behaviors were observed, the highest conversions being about 70% (E-cat D, 12 s, 550 °C) and the selectivities to gasoline 60% and 50% at 500 and 550 °C, respectively.

However, the gasolines produced by each catalyst are clearly different in their composition. It can be seen in Figure 3 for the case example of reaction temperature 550 °C that, even though the octanes are similar (RONs are approximately 95 at 500 °C and 97.5 at 550 °C), the gasoline from E-cat D has significantly lower olefins and higher aromatics and iso-paraffins contents than the gasoline from E-cat O. Essentially the same differences between catalysts were observed at the lower temperature. These differences can be assigned to a much higher overall hydrogen transfer activity in E-cat D. Even though the unit cell sizes of the zeolite component are the same, this being the most important parameter in relation to hydrogen transfer,<sup>8</sup> it is well-known that the addition of rare earths contribute positively,<sup>12</sup> and that is the main difference between the catalysts tested. These distributions of hydrocarbon types in gasoline can be considered usual<sup>13</sup> and, as expected due to the similar properties of the catalysts, the carbon number distributions within each of the gasoline lumps are essentially the same (data not shown).

Qualitatively, the same distribution of the hydrocarbon types in gasoline was observed for both catalysts in the conversion of *n*C16. In effect, the amount of olefins in gasoline was higher and the amount of

aromatics and iso-paraffins was lower in E-cat O at both temperatures. For example, at 550 °C for E-cat D and E-cat O, respectively, the gasoline compositions (percentage) were approximately: olefins, 25 and 35; aromatics, 16 and 11; iso-paraffins, 45 and 35. At 500 °C, the gasoline compositions (percentage) were approximately: olefins, 21 and 29; aromatics, 11 and 9; iso-paraffins, 50 and 42. As expected due to the different nature of the reactants, the selectivities are different when compared with VGO, e.g., the proportion of aromatics compounds in gasoline is much lower with *n*C16.

As mentioned previously, olefins are indicated in an overall view as the most important contributors to the formation of gum in gasolines. Among them, straight chain molecules produce minimum gum, while branching generally increases the trend, depending on the position of branching, and cyclic unsaturated molecules, particularly di-cyclo-olefins, are the most important producers of gum.<sup>2</sup> Particularly, conjugated dienes, due to their high chemical reactivity, are considered the initiators of the chain reactions leading to the polymeric residua. This is confirmed by simple experiments of oxidation of naphthas that show that the concentration of dienes and cyclic olefins in the C5 and C6 groups decrease significantly while, simultaneously, gum deposits are formed.<sup>14</sup> Thus, given the relationship between the formation of gums, which are usually determined by means of ASTM standard D 873 ("potential gums"), and the amount of olefins and dienes in the gasoline, these hydrocarbons are used to predict product stability.<sup>2</sup>

Since most of the olefins present in the gasoline belong to the light fraction,<sup>15</sup> it was decided to study the yields of those hydrocarbons in the C5 fraction, considering their behavior as representative of the other olefins in the gasoline cut. In this study, C5 olefins represented between 7 and 12% of the gasoline in the conversion of VGO, depending on the catalyst and reaction temperature used, and accounting for 38 to 45% of all the olefins in gasoline. Moreover, it is possible to have a detailed analysis of products in this range of boiling points and, particularly, to notice the evolutions of the yields of conjugated dienes (isoprene (2-methyl-1,3-butadiene), *c*- and *t*-1,3-pentadiene) and cyclic olefins (cyclopentene). Since the relationship between reaction time and conversion is direct (refer to Figure 2), the corresponding analysis can be performed as a function of any of these parameters.

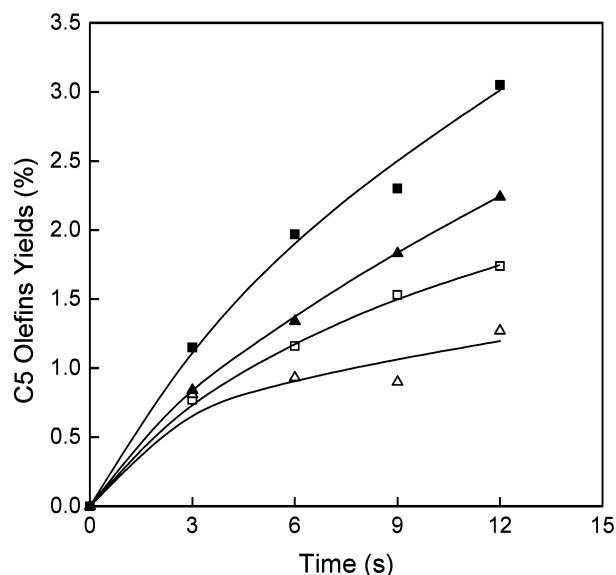
The yield of C5 olefins in VGO conversion is shown in Figure 4, where it can be seen that, for each catalyst at a given reaction temperature, it increases continuously as a function of reaction time. The maximum values observed were 3% for E-cat O at 550 °C, 12 s. The yields also increase with temperature, in response to the higher thermal sensitivity (energy of activation) of the cracking reactions as compared to others, like hydrogen transfer. E-cat O yields more olefins than E-cat D, as expected considering their particular characteristics. The same behavior was observed in the conversion of *n*C16, but in this case the yields of C5

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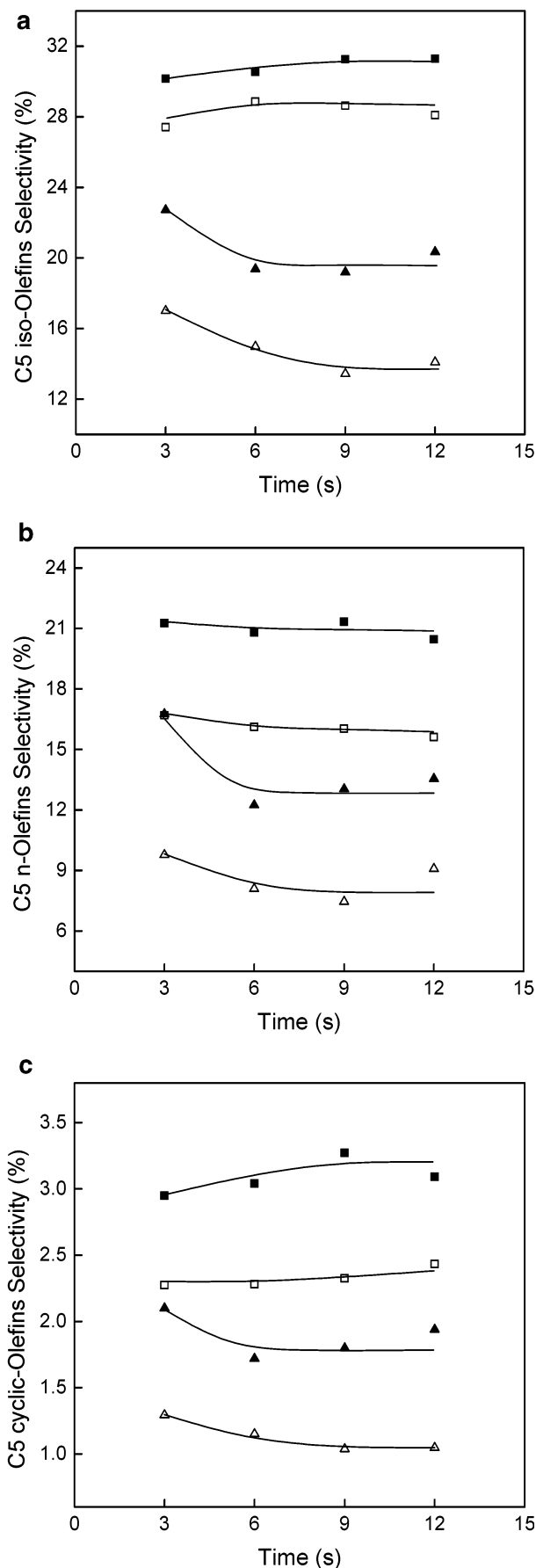
**Figure 4.** Yield of C5 olefins as a function of reaction time. Symbols: E-cat O (■), E-cat D (▲). Temperature: 500 °C (open symbols), 550 °C (closed symbols).

olefins are higher; the maximum value was 6% for E-cat O, at 550 °C and 12 s reaction time.

The distribution of olefins in the C5 group in the conversion of VGO is shown in Figure 5 in terms of selectivity, which is defined as the ratio between the yield of a given olefin and the addition of the yields of all the compounds (hydrocarbons) with the same C atom number. It can be seen that the selectivities for the different types of olefins, iso- (Figure 5a), *n*- (Figure 5b) and cyclic (Figure 5c), all are higher when the reaction was performed at the highest temperature. Moreover, this distribution also confirms the individual characteristics of the catalysts in the sense that the activity of hydrogen transfer in E-cat D is always significantly higher than that of E-cat O and, consequently, olefins are consumed at a higher degree. Iso-olefins are the most important in the group, accounting for 28–30% of the total C5 hydrocarbons in E-cat O and 16–20% in E-cat D; on the contrary, the lowest yields and selectivities belong to the cyclic olefin cyclopentene. It can be noticed that the various selectivities are nearly constant in the range of conversions studied for catalyst E-cat O, while a slight decrease is apparent in the profiles of E-cat D that may reflect the higher relative incidence of secondary reactions, like hydrogen transfer, when conversion increases.

In the case of using nC16 as the reactant, the behavior of both catalysts in relation to the distribution of C5 olefins was qualitatively the same as the one observed with VGO at every condition, yields being higher, in general. As an example, Table 3 shows that the selectivities to the different types of olefins follow the same trends as those observed with VGO, although a higher selectivity to cyclopentene was observed.

In relation to C5 diene compounds formed in the conversion of VGO, isoprene is the most important, its yield approaching 0.08% when conversion was 45.4% on E-cat O at 550 °C and 12 s reaction time. On the other hand, *c*- and *t*-1,3-pentadiene yields are lower than 0.04% under the same conditions. No other diene isomer was observed. However, the maximum value of isoprene

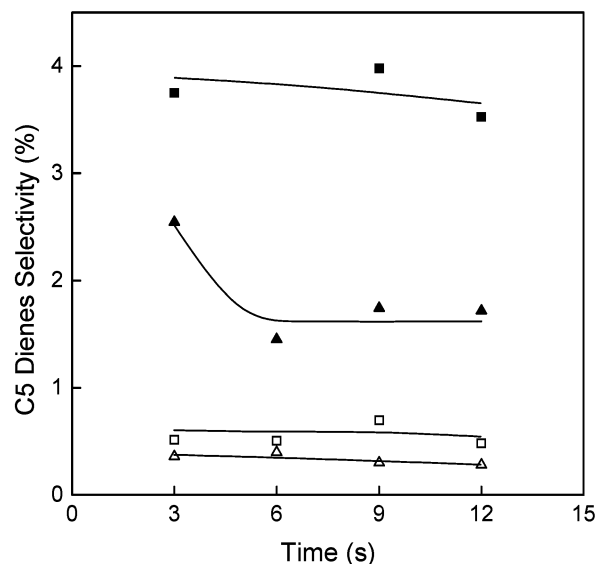


**Figure 5.** Selectivities to olefins in the C5 group as a function of reaction time. Symbols: E-cat O (■), E-cat D (▲). Temperature: 500 °C (open symbols) and 550 °C (closed symbols). (a) iso-olefins, (b) *n*-olefins, (c) cyclic olefins.



**Table 3. Yield of C5 Olefins and Selectivities to Iso-, *n*-, and Cyclic Olefins in the Conversion of NC16; Reaction Time 6 s**

catalyst	temperature (°C)	C5 olefins yield (%)	selectivities (%)		
			iso-	<i>n</i> -	cyclic
E-Cat D	500	3.1	17.6	10.5	6.5
	550	3.9	18.3	11.6	8.4
E-Cat O	500	3.5	24.0	15.3	9.7
	550	4.6	27.1	18.9	13.5

**Figure 6.** Selectivity to C5 dienes as a function of reaction time. Symbols: E-cat O (■), E-cat D (▲). Temperature: 500 °C (open symbols) and 550 °C (closed symbols).

selectivity, 2%, was observed on E-cat O at the lowest tested reaction time of 3 s, then decreasing at higher values of reaction times due to its high reactivity or adsorption. The variations in the selectivity to dienes in the C5 group are shown in Figure 6, where it can be seen that the same trends as those with mono-olefins are kept, in the sense that the higher the temperature, the higher the C5 dienes yield and that the yields of E-cat O are always higher. However, it is possible to observe a singular effect of reaction temperature on the yield of dienes, which seems to be much more important than the one on the yield of mono-olefins (refer to Figure 5). In effect, when the reaction is conducted at 550 °C, diene yield increases by a factor of 9 and 6 times over the yield at 500 °C, for E-cat O and E-cat D, respectively. However, it is to be noted that the same factor amounts to a maximum of only 1.5 for mono-olefins. These evidences suggest that thermal cracking reactions may have a strong impact on diene yields,<sup>16</sup> a fact that could be congruent with previous commercial observations that the operation of FCC units under high severity conditions, or high temperatures in the regenerator, lead to gasolines with lower stability.<sup>3</sup>

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The yield of dienes is comparatively higher when the reactant is *n*-hexadecane; for example, maximum observed yields of 0.6% of isoprene (E-cat O, 550 °C, 12 s reaction time) impose selectivities of up to 4.5%. However, the overall qualitative variations are the same as with VGO. Additional information was gathered from experiments performed with fresh catalyst O (results not shown), where it was demonstrated that the yield of dienes is much lower than the ones observed on E-cats under the same conditions; this could be explained on the basis of the combination of high activity of these catalysts and high reactivity of diene hydrocarbons.

An a-priori analysis, then, would predict that under the same operative conditions and for a given feedstock, E-cat O would yield gasolines that are more unstable than those from E-cat D. A simple method could be devised in the methodology of catalyst evaluation procedures in order to define its trends to gum formation; the method could include a small number of experiments performed in a Riser Simulator reactor under typical FCC conditions with the equilibrium catalysts. Either the standard feedstock or *n*-hexadecane, which showed more sensitivity to C5 olefins, could be used as the reactant.

## Conclusions

The conversion of VGO on two equilibrium commercial catalysts was studied in relation to the yield of mono-olefins and dienes in the gasoline cut that may be associated with the respective gum formation trends. The composition of the gasoline was very sensitive to the catalyst formulations and the resulting hydrogen transfer capabilities. Particularly, the yield of olefins (*n*-, iso-, and cyclic), and dienes in the group C5 was observed to increase as a function of contact time and temperature.

Similar conclusions in terms of yields and selectivities of C5 olefins can be stated for the case of using *n*-hexadecane under the same conditions, its utilization being simpler. nC16 also showed higher sensitivity for the dienes in the C5 group.

A method could be established to test for gum formation trends in the catalysts or the feedstocks, based on a small number of laboratory experiments under typical FCC conditions in a Riser Simulator reactor. nC16 could be a good choice for the reactant and, to increase the sensitivity of the method, high temperature would be convenient.

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