

## RESEARCH NOTES

## Factors Influencing the Isobutane Yield during the Conversion of Vacuum Gas Oil (VGO) under Fluidized Catalytic Cracking (FCC) Conditions

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Five equilibrium fluidized catalytic cracking (FCC) catalysts of different types, with unit-cell sizes in the range of 24.23–24.29 Å, were evaluated in the conversion of three commercial vacuum gas oil (VGO) feedstocks in a CREC Riser Simulator laboratory reactor at temperatures of 500 and 550 °C, a catalyst-to-oil ratio of 6.1, and reaction times in the range of 3–30 s. The results have allowed us to define the main characteristics of the catalysts, in terms of various indexes, such as activity, gasoline yield and quality, and individual yields (using isobutane as a case example). In all cases, isobutane was essentially a primary product. It was observed that the yield of isobutane was linked to the hydrogen transfer properties and the activity of the catalysts. For a given catalyst, the higher the temperature, the less isobutane is formed at the same conversion, because of the lower incidence of hydrogen transfer reactions. The type of feedstock influences the isobutane yields, particularly on low-activity, low-hydrogen-transfer catalysts. The approach is shown to be a proper tool to evaluate commercial FCC catalysts (in this case, in the search for the optimum isobutane yield) and demonstrate that knowledge of the integral evaluations (feedstock, catalyst, and process conditions) is necessary.

## Introduction

The fluidized catalytic cracking (FCC) of hydrocarbons is a key conversion process in refineries; the market of catalysts for this process makes knowledge of the procedures for laboratory evaluation and selection critical.<sup>1</sup> Although it is not common practice to focus all of the evaluation process on the yield of particular compounds, isobutane is one of the main raw materials derived from FCC, which is mainly used for the alkylation process; yet, it is given less importance as a product than other compounds. Isobutane has been considered to be a true product from the reactions of catalytic cracking<sup>2</sup> and deserves mechanistic significance.<sup>3</sup> It is known that, besides primary conventional  $\beta$ -scission reactions, secondary hydrogen transfer reactions have an important role in the control of the relative amounts of product isobutane and olefins, among the gas products;<sup>4</sup> then, some catalyst properties, such as zeolite unit cell size, rare-earth content, and zeolite load, along with reaction conditions, could have a significant influence and become important issues in the selection of catalysts when increases in the yield of isobutane are also desirable.

The objective of this work is to contribute to the elucidation of the incidence of the most important reaction parameters and properties of the equilibrium FCC commercial catalysts on the yield and selectivity of isobutane in the conversion of vacuum gas oils (VGOs). Contrary to laboratory practice with test reactants and standard fixed-bed reactors,<sup>5–7</sup> commercial VGO feedstocks and a CREC Riser Simulator laboratory reactor were used.

## Experimental Section

Five equilibrium commercial FCC catalysts that had been sampled from operating refineries were used; their main properties are shown in Table 1. The characteristics of the three feedstocks used (VGO-B, VGO-P, and VGO-M) are shown in Table 2. The experiments were performed in a batch fluidized-bed laboratory unit with internal recirculation, the CREC Riser Simulator reactor,<sup>8</sup> which was specifically designed for FCC studies; additional descriptive details of the reactor can be found in, e.g., the reported work of Passamonti et al.<sup>9</sup> The reaction temperatures were 500 and 550 °C, and the mass ratio of catalyst to oil was 6.1; in all cases, 0.14 mL of VGO feedstock were injected, with reaction times in the range of 3–30 s. The mass balance calculations were within  $\pm 5\%$  in all cases. Reaction products were analyzed by standard capillary gas chromatography, and coke yields were assessed by combustion. The conversion (expressed as a percentage) in each experiment was defined as

$$\text{conversion} = 100 - (\% \text{boiling at } > 344 \text{ } ^\circ\text{C})$$

where the term given in parentheses represents the percentage of material that boils at a temperature of  $> 344$  °C. The selectivities were calculated as the relationship between the yield of a certain product and the conversion. The research octane numbers (RON) of the gasoline cut were assessed using a modified version of Anderson's method.<sup>10</sup>

## Results and Discussion

**Catalyst Activity.** The conversions observed were in the range of commercial interest. For the example of the feedstock VGO-M, conversions at 25 s and 550 °C were determined to

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

catalyst	unit-cell size <sup>a</sup> (nm)	rare-earth oxide (%)	BET surface area <sup>b</sup> (m <sup>2</sup> /g)	zeolite load <sup>c</sup> (%)	type
E-Cat D	2.423	1.26	139	16.9	octane-barrel
E-Cat M	2.426	1.19	158	18.0	octane-barrel
E-Cat O	2.424	0.00	151	15.9	octanes
E-Cat P	2.429	3.05	137	14.0	max. gasoline
E-Cat R	2.427	2.94	125	14.8	resid

<sup>a</sup> According to ASTM Standard Test Method D-3942-85. <sup>b</sup> According to the BET method, using N<sub>2</sub> adsorption. <sup>c</sup> According to Johnson's method<sup>18</sup> with N<sub>2</sub> adsorption.

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

property	Value		
	VGO-B	VGO-M	VGO-P
distillation (°C)			
10 vol %	402	361	389
50 vol %	464	432	449
90 vol %	534	494	510
density (g/cm <sup>3</sup> )	0.9240	0.9160	0.9207
sulfur (%)	0.57	2.03	1.57
Conradson carbon residue, CCR (%)	0.50	0.11	0.16
character	aromatic	paraffinic	paraffinic

**Table 3. Liquefied Petroleum Gas (LPG) and Isobutane Yields in the Conversion of Vacuum Gas Oil (VGO)<sup>a</sup>**

catalyst	VGO-B		VGO-M		VGO-P	
	at 500 °C	at 550 °C	at 500 °C	at 550 °C	at 500 °C	at 550 °C
LPG Yield (%)						
E-Cat D	10.0	11.5	10.3	12.9		
E-Cat M	10.3	11.7	10.7	12.9	10.2	12.5
E-Cat O	8.8	10.4	10.1	12.0		
E-Cat P	7.3	9.6	8.7	11.3	8.7	11.1
E-Cat R	7.9	9.9	8.5	10.2		
Isobutane Yield (%)						
E-Cat D	4.2	3.3	4.0	3.9		
E-Cat M	4.1	3.3	4.2	3.6	4.0	3.8
E-Cat O	2.5	1.7	2.7	2.4		
E-Cat P	2.0	1.8	2.9	2.8	2.8	2.8
E-Cat R	2.2	2.1	2.6	2.3		

<sup>a</sup> At 50% conversion.

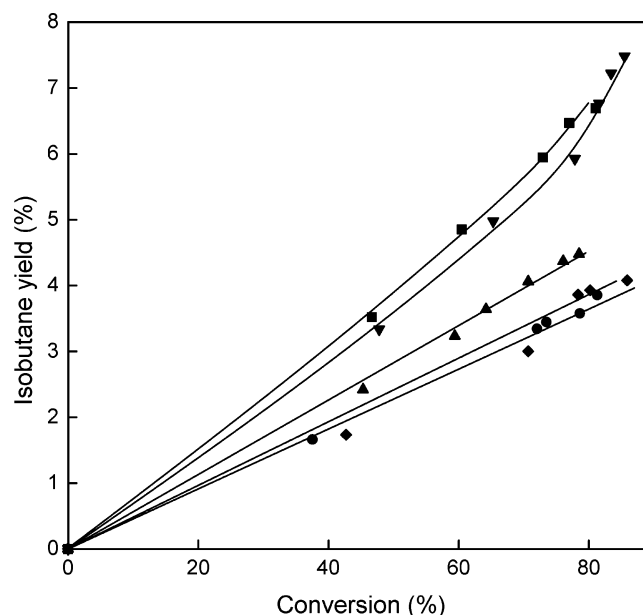
range from 76% (catalyst E-Cat P) to 83% (catalyst E-Cat M), and the ranking of catalysts' activities was

$$\text{E-Cat M} > \text{E-Cat D} \approx \text{E-Cat O} > \text{E-Cat R} > \text{E-Cat P}$$

When the temperature was 500 °C, the results were qualitatively similar, with lower conversion values. A similar behavior was observed in the cases of the other feedstocks (VGO-B and VGO-P). Among the most active catalysts, catalysts E-Cat D and E-Cat M do not have the largest unit-cell size, which is usually linked to catalyst activity; however, the high zeolite loads and the content of rare earths justify their high activity.<sup>11</sup> The high activity of catalyst E-Cat D also reflects a high average coke yield (7.5% and 8.5% at 500 and 550 °C, respectively, for both feedstocks VGO-B and VGO-M, in comparison to the minimum yields of 3.5% and 4.5% for catalyst E-Cat P.

The yields and selectivities of gasoline indicate usual values,<sup>12</sup> from 48% (catalyst E-Cat D) to 60% (catalyst E-Cat P), depending on the feedstock and the reaction temperature. The gasoline quality (RON) at 550 °C showed maximum values of ~97.5 on catalysts E-Cat D and E-Cat O, and minimum values of ~95.9 on catalyst E-Cat P. The observed gasoline qualities and selectivities confirmed the type of catalyst in each case.

Table 3 shows that the differences in the yields of liquefied petroleum gas (LPG) are significant, with maximum differences



**Figure 1.** Isobutane yield using various catalysts, as a function of conversion, for feedstock VGO-M at a temperature of 550 °C. Symbols: (■) E-Cat D, (●) E-Cat O, (▲) E-Cat P, (▼) E-Cat M, and (◆) E-Cat R.

of up to 41% over the lowest value for the same feedstock. In particular, catalyst E-Cat P is the one that exhibited the lowest yields in all the cases, whereas catalysts E-Cat D and E-Cat M showed the highest yield values. These yields imply LPG selectivities that can be considered to be typical.<sup>13</sup> On the other hand, it was observed, for a given catalyst, that the LPG yields were generally lower with the VGO-B feedstock (aromatic), in comparison to the VGO-M or VGO-P feedstocks (paraffinic).

**Isobutane Yield and Selectivity: Effect of Catalyst Properties.** The isobutane yield curves are shown in Figure 1 for the example of VGO-M at 550 °C. It can be seen that isobutane is essentially a primary product, with some degree of secondary character when conversions are >70% in the cases of the most active catalysts (catalysts E-Cat M and E-Cat D). According to the shape of these yield curves, then, the selectivity of isobutane in LPG is directly determined by the slope of the curves. Generally, the lower the temperature, the higher the isobutane yields (see Table 3). This suggests that cracking reactions are not the only factor that is responsible for isobutane yields, because, if that were the case, higher yields should be observed at higher temperatures.

As mentioned, isobutane has been considered to be an index of the extension of catalytic cracking reactions of different hydrocarbons on acidic catalysts.<sup>2</sup> This view is consistent with the mechanism of conventional  $\beta$ -scission catalytic cracking,<sup>14</sup> which leads to more-stable tertiary carbocations on the catalytic surfaces, which, in turn, desorb as branched products. However, the relationship between isobutane yield and catalyst activity is not straightforward. In effect, Figure 1 shows that the order of isobutane yields in the various catalysts is

$$\text{E-Cat M} \approx \text{E-Cat D} > \text{E-Cat P} > \text{E-Cat O} \approx \text{E-Cat R}$$

with neat differences, whereas the order of activities for the same feedstock and temperature was

$$\text{E-Cat M} > \text{E-Cat D} \approx \text{E-Cat O} > \text{E-Cat R} > \text{E-Cat P}$$

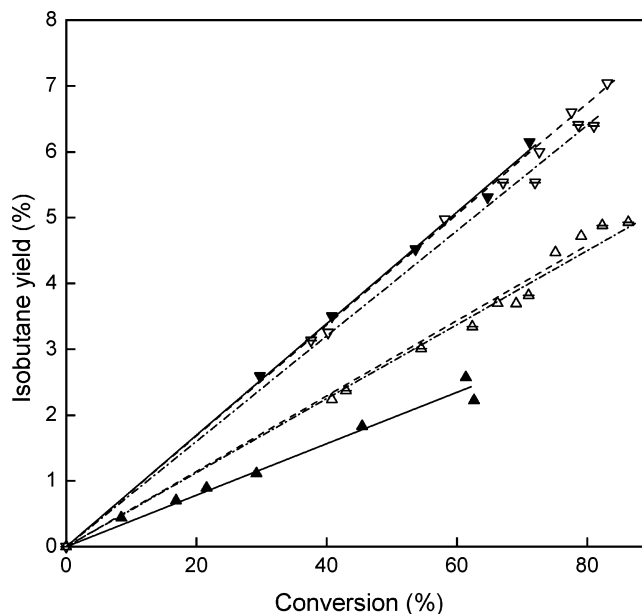
The same ranking of isobutane yields for the various catalysts was observed at the lower temperature. The maximum isobutane yields, which are  $\sim 5.9\%$  at a typical conversion of 70%, were observed on catalysts E-Cat D and E-Cat M at 500 °C.

In the case of VGO-B, the ranking of the catalysts, in terms of isobutane yield, changes to some extent. For this feedstock, the isobutane yields for catalyst E-Cat P decrease significantly and become the lowest at 500 °C. It is also seen that, as in the case of VGO-M, the highest isobutane yield ( $\sim 5.9\%$  at 500 °C and  $\sim 4.8\%$  at 550 °C, both at 70% conversion) are obtained with catalysts E-Cat D and E-Cat M. These observations are also reflected in the proportions of isobutane in LPG at both reaction temperatures (refer to Table 3).

According to the previous data analysis, for a given feedstock, the isobutane yields are dependent on the catalyst properties, reaction temperature, and conversion level. However, it might be interesting in some refineries to selectively favor isobutane against other products. Different factors must be considered in relation to the observations about isobutane yields and selectivities in LPG, which could be explained more consistently, considering that the main sources for isobutane are the hydrogen transfers to isobutylene<sup>5</sup> or to adsorbed isobutyl cations. The observed rankings of isobutane yields and selectivities can be somewhat linked to the hydrogen transfer ability of the various catalysts; in effect, although catalysts E-Cat D, E-Cat M, and E-Cat O have similar, low unit-cell sizes, catalysts E-Cat D and E-Cat M have rare earths that have been added, whereas catalyst E-Cat O does not. Rare earths are considered to be a key factor to improving hydrogen transfer properties; however, if the load is high, such as that in the case of catalysts E-Cat R and E-Cat P, with a relatively large unit-cell size but with rare-earth oxide amounts of  $\sim 3\%$ , the neat effect could be detrimental, because of the interaction between the rare-earth cations. Lemos et al.<sup>15</sup> showed that the formation of  $-\text{OH}$  bridges between rare-earth cations, when they are present in high concentrations, leads to an important decrease in the catalyst acidity, if compared against the expected hydrolysis of the individual rare-earth cations.

Nevertheless, it is apparent that the hydrogen transfer capacity of a given catalyst is not the only parameter that controls isobutane selectivity. For example, if the isobutane yields obtained with feedstocks VGO-B and VGO-M are compared to other index of hydrogen transfer (e.g., the relationships between isopentane and isoamylenes) observed in the conversion of the same feedstocks, it becomes clear that catalyst E-Cat O—that is, the catalyst with expected lowest hydrogen transfer ability, given its unit-cell size and the lack of rare earths—has an isobutane selectivity similar to that of catalysts E-Cat P and E-Cat R, which, according to the index mentioned, should have higher hydrogen transfer ability.

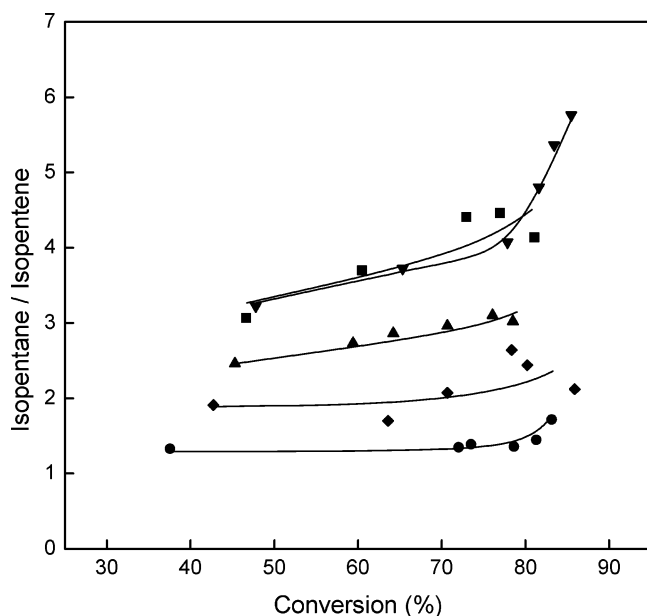
**Isobutane Yield and Selectivity: Effect of Feedstock Properties.** The effect of the feedstock composition on the yield of isobutane over catalysts E-Cat P and E-Cat M is shown in Figure 2. These catalysts were selected because of their very different selectivities to isobutane for a given feedstock. It can be observed that the feedstock composition does not have a significant impact in the case of the catalyst with high isobutane selectivity (catalyst E-Cat M), but it is very important in the case of the catalysts with low isobutane selectivity. The



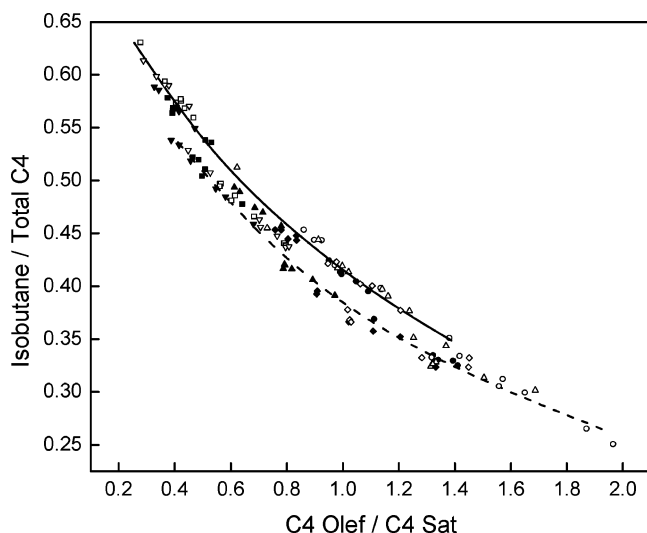
**Figure 2.** Isobutane yield using various catalysts, as a function of VGO conversion, at a temperature of 500 °C, shown via a comparison of different feedstocks. Upright triangular symbols represent catalyst E-Cat P, and inverted triangular symbols represent catalyst E-Cat M. Data for feedstock VGO-B are represented by closed symbols and a solid line; data for feedstock VGO-M are represented by open symbols and a dashed line; and data for feedstock VGO-P are represented by open symbols with a line struck through them and a dash-dotted line.

feedstocks differ in composition: VGO-M and VGO-P both have paraffinic character, whereas VGO-B is mainly aromatic. In the case of catalyst E-Cat P, the higher selectivities observed with VGO-M and VGO-P, in comparison to VGO-B, could be justified, considering the paraffinic quality of those feedstocks. In the case of catalyst E-Cat M, its high activity and hydrogen transfer could attenuate the impact of feedstock composition. The effect of feedstock composition on the yield of isobutane can be analyzed considering the simple description of hydrogen transfer reactions between olefins and naphthenes to yield paraffins plus aromatics. If the feedstock is aromatic, as is the case for VGO-B, those compounds will hinder hydrogen transfer more considerably in the catalysts with low activity for those reactions (catalysts E-Cat O and E-Cat P). In contrast, the catalysts with high hydrogen transfer activity (catalysts E-Cat M and E-Cat D) will not be affected as much. Moreover, this negative impact of aromatic feedstocks was confirmed to be less important at lower temperatures, because, at such temperatures, hydrogen transfer reactions are selectively favored.

**Relationships between Isoparaffins and Iso-olefins.** The relationship between isobutane and isobutylene, as governed by hydrogen transfer,<sup>5</sup> was tracked by observing the relationship between isopentane and isoamylenes, because the mechanisms that control their yields and ratios are homologous.<sup>6,16</sup> For the sake of clarity, only results that were obtained in the conversion of paraffinic VGO-M are shown in Figure 3 at 550 °C, because the information gathered in the other cases is qualitatively similar. It can be observed that the amount of isopentane increases, relative to isoamylenes, as a function of conversion, because of the increasingly higher incidence of hydrogen transfer reactions, which are secondary and consume olefins. Moreover, for all of the catalysts, the lower the temperature, the higher the proportion of isopentane, which is consistent with the impact of temperature on the lower activation energy of hydrogen transfer, in comparison to cracking reactions.<sup>17</sup> Both observations confirm the key role of these reactions in the control of



**Figure 3.** Mass ratio of isopentane to isoamylenes, as a function of conversion, for feedstock VGO-M at a temperature of 550 °C. Symbols: (■) E-Cat D, (●) E-Cat O, (▲) E-Cat P, (▼) E-Cat M, and (◆) E-Cat R.



**Figure 4.** Mass ratio of isobutane to total C4, as a function of the mass ratio of butenes to butanes. Symbol shapes are the same as those presented in Figure 1, except, here, the closed symbols represent feedstock VGO-M and the open symbols represent feedstock VGO-B. The solid line represents data obtained at 550 °C, and the dashed line represents data obtained at 500 °C.

branched saturated/unsaturated light hydrocarbons. It then can be deduced, for a given catalyst, that isobutane is favored against isobutylene at higher conversions and lower temperatures. The observed ranking for this relationship is

$$\text{E-Cat M} \approx \text{E-Cat D} > \text{E-Cat P} > \text{E-Cat R} > \text{E-Cat O}$$

and it must be noted that the ranking is not exactly the same as that which was observed for isobutane selectivity. However, isobutylene as well as other olefins in the C4 group can be hydrogen acceptors, as shown by Cheng et al.,<sup>6</sup> who also estimated that, because of relative cation stabilities, branched olefins are ~16 times more active than linear olefins, thus impacting on the relationship between saturates and unsaturated hydrocarbons. This is confirmed by the fact that similar results are obtained if the analysis is extended to the ratio between butenes and butanes (results not shown).

Another index of the impact of hydrogen transfer on selectivity can be observed in the analysis of the degree of branching in C4 compounds. Corma et al.<sup>7</sup> postulated that bimolecular condensation plus cracking as series reactions lead to a high proportion of C4–C6 branched products. If this occurs, hydrogen transfer would be necessary to promote desorption. Figure 4 shows that there exists a neat relationship between the degree of branching (isobutane) in the products in the C4 group and the hydrogen transfer ability of the catalysts (represented by the ratio of butenes to butanes): the lower the hydrogen transfer ability, the less branching in the products. Note that these facts were observed on five different equilibrium commercial FCC catalysts, with three different VGO feedstocks and at two thermal levels, thus confirming the reliability of this index. The variations with the temperature are consistent with the impact that it has on the relationship between hydrogen transfer and other reactions.

## Conclusions

Methods for the laboratory evaluation of the performance of commercial equilibrium fluidized catalytic cracking (FCC) catalysts can be developed based on the use of the CREC Riser Simulator reactor. Conditions that are typical of the commercial process, in terms of reaction temperatures, catalyst-to-oil ratios, and reaction times can be used to reveal not only the main characteristics of each catalyst, but also some specific evaluation parameters, such as activity and product selectivity and yields. In this way, comparative rankings can be established for conversion, gasoline yield, liquefied petroleum gas (LPG) yield, and individual products yield. In the case of isobutane, it is essentially a primary product in the conversion of vacuum gas oil (VGO). It was shown that activity and hydrogen transfer ability are important catalyst properties that affect isobutane yield. If the catalyst is comparatively less active and has low hydrogen transfer ability, the type of feedstock has a strong impact on isobutane yields: aromatic VGOs lead to lower yields. The impact is lower when very active catalysts with high hydrogen transfer are used. Clearly, complete evaluations (feedstock, catalyst, process conditions) must be performed to predict isobutane yields more safely. This type of test can help in the overall evaluation procedure of the FCC catalyst.

## Acknowledgment

This work was performed with the financial assistance of Universidad Nacional del Litoral, Secretaría de Ciencia y Técnica (Santa Fe, Argentina) (under Project 01-07), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (under Contract No. PIP 6285/05), and Agencia Nacional para la Promoción Científica y Tecnológica (under Project No. PICT00 14-08990).

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Received for review June 27, 2007

Revised manuscript received November 7, 2007

Accepted November 8, 2007

IE070880R