Recycling of Low-Value Hydrocarbon Cuts by Means of Multiple Injections to FCC Units

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The upgrading of a visbreaker naphtha by recycling it into an FCC unit was studied following the approach of multiple injections (with the naphtha in the first one) using a laboratory riser simulator reactor and an equilibrated catalyst. The experimental work comprised three different stages: a study of the crackability of the naphtha under conventional FCC conditions (500–550 °C, CATOIL 6.1, short contact times), a study of the conversion of the naphtha under a regime of high severity (CATOIL 37), and a study of the impact of this injection on the overall FCC operation. Heavy C_7-C_9 olefins and *n*-paraffins are converted, and aromatics and C_4-C_6 *i*-paraffins are the most noticeable products. Even though the RON in the gasoline cut of the products does not change, modifications in the composition are advantageous because heavy olefins and *n*-paraffins are selectively converted. The high-severity regime induces more profound changes in the composition of the gasoline cut that significantly improve the blending properties. More importantly, the first injection would not interfere with the standard feedstock injection, because catalyst properties and performance are not altered, as shown by experiments with coked and regenerated catalyst.

Introduction

The fluid catalytic cracking (FCC) of hydrocarbons is one of the most important petroleum refining processes, because it is not only a major fuel producer but also a supplier of raw materials for a number of downstream processes.¹ FCC technology has changed continuously as a result of economic, environmental, or even political demands. Today, one of the most important concerns is the control of the product profile, an issue that has been addressed by means of innovative or evolutionary developments in catalysts, hardware, and operating conditions or modes.²

A technology with split feed injections was claimed as a method for increasing light olefin yields and gasoline octanes. The concept was based on the observation that low-molecular-weight stocks give higher conversion and gasoline yields when cracked by themselves than when cracked in blends with heavier feedstocks.³ The scheme proposed that low-boiling feed be charged to a bottom injector, while heavier feed is charged to a second, upper injector. The idea also included splitting the same feed into two fractions injected at two different points in the riser,⁴ with the larger fraction to be charged in the first injection point. This concept was studied at the pilot-plant level with commercial feedstocks and at the laboratory level with *n*-hexadecane as a test reactant.⁵ Pilot-plant studies showed that light olefin yields and gasoline octanes can be increased as compared to a base case, and the changes were rationalized as the consequence of a combination of effects: high-severity cracking in the first portions of the riser, quenching of the products of those portions by the second injection, and reduced hydrogen transfer in the upper part of the riser.³

On the other hand, laboratory tests with different split ratios and simulated riser heights for the second

injection⁵ showed that conversions and gasoline yields were equal to or lower than those obtained in standard operation, that the yields of different hydrocarbon groups were essentially unaltered, and that coke yields were always lower. Moreover, important changes were observed in product C_4-C_6 light olefins because, at the same conversion, the split injections increased the selectivities, with more important improvements at lower temperature and higher split ratio, while the influence of the position of the second injection was less important. The shifts were explained as resulting from the partial catalyst deactivation caused by the coke formed during the first step that, more importantly, interfered with hydrogen-transfer reactions in the second step.

Some hydrocarbon streams produced in the refineries are lower-value cuts that, depending on particular conditions, need to be upgraded for further use, such as blending into the gasoline pool. Among them, naphthas from thermal processes such as coking and visbreaking might have some components in excess (for example, linear paraffins or heavy olefins) that might interfere with blending operations.⁶ One option for upgrading low-value cuts is to recycle them into the FCC units, either mixed with the standard feedstock or injected separately at a different point in the reactor. However, the literature related to this subject is very scarce. Straight-run or coker naphthas were chosen for a particular study in which they were injected prior to a standard VGO feedstock;⁷ in this way, considering that the naphthas were a fraction of the primary feed rate, not only the catalyst-to-naphtha ratio, but also the temperature, was very high. The most important consequence was an increase in the LPG yield. It is clear that the composition of the recycled streams, and consequently their crackability, will have an impact on this approach.

It is the objective of this work to study the feasibility of upgrading a visbreaker naphtha by recycling it into

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Table 1. Overall Composition of the Visbreaker Naphtha

fraction	hydrocarbons	wt %
$C_{4^{-}}$	69	1.2
	<i>n</i> -paraffins <i>i</i> -paraffins	21.3 20.7
$C_5 - C_{12}$	olefins	31.5
	aromatics	13.5

the FCC process and, simultaneously, to confirm that operation with multiple injections at different heights in the riser is suited for this option. The experimental approach was developed using a riser simulator laboratory reactor operated for three stages with commercial and test reactants.

Experimental Section

The catalyst used was an equilibrium sample of a commercial octane-type catalyst with rare earths (E-Cat, Vision 418, FCC S.A., Brazil), that was obtained from a sampling device in a running refinery. The unit cell size of this catalyst was 24.23 Å, the zeolite content was 16.9 wt %, the rare earths content was 1.26 wt %, and the specific surface area was 139 m² g⁻¹. The visbreaker naphtha (VN) used as the recycle stream (density = 0.7194 g cm⁻¹; see overall composition in Table 1) was obtained from another refinery. *n*-Hexadecane (Fluka, \geq 99.5 wt %) was used as the test reactant.

The laboratory reactor used, called a riser simulator,⁸ was designed specifically for studies of FCC issues. The basic design concept considers that a small slice of an ideal riser, comprising the mixture of catalyst particles and hydrocarbons that "see" each other while moving along the riser after being put into contact, can be located in a batch reactor with internal recirculation; thus, the residence time and position along the riser are

equivalent to the reaction time in the riser simulator. Then, injections at a given position in an ideal riser reactor can be simulated by injections at different times in the laboratory reactor (see 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 conditions, the reactant is fed through an injection port, and immediately after the reaction time is attained, products are evacuated instantly and analyzed by gas chromatography. Coke yields were determined by means of a temperatureprogrammed oxidation and further methanation procedure.9

The experimental strategy for this work, comprising three different stages, was as follows: step I, conversion of VN, in which the naphtha stream was cracked under "conventional" conditions to study its crackability and observe the main products; step II, cracking of VN under high-severity conditions, that is, simulation of the first portion of an FCC riser, where only the VN would contact the catalyst, under a scheme of two injections of different compositions, with the first feedstock being the naphtha; step III, conversion of the test reactant *n*-hexadecane over catalyst samples that had been previously coked by the conversion of the VN under high-severity conditions, that is, simulation of the upper portion of an FCC riser to determine the impact of the previous naphtha conversion, by comparison with the results of the reaction of n-hexadecane under standard conditions on regenerated catalyst. A schematic representation of the approach and the experimental conditions used in each of the stages are presented in Figure 2 and Table 2 respectively, where CATOIL refers to the mass catalyst-to-reactant ratio. Unless otherwise stated



Figure 1. Riser simulator reactor: (a) basic design concept, (b) schematic representation.

Table 2.	Experimental	Conditions for	or the	Various	Step	S
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step	feedstock	<i>T</i> (°C)	catalyst mass (g)	volume injected (mL)	reactant initial partial pressure	CATOIL	reaction time (s)
Ι	VN	500 - 550	0.8	0.18	p_0	6.1	3, 6, 9, 12
II	VN	550	0.6	0.06	$p_0/3$	13.9	3, 5, 7
		550	0.8	0.06	$p_0/3$	18.5	3, 5, 7
		550	1.0	0.06	$p_0/3$	23.2	3, 5, 7
		550	1.2	0.06	$p_0/3$	27.8	3, 5, 7
III	VN ^a	550	0.8	0.03	$p_0/6$	37.0	3
	$n - C_{16}^{b}$	550	0.8	0.17	$p_{c16,0}$	6.1	3, 6, 9, 12

^a Five identical experiments to collect coked catalyst. ^b Two series of identical experiments performed with coked and regenerated catalyst.



Figure 2. Schematic representation of the experimental approach.

(e.g., some experiments in step III), all of the experiments were performed with regenerated catalyst.

Reaction products were analyzed on-line by gas chromatography using a Hewlett-Packard 6890 Plus chromatograph and a capillary column (HP-1 cross-linked methyl silicone gum, 25-m length, 200- μ m i.d., and 0.33- μ m film thickness). The research octane numbers (RONs) of the various cuts were assessed by means of Anderson's method.¹⁰

Results and Discussion

Results are presented and discussed in view of the experimental steps defined above. It should be noted that, for these experiments with naphtha feedstock, conversion cannot be defined in the usual way, because many hydrocarbons that are products from the conversion of the naphtha are in the same range of molecular weights as the feedstock; that is, interconversion is significant. This fact can be clearly exemplified by the increase in *i*-paraffins and aromatics compounds in the C_5-C_{12} range (see below). Some representative indexes could be used to characterize feedstock conversion; for example, the total yield of hydrocarbons with four or fewer carbon atoms per molecule, C4-, which are not present in meaningful amounts in the reactant and which are formed approximately proportionally to the conversion of these complex hydrocarbon mixtures.^{11,12} However, the results are generally expressed as a function of reaction time.

Step I. The first step of the research was dedicated to the study of the performance of the naphtha as a feedstock under typical commercial FCC conditions (see Figure 2). The yield of gasoline showed a decreasing profile as a function of reaction time, reaching values of 77.9% at 500 °C and 71.2% at 550 °C, at the reaction time of 9 s. Indeed, these decreasing profiles indicate to some degree the conversion of the naphtha. It is to be noted, then, that a substantial mass fraction of the naphtha, with important changes in composition that are discussed below, would remain inside the FCC



Figure 3. Yields of aromatics compounds as a function of reaction time. Feed, VN; CATOIL, 6.1; T = 550 °C. Symbols: (**■**) benzene, (**●**) toluene, (**▲**) C₈, (**▼**) C₉, (**♦**) C₁₀-C₁₂.

naphtha cut and would contribute to the gasoline pool. At a given reaction temperature, for example 500 °C, most of the other products are LPG (about 17%), with the coke and dry gas yields amounting to 4.5 and 0.7%, respectively. When the temperature is increased to 550 °C, the yields of these hydrocarbon groups shift accordingly; that is, the dry gas, LPG, and coke yields increase, and the gasoline yield decreases. Moreover, it can be observed that the yields of coke are similar to those obtained in the conversion of much heavier feedstocks, such as vacuum gas oil, thus suggesting a significant coke-forming trend for VN.

The various hydrocarbon types in the C_4-C_{12} products exhibit clearly different responses. The overall behaviors as a function of reaction time indicate that, in the case of the 550 °C reaction temperature, the yield of iparaffins increases from 20.7 to 31.3%, the yield of aromatics increases from 13.5 to 19.3%, the yield of olefins decreases significantly from 32.0 to 11.2%, the yield of naphthenics decreases from 11.8 to 5.6%, and the yield of *n*-paraffins remains approximately constant at 21.5%. Nevertheless, important changes can be observed according to the hydrocarbon molecular weights. For the case of 550 °C, then, it can be observed in Figure 3 that the overall increase in yield for aromatics is mainly due to toluene and C8 compounds. For i-paraffinic compounds, it can be seen in Figure 4 that the most substantial changes are the increase in the yield of C4-C₅ hydrocarbons, particularly isobutane, together with the consumption of C_8-C_9 compounds. The same trends are observed for *n*-paraffins (see Figure 5). The high reactivity of olefins, particularly those with higher



Figure 4. Yields of C_4-C_{12} *i*-paraffins as a function of reaction time. Feed, VN; CATOIL, 6.1; T = 550 °C. Symbols: (\triangledown) C_4-C_5 , (\blacksquare) C_6 , (\spadesuit) C_7 , (\blacktriangle) C_8-C_9 , (\bigstar) $C_{10}-C_{12}$.



Figure 5. Yields of C_4-C_{12} *n*-paraffins as a function of reaction time. Feed, VN; CATOIL, 6.1; T = 550 °C. Symbols as in Figure 4.

molecular weight, C_7-C_9 , which, moreover, are the most important olefinic components of VN, is clearly shown in Figure 6. In contrast, C_4-C_5 olefins are reaction products. Naphthenics (results not shown) increase slightly in the C_5-C_6 range and decrease in the C_7-C_{12} range. All of these observations, together with the important LPG yields, are consistent with the overall expected reaction mechanisms of the cracking of complex hydrocarbon mixtures^{13,14} under the experimental conditions used. In effect, for example, the important increase in C_4-C_6 *i*-paraffins and *i*-olefins is probably a consequence of the cracking of olefins with higher molecular weights and paraffins in the C_7-C_{10} range.

The quality as a fuel of the product C_5-C_{12} cut can be analyzed in terms of its composition. In that sense, two factors are negative if the blending characteristics of the naphtha feedstock are considered: it has a low RON of 74.2 and a high concentration of relatively heavy olefins and linear paraffins. The RON of the C_5-C_{12} cut formed after different reaction times is quite steady around the value for VN (74.2). The constant RON value can be explained in view of the changes in the concen-



Figure 6. Yields of C_4-C_{12} olefins as a function of reaction time. Feed, VN; CATOIL, 6.1; T = 550 °C. Symbols as in Figure 4.



Figure 7. Olefinicity of C₄ group as a function of conversion. Feed, VN; CATOIL, 6.1; $T = (\bullet)$ 500 and (\blacktriangle) 550 °C.

trations of the various hydrocarbon types and their relative contributions to fuel's antiknock properties. For example, overall, for the particular case of the experiment at 550 °C and a 9-s reaction time, aromatics increase 80% and *i*-paraffins 40%, whereas olefins decrease 60% and naphthenics 30%. Although this indicates that gains in RON are not obtained, the important changes in composition mentioned above have to be considered, because the blending performance of the cut is much improved after the significant reductions in heavy olefins and *n*-paraffins. Similar results in terms of the dry gas, LPG, and gasoline yields and changes in the composition of the liquid fraction were reported by Fernández et al.¹⁵ for the conversion of a visbreaker naphtha.

Because of their high demand, it is interesting to assess how much light olefin is formed from VN. As an example that can be considered representative of the C_4-C_6 range, the olefinicity of the C_4 group (C_4 olefins/ C_4 total) is shown in Figure 7 as a function of conversion (defined as the yield of C_4 -hydrocarbons). The "initial" value of 0.43 should not be taken into account because of the very low amount of C_4 hydrocarbons present in



Figure 8. Yields of (\blacksquare) dry gas, (\bullet) LPG, (\blacktriangle) gasoline, and (\checkmark) coke as a function of reaction time. Feed, VN; CATOIL, (-) 13.9 and (-) 27.8; T = 550 °C.

the feedstock. It can be seen that olefinicity decreases as a function of conversion, a fact that can be ascribed to the increasingly higher incidence of secondary hydrogen-transfer reactions,¹⁴ and that it increases with reaction temperature, because of the selective increase in cracking reactions.^{13,16} For this C₄ group, olefinicity ranges from about 0.34 to 0.23, which compares negatively with average values of 0.60 to 0.70 in commercial VGO cracking.¹⁷ This fact suggests a decrease in the light olefins yield when a VN is recycled into an FCC unit.

Step II. This experimental stage studied the conversion of VN in the high-severity, short-contact-time regime that it would face if it were injected at a position prior to the standard one in this recycling approach (see Figure 2). It can be anticipated that, because catalyst circulation is to be kept constant, CATOIL will be very high for the naphtha. For example, for a recycle ratio of 15% of the VN in the total feedstock, CATOIL would be about 40. VN would have a relatively low partial pressure, which was also simulated in the laboratory. Moreover, the temperature at this point would be higher because of the contact with catalyst coming from the regenerator, a fact that was not investigated in this study.

The yields of the most important hydrocarbon groups, dry gases, LPG, gasoline, and coke, are shown in Figure 8 as a function of reaction time. For the sake of clarity, the lowest and highest values of CATOIL used (13.9 and 27.8, respectively) are included. As expected, the yields of dry gas, LPG, and coke increase as a function of both reaction time and CATOIL. In contrast, the gasoline yield decreases as a function of reaction time and CATOIL, indicating that feedstock conversion increases. Although a direct comparison between this laboratory study and actual commercial FCC operation with VGO under standard conditions is not possible, these results suggest that an overcracking regime, that is, excessive naphtha conversion to lighter products, is not certain. Moreover, in the case of recycling a visbreaker naphtha under these conditions, about 65% of the VN would remain in the FCC naphtha cut.

The increase in coke yields is perceptible when compared with the yields observed at conventional



Figure 9. Yields of (\bullet) *n*-paraffins, (\blacktriangle) *i*-paraffins, (\blacklozenge) olefins, (\blacktriangledown) naphtenics, and (\blacksquare) aromatics in the range C₄-C₁₂ as a function of reaction time. Feed, VN; CATOIL, (-) 13.9 and (- -) 27.8; *T* = 550 °C.

Table 3. Yields of Dry Gas, LPG, Gasoline, and Coke Observed in Steps I and II $\,$

		reaction		yield	(wt %)	
step	CATOIL	time (s)	dry gas	LPG	gasoline	coke
Ι	6.1	9	2.0	22.0	71.2	4.8
II	27.8	7	2.3	21.1	65.4	11.1

CATOIL values, a fact that is to be expected with the much higher severity used in this stage. The highest coke yield amounts to 11% when the CATOIL ratio is 27.8. The eventual consequences of this issue should be revised if the multiple injections method is to be applied for recycling a visbreaker naphtha to an FCC unit (see below, step III).

Although the yields of dry gas and LPG are similar to those observed in step I, where a much lower CATOIL was used (see Table 3), it has to be considered that the reactant partial pressure in step II is 3 times lower, and because the cracking of complex hydrocarbon mixtures shows reaction orders that are close to 2,¹⁸ the effect of reactant partial pressure on the chemical reaction rate and yields is more significant. Then, on a comparative basis, the conversion and the variations in the yields of various groups should be considered much higher in step II, under a high-severity regime. For the examples in Table 3, the shorter reaction time also supports this evidence.

The overall yield profiles of the various hydrocarbon types as a function of reaction time are consistent with the observations in step I, that is, decrease in the yields of olefins and naphthenics, an increase in the yield of *i*-paraffins, and essentially steady profiles in the cases of *n*-paraffins and aromatics (see Figure 9). It is to be noted that xylenes and C_9 aromatics now appear to be affected by the high severity and lower reactant partial pressure and do not increase their yields as a function of reaction time (data not shown). The effect of increasing CATOIL is moderate, as can be observed in Figure 9. However, the hydrocarbons in the groups showed different behaviors according to their molecular size; in that respect, the variations were qualitatively the same as those observed in step I (see Figures 3–6).

The RON of the gasoline cut in the products did not change as compared to that for the unreacted naphtha, according to the variations in composition, and the influence of CATOIL is negligible, because the RON values are all very close to 74.2. However, changes in composition (e.g., decrease in heavy olefins) are more pronounced with these high CATOIL values. For example, on average, a comparison with the unreacted naphtha shows that the gasoline cut in the product has 70% less C_8-C_{10} olefins, 170% more C_5-C_7 *i*-paraffins, and 40% more aromatics. Thus, it is confirmed that recycling a visbreaker naphtha under the conditions of step II significantly improves its blending potential.

As also expected, the olefinicity in C_4-C_6 groups is higher than that observed in experiments with typical CATOIL values. For example, on average, the values observed at 20% conversion (C_{4^-} yield) for the high CATOIL and standard operations were 0.36 and 0.34, 0.32 and 0.28, and 0.28 and 0.22 for C_4 , C_5 , and C_6 groups, respectively.

Step III. This stage is devoted to ascertaining eventual changes in the catalyst properties and behavior under an operating scheme of multiple injections of different compositions, with the first injection being the recycled visbreaker naphtha (see Figure 2). A test reactant, *n*-hexadecane, was used instead of a commercial feedstock in the second injection. The VN stream was assumed to be about 15% of the total feed, and the CATOIL value and initial reactant partial pressure were adjusted accordingly to generate coked catalyst that was used to convert *n*-hexadecane and compare the results with those of the same reactant over regenerated catalyst under the same conditions.

The catalyst was contacted with the VN for 3 s at 550 °C, resulting in a coke deposition on the catalyst of 0.22%, corresponding to a coke yield of about 8%. It has been shown that equilibrium FCC catalysts maintain a certain activity level after being coked and that coke deposition along the riser is very fast because, after about 10% of the total length, coke increases very slowly. MAT activities after this position remain stable at about 68.¹⁹ Regenerated catalysts that had MAT activities of 69, 73, and 74 had corresponding spent-catalyst MAT activities of 58, 63, and 62 with coke loadings of 0.75, 0.70, and 0.78 wt %, respectively.²⁰ Another study²¹ showed that 0.75 wt % coke on the catalyst induced a drop in MAT activity of about 19%. Coke loads of 0.59% converted 37% of a VGO feedstock in a riser simulator reactor, whereas the regenerated catalyst converted 54% under the same conditions.¹² In view of these results, it is expected that the loss of activity due to the coke load generated by the first injection of VN should be relatively low.

Figure 10 shows the yields of dry gases, LPG, and gasoline as a function of reaction time observed with both the naphtha-coked and regenerated catalysts. It can be seen that the specific yield profiles are essentially the same; that is, the two catalysts behave in the same way provided the conditions are the same. This observation suggests that the effect of the coke load due to contact with the VN for 3 s (0.22% coke on catalyst) is negligible. Indeed, a very small difference was observed in the yields of dry gases.

The comparison of coke yields deserves special consideration. They are shown in Table 4, where it can be seen that the amount of coke produced by the previously coked catalyst, that is, the coke formed on top of that produced by the naphtha injection, is always lower than the amount of coke produced by the regenerated cata-



Figure 10. Yields of (**■**) dry gas, (**●**) LPG, and (**▲**) gasoline as a function of reaction time. Feed, *n*-hexadecane; CATOIL, 6.1; closed symbols, regenerated catalyst; open symbols, coked catalyst; T = 550 °C.

Table 4. Coke Yields in the Conversion of n-Hexadecaneover Regenerated and Naphtha-Coked Catalysts^a

reaction time (s)	coke yield (wt %)		
	regenerated catalyst	naphtha-coked catalyst	
3	1.09	0.31	
6	1.92	0.64	
9	2.07	0.79	
12	2.19	1.04	

^{*a*} T = 550 °C, CATOIL = 6.1.

lyst. A simple calculation shows that, at a 12-s reaction time, the standard operation (single injection, regenerated catalyst) forms about 8% less coke than the mode with two injections. In general terms, this additional coke with multiple injections should not represent a problem for the operation of FCC units; however, present technology is able to manage high coke production, such as that found in residue cracking,²² with different solutions. Moreover, it has to be considered that the test reactant used in step III in these experiments has a very low coking trend and, consequently, the impact of the coke formed by the recycle stream in the first injection is undoubtedly more important. In contrast, it can be predicted that, in the case of commercial feedstocks such as VGO that yield much more coke than *n*-hexadecane, the incidence of coke formation would be much lower.

The fuel quality of the gasoline in the reaction products is not affected either, as the RON is 90.9 in the case of the regenerated catalyst and 90.0 in the case of the coked catalyst.

Another manifestation of the same behavior on the two catalysts was verified by the fact that the different types of hydrocarbons followed the same yield curves as a function of time on both catalysts (results not shown). However, it is understood that the performance of coked catalysts clearly depends on the particular catalyst properties.¹²

Conclusions

It was shown that it is possible to upgrade a visbreaker naphtha by recycling it into an FCC unit using multiple injections, with the naphtha injected before the conventional feedstock. In that way, a very severe contact regime (CATOIL of about 40) is assured for the naphtha, and changes in the gasoline cut are produced that are positive, mainly from the standpoint of fuel composition. Heavy C_7-C_9 olefins and *n*-paraffins are converted, and aromatics and C_4-C_6 *i*-paraffins are the main products. *n*-Hexadecane tests on both regenerated and naphtha-coked catalysts showed that the performance of the catalyst is not altered by the first injection and that the increase in coke yield would be manageable. The laboratory reactor riser simulator was confirmed to be a useful tool for FCC studies.

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