

PETROCHEMICAL PROMOTERS IN CATALYTIC CRACKING

Maria-Elizabeth Gómez*¹, Clemencia Vargas¹ and Javier Lizcano²

¹ Ecopetrol S.A - Instituto Colombiano del Petróleo, A.A. 4185 Bucaramanga, Santander, Colombia

² UT TIP - Petrolabin, Piedecuesta, Santander, Colombia

e-mail: mariael.gomez@ecopetrol.com.co

(Received May 5, 2009; Accepted October 10, 2009)

This study is based on the current scheme followed by a refinery with available Catalytic Cracking capacity to process new feedstocks such as Straight Run Naphtha and Naphthas from FCC. These feedstocks are of petrochemical interest to produce Ethane, Ethylene, Propylene, i-Butane, Toluene and Xylene.

To evaluate the potential of these new streams versus the Cracking-charged Residues, it was performed a detailed chemical analysis on the structural groups in carbons [C1-C12] at the reactor product obtained in pilot plant. A catalyst with and without Propylene - Promoter Additive was used.

This study analyzes the differences in the chemical composition of the feedstocks, relating them to the yield of each petrochemical product. Straight Run Naphthas with a high content of Naphthenes, and Paraffines n[C5-C12] and i[C7-C12] are selective to the production of i-Butane and Propane, while Naphthas from FCC with a high content of n[C5-C12] Olefins, i-Olefins, and Aromatics are more selective to Propylene, Toluene, and Xylene.

Concerning Catalytic Cracking of Naphthas, the Additive has similar selectivity for all the petrochemical products, their yields increase by about one point with 4%wt of Additive, while in cracking of Residues, the Additive increases in three points Propylene yield, corresponding to a selectivity of 50% ($\Delta C3 = / \Delta LPG$).

Keywords: propylene, catalytic cracking, i-butane, ethylene, naphthas, petrochemicals, Residues, ZSM-5.

* To whom correspondence may be addressed

El presente estudio se basa en el esquema actual de una refinería con capacidad disponible en Cracking Catalítico, para procesar nuevas cargas tales como Naftas Vírgenes y Naftas de URC (Unidad de Ruptura Catalítica), las cuales son de interés Petroquímico en productos tales como Etano, Etileno, Propileno, i-Butano, Tolueno y Xilenos.

Para evaluar el Potencial Petroquímico de estas corrientes frente al de los Residuos cargados a Cracking, se realizó un análisis químico detallado de los Grupos Estructurales de los Carbonos [C1-C12] en el producto reactor obtenido en planta piloto, utilizando un catalizador con y sin Aditivo promotor de Propileno.

El estudio analiza las marcadas diferencias en la composición química de las cargas, y las relaciona con los rendimientos de cada uno de los productos petroquímicos. Las Naftas Vírgenes con mayor contenido de Naftenos y de Parafinas n[C5-C12] e i[C7-C12] son selectivas hacia la producción de i-Butano y Propano, mientras que las Naftas de URC con altos contenidos de n[C5-C12] Olefinas, i-Olefinas, y Aromáticos son más selectivas hacia Propileno, Tolueno y Xilenos.

En el craqueo de las Naftas, el Aditivo tiene la misma selectividad para todos los productos petroquímicos, sus rendimientos incrementan en valores cercanos a un punto con 4% peso de Aditivo; mientras que en el craqueo de los Residuos el aditivo incrementa en 3 puntos el rendimiento de Propileno, lo que corresponde a una selectividad del 50% ($\Delta C3 = / \Delta LPG$).

Palabras Clave: propileno, craqueo, i-butano, etileno, naftas, petroquímicos, residuos, ZSM-5

NOMENCLATURE

<i>LCO</i>	Light Cycle Oil
<i>C/O</i>	Catalyst / Oil ratio
<i>DCR</i>	Davison Circulating Riser
<i>FCCU</i>	Fluid Catalytic Cracking Unit
<i>LPG</i>	Liquefied Petroleum Gas
<i>H₂</i>	Hydrogen
<i>iC₄</i>	i-Butane
<i>iC₅</i>	i-Pentane
<i>i[C₄-C₆]</i>	i-Paraffines C ₄ -C ₆
<i>i[C₇-C₁₂]</i>	i-Paraffines C ₇ -C ₁₂
<i>iP</i>	i-Paraffines
<i>Naft</i>	Naphthenes
<i>nC₂</i>	Ethane
<i>C₂=</i>	Ethylene
<i>nC₃</i>	Propane
<i>nC₃=</i>	Propylene
<i>nC₄</i>	Butane
<i>n[C₁-C₄]</i>	n-Paraffines C ₁ -C ₄
<i>n[C₂-C₄]Olefins</i>	n-Olefins C ₂ -C ₄
<i>n[C₅-C₁₂]</i>	n-Paraffines C ₅ -C ₁₂
<i>n[C₅-C₁₂]Olefins</i>	n-Olefins C ₅ -C ₁₂
<i>nP</i>	n-Paraffines
<i>PIANO</i>	Paraffines, i-Paraffines, Aromatics, Naphthenes and Olefins
<i>SimDis</i>	Simulated distillation
<i>UVVIS</i>	Visible ultraviolet
<i>VGO</i>	Vacuum Gas Oil
$\Delta C_3= / \Delta LPG$	Propylene Selectivity with Additive: [C ₃ =increase] / [LPG increase]

INTRODUCTION

The operational constraints of a Fluid Catalytic Cracking Unit (FCCU) to produce certain products not only depend on its technology or operating conditions, but also on the characteristics and quality of the feedstock that determine its potential to produce the desired product.

The objective of this study is to determine and compare the petrochemical potential of different types of Naphthas for a Refinery that has four units of different FCCU technology, processing different type of feedstocks, as follows: one Model IV processing Vacuum Gas Oil (VGO), two Universal Oil Product Units (UOP) and one Orthoflow Unit processing a mixture of Residues with VGO, and Vacuum Bottoms with or without further hydrotreatment.

The products of interest are Ethane, Ethylene, Propylene, i-Butane, Toluene and Xylene. Ethane is pyrolyzed and converted in Ethylene. The Propane-Propylene current is separated in a splitter and the Propylene is sent to a polymerization plant, while i-Butane is required as a feedstock for alkylation. The current scheme of the Refinery includes the production of Motor Gasoline and therefore, there are no facilities to separate the Aromatic fraction. This fraction can be separated by applying the process patented by Timken, H. K. C., & Angevine, P. J. (1997) consisting of Naphtha hydrotreatment to eliminate sulfur, followed by the recovery of the Aromatic fraction by distillation. This process co-produces Naphthas with low-sulfur and relatively high octane.

THEORETICAL FRAMEWORK

The reactions occurring in the cracking of Naphtha are less complex than those involved in the cracking of heavy oil. Nevertheless, they involve hundreds of compounds interacting in thousands of reactions (Yang, *et al.* 2008). Based on their decreasing reactivity, these reactions are usually grouped as follows (Wang, L., Yang, B., & Wang, Z., 2005):

Olefins > Aromatic Side Chains > i-Paraffines > Naphthenes > n-Paraffines >> Aromatic Rings.

Studies conducted on catalytic cracking of Gas Oil with catalysts using Propylene Additive ZSM-5 (Zhao, X., & Harding, R. H. 1999) demonstrated that the yield of Olefins induced by the Additive decreases with the content of Naphthenes in the feedstock. This behavior is attributed to the fact that Naphthenes participate in the hydrogen-transfer reactions that saturate Olefins. It is therefore concluded that the Additive effect is maximized when catalysts of low activity in hydrogen transfer reactions are used. These catalysts are characterized by the low density of acid sites and low content of rare earth elements. Regarding the catalytic cracking of Naphtha from FCC, the work done by Hollader, M. A., *et al.* (2002) concludes that the only significantly reactive compounds in Naphtha from FCC are the olefins with more than 6 atoms of carbon. It is also demonstrated that bimolecular reactions of hydrogen transfer occur on the catalyst and not on the Additive. By contrast, the Additive with smaller pore size promotes monomolecular reactions only to produce light olefins. It is important to understand how Naphtha composition can affect product selectivity during catalytic cracking reactions. Therefore, the approach in this study is to analyze the behavior of each type of hydrocarbon in detail.

EXPERIMENTAL DEVELOPMENT

The industrial Naphthas selected for this study were: Paraffinic and Naphthenic Naphthas from atmospheric distillation and Naphthas from the 4 FCCUs (Table 1).

All Naphthas and Residues from each Unit were evaluated in the pilot plant in a broad operating window, using different C/O severities, within the operating restrictions of the industrial plant. Reaction temperature was 545°C (1000°F) for Naphthas and 525°C (977°F) for Residues. An industrial equilibrium catalyst was used in all cases.

Additionally, in the case of Naphtha, the effect of the Propylene-Promoter Additive, ZSM-5, was evaluated by using a concentration of 4%, and for Residues 2, 4, and 6%.

Table 1. Quality of Residues and Naphthas to Pilot Plant

	RESIDUES			NAPHTHA							
	ModIV	Ortho	UOPII	Naphthenic	Paraffinic	ModIV-		UOPII-		Ortho-	UOPI
						DBP	Liv	Liv	Pdt	Pdt	Liv
°API	20,4	19,5	19,6	53,2	50,1	52,8	60,0	60,3	58,6	52,3	62,3
CCR, %wt	0,7	2,5	1,9	-	-	-	-	-	-	-	-
SimDis	D-5307,%wt, °F			D-3710,%vol, °F							
5%	381	410	407	188	99	87	84	84	80	89	85
30%	764	792	799	240	193	208	129	110	111	187	110
50%	833	885	892	269	219	278	200	183	196	255	181
95%	1038	-	-	355	371	423	410	355	385	429	338
UVVIS (%wt)											
Total Aromatics	15,0	15,5	14,8								
Mono Aromatics	4,6	4,6	5,1								
Di-Aromatics	3,7	3,6	3,2								
Tri-Aromatics	3,8	3,7	3,3								
Tetra+ Aromatics	2,9	3,6	3,2								
SARA (%wt)											
Saturateds	47,9	43,1	44,1								
Aromatics	44,7	49,3	48,9								
Resins	5,0	7,6	7,0								

Note: UVVIS and SARA analysis are not applied to Naphtha.

ModIV-DBP: Model IV Low Pressure Distillate
 ModIV-Liv: Model IV Light Naphtha
 UOPII-Liv: UOPII Light Naphtha
 UOPII-Pdt: Total Naphtha from UOPII
 Ortho-Pdt: Total Naphtha from Orthoflow
 UOPI-Liv: UOPI Light Naphtha

Experimental Equipment

Pilot Plant. All feedstocks were evaluated in a continuous Davison Circulating Riser (DCR). The unit operates with 3,3 kg of catalyst that continuously reacts and regenerates itself. The operation was carried out maintaining an isothermal profile along the Riser, with a feed flow of 0,8 kg/h.

Gas Chromatograph. Gases were analyzed in an ANGILENT 6890 model chromatograph, following the standard UOP-539, with a repeatability reported by the laboratory of $\pm 0,014\%$ vol, on average for each compound. The liquid product was characterized using two methods: the first method consisted of the simulated distillation described in ASTM D-7213 where the product was separated into three fractions as follows: Naphtha (<430°F), LCO (430-650°F) and Slurry (>650°F); the second is PIANO (Paraffines, i-Paraffines, Aromatics, Naphthenes and Olefins) as

described by ASTM D-6729, that separates all compounds less than or equal to C12, with a repeatability of $\pm 0,087\%$ wt on average for each compound reported by the laboratory. Coke yield was calculated from the composition of the flue gas analyzed following the ASTM D-1945, with a repeatability reported by the laboratory of $\pm 0,035\%$ vol. on average for each reported compound.

RESULTS

The results discussed in this study are PIANO of pilot plant feedstocks (FCC and Straight-run Naphthas), Chromatographic and PIANO reports from the pilot plant effluents. These results are normalized through a mass balance and reported in Table 2 as reactor products.

Table 2. Pilot Plant Yields (%wt) from Catalytic Cracking of Naphthas and Residues, with and without ZSM-5 Additive.

Severity C/O	PIANO NAPHTHA FEEDSTOCK				yields C1-C12 %wt										
	Naph-thenic	Para-ffinic	ModIV-Liv	UOPII-Pdt	NO ADDITIVE					WITH ADDITIVE 4%wt					
					Naph-thenic	Para-ffinic	ModIV-Liv	UOPII-Pdt	Residue UOPII	Naph-thenic	Para-ffinic	ModIV-Liv	UOPII-Pdt	Residue UOPII	
-	-	-	-	15					6	15					6
Paraffines	42,2	56,7	42,0	28,4	43,1	51,0	43,5	33,4	16,0	43,3	50,2	41,2	35,1	15,0	
n-Paraffines	10,5	22,5	7,0	5,7	16,4	23,5	12,9	9,8	5,7	18,0	23,8	12,8	11,2	6,2	
n[C1-C4]	0,1	-	0,2	0,5	9,1	8,9	7,0	5,1	4,4	11,5	10,1	7,5	6,3	4,6	
n[C5-C12]	10,4	22,5	6,8	5,2	7,3	14,6	5,9	4,7	1,3	6,5	13,7	5,3	4,9	1,6	
nC1	-	-	-	-	1,1	1,0	1,6	1,3	1,6	1,4	1,1	1,6	1,4	1,5	
nC2	-	-	-	-	0,6	0,6	0,7	0,7	1,2	0,8	0,7	0,9	0,8	1,2	
nC3	-	-	-	-	5,0	4,9	3,2	1,7	1,1	6,4	5,6	3,5	2,6	1,4	
nC4	-	-	-	-	2,4	2,4	1,5	1,4	0,5	2,9	2,7	1,5	1,5	0,5	
i-Paraffines	31,7	34,2	35,0	22,7	26,7	27,5	30,6	23,6	10,3	25,3	26,4	28,4	23,9	8,8	
i[C4-C6]	1,5	8,4	18,6	11,5	18,6	19,4	23,8	19,1	5,0	19,0	19,0	22,4	19,1	4,7	
i[C7-C12]	30,2	25,8	16,4	11,2	8,1	8,1	6,8	4,5	5,3	6,3	7,4	6,0	4,8	4,1	
iC4	-	-	-	-	9,1	8,1	5,4	3,8	2,0	10,3	8,4	5,7	4,8	2,3	
iC5	0,3	1,7	12,6	7,7	7,0	6,1	12,6	11,0	1,5	6,5	5,7	11,7	10,4	1,2	
Olefins	7,5	1,3	20,8	33,7	17,8	17,2	17,1	20,7	25,6	17,0	17,9	18,0	20,4	28,4	
n-Olefins	0,3	0,1	5,9	10,4	12,7	13,9	13,1	15,8	15,3	12,5	14,8	14,6	16,4	19,0	
n[C2-C4]Olefins	-	-	0,2	1,3	11,9	13,4	11,9	14,1	11,9	11,9	14,1	13,7	15,7	16,6	
n[C5-C12]Olefins	0,3	0,1	5,7	9,1	0,8	0,5	1,2	1,7	3,4	0,6	0,7	0,9	0,7	2,4	
nC2=	-	-	-	-	1,5	1,6	1,6	1,5	1,2	2,0	1,9	2,0	2,2	1,6	
nC3=	-	-	-	-	6,4	7,5	6,4	7,1	5,2	6,6	7,8	7,5	8,4	8,4	
i-Olefins	4,2	1,2	12,0	17,9	3,7	2,5	3,4	4,2	7,3	3,3	2,3	2,8	3,4	6,4	
Naft-Olefins	3,0	-	2,4	4,3	1,2	0,6	0,4	0,5	2,2	1,1	0,6	0,4	0,5	2,3	
di-Olefins	-	-	0,5	1,1	0,2	0,2	0,2	0,2	0,8	0,1	0,2	0,2	0,1	0,7	
Aromatic	15,7	13,2	26,1	29,7	24,5	19,1	27,8	33,5	15,9	26,9	20,3	28,2	33,2	14,9	
Benzene	0,3	1,1	0,6	0,9	1,4	1,7	1,4	1,5	0,4	1,5	1,7	1,6	1,9	0,4	
Toluene	2,5	3,1	2,5	4,5	6,2	5,8	6,3	7,9	1,7	6,5	5,9	6,8	8,9	1,8	
Xylenes	6,2	3,3	4,6	7,4	9,5	6,4	8,9	10,8	3,2	9,8	6,5	9,2	11,0	3,0	
Naphthenes	34,6	28,8	11,1	8,2	10,0	9,1	3,9	3,6	3,7	7,4	7,3	3,8	3,1	3,3	
REACTOR PRODUCT STANDARD CUT															
H ₂					0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,2	0,1	0,1	
Total Dry Gas					3,2	3,2	3,9	3,9	4,4	4,2	3,7	4,5	4,4	4,7	
Total LPG					26,9	27,2	20,4	20,4	14,3	29,5	28,9	22,4	22,4	19,2	
Naphtha (C5-430°F)					65,3	66,0	68	68	42,9	60,9	63,1	64,3	65,0	37,7	
LCO (430-650°F)					1,8	1,2	3,3	3,3	18,3	1,8	1,5	3,5	4,1	18,2	
Slurry (>650°F)					0,6	0,5	1,0	1,0	14,7	0,7	0,6	1,4	1,2	14,7	
Coke					2,1	1,8	3,3	3,3	5,3	2,8	2,1	3,7	2,8	5,4	
Total					100	100	100	100	100	100	100	100	100	100	
Additive Selectivity ($\Delta C3= / \Delta LPG$)					-	-	-	-	-	-	-	55%	45%	65%	

Table 2 shows the most representative results of this study. This provides a more general outlook of the changes in structural composition resulting from the cracking reactions.

LCO, Slurry, and Coke are also produced in the catalytic cracking of Naphtha in yields between 4 and 9%. This usually comes from aromatic dehydrogenation and condensation reactions (Table 2). Naphthas from FCC produce a higher yield of these products which, in turn, is related to its greater Aromatic content.

For the cracking of Residues, the sum of LCO, Slurry, and Coke yields is nearly 40%. This means that the remaining 60% corresponds to the C1- C12 fraction analyzed in detail at the top of Table 2.

Since these Naphthas are injected into the Riser bottom in smaller proportions as compared to Residue, Table 2 shows the comparison of Reactor Product yields of Naphthas and Residues at different C/O severities: 15 for Naphthas and 6 for Residues like the Industrial Plant.

ANALYSIS OF RESULTS

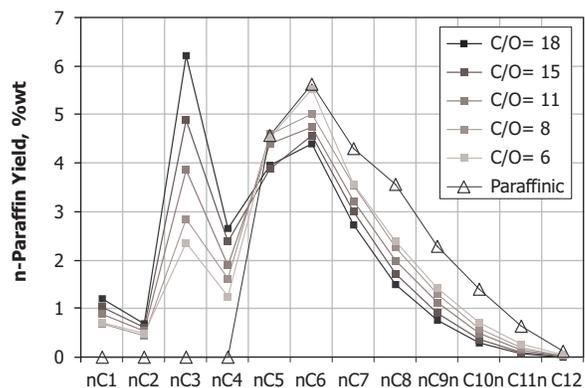
Since the potential of petrochemical products are within Naphtha, LPG and dry gas streams, the analysis of results focuses on the detailed study of compounds C1-C12, which are grouped in the following families: Paraffines, Olefins, Aromatics and Naphthenes.

n-Paraffines

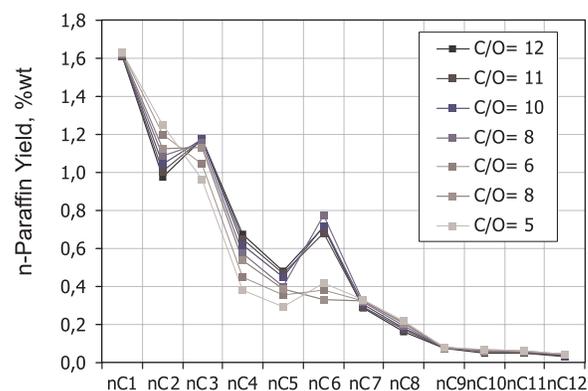
Figure 1a shows the yield profile of n-Paraffines obtained by the catalytic cracking of Paraffinic Naphtha. Similar profiles were observed with all the studied Naphthas. The yield of nC3 increases significantly and is sensitive to variations in C/O severity. The same is observed with all the other Naphthas.

Regarding Naphtha and Residues (Figure 1), Methane and Ethane yields are between 0,5 and 1,5% and are due to thermal cracking, therefore, these products do not depend on the type of Naphtha and are not significantly affected by the severity or the Additive (Table 2).

Even though nC3 is not directly a petrochemical product for this refinery, it is important to be considered when the objective of FCC is nC3 =, since greater nC3 production results in increased congestion of the compression and recovery zone by less-valuable products.



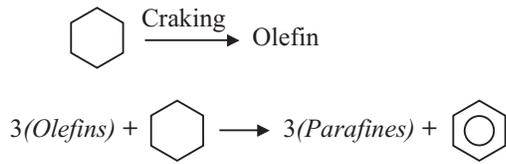
a. Cracking of Paraffinic Naphtha



b. Cracking of Orthoflow Residue

Figure 1. Distribution profile of n-Paraffin Yields

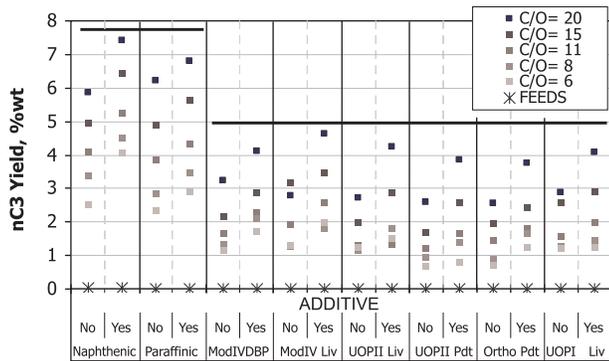
Yield of nC3 is more selective than nC4 (Figure 1) and Straight Run Naphthas are much more selective to nC3 than Naphthas from FCC (Figure 2a). This difference is due to the fact that Paraffinic Naphtha has a higher content of n[C5-C12] than Naphthas from FCC (22% vs. 6%) (Figure 2b). Based on the composition of Naphthenic Naphthas, the higher nC3 yield is due to the high content of i[C7-C12], which crack to lighter compounds and Naphthenes. Furthermore, these Naphthenes crack to produce Olefins, and are then saturated with more Naphthenes by hydrogen transfer reactions.



The n[C5-C12] in Naphthas from FCC do not crack (Figure 2b), then nC3 must be produced from other reac-

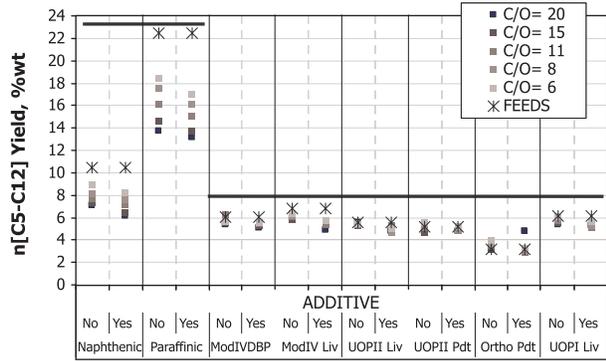
tions, where Olefins saturation is one of the most likely to occur, considering that there is a high concentration of Olefins in these Naphthas ($\pm 30\%$) (Table 2) (Zhao, & Harding, 1999).

For all Naphthas, the application of Additive increased nC3 yields by ± 1 (Figure 2a) and for Residues by $\pm 0,5$ (Figure 3a). No effect of the Additive is observed on n[C5-C12] (Figures 2b and 3b).



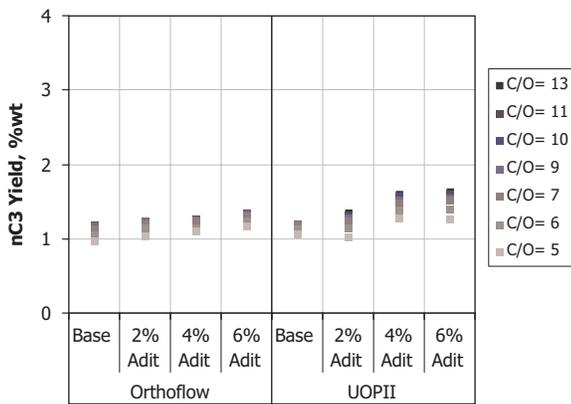
No : Without Additive
Yes : With Additive

a. nC3

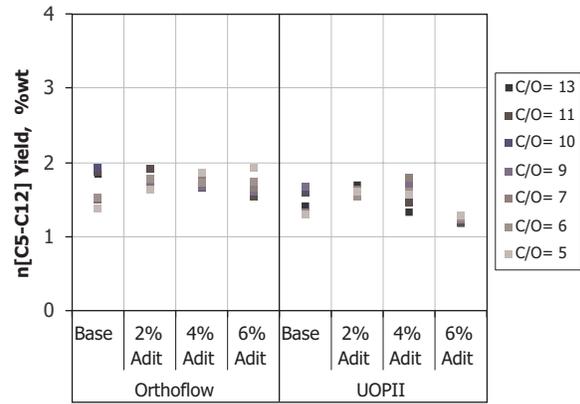


b. n[C5-C12]

Figure 2. n-Paraffin Yields in Catalytic Cracking of Naphthas



a. nC3



b. n[C5-C12]

Figure 3. n-Paraffin Yields in Catalytic Cracking of Residues

i-Paraffines

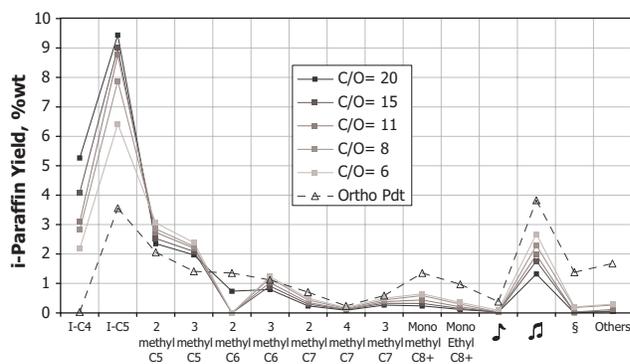
Selectivity of i-Paraffines in catalytic cracking of Naphthas is clearly directed toward iC4 and iC5 production (Figure 4). These yields partially come from cracking of i[C7-C12] which are reduced during the process (Figure 5b). Naphthenic and Paraffinic Straight Run Naphthas have higher content of i[C7-C12] ($\pm 30\%$), and higher selectivity toward iC4 than Naphthas from FCC, 9 vs. 5% (Figure 4b and 5).

The most abundant i-Paraffin in the catalytic cracking of Naphthas from FCC is iC5 (Figure 4a), reaching values up to 12% wt (Table 2).

Naphtha from ModIV is a special case because, unlike others, this plant does not process Residues but Light Gas Oil.

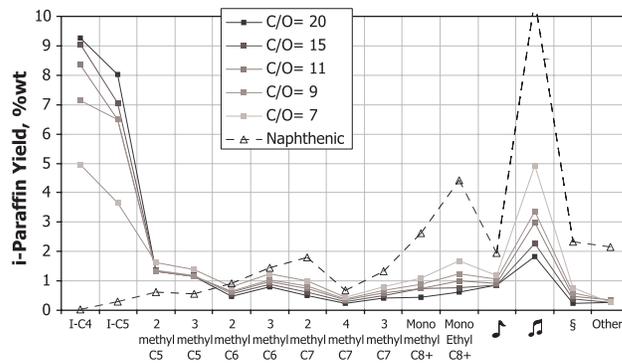
Therefore, in most cases, it shows an intermediate behavior between Straight Run Naphthas and Naphthas from FCC.

The Additive boosts iC4 yields within ± 1 point for all Naphthas (Figure 5a), and $\pm 0,5$ points for cracking of Residue (Figure 6a); however, the total content of i-Paraffines, both in Naphtha (Table 2) and Residues, (Figure 6b) decreases.



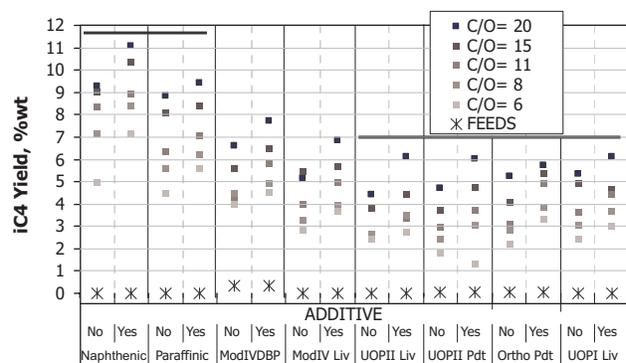
♯: amount of i-Paraffines C8+ with 2 branches (Methyl and/or Ethyl) at the same Carbon position.
 ♯: amount of i-Paraffines C8+ with 2 branches (Methyl and/or Ethyl) at different Carbon position.
 §: amount of i-Paraffines C8+ with 3 branches (Methyl and/or Ethyl).

a. Cracking of Orthoflow Naphtha

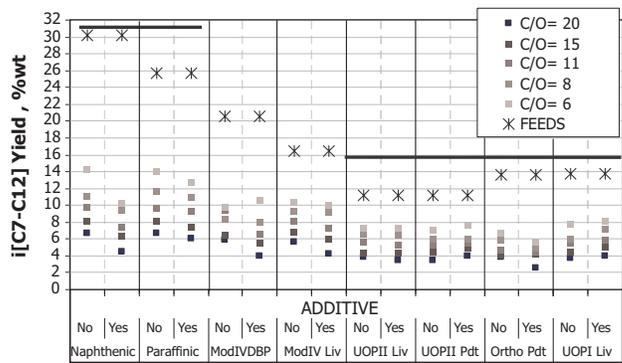


b. Cracking of Naphthenic Naphtha

Figure 4. Distribution profile of i-Paraffin Yield



a. iC4



b. i[C7-C12]

Figure 5. i-Paraffin Yields in Catalytic Cracking of Naphthas

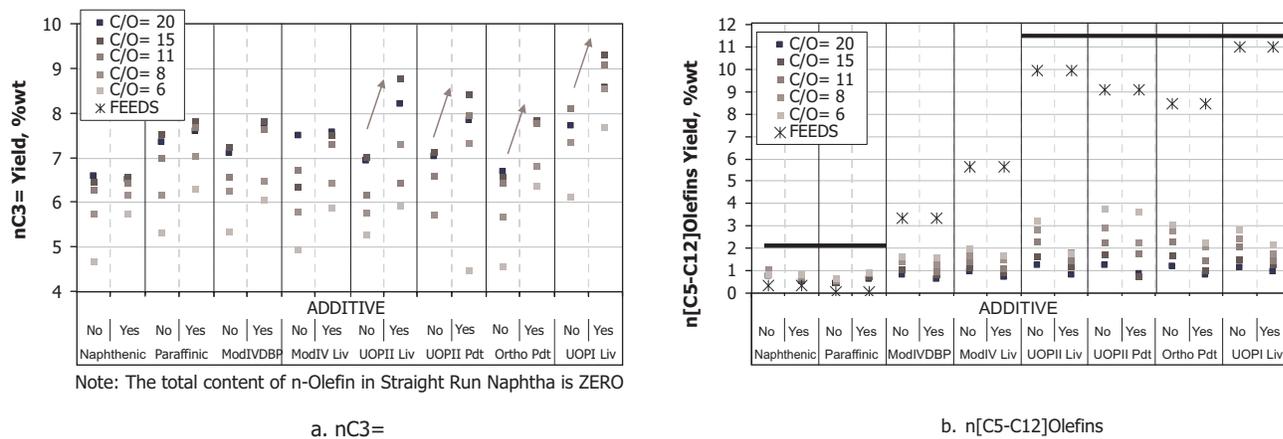


Figure 8. n-Olefin Yields in Catalytic Cracking of Naphthas

tive. This means that the industrial use of the Additive is not justified with this type of feedstock. Regarding Naphthas from FCC, Additive increases nC3= yields by more than one point (Figure 8a).

of Additive in the Catalyst. This matches with the selectivity specifications (greater than 50%) given by Additive Suppliers in the cracking of heavy feedstocks (Table 2).

Concerning Cracking of Residue, the Additive is much more selective toward nC3= as compared to cracking of Naphthas, increasing yield by up to 4 points in UOPII case (Figure 9a) when using 6%

As far as Ethylene (C2=), all Naphthas showed a similar yield of ± 1,8% and Residues ± 1,0% (Figure 10). Unlike cracking of Residues, cracking of Naphtha increases yield to Ethylene upon increase in C/O severity.

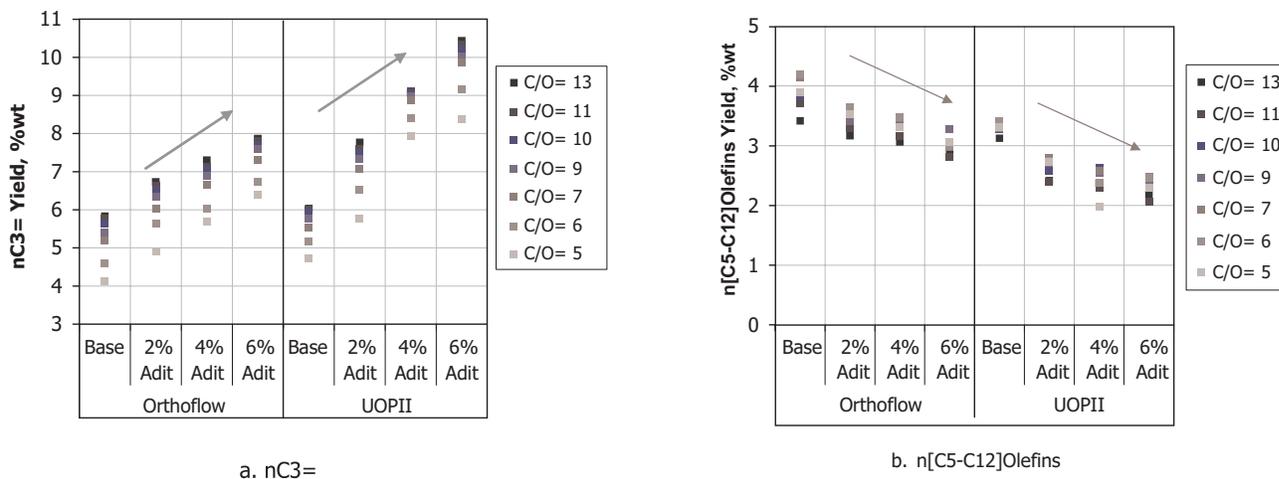


Figure 9. n-Olefin Yields in Catalytic Cracking of Residues

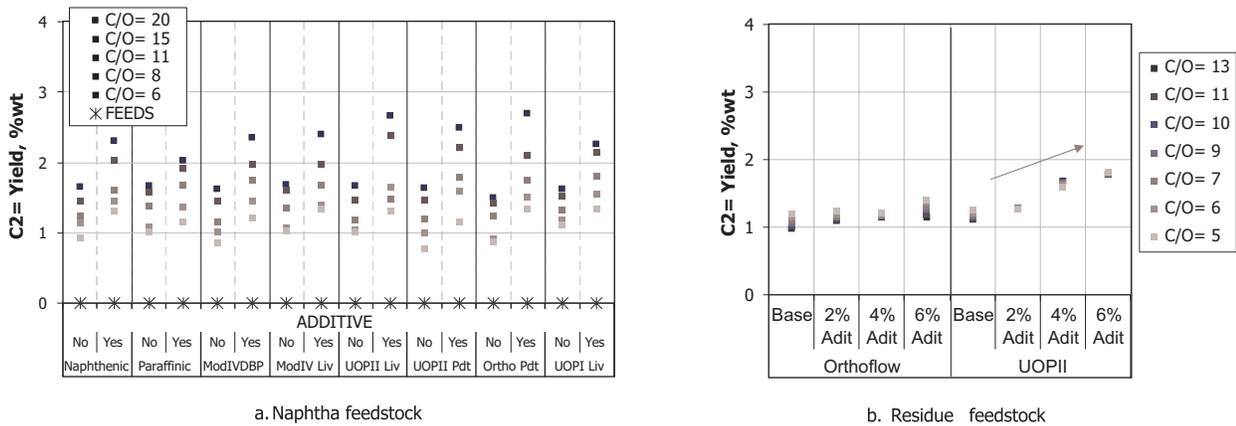


Figure 10. C2= Yield in Catalytic Cracking of Naphthas and Residues

The Additive promotes the C2= yields for all Naphthas, particularly in Naphthas from FCC (Figure 10). For Residues, the effect of Additives is better observed in UOPII, where an increase of Additive results in a slight linear increase of C2=. Other papers on Gas Oil cracking have reported the same trend for C2= (Zhao & Roberie, 1999).

i-Olefins

i-Olefins are very reactive and are almost fully consumed during cracking reactions, from ±19% to 2% (Figure 11a). i-Olefins, like n-Olefins, are nC3=

promoters that favor proper Additive performance. (Hollander *et al.*, 2002).

According to Buchanan, J., S. (1998), i-Olefins on Additives exhibit the highest reaction rate. They crack to produce n-Olefins of low molecular weight. Naphthas from FCC have high i-Olefin content (±19%) (Figure 11a): consequently, they have high nC3= yields with the use of the Additive (Figure 8a). For cracking of Residues (Figure 11b), only UOPII, that has higher nC3= yields, shows a progressive reduction in i-Olefins yields as the use of Additive increases (Figure 9a).

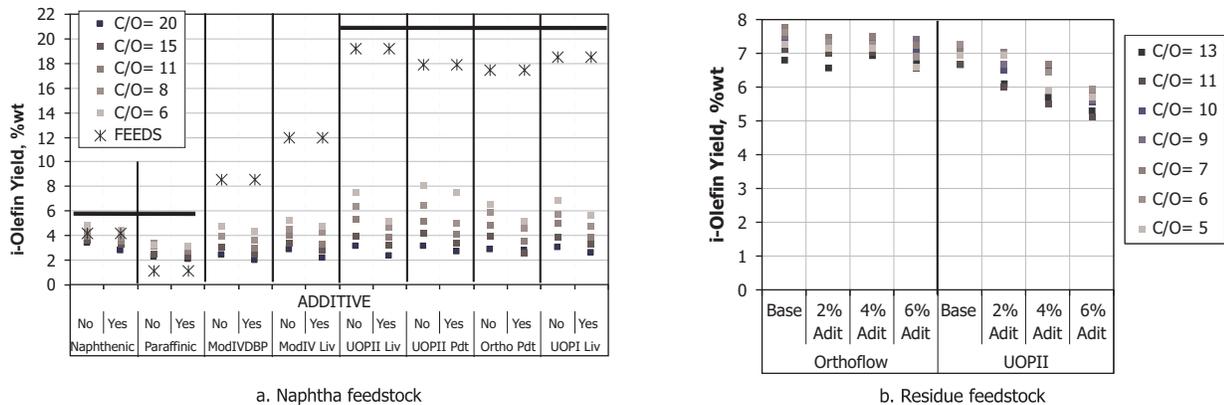


Figure 11. i-Olefin Yields in Catalytic Cracking of Naphthas and Residues

Naphthene Olefins

Naphthene Olefins content is higher in Naphthas from FCC (except ModIV) than in Straight Run Naphthas. Like i-Olefins, they are reduced to almost nothing as C/O severity increases (Figure 12a).

Naphthenic compounds do not interact over the Additive since these molecules are bigger than the accessibility diameter of ZSM-5 (5,4 Å), (Hollander *et al.*, 2002) (Figure 12b).

Aromatics

During cracking reactions, total Aromatic compounds in products increase (Table 2). Mono Aromatic

compounds in Naphthas are generally the result of hydrogen transfer reactions between Olefins and Naphthenes (Wang *et al.*, 2008, Wang, L., Yang, B., & Wang, Z. 2005). Therefore, Straight Run Naphthas with higher Naphthenes content cause a larger increase in yield toward total aromatic compounds, from 15 to 24% (Table 2). However, total Aromatic content is higher in Naphthas from FCC.

The Aromatic distribution profile (Figure 13a and 13b) shows that the main Aromatic compound resulting from catalytic cracking of Naphtha is Toluene, followed by m-Xylenes. For Residues, Toluene and m-Xylene yields are produced in equal proportion (Figure 13b).

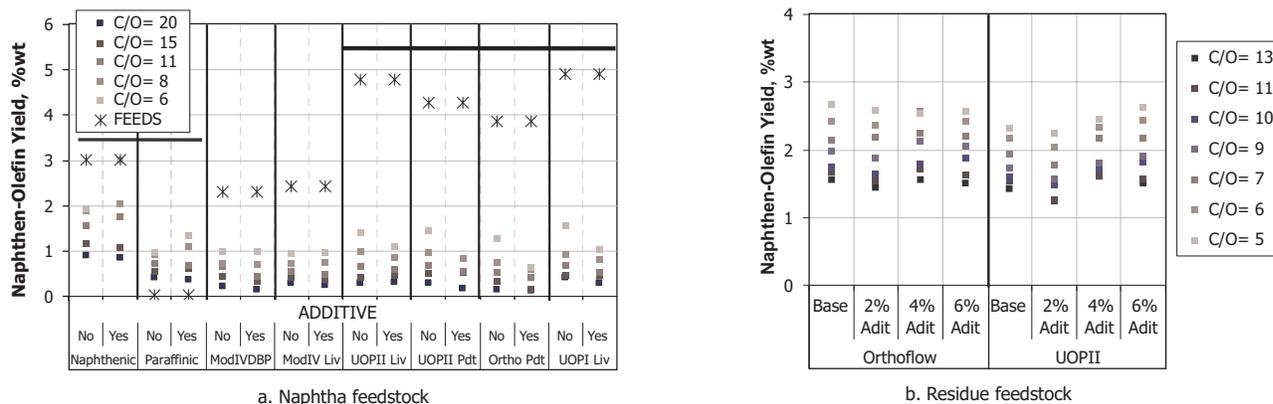


Figure 12. Naphthen-Olefin Yields in Catalytic Cracking of Naphthas and Residues

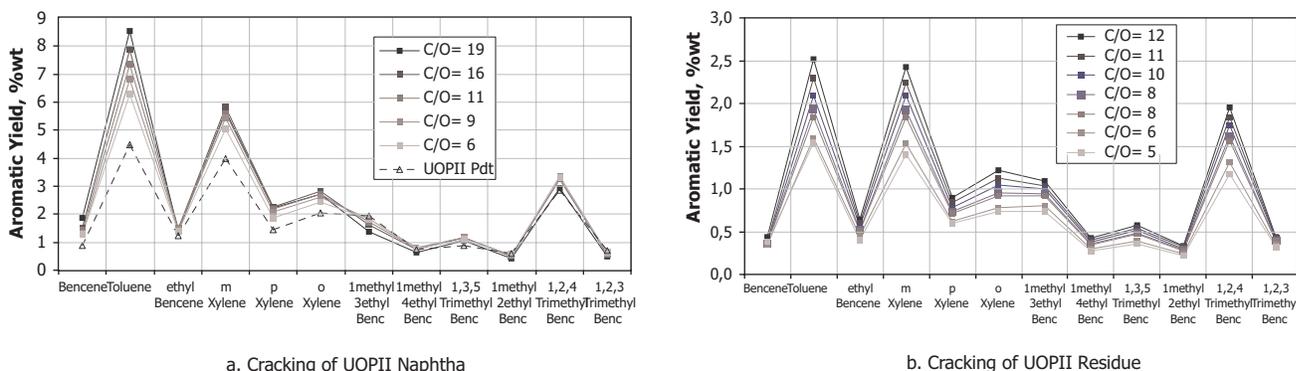
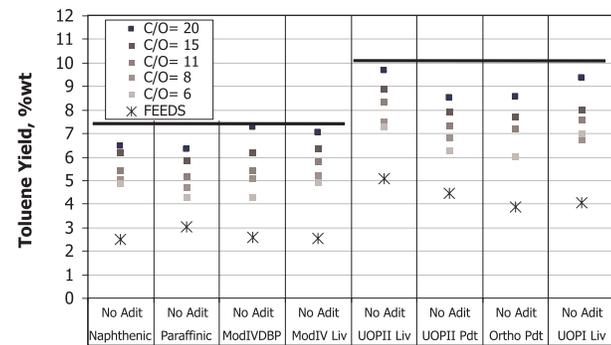
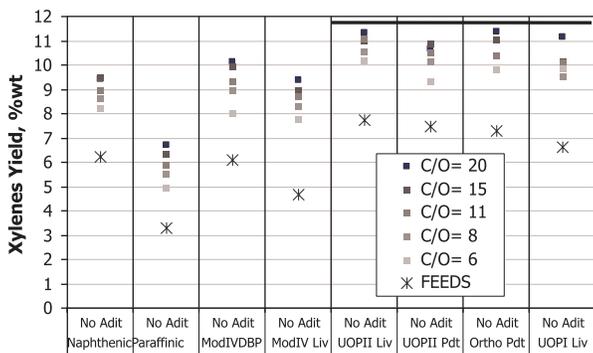


Figure 13. Distribution profile of Aromatic Yields

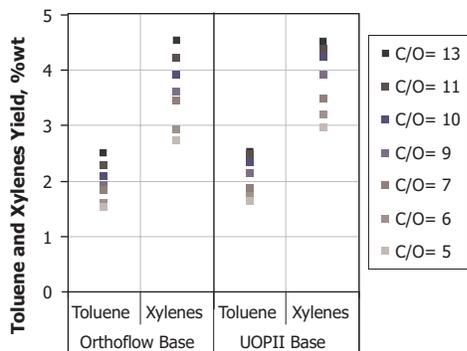
In Naphthas from FCC, total Toluene and Xylenes yields are greater than in Straight Run Naphthas (Figure 14a and 14b). This is not due to higher selectivity but to the fact that Naphthas from FCC feedstocks have higher initial content of these compounds than Straight Run Naphthas. Toluene and m-Xylene yields are significantly affected by C/O severity.



a. Toluene in Naphtha Feedstock



b. Xylenes in Naphtha feedstock



c. Toluene and Xylenes in Residues

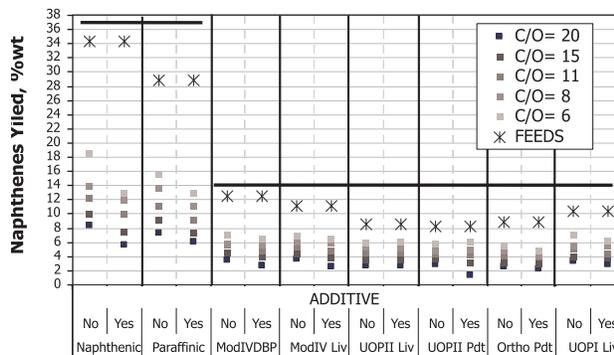
Figure 14. Aromatic Yields in Catalytic Cracking of Naphthas and Residues

The yields of Toluene and Xylene in the cracking of Residues are too much lower than those from cracking of Naphthas (Figure 14).

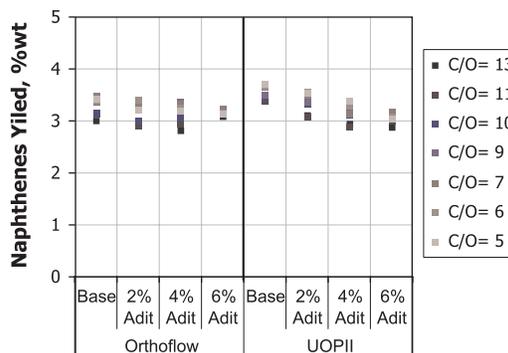
Naphthenes

According to Figure 15, Naphthenes are always reduced during cracking reactions (Table 2). Since Naphthenes are the main components in Straight Run Naphthas ($\pm 34\%$), their reactivity is higher because there is no competition with Olefins for active sites (Straight Run Naphthas do not have Olefins). Their reactivity is evident in their sensitivity to C/O severity.

Based on the above, Naphthenes become indirect Propylene promoters in the cracking of Straight Run Naphthas due to the fact that they have no Olefins and, therefore, they are produced by cracking of Naphthenes.



a. Naphtha feedstock



b. Residue feedstock

Figure 15. Naphthene Yields in Catalytic Cracking of Naphthas and Residues

Due to their molecular size, Naphthenes cannot access the ZSM-5 Zeolite. Therefore, the reduction observed in Figure 15a can be attributed to additional reactions of Naphthenes with Olefins, being the latter promoted by ZSM-5.

CONCLUSIONS

The differences between the composition of Straight Run Naphthas and Naphthas from FCC are significant. Straight Run Naphthas have higher content of n[C5-C12] i[C7-C12], and Naphthenes than Naphthas from FCC. Compared to Straight Run Naphthas, Naphthas from FCC are rich in Aromatics, n[C5-C12], Olefins, and i-Olefins (Table 2).

These marked differences in feedstock composition result in the orientation of yields toward a specific petrochemical compound after catalytic cracking of Naphthas, as follows:

- Straight Run Naphthas are selective toward i-Butane, and their yields are almost double the amount produced by Naphthas from FCC (9% vs. 5%). An increment of one point in iC4 yield is obtained for all Naphthas with the use of the Additive. i-Butane yields are directly related to compounds of the same family, i.e., with the high i[C7-C12] content in the feedstock (30% in the cases studied).
- Straight Run Naphthas produce the same Propylene yields as Naphthas from FCC (between 6 and 8%). Propylene yields are directly related to the content of both n[C5-C12]Olefins and i-Olefins. In the Straight Run Naphtha with very low content of olefins, the high content of Naphthenes (34%) act as promoters which are cracked into olefins and produce the same yield of Propylene as Naphthas from FCC. However, Straight Run Naphthas do not have enough Olefins to produce additional yields with the use of the Additive. Therefore, the use of the Additive ZSM-5 is not advisable when the feedstock is composed of Straight Run Naphthas.

- Straight Run Naphthas are highly selective toward Propane. The yields are almost double when compared to Naphtha from FCC (6% vs. 3%). The Additive increases by approximately one point for all Naphthas. Propane yields are directly correlated with high n[C5-C12] contents in these feedstocks (10 - 22%) or with Naphthenes and i-Paraffines also in high concentration (30 and 34% respectively in the cases studied).
- Yields toward Ethane and Ethylene for all Naphthas are between 0,5% and 1,0% for Ethane and $\pm 1,8\%$ for Ethylene. The Additive promotes ± 1 point increase in Ethylene yields in Naphthas.
- Naphthas from FCC can produce up to 10% of Toluene and 10% Xylenes.

In general terms, the yields of petrochemical products from catalytic cracking of Naphthas from FCC, except Propylene, are about twice those obtained by cracking of Residue.

In Naphthas, the Additive has the same selectivity for all petrochemical products. Its application increases Ethylene, Propane, Propylene and i-Butane yields in about one point each.

On the other hand, for the same concentration of Additive used in Naphthas, i.e., 4%, the Additive on Residues increases Propylene yields by 3 points, that means a Propylene selectivity of 50%.

ACKNOWLEDGEMENTS

The authors express their gratitude to the personnel at the Catalytic Cracking Pilot Plant and Laboratories of Refining and Transport located at the ICP for their cooperation in trial development. The authors also thank CT&F editors and evaluators who made the publication of this article possible with their careful observations.

REFERENCES

- ASTM D1945. (2003). Standard Test Method for Analysis of Natural Gas Chromatography.
- ASTM D6729. (2004). Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography.
- ASTM D7213. (2005). Standard Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 to 615°C by Gas Chromatography.
- Buchanan, J., S. (1991). Reactions of model compounds over steamed ZSM-5 at simulated reaction conditions. *Appl. Catal.* 74: 83-94.
- Buchanan, J., S. (1998). Gasoline selective ZSM-5 FCC Additives: Model reaction of C6-C10 olefins over steamed 55:1 and 450:1 ZSM-5. *Appl. Catal. A: Gen.*, 171: 57-64.
- Hollander, M., A., Wissink, M., Makken, M. & Moulijn, J. A. (2002). Gasoline conversion: reactivity towards cracking with equilibrated FCC and ZSM-5 catalysts. *Appl. Catal. A: Gen.*, 223: 85-102.
- Timken, H. K. C. & Angevine, P. J. (1997). Production of Benzene, Toluene, and Xylene (BTX) from FCC Naphtha. *United States Patent, Patent number: 5,685,972*, Nov. 11.
- UOP 539. (1997). Refinery Gas Analysis by Gas Chromatography.
- Wang, L., Yang, B. & Wang, Z. (2005). Lumps and kinetics for the secondary reactions in catalytically cracked gasoline. *Chem. Eng. J.*, 109: 1-9.
- Wang, G., Yang, G., Xu, C. & Gao, J. (2008). A novel conceptual process for residue catalytic cracking and gasoline reformation dual-reactions mutual control. *Appl. Catal. A: Gen.*, 341 (1-2), 98-105.
- Wang, Gang., Xu, Chunming. & Gao, Jinsen. (2008). Study of cracking FCC naphtha in a secondary riser of the FCC unit for maximum propylene production. *Fuel Processing Technology*, 89 (9), 864-873.
- Yang, B., Zhou, X., Chen, C., Yuan, J. & Wang, L. (2008). Molecule simulation for the secondary reactions of fluid catalytic cracking gasoline by the method of structure oriented lumping combined with Monte Carlo. *Ind. Eng. Chem. Res.*, 47 (14), 4648-4657.
- Zhao, X. & Harding, R., H. (1999). ZSM-5 Additive in fluid catalytic cracking. 2. Effect of hydrogen transfer characteristics of the base cracking catalysts and feedstocks. *Ind. Eng. Chem. Res.*, 38 (10), 3854-3859.
- Zhao, X. & Roberie, T., G. (1999). ZSM-5 Additive in fluid catalytic cracking. 1. Effect of Additive level and temperature on light olefins and gasoline olefins. *Ind. Eng. Chem. Res.*, 38 (10), 3847-3853.