FCC FEED FRACTIONATION. AN ANALYSIS OF CONTRIBUTIONS AND SELECTIVITIES OF DISTILLATION CUTS TO OVERALL CONVERSION

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Abstract. *Petroleum refining is engaged with upgrading of petroleum atmospheric and vacuum distillation streams, being each a complex mixture of hydrocarbons. FCC process reactions network is very complex, demanding high levels of resources and time, if one is to define the detailed molecular interactions involved. Therefore and for practical purposes, it may be of interest to separately test less complex fractions derived from the feed and obtain information that can be used in driving latter work on related kinetic evaluation. Accordingly, to study the effect of feed composition in overall conversion and yields of individual products, in this work, a feed to FCC process was fractionated into six cuts of narrow boiling point distillation range. Each one of these distilled cuts (DC) can be considered as an individual lump of more precise average carbon number, and with different response to cracking. By comparison of selected physical properties reported for each DC one may predict different chemical behavior and distribution in their reaction product slates, under otherwise equal reaction conditions. Chemical performance tests were realized in a micro-reaction unit under different severity levels, in presence of an industrial equilibrium catalyst. Results are compared considering individual DCs as part of the feed compared and also as independent feeds*

Key words: *FCC, catalytic cracking, gasoline, reaction selectivity, vacuum gasoil, conversion.*

Introduction

Petroleum refining deals with the upgrading of process streams, representing each a complex mixture of hydrocarbons, usually characterized by boiling range, CCR and specific gravity. A typical FCC feedstock is a mixture of light and heavy vacuum gas oils, with properties considered important variables of the process, and of great influence on operational conditions, catalyst selection and product quality. A typical feedstock can be defined as a mixture of paraffins, iso-paraffins, naphthenic, and aromatic hydrocarbons. As hydrocarbon molecular weight increases in the distillation curve, the proportion of hybrid hydrocarbons (more than one hydrocarbon type represented per molecule) becomes more important. Additionally, polar compounds containing oxygen, sulphur, nitrogen and heavy metals are also present, in amounts depending on vacuum tower separation efficiency.

FCC reaction network is very complex as well, and its study demands high level of resources and time, if one is to define the detailed molecular interactions involved. For practical purposes and whenever a kinetic model is needed, it is then advisable to make valid assumptions in order to choose those reaction paths of the network that seem more important for yield and quality prediction.

There is a huge amount of technical reports dealing with kinetic models developed to predict product yields at the riser. Pitault et al. [1] reported a kinetic model based on the well known lumping strategy. Each lump integrates paraffins, olefins, naphthenics, aromatics and polar compounds, determined by MS analysis of three feedstocks with different levels of paraffins content. They correlate conversion with MAT yields and composition of light cycle oil (LCO), gasoline (GSLN) and liquid phase gas (LPG), in order to predict chemical behavior of such feedstocks.

Harding et al. [2] studied gas oil feedstock behavior by its separation into fractions according to boiling range and also into paraffinic, aromatic and polar fractions. Gas oil is then doped with different amounts of each hydrocarbon fraction, thus obtained, to establish its effect on product selectivity. Authors noted that reported incremental yields are only slightly affected by adding individual distillation fractions, but are very much influenced when addition is done by chemical type.

Christensen et al. [3], built a process model that describes fundamental cracking chemistry of FCC feedstocks using more than 3,000 molecular species. They claim the use of structure oriented lumping (SOL) and more than 60 reaction rules which application renders a network of more than 30,000 elementary chemical reactions. The riser kinetic model is coupled with equipment models to form an integrated FCC process model. One important disadvantage of this approach is the detailed analysis of feedstock and products required.

Lappas et al. [4] studied the catalytic cracking rate of aromatic fractions separated from an industrial FCC feedstock and its contribution to the gasoline product fraction. They confirmed that low contribution to gasoline and LPG is obtained from these aromatics, particularly highly condensed structures, which also exhibit a high coke forming tendency. Fisher [5] studied a series

of different feedstocks and reported a procedure to predict distribution of major products, based on MS analysis of raw materials, and confirmed by comparison with MAT experimental data.

Green et al. [6] studied a series of FCC feedstocks and proposed a conceptual model for prediction of yields on the basis that primary production of gasoline and C3/C4 gases derive from alkyl side chains and acyclic paraffins in feed, with simultaneous conversion of aromatic and naphthenic cores to cycle oils. White [7] studied the existing relation between feedstock hydrocarbon groups and FCC yields, and explained the benefits of correlating them. In a similar approach, Hinds [8] classified the component structures and hydrogen content in feedstock and related them to the kind of products obtained. Probability assumptions based on carbenium ion chemistry should be made as the first approach towards prediction of product slate from reaction of a given molecule [9].

Experimental

An industrial feedstock was fractionated into six distillation cuts (DC) of narrow boiling ranges as depicted in Table 1.

Each distillation cut and the integrated feed (IF) were tested in a micro-reaction unit under conditions shown in Table 2, using an industrial catalyst which properties are reported in the same table.

Achieved conversion and yields are reported in Table 3. Experimental data in this table is affected by corresponding wt % contribution of each DC on feed composition; therefore, the sum of individual yields and conversion should approximate experimental data obtained for the integrated feed.

Table 4 shows a comparison of results for different severities, under otherwise equal conditions, observed when the sum of contributions from all DCs are considered.

It should be mentioned that experimental tests were realized in presence of aliquots of same industrial equilibrium catalyst, contaminated with impurities, such as nickel and vanadium; then, particularly coke formation from light DCs is not a result of feedstock composition alone.

Results and Discussion

General Comments

Knowledge of detailed feedstock composition is the most reliable support to establish a strategy for predicting product yields and quality parameters from the chemistry involved in FCC processing. Thus, individual contributions of chemical classes to feed composition can be used with advantage to correlate physical and thermodynamic properties as well as for the development of kinetic models. Since the number of possible components in the mixture is too high, lumping is always necessary. Moreover, the lumping strategy is of paramount importance to obtain results of industrial interest. Detailed analysis of feedstock, obtained by advanced laboratory analytical tools, should be applied in forecasting product quality by using preferential reaction paths to explain product composition and properties.

The most important reactions which occur in FCC process are based mainly on cracking of carbon-carbon bonds in paraffinic, and saturated cyclic structures, including alkyl groups

Table 1. Properties of feed and its distillation cuts (TBP distillation).

	Light End (LE)			Heavy End (HE)			
DC	1	2	3	4	5	6	Feed
Boiling Point, °C	IBP-363	363-403	403-443	443-463	463-483	483+	IBP-FBP
wt % on feed	16.68	17.46	6.88	20.23	19.55	19.20	100
°API	27.28	23.4	21.2	20.6	19.4	18.0	21.82
Density,	0.8913	0.9135	0.9266	0.9303	0.9377	0.9465	0.9229
ACN	20.23	22.83	25.82	28.12	29.81	32.38	30.7
AMW	277.62	312.77	347.99	380.15	410.21	445.39	439.2

IBP-FBP: Initial Boiling Point-Final Boiling Point; ACN-Average Carbon Number; AMW-Average Molecular Weight (Mass Spectrometry).

Table 2. Test conditions and catalyst properties

Test Conditions	
Catalyst, g	4.0
Temperature, °C	520
Severity C/O ratio	3, 4, 5, 6
WHSV, h^{-1}	16
Equilibrium Catalyst Properties	
Density, g/cm^3, (UOP-254)	0.8871
Surface area, m^2/g, (BET)	152.6131
Micro-pore volume, cm^3/g	0.046648
Activity, wt%	66.0
Ni, ppm	327.0
V, ppm	1500.0

attached to aromatic rings. Today, it is accepted that detailed characterization of feed and the application of corresponding chemistry rules involved in the process, are key elements in prediction of product yields and composition.

In general, the main reactions in catalytic cracking are:
- Cracking of paraffins
- Cracking of naphthenics
- Cracking of alkyl groups in aromatic structures
- Cracking of intermediate olefinic species
- Isomerization of olefins and paraffins
- Hydrogen transfer
- Coke formation

Table 3. DCs contributions to overall yields and conversion (wt%).

C/O = 3	Distillation Cut (DC)					
	1	2	3	4	5	6
DG	0.19	0.21	0.08	0.26	0.26	0.28
LPG	2.57	2.22	0.82	2.22	1.78	1.31
GSLN	6.96	6.70	2.54	7.26	6.65	6.00
Coke	0.34	0.50	0.21	0.71	0.73	0.79
LCO+DO	6.65	7.84	3.16	9.83	10.14	10.82
Contrib. to overall conv.	10.05	9.62	3.66	10.44	9.41	8.38
C/O = 4						
DG	0.22	0.24	0.10	0.30	0.30	0.33
LPG	2.78	2.58	0.95	2.64	2.40	1.95
GSLN	7.26	7.18	2.77	7.92	7.33	6.52
Coke	0.42	0.57	0.25	0.77	0.84	0.93
LCO+DO	5.97	6.88	2.85	8.60	8.68	9.47
Contrib. to overall conv.	10.68	10.58	4.07	11.63	10.87	9.73
C/O = 5						
DG	0.25	0.27	0.11	0.33	0.35	0.37
LPG	2.98	2.92	1.09	3.02	2.85	2.56
GSLN	7.55	7.57	2.96	8.61	7.86	7.08
Coke	0.53	0.71	0.29	0.88	0.95	1.06
LCO+DO	5.37	5.99	2.43	7.39	7.55	8.13
Contrib. to overall conv.	11.31	11.47	4.45	12.84	12.00	11.07
C/O = 6						
DG	0.27	0.29	0.12	0.36	0.37	0.40
LPG	3.17	3.07	1.16	3.28	3.07	2.88
GSLN	7.99	7.95	3.08	8.97	8.38	7.80
Coke	0.61	0.81	0.32	1.03	1.08	1.22
LCO+DO	4.64	5.34	2.20	6.59	6.64	6.89
Contrib. to overall conv.	12.04	12.12	4.68	13.64	12.91	12.31

DG - Dry Gas; LPG – LP Gas; GSLN – Gasoline; LCO – Light Cycle Oil; DO - Decanted Oil.

Table 4. Comparison of DCs contributions with integrated feed yields and overall conversion.

C/O	3		4		5		6	
	ÓDC	FEED	ÓDC	FEED	ÓDC	FEED	ÓDC	FEED
DG	1.28	1.17	1.51	1.42	1.68	1.71	1.81	1.85
LPG	10.90	11.71	13.31	13.72	15.42	15.39	16.63	16.51
GSLN	36.10	36.05	38.96	39.08	41.62	42.22	44.18	46.06
LCO	22.30	22.94	20.24	21.87	18.18	19.99	16.12	19.06
DO	26.12	25.42	22.21	18.25	18.68	15.40	16.18	11.93
COKE	3.28	2.70	3.78	3.30	4.42	3.96	5.08	4.59
Conversion	51.57	51.64	57.56	57.52	62.03	63.28	67.70	69.01

Product distribution derived from cracking a molecule, firstly depends on the feasibility of generating an ion; secondly, on the ability of this initial ion to migrate to different allowed positions in the molecule producing isomers, and finally, on the cracking reaction itself. In general, ion formation is achieved by hydride abstraction from a saturated molecule by a strong Lewis acid or by protonation in presence of a strong Bronsted acid. Charge migration in the ion is restricted by the initial basic structure of the reacting molecule and is related to the stability level that each position of this unsaturation center may achieve. Which bond is more exposed to cracking depends on the molecular arrangement of the reacting ion and its carbon number.

Fractionation of feedstock into six narrow boiling range distillation cuts offers the option to establish yield contributions from its individual cracking behavior. That can be done either by affecting obtained experimental yields and conversions with corresponding DC weight percent contribution on distilled integrated feed, or by considering each DC as a separated feed. The results are different because in the former case, DC yields are consequence of inherent reactivity added to weight percent contribution on feed, while in the latter, yields exhibit solely the reactivity or ease of cracking of each isolated DC. From the industrial point of view, the overall result is important; but for the development of predicting and modeling strategies, measurement of exhibited reactivity of each DC is crucial. It is important to bear in mind that all DCs lie in the decanted oil (DO) boiling range (343ºC+), except for lighter DC-1, most of it boiling in the LCO (221 -343ºC) range (Table 1).

Next, the first case will be addressed in terms of overall yields and conversion, and then reactivity will be discussed as selectivity patterns.

Yields and Conversion

When moving towards DCs with higher boiling range, average molecular weight shows an increasing trend (Table 1) due to a constant increase in content of more refractory heavy material, which gradually changes in nature becoming more complex. The characteristic composition of each DC has an important effect on its reaction behavior.

When comparing conversions for LE-DCs (DC-1 to -3) against those for HE-DCs, as groups, it is observed that for the former it increases by 5 units as severity moves from 3 to 6, against 10 units for the latter, as shown in Table 5.

Table 5. Light End vs Heavy End conversion.

C/O	LE	HE	Total
3	23.33	28.24	51.57
4	25.32	32.23	57.56
5	27.23	35.91	63.14
6	28.85	38.85	67.70

As a result, a diminishing trend in contribution to overall conversion from LE-DCs is observed; these effects are evident also in Figure 1, which shows a steepest upward gradient for heavy DCs.
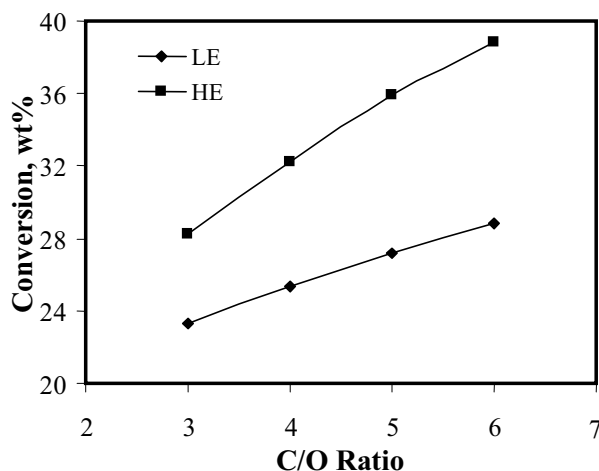

Figure 1. LE and HE Conversion Changes with Severity.

As for coke formation from individual DCs, DC-3 does not lie were it is expected with relation to the others, and this is so, because its contribution with respect to overall feed composition is low (6.88 wt %), as depicted in Table 1. Otherwise, coke yields show the expected trend, with the heavier DC-6 as the greatest coke forming DC; in fact, coke forming potential from any HE-DC is always higher than those from LE-DCs (Figure 2).
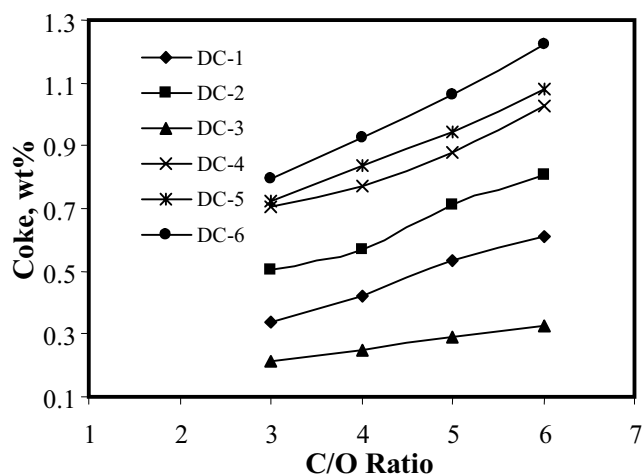

Figure 2. Coke Formation from DCs

Gasoline yields are more or less close except for DC-3, which again are very low in the whole severity range, due to the same mentioned reason (Figure 3).

Similarly, LPG exhibits the same trend, and therefore, production of both important products is very much related to fractional contribution in the original distillation curve of the feedstock.

In all cases, gasoline and LPG production potential is very much masked by DCs fractional contribution to the original feed; in other words, all DCs seem to have close gasoline and LPG production potential, with little influence of their composition.
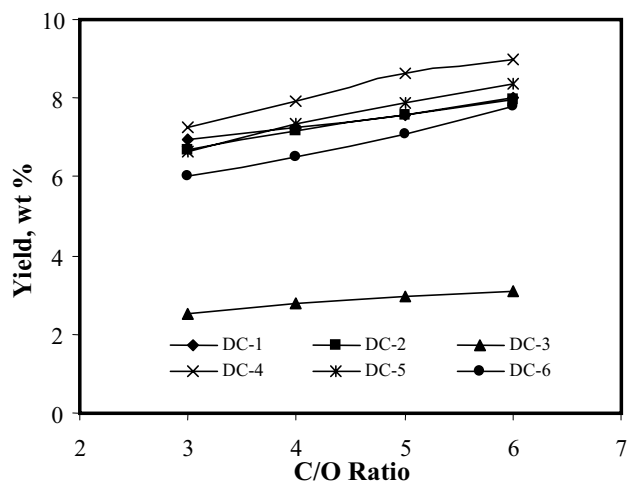
Figure 3. Gasoline forming Trends.

Figure 5. Selectivity to gasoline

Figure 6. Selectivity to LPG

Selectivity patterns

From a qualitative point of view, there is a substantial difference in reaction performance of light and heavy cuts, as defined by their boiling range and hence, their inherent composition. When taken as individual feedstocks and not considering them as a fractional contribution, light DCs show greater conversion levels at all severities (Figure 4).
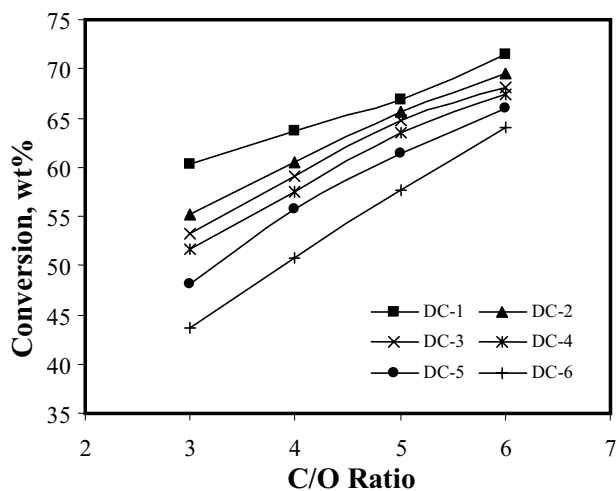

Figure 4. Distillation Cuts. Conversion at Different Severities.

Selectivity curves meant as –(yield of product)/(overall conversion)-, illustrates the relative changes in product yields as conversion increases. Conversion is taken as the sum of gasoline, LPG, dry gas and coke yields. Gasoline selectivity is illustrated in Figure 5, where it is evidenced that at low severities heavier DC-5 and -6 attain the higher yields to gasoline, but also have the greatest decline.

For lighter DC-1 to -3, gasoline formation is comparable and less sensible to changes in severity, as it is for heavier DCs. Increased catalyst contact (higher C/O) with feed, mainly with HE-DCs, produces a great amount of gasoline over-cracking, which mostly contributes to higher yields of LPG (Figures 5 and 6).
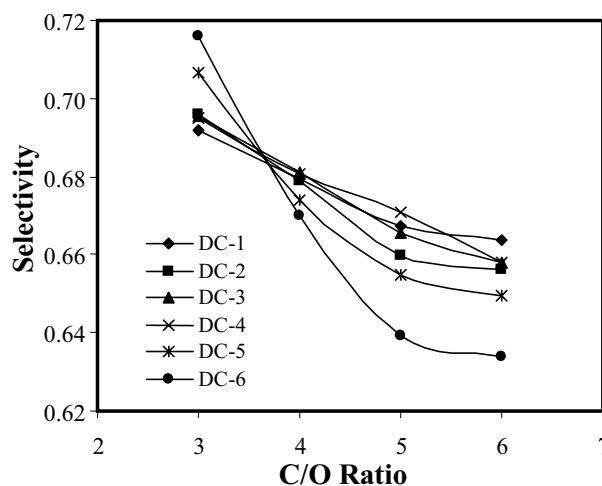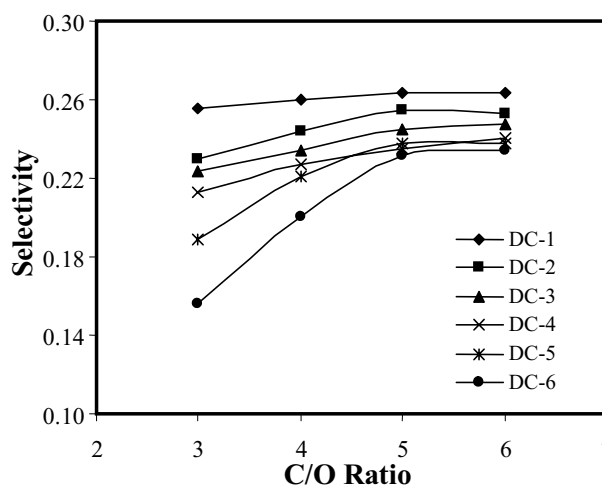
Graphical representation (Figure 7) of LCO and DO yields denotes clear differences in reaction behavior for light and heavy DCs; as said and except for DC-1, all DCs have boiling points in the range of what is defined as DO (343°C+), meaning that DC-2 to -6 have initial DO-like composition, with differences in quality directly related to its position in the feed boiling curve. While LCO/DO yields ratio for light DCs is equal or greater than one, for heavy DCs is always lower than one.
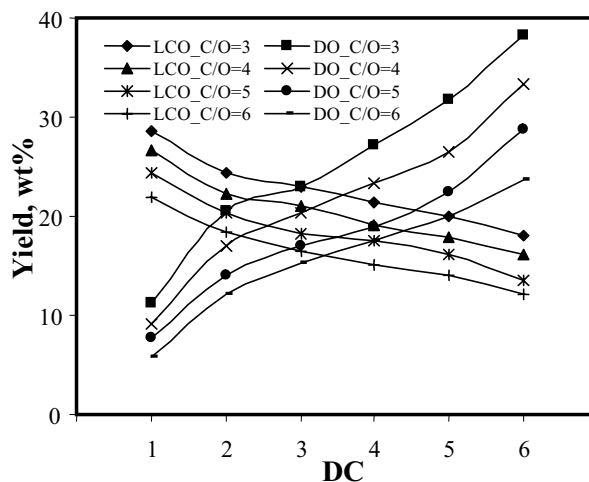

Figure 7. LCO and DO Yield Profile

DC-1 has a very high content of hydrocarbons boiling in the range of LCO and therefore it is not surprising its high content in the product even when high conversion to lighter products is expected. DC-2 and DC-3 do not have hydrocarbons in the LCO boiling range but contain rather light, easy to crack, DO-like hydrocarbons. From DC-4 on (443°C+), higher concentration of more complex polycyclic material requires higher severity levels in order to increase conversion. DO and LCO are readily converted to gasoline and LPG as severity is increased from C/O 3 to 6. Light DCs crack substantially at low severity and therefore, there is no important additional contribution to overall conversion (gasoline and lighter) at higher severity levels, other than some additional cracking to dry gas and coke, since gasoline over-cracks almost quantitatively to LPG. From Figure 7 it is observed that for DC-1, and with regard to severity effects, the intermediate light (LCO boiling range) and heavy (DO boiling range) products crack equally well. As for DC-6, it is observed that heavier DO boiling range hydrocarbons crack more easily than those boiling at the LCO range. The tested distillation cuts could be thought of as a representative simulation of feedstocks of the kind, since their particular behavior.

Light DCs exhibit the lowest selectivity for Dry Gas (DG) and coke, as compared to heavier DCs (Table 2). These relative trends are in accordance with what is generally expected from light and heavy feedstocks to the process, however, here there is a clear consequence of the specific boiling range of each DC. Heavy DC-5 and -6 are the ones that contribute the most to DG and coke production. Nevertheless, it is important to review that coke formation has a very complicated mechanism and it may originate from different sources; poliaromatic structures from any feedstock are important contributors, but also there should be an important proportion generating from olefinic intermediates which react to di-olefins through hydrogen transfer reactions to aromatics, and then to coke. Nickel always present in heavier DCs deposits in the catalyst and promotes dehydrogenation reactions, and hence, coke formation.

Conclusions

As for DC-1, reactions take place under otherwise clean environment, that is, absence of metals and the lowest, if any, of polycyclic material. It then exhibits a controlled but initially (low severity) high enough level of cracking with relatively low coke production; on the other hand, cracking of DC-6 requires higher number of catalyst active sites (C/O = 6) to crack not only existent saturated molecules, but also available alkyl functional groups as well as some saturated rings in polycyclic molecules, in order to achieve conversion levels comparable to those reported by DC-1 at the lower severity.

In the case of gasoline formed from heavier DC-5 and DC-6, it exhibits the greatest decline with severity even though their initial selectivity at low severity is higher than for light DCs. DC-5 and DC-6 evidence also the lowest selectivity to LPG, and although it is considerably improved with increasing severity, it never reaches the selectivity values for DC-1.

The study of distillation cuts obtained from a feedstock to FCC process draws advantages which can be translated in better decision making with regard to the best mixing strategy of hydrocarbon streams in the refinery. This will conclude in an enhanced performance of a particular industrial unit with specific objectives. Additionally, gathered information could also be used in the development of kinetic models able to predict not only yields but also main products quality.

Acknowledgements

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