Hydrocarbon Yield Structure in the Conversion of Heavy Model Molecules (Quinolin-65) on Fluidized Catalytic Cracking Catalysts

Alejandra Devard, Richard Pujro, Gabriela de la Puente, and Ulises Sedran*

Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), FIQ, UNL-CONICET, Santiago del Estero 2654, 3000 Santa Fe, Argentina

ABSTRACT: The reactivity of a heavy model molecule (quinolin-65, named Q65, a 2,3,7,8-dibenzopyrene derivative) over two different equilibrium fluidized catalytic cracking catalysts of the conventional and resid types was studied at 550 °C and with reaction times that varied from 5 to 20 s, in a batch fluidized-bed laboratory reactor. Two types of experiments were performed to determine the hydrocarbon products resulting from the conversion of Q65. This compound is solid at room temperature, and a solution of Q65 at 4.6 wt % in toluene and pure toluene were used. Conversions and yields were assessed by means of careful mass balances. The product distributions showed that Q65 produced a wide range of hydrocarbons from C1 to C20. These distributions were different according to the formulations of the catalysts. Olefins were predominant among gases and, neatly, aromatics among liquids. Coke yields were high, exceeding 12 wt %. The characteristics of the catalysts were also revealed through the higher activity and hydrogen-transfer ability of the conventional catalyst and the better coke selectivity of the resid catalyst. It was shown that both the linear alkyl chain and the multi-ring core react.

INTRODUCTION

The increasing demand to process heavier, lower quality crudes and the need to maximize the yields of petrochemical raw materials are among the most stressing issues in petroleum refining. These two points have a significant impact on the process of fluidized catalytic cracking (FCC) of hydrocarbons, which is central in refineries.[1] One of the consequences of these concerns is that FCC catalysts, which are based on Y zeolite as the main component, are demanded that can operate efficiently in the conversion of residual or nonconventional hydrocarbon cuts added to typical vacuum gas oil (VGO) feedstocks. Even processes were developed that can use fully residue feedstocks. Because extremely large molecular structures and high-contaminant metal contents are inherent to the resid FCC,[2] resid catalysts are characterized by their better bottoms cracking activity, accessibility properties, and coke selectivity.[3]

The catalytic cracking of hydrocarbons on Y zeolite is conditioned by the mass transport of the chemical species involved.[4] However, it has been generally assumed that the chemical reaction on the active sites is the limiting step in the overall process, which includes diffusion, adsorption, and reaction. Consequently, the evaluation of commercial FCC catalysts typically ignores the restrictions to mass transfer. In processing resids, diffusion can be an important limiting factor in the global reaction rate, considering that the catalysts are compound, with Y zeolite deposited on a matrix together with other components, such as binders, fillers, and additives.[5] Commercially, the Albermarle accessibility index (AAI)[6] is an attempt to characterize diffusion issues and constitutes an overall property. The index is a relative measure of the initial slope of the curve, which represents the evolution as a function of time of the ultraviolet (UV) absorption by large organic molecules from a petroleum fraction, containing asphalthenes, which is dissolved in a solution that is put into contact with the catalyst particles; the faster the evolution, the higher the index and the accessibility in the catalyst.

Alternative approaches could be developed on the basis of the diffusion and reaction processes of a proper model molecule; for example, to assess accessibility, the cracking of bulky molecules could be used. Some of the model compounds used with identical or similar aims had been 1,3-diisopropyl-benzene (1,3-DIPB),[4] 1,3,5-triisopropylbenzene (TIPB),[7] or, in some cases, cumene.[4] However, the molecular structure and size of these hydrocarbons are far from representing those of the fractions typically present in resid feedstocks, such as asphalthenes or resins.

López-Linares et al.[8] reported the use of molecules of a well-known structure. Given their molecular weight, aromaticity, naphthenicity, heteroatom content, and nature of the functional groups present, they resulted in being useful to generate information on the adsorption behavior of asphalthene fractions from various resids over kaolin surfaces. One of those molecules was quinolin-65 (Q65), a 2,3,7,8-dibenzopyrene derivative, which includes nitrogen, oxygen, and sulfur atoms. The molecule is shown schematically in Figure 1. The authors concluded that Q65, which is slightly soluble in *n*-heptane and soluble in aromatics, such as toluene (TOL), can be
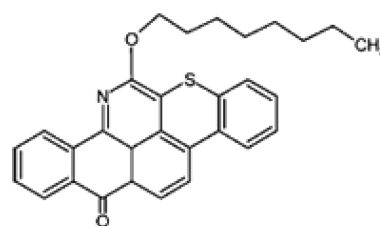

Figure 1. Schematic representation of Q65.

representative of asphalthene fractions when considering adsorption matters.

It is the objective of this work to analyze the reactive behavior of Q65 over two different equilibrium commercial FCC catalysts under conditions of the commercial process. Experiments were performed to define the potential of Q65 as a model molecule for certain fractions in residues. These experiments were performed in the Chemical Reactor Engineering Centre (CREC) riser simulator laboratory reactor,[9] which was specifically designed for the study of FCC issues.

■ EXPERIMENTAL SECTION

Materials. Two equilibrium commercial FCC catalysts provided by refineries were used; the first one named E-cat D (conventional type), and the second one named E-cat R (resid type), with their main properties being shown in Table 1.

Table 1. Properties of the Catalysts Used

catalyst	UCS[a] (nm)	Sg[b] (m² g⁻¹)	zeolite[c] (wt %)	REO[d] (wt %)	AAI[e]
E-cat R	2.427	125	14.8	2.94	8.3
E-cat D	2.423	139	16.9	1.26	5.5

[a]Unit cell size from American Society for Testing and Materials (ASTM) D-3942-85. [b]BET specific surface area using N_2 adsorption. [c]Zeolite content using Johnson's method.[10] [d]Rare earth oxide content. [e]According to ref 6.

The molecular weight of Q65 ($C_{30}H_{29}NO_2S$, Sigma-Aldrich) is 467.62 g mol⁻¹. Q65 is solid at room temperature, with its melting point being 178−193 °C. TOL (Cicarelli, 99.5 wt %) was used as the solvent.

Reaction Equipment. The experiments were performed in a CREC riser simulator laboratory reactor.[9] The reactor has a turbine on the top of a chamber that holds the catalyst bed between porous metal plates. The turbine rotates at 7500 revolutions per minute (rpm), thus inducing a low-pressure area in the upper central zone in the reactor that makes gases recirculate in the upward direction through the chamber, thus fluidizing the catalyst bed. When the reactor is at the desired experimental conditions, the reactant is fed with a syringe through an injection port and vaporizes instantly, thus setting the initial time. After the desired reaction time is reached, the gaseous mixture is evacuated immediately and products can be sent to analysis. Additional descriptive details can be found in refs 11 and 12. The reactor was previously used in the study of various subjects, such as catalyst evaluation,[13] kinetic and diffusive modeling,[14,15] and studies of new operative modes.[16−18]

Experimental Procedure. Q65 was used dissolved at 4.6 wt % in toluene (TOL−Q65) at 550 °C, with reaction times that varied from 5 to 20 s and with a catalyst/reactant relationship of 5.0, achieved with a catalyst mass of 0.8 g. Identical experiments were performed using only pure TOL, to produce comparative background information and to discern the particular contributions made by solvent and Q65 molecules to the product distribution. This experimental approach was developed to facilitate the handling of very viscous or solid reactants in laboratory reactors and has been used to study, for example, the conversion of recycled plastics[19] or residual hydrocarbon feedstocks[20] over FCC catalysts. The contribution from thermal reactions was considered negligible, because experiments with pure TOL and no catalyst in the reactor showed conversions lower than 1.1%.

The reaction products were analyzed by online conventional capillary gas chromatography. Coke yields were assessed by means of the temperature-programmed oxidation of the coke deposits and further methanation of the carbon oxides formed. Products were classified into the following groups, which are typical of the FCC operation: dry gas (C1−C2), liquefied petroleum gas (LPG, C3−C4),

products in the range of gasoline (C5−216 °C), and light cycle oil (LCO, 216−344 °C) boiling points and coke.

■ RESULTS AND DISCUSSION

A comparison between typical elemental compositions of asphalthene fractions in heavy oil (Table 2 shows the examples

Table 2. Elemental Composition of Q65 and Asphalthene Fractions (wt %)

	Q65	asphalthenes[a]	asphalthenes[b]
C	77.05	85.69	76.80
H	6.25	11.15	10.00
N	3.00	2.21	2.21
S	6.84	0.72	2.69
O	6.86	0.23	8.27

[a]According to ref 21. [b]According to ref 22.

from two Chinese heavy oils)[21,22] and the Q65 molecule can be helpful to back its use as a model compound. It can be seen that the most important differences are located in some of the heteroatom contents.

In the experiments with the TOL−Q65 solution, no components eluting after the n-C20 retention time (the boiling point of n-C20 is 344 °C, which usually defines the final point of the LCO cut in FCC) were observed in the chromatograms. Then, the hydrocarbon products resulting from the conversion of Q65 had boiling points lower than 344 °C or took part of the coke deposits.

To analyze with more detail the mass balances in the experiments and the yields of the various hydrocarbon groups produced by the conversion of the Q65 molecules, the corresponding masses of hydrocarbons can be calculated by subtracting from the total mass of a given group in the experiments with TOL−Q65 the mass formed by the solvent alone. This mass is known from the yield curves in the experiments with pure TOL under the same conditions. Then, the hydrocarbon yields from Q65, including coke, can be determined with eqs 1 and 2, which imply the assessment of careful mass balances.

$$y_i\,(\%) = \frac{m_{i,\text{Q65}}}{m_{\text{Q65}}}100$$

(1)

$$m_{i,\text{Q65}} = m_i - m_{i,\text{TOL}}$$

(2)

For the group i, $m_{i,\text{Q65}}$ is the mass produced by the conversion of the Q65 molecules, m_i is the mass of the group produced by the TOL−Q65 solution, $m_{i,\text{TOL}}$ is the mass produced by the solvent TOL alone, and m_{Q65} is the mass of Q65 fed to the reactor.

To solve the mass balances, this procedure assumes that no interactions exist between the components of the Q65 and TOL reacting systems and that the actual differences in the yields in the experiments performed using the solution or only the solvent (e.g., because of small changes in true TOL partial pressure) have no significance. Moreover, the conversion of Q65 into hydrocarbons can be calculated from the various yields.

$$x\,(\%) = y_{\text{C1−C2}}\,(\%) + y_{\text{C3−C4}}\,(\%) + y_{\text{C5−216 °C}}\,(\%)$$
$$+ y_{\text{216−344 °C}}\,(\%) + y_{\text{coke}}\,(\%)$$

(3)

Table 3. Mass Balances for the Experiments at a 15 s Reaction Time[a]

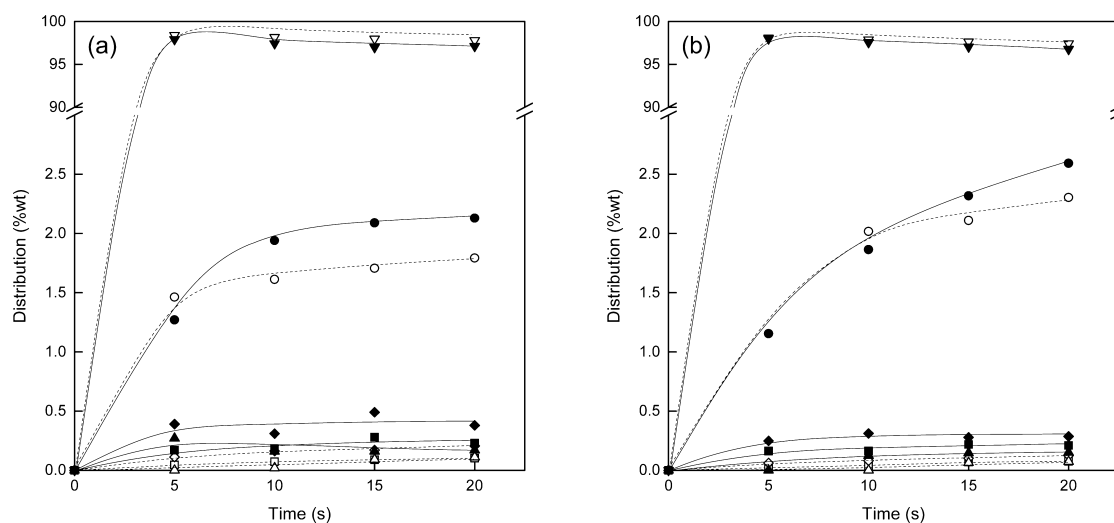| catalyst	m_{Q65}	multi-ring core	side chain	m_{C1-C2}	m_{C3-C4}	$m_{C5-216\ °C}$	$m_{216-344\ °C}$	m_{coke}	$m_{prod,Q65}$	x (%)
E-cat D	7.14	5.43	1.71	0.30	0.53	3.19	0.15	0.88	5.04	70.6
E-cat R	7.71	5.86	1.85	0.23	0.29	3.45	0.15	0.71	4.83	62.6

[a]Masses in milligrams.

Figure 2. Product distribution (wt %) of the main hydrocarbon groups in the conversion of TOL−Q65 (closed symbols and full lines) and pure TOL (open symbols and dashed lines): (a) catalyst E-cat D and (b) catalyst E-cat R. Symbols: (■ and □) C1−C2, (◆ and ◇) C3−C4, (▼ and ▽) C5−216 °C, (▲ and △) 216−344 °C, and (● and ○) coke.
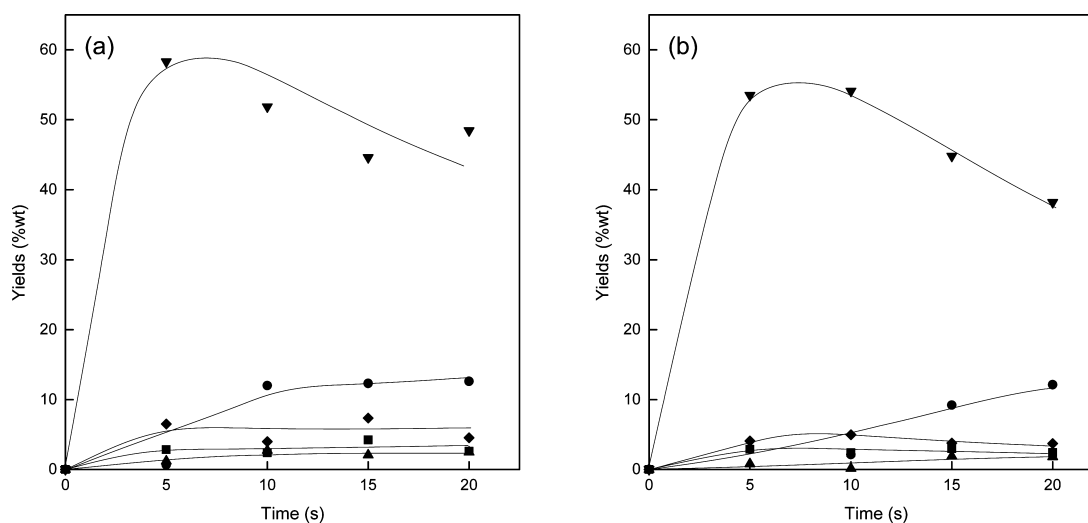

Figure 3. Yields (wt %) of the main hydrocarbon groups in the conversion of Q65: (a) catalyst E-cat D and (b) catalyst E-cat R. Symbols are the same as in Figure 2.

Conversions over the two catalysts were essentially constant in the experiments, with average values of 70.9 and 58.9% for catalysts E-cat D and E-cat R, respectively. These values confirm a higher activity for catalyst E-cat D.[23,24] Because the total mass of products from Q65 in the gas phase and coke is higher than the mass corresponding to the eight carbon atoms linear aliphatic side chain (see Figure 1), it can be deduced, from the mass balances, that the multi-ring core of the Q65 molecule also reacts or takes part of the coke deposits on the catalyst. This is also supported by the fact that the mass of coke produced by the Q65 molecules is smaller than the mass corresponding to the multi-ring cores. Examples of the mass balances are shown in Table 3.

Some speculations can be performed about possible points for acid chemical attack. For example, from the analysis of the Q65 molecular structure (see Figure 1), those positions where heteroatoms are located (O linked to the side chain, S in the core, and carbonilic O and N) are candidates, because of the higher electronic density in those areas.

The yields of the main hydrocarbon groups as a function of the reaction time in the experiments with TOL−Q65 are shown in Figure 2 compared to those in the experiments with pure TOL. It had been shown that when pure TOL is converted over FCC catalysts under this range of experimental conditions,[12] it produces mainly benzene and xylenes, which result from the disproportionation reaction, and also very small

amounts of open-chain hydrocarbons with six or less carbon atoms per molecule, C9 aromatics, naphthalene, and methyl naphthalene. It can be seen that, in all of the hydrocarbon groups, Q65 produces an increase in their yields compared to the cases of pure TOL. The only exception was in the gasoline boiling range, where significant differences are not observed in the yields from both feedstocks (TOL−Q65 and TOL).

Figure 3 shows the yields of the various hydrocarbon groups resulting from the conversion of Q65 as a function of the reaction time over both catalysts. According to the higher activity of E-cat D, the yields of all of the groups were slightly higher than those with catalyst E-cat R. The yields of C1−C2 hydrocarbons, which are mainly formed by the reactions of thermal cracking,[25] show a very slightly increasing profile and selectivities of 3.4 and 4.0 wt % on catalysts E-cat D and E-cat R, respectively. It is expected that these reactions affect particularly the eight carbon atoms linear aliphatic chain in the Q65 molecule. In studies with linear C8 paraffins over Y and USY zeolites at 500 °C, these hydrocarbons were also observed with low selectivities (average of 5.6 wt %).[26]

The yields of C3−C4 hydrocarbons show profiles that are essentially stable in both catalysts. The majority of the products in the group are C3 hydrocarbons and butenes, while n-butane and isobutane are produced in about the same magnitude, as seen in Table 4 for the example of the experiments at 10 s. This

Table 4. Product Selectivities in C3−C4 Hydrocarbon Group (wt %)[a]

	E-cat D	E-cat R
C3	43.27	43.84
isobutane	16.70	11.63
n-butane	14.83	9.36
butenes	25.20	35.16
C4/C4=	1.25	0.60

[a]Reaction time = 10 s.

distribution shows a lower proportion of isobutane and a much higher proportion of butenes if compared to the products in the same range observed in the conversion of linear C8 paraffins.[26]

The highest yield in the conversion of Q65 corresponded to hydrocarbons in the gasoline boiling range. It showed a maximum and then decreased as a function of time, suggesting that the components of the group are forming coke or, in the case of aromatics, alkylated to LCO-range products.

Because the solvent TOL produces insignificant amounts of non-aromatic compounds in the gasoline boiling range,[12] the yields of these paraffinic and olefinic hydrocarbons in the group can be considered only as the result of the conversion of the Q65 molecules. Branched paraffins are observed in the C5−C9 range (mostly isopentane and 2- and 3-methylpentane), and linear paraffins are observed in the C5−C12 range (mostly n-pentane). Branched olefins (mostly 2- and 3-methyl-1-butene and 2-methyl-2-butene) and linear olefins (mostly pentenes: 1-pentene, c-pentene, t-pentene, and 1-hexene) are produced in lower amounts, and minor yields of cyclopentane are also observed. The aromatic compounds in the group, which control the gasoline yield curve profile, are mostly monoaromatics, which can be produced from both the linear side chain and, more directly, from the core of the Q65 molecule. A summary of the composition of these groups, which was very similar for both catalysts, is shown in Table 5. Moreover, while the proportion of aromatics was stable as a function of time, the

concentration of olefins and paraffins showed a slightly decreasing profile.

Table 5. Composition of the C5−216 °C Cut (wt %)[a]

	E-cat D	E-cat R
aromatics	83.5	83.7
olefins	2.4	3.1
saturated	11.8	13.2

[a]Reaction time = 10 s.

The yield of hydrocarbons in the LCO boiling range is similar in both catalysts. The hydrocarbons observed in the cut are almost completely aromatics, with the most important one being methyl naphthalene, although some C3-naphthalenes and methyl fluorene were also observed. These products could be the result of the alkylation of aromatics in the gasoline range by light olefins, and this can be one of the reasons for the decrease in the yield of the C5−216 °C group. They could also be originated from the aromatic core of the Q65 molecules.

The molecular structure of Q65 strongly suggests that it can be a promoter of coke formation, a fact that is confirmed by the high yields shown in Figure 3. The combustion profiles in all of the cases showed single peaks with the maxima located after the highest temperature in the program (700 °C) was achieved, thus suggesting high condensation. Moreover, the coke yield with the conventional catalyst E-cat D is higher than that with the resid catalyst E-cat R, consistent with their respective formulations. Catalyst E-cat R also showed a better coke selectivity in the conversion of residual feedstocks.[23,24] These results are also consistent with the higher activity and hydrogen-transfer capability exhibited by catalyst E-cat D (reflected in, e.g., the lower olefinicity in the C4 hydro-carbons;[27] see Table 4), which could result in higher coke yields. It must be considered, however, that the hydrogen-transfer capability of catalyst E-cat D is not completely coherent with its content of rare earth ions, which is lower than that of catalyst E-cat R; this can be rationalized considering that, if the load is above approximately 3%, such as in the case of catalyst E-cat R, rare earth ions may form OH bridges between them, leading to a decrease in the catalyst acidity, below that expected from the hydrolysis of the individual cations.[28]

Considering that the Q65 molecule has some of the characteristics of asphaltenes, such as condensed polyaromatic rings with aliphatic chains and heteroatoms (nitrogen, oxygen, and sulfur), its definition as a model to represent asphaltenes or other fractions in resids requires comparisons against the behavior of "pure" fractions. However, the information about the reactivity and product slates from residues in FCC is scarce.[29] Moreover, the fact that the composition of the fractions in residues changes depending upon the fractionation method, as well as their definition in terms of solubility (which implies that they are not true chemical families), has to be taken into account.[30]

■ CONCLUSION

Q65 is a compound with some characteristics that can be associated with asphaltene structures. Its conversion over equilibrium commercial FCC catalysts of different types at high temperature and short reaction times was useful to characterize some catalyst properties. Activity and hydrogen-transfer ability (higher in the conventional catalyst) and coke selectivity, which is better in the resid catalyst, are examples.

It was shown that both the eight carbon atoms linear aliphatic side chain and the multi-ring core of the Q65 molecule react, leading to hydrocarbon product distributions that cover a wide range from C1 to C20. The distributions showed some differences according to the formulation of the catalysts. However, overall, olefins prevailed among gases and, neatly, aromatics among liquids. Coke yields were high, exceeding 12 wt %.

Although the reaction suggested high sensitivity to some key issues in resid FCC catalysts, e.g., coke selectivity, the potential of Q65 as a model molecule needs to be confirmed by comparison to the products from the conversion of residue fractions under the same conditions.

■ AUTHOR INFORMATION

Corresponding Author
*Telephone: +54-342-4528062. Fax: +54-342-4531068. E-mail: usedran@fiq.unl.edu.ar.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ NOMENCLATURE

TOL = toluene
Q65 = quinolin-65
m = mass (g)
x = conversion (%)
y = yield (%)

Subscripts

Q65 = refers to quinolin-65
TOL = refers to toluene
C_1–C_2 = refers to dry gas
C_3–C_4 = refers to liquefied petroleum gas
C_5–216 °C = refers to products in the range of gasoline
216–344 °C = refers to light cycle oil
coke = refers to coke

■ REFERENCES

(1) O'Connor, P. *Stud. Surf. Sci. Catal.* **2007**, *166*, 227–251.
(2) Yung, K. Y.; O'Connor, P. O.; Janik, S. J.; Bruno, K. *Catal. Cour.* **2003**, *53*, 2–8.
(3) Schlosser, C. R.; Baptista, R. D.; Brazil, H. Q.; Chamberlain, O.; Pinho, A.; Sandes, E. F.; O'Connor, P.; Torem, M. A. *Proceedings of the Akzo Nobel ECO-MAGIC Catalysts Symposium*; Noordwijk, The Netherlands, June 10–13, 2001; Contribution F8.
(4) Al-Khattaf, S.; de Lasa, H. *Appl. Catal., A* **2002**, *226*, 139–156.
(5) Scherzer, J. *Catal. Rev. Sci. Eng.* **1989**, *31*, 215–354.
(6) Hakuli, A.; Imhof, P.; Kuehler, C. *Proceedings of the Akzo Nobel ECO-MAGIC Catalysts Symposium*; Noordwijk, The Netherlands, June 10–13, 2001; Contribution F4.
(7) Falco, M.; Morgado, E.; Amadeo, N.; Sedran, U. *Appl. Catal., A* **2006**, *315*, 29–34.
(8) López-Linares, F.; Carbognani, L.; Gonzalez, M.; Sosa-Stull, C.; Figueras, M.; Pereira-Almao, P. *Energy Fuels* **2006**, *20*, 2748–2750.
(9) de Lasa, H. U.S. Patent 5,102,628, 1992.
(10) Johnson, M. F. L. *J. Catal.* **1978**, *52*, 425–431.
(11) Passamonti, F.; de la Puente, G.; Morgado, E.; Gilbert, W.; Sedran, U. *Chem. Eng. J.* **2012**, *183*, 433–447.
(12) Al-Khattaf, S. *Ind. Eng. Chem. Res.* **2007**, *46*, 59–69.
(13) Gilbert, W. R.; Morgado, E., Jr.; de Abreu, M.; de la Puente, G.; Passamonti, F.; Sedran, U. *Fuel Process. Technol.* **2011**, *92*, 2235–2240.
(14) de la Puente, G.; Sedran, U. *Chem. Eng. Sci.* **2000**, *55*, 759–765.
(15) Bidabehere, C.; Sedran, U. *Ind. Eng. Chem. Res.* **2001**, *40*, 530–535.
(16) Tiscornia, I. S.; de la Puente, G.; Sedran, U. *Ind. Eng. Chem. Res.* **2002**, *41*, 5976–5982.
(17) de la Puente, G.; Chiovetta, G.; Sedran, U. *Ind. Eng. Chem. Res.* **1999**, *38*, 368–372.
(18) Spretz, R.; Sedran, U. *Appl. Catal., A* **2001**, *215*, 199–209.
(19) de la Puente, G.; Klocker, C.; Sedran, U. *Appl. Catal., B* **2002**, *36*, 279–285.
(20) de la Puente, G.; Devard, A.; Sedran, U. *Energy Fuels* **2007**, *21*, 3090–3094.
(21) Chen, Y.; Yang, Ch.; Wang, Y. *J. Anal. Appl. Pyrolysis* **2010**, *89*, 159–165.
(22) Chen, Y.; He, J.; Wang, Y.; Li, P. *Energy* **2010**, *35*, 3454–3460.
(23) Devard, A.; de la Puente, G.; Sedran, U. *Fuel Process. Technol.* **2009**, *90*, 51–55.
(24) Devard, A.; de la Puente, G.; Sedran, U. *Appl. Catal., A* **2009**, *353*, 223–227.
(25) Moldoveanu, S. C. *Techniques and Instrumentation in Analytical Chemistry*; Elsevier: Amsterdam, The Netherlands, 2010; Chapter 6, pp 111–127.
(26) Smirniotis, P. G.; Ruckenstein, E. *Ind. Eng. Chem. Res.* **1994**, *33*, 800–813.
(27) Cheng, W. C.; Suarez, W.; Young, G. W. In *Advanced Fluid Catalytic Cracking Technology*; Chuang, K. C., Young, G. W., Benslay, R. M., Eds.; American Institute of Chemical Engineers (AIChE): New York, NY, 1992; AIChE Symposium Series *291*, pp 38–44.
(28) Lemos, F.; Ramoa Ribeiro, F.; Kern, M.; Giannetto, G.; Guisnet, M. *Appl. Catal.* **1988**, *39*, 227–238.
(29) Gilbert, W.; Baptista, C.; Teixeira, M. A. *Pet. Technol. Q.* **2000**–**2001**, *Winter*, 49–53.
(30) Gonzalez, M. F.; Sosa-Stull, C.; López-Linares, F.; Pereira-Almao, P. *Energy Fuels* **2007**, *21*, 234–241.