Bulk Molecular Characterization Approach for the Simulation of FCC Feedstocks

2 AUTHORS, INCLUDING:

George Bollas
University of Connecticut
43 PUBLICATIONS **273** CITATIONS

Bulk Molecular Characterization Approach for the Simulation of FCC Feedstocks

G. M. Bollas* and I. A. Vasalos

*Laboratory of Petrochemical Technology, Department of Chemical Engineering,
Aristotle University of Thessaloniki, 57001 Thessaloniki, Greece*

A. A. Lappas, D. K. Iatridis, and G. K. Tsioni

*Chemical Process Engineering Research Institute (CPERI),
Centre for Research and Technology Hellas (CERTH), P.O. Box 361, 57001 Thermi-Thessaloniki, Greece*

Feedstock quality affects the fluid catalytic cracking (FCC) process to such an extent that even the operating variables or the catalyst selection seem to be of secondary importance. This paper focuses on the way that the bulk properties of an FCC feedstock can explain the extent of catalytic reactions (crackability) and coke production (coking tendency). The final goal of this effort is to develop a model for the characterization of fluid catalytic cracking feedstocks on the basis of standard analytical procedures accessible to the average refinery. Using different approaches to the characterization of petroleum fractions, a model was developed for the prediction of the behavior of fluid catalytic cracking feedstocks under real FCC conditions. A large database of experiments, performed in the FCC pilot plant of the Chemical Process Engineering Research Institute (Thessaloniki, Greece), was used for the development of the feedstock characterization procedure. The aromatic carbon, the average carbon number, and the total nitrogen and sulfur contents were appropriately combined to predict the effect of feedstock quality on the conversion and coke yield of the fluid catalytic cracking process. The simulation results reveal the ability of this approach to predict accurately the crackability and coking tendency of an FCC feedstock from easily measured properties and to explain the impact of these properties on the FCC outcome.

Introduction

The modeling of fluid catalytic cracking (FCC) units is of pivotal interest, because of their complexity and associated economic incentives. The effective simulation of FCC units requires a thorough understanding of the combined kinetics and hydrodynamics of the two interconnected reactors, the riser and the regenerator. Furthermore, understanding the interacting effects of the two leading factors in the catalytic reactions, the feedstock and the catalyst, is crucial. Although numerous efforts have been made to add knowledge through the simulation of FCC operations and to develop advanced catalytic systems, a relative gap appears in the area of the simulation of the effect of the feed on the FCC process. In fluid catalytic cracking, feed quality is especially critical because it affects the heat balance and the ultimate cracking severity, in addition to its fundamental effects on the inherent crackability of the molecular structures. FCC feeds include straight-run distillates, vacuum gas-oils, and atmospheric and vacuum residua, which are unidentified complex hydrocarbon mixtures, thus increasing the degree of complexity of FCC modeling. The number of components and hydrocarbon types in FCC feeds increases with boiling range, which causes increased difficulties in the degree of possible analytical identification. The theoretically pos-

sible number of paraffin isomers gives an idea of the complexity of the problem: 75 isomers with 10 carbon atoms can exist, so at a carbon number of 20, about 3.66 × 10^{5} paraffin isomers can be found, whereas at a carbon number of 100, the number of possible existing isomers increases to 5.92 × 10^{39}.[1]

Ideally, the ultimate goal in FCC processing would be to relate the feed composition to product yields and qualities for particular operating conditions. However, because complete characterization of FCC feedstocks is not practical for economic and technical reasons, the industry developed methods to correlate combined feed properties with the FCC outcome. Characterization methods can vary widely in sophistication. Different end uses (for instance, daily routine for unit operation, process simulation, process design, catalyst research, etc.) require different methods. Whatever the purpose, understanding feed properties, feed characterization, and analytical limitations is crucial.

Generally, one can distinguish three major trends in the area of FCC feed characterization: (a) parametric models,[2−4] which incorporate important feed properties in mathematical models without adding much knowledge about the actual effect of each property; (b) lumping models,[5−7] in which the different types of hydrocarbons are lumped into groups that are assumed to characterize the behavior of the total feed according to a pseudo-reaction scheme; and (c) modern "single-event" kinetic representations of the feed,[8,9] which permit a mechanistic description of catalytic cracking based on the well-known mechanisms of the various reactions involving carbenium ions.

* To whom correspondence should be addressed. Address: G. M. Bollas, Chemical Process Engineering Research Institute, Centre for Research and Technology Hellas, 6th km. Charilaou−Thermi Rd., P.O. Box 361, Thessaloniki GR-570 01, Greece. Fax: +30 2310 498380. E-mail: gbollas@cperi.certh.gr

Each approach appears to have its own pros and cons according to its purpose and its applicability at the real process level. Parametric models are easily adopted within industrial real-time operations, because they involve properties that are easily measured on a daily basis in any refinery laboratory, such as the density of the feed, its boiling point, refractive index, etc.[10] The main disadvantage of parametric models is that they are entirely empirical, and their lack of fundamentality makes them applicable only for the specific process setup for which they were developed, while the range of the original training dataset restricts their accuracy. On the other hand, the more fundamentally based lumping models aim to provide insight into how feed quality affects the cracking reactions. The general idea of these models is to define paraffinic, naphthenic, and aromatic lumps while splitting the total FCC feed in two fractions: (a) the heavy fraction containing the long-chain paraffinic molecules and high-carbon-number polycyclic aromatic and naphthenic molecules and (b) the light fraction that involves hydrocarbon molecules with average carbon numbers up to 20.[5] The clear advantage of these types of models is that they are consistent with the general theory of how each hydrocarbon group contributes to catalytic cracking and, of course, with experimental evidence. However, the laboratory requirements for complex experimental measurements are not convenient and often are not a practical option at all for refineries, from both economic and laboratory-capabilities perspectives. Finally, the modern and more advanced single-event kinetic modeling approach aims to lead to kinetic parameters that are truly independent of the bulk feedstock quality. The analysis of the feedstock is made by means of liquid chromatography and GC-MS. However, the application of such models to the catalytic cracking of industrial FCC feedstocks is far from practical, as a result of the required analytical complexity and the corresponding computational limitations.

In parallel to these three major trends in feed characterization, a significant effort is being made to interrelate the various bulk properties of petroleum fractions and to produce techniques for their molecular characterization from easily measured petroleum properties. In the characterization of petroleum fractions, two different classification schemes dominate. The first is hydrocarbon classification according to structural elements such as aromatic and naphthenic rings, aromatic carbons, etc., which is mainly performed by nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR) spectroscopy and is successfully predicted by the empirical method of Van Nes and Van Westen,[11] widely known and used as the ndM method. The second classification corresponds to the molecular type of the hydrocarbons contained in a petroleum fraction, which is handled by mass spectroscopy and is satisfactorily predicted by the empirical correlation of Riazi and Daubert.[12] Furthermore, new correlations for the molecular and structural characterization of petroleum fractions have been presented in the literature in the recent years. Dhulesia[13] presented the total equation, which claimed to override the problems with overpredictions of the ndM method, whereas the G−L method of Guilyazetdinov[14] and the DBE concept presented by Korsten[15] aimed at an even more analytical characterization of petroleum fractions on the basis of a number of logical assumptions about the average hydrocarbon structure.

The emerging need for more accurate petroleum characterizations led the research community to the idea of splitting the total petroleum sample into a manageable number of fractions (pseudocomponents) and then examining these fractions separately to define critical properties and all other required information. It is widely accepted that a proper description of the physical properties of these subfractions is essential for reliable compositional studies. The analysis of the total fraction into pseudocomponents is based on distillation analysis, typically a true boiling point (TBP) test, which is the only available information for the distribution of the hydrocarbon fractions. With the TBP distribution known, the prediction of the complete distributions for various properties of a C_{7+} fraction is possible, using the bulk properties of the mixture and an appropriate distribution model. Whitson[16,17] used a γ-distribution model to describe the molecular weight per mole fraction relation for the C_{7+} fraction, and by assuming a constant Watson's factor (K_W), he generated the specific gravity distribution.[17] Ahmed[18] used a two-parameter exponential function for the molecular weight distribution, whereas Pedersen et al.[19] suggested a logarithmic distribution of the molar fraction versus the carbon number. Riazi[20] reviewed several distribution models and concluded that the exponential distribution model is not suitable for representing boiling point, density and refractive index distributions. Furthermore, Riazi proposed a reduced two-parameter γ-distribution model according to his set of equations and assumptions.[20] Nevertheless, all of the above researchers stressed the importance of splitting the wide-boiling-point fraction into narrow-boiling-point pseudo-fractions to increase the accuracy of predictions.

The aim of this paper is to combine the correlations available in the literature for petroleum characterization and classification to develop a system of equations for the most complete description of FCC feeds possible from easily measured properties. Thus, sufficient knowledge would be accomplished for the influence of each property on catalytic cracking. On the basis of the experimental results of the FCC pilot plant operated in Chemical Process Engineering Research Institute (CPERI), the impact of the feed on catalytic cracking was clearly distinguished from the effect of the other process variables. Thirteen different feedstocks with a wide range of properties were examined under real FCC conditions, and their relative (compared to a reference FCC feed) potentials to enhance catalytic cracking, named crackability, as well as their tendencies to produce coke, named coking tendency, were determined. The bulk properties of each feedstock were properly combined to create functional groups that can be used to explain the cracking results. The crackability of an FCC feedstock and its tendency to produce coke and to poison the catalyst were then expressed via these functional groups, which were coupled into an integrated model for predictions of the conversion and coke yield (both in units of weight percentages). Finally, using an appropriate distribution model, the total fractions of the feedstocks studied were split and lumped into heavy and light fractions, and the contribution of each fraction to the cracking behavior of the feedstocks was examined.

How Feed Quality Affects Catalytic Cracking

In the past several decades, significant experience was established regarding the ways in which different

FCC feedstocks influence the conversion and product yield and quality of catalytic cracking.[2,5,21−24] These research efforts were focused on defining the ways in which different hydrocarbon types react in the FCC environment and understanding the effects of non-hydrocarbon contaminants on cracking operations. In this section, the main conclusions of the various ways that feed quality affect catalytic cracking are summarized.

Each type of hydrocarbon reacts under catalytic cracking conditions in certain definite ways. The major difference among hydrocarbons of a particular type is in their crackability or extent of conversion for a given set of operating conditions. In all cases, for each type of molecule, increasing the molecular weight or carbon number increases the crackability. A variety of primary and secondary reactions take place during catalytic cracking. These include chain rupture, isomerization, cyclization, dehydrogenation, polymerization, hydrogen transfer, and condensation. Hence, the result of cracking even a simple molecule such as a normal paraffin is complex.

Normal paraffins crack mostly to olefins and paraffins and give fair yields of very light gasoline (mostly C_5 and C_6 hydrocarbons). The normal paraffins are fairly difficult to crack. The reaction rates and products of paraffin cracking are determined by the molecular size and structure. Paraffinic molecules containing tertiary carbon atoms crack most readily, whereas quaternary carbon atoms are more resistant to cracking.

Naphthenes and isoparaffins tend to crack at about the same rate, but the product distributions are much different. Naphthenes produce relatively little gas and give excellent yields of gasoline. The gasoline is of better quality than that from paraffin cracking and contains appreciable quantities of aromatics, resulting from dehydrogenation of the naphthene rings.

Aromatics crack in several ways. The benzene ring is practically impossible to crack. Condensed-ring aromatics without side chains are converted to a limited extent, but almost entirely to coke. Alkylaromatics with side chains containing at least three carbon atoms crack extensively by shearing off the entire side chain. With long side chains, secondary reactions will occur, resulting in products similar to those from the cracking of olefins and paraffins. Generally, more aromatic feeds give poorer FCC yields. A contributing factor to this general trend is that, as the number of ring structures in the feed increases, the likelihood increases that dehydrogenation from contaminant metals will cause multi-ring aromatics to form, leading to condensation and coking of the catalyst. The molecular structure of the aromatic hydrocarbons is another important issue regarding their crackability. The distribution of aromatics among the degree of condensation clearly affects the rate of cracking. As the number of rings in a polynuclear aromatic molecule increases, the rate of cracking decreases, although the aromatic content appears to remain the same.[21] The net result of the catalytic cracking of aromatic hydrocarbons is moderate yields of gas, very little gasoline, large quantities of very aromatic cycle stock, and high coke yields.

Olefins seldom appear in catalytic cracking feeds, but their reactions are of interest because they are the primary products of other cracking reactions. Olefins heavier than about C_6 are extremely reactive. The products of olefin cracking are primarily propylene and butenes, along with butanes from secondary reactions.
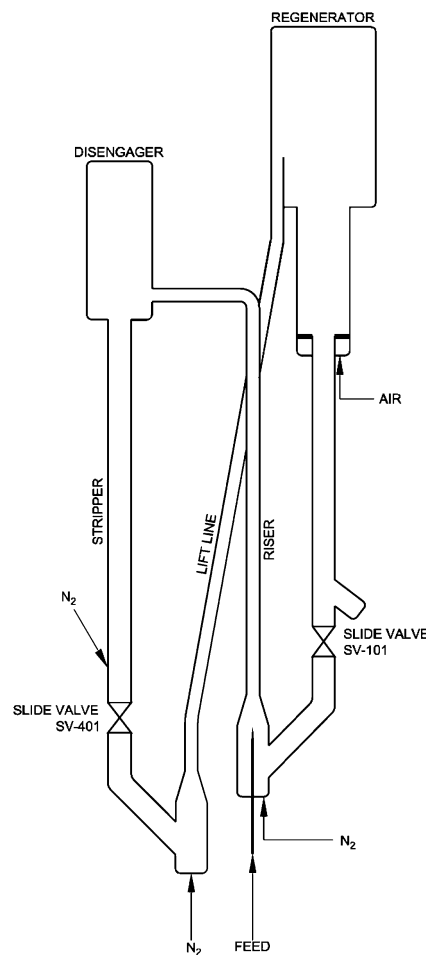

Figure 1. Schematic diagram of the pilot pant of CPERI.

Some polymerization and cyclization takes place in olefin cracking to produce a small amount of cycle stock and fairly high coke yields.

Non-hydrocarbon contaminants, such as nitrogen, iron, nickel, vanadium, and copper compounds, act as poisons to cracking catalysts. Nitrogen, being basic, reacts with the acid centers on the catalyst and lowers the catalyst activity. However, the basicity of nitrogen compounds at cracking conditions can vary widely.[25] Thus, the total nitrogen content is considered as a better indicator for cracking inhibition by basic nitrogen compounds.[24] The metals deposit and accumulate on the catalyst and cause a reduction in throughput by increasing coke formation. Finally, the sulfur content of an FCC feed has no major effect on the crackability of the feed, but it strongly affects the product distribution and quality.[23,24]

Experimental Setup

The FCC pilot plant of CPERI operates in a fully circulating mode and consists of a riser reactor with a 7-mm i.d., a fluid-bed regenerator, a stripper, and lift lines (Figure 1). At the reactor bottom, the gas-oil contacts the hot catalyst (which flows from the regenerator) and evaporates, and the catalyst is kept in a fluidized state by means of nitrogen flow. In the riser, the cracking reactions take place, and at the riser exit, the mixture enters the stripper vessel where the separation (stripping) of gases from the solid catalyst occurs. The fluid-bed regenerator reactor is used to burn off the carbon deposited on the catalyst surface as a byproduct

of the cracking process. A more analytical description of the CPERI FCC pilot plant can be found in the literature.[26] The main advantage of the use of pilot plants in the modeling of FCC units is that their kinetic characteristics simulate the real process of commercial units with the maximum possible accuracy. Furthermore, operation of the pilot unit provides the ability to examine the process under steady feed and/or catalyst properties, to isolate their respective effects on cracking and develop property-oriented correlations for each subset of process variables. The main difference between the pilot plant of CPERI and commercial FCC units arises from the differences in geometry. In small-diameter FCC risers, the gas and solids rise with different velocities, corresponding to different residence times of the two phases. This should mainly affect the catalyst residence time and the catalyst deactivation rate.[26] However, it is expected that the effect of feedstock quality on the product yields, which mainly concerns the actual reaction kinetics of the process, should not differ between commercial units and the pilot plant.

In the study of the effect of feed quality on the cracking reactions, a set of experiments with 10 different FCC feedstocks was used for model development, and a set of experiments with three feedstocks was used for model validation. The properties of these feeds are presented in Tables 1 and 2 and were measured according to ASTM standards. That is, the total nitrogen, sulfur, and carbon contents (wt %) were measured according to methods D4629, D4294, and D5291, respectively, whereas the API gravity, refractive index, and Conradson carbon residue were measured according to methods D4052, D1218, and D4530, respectively.

Model Development

Background. The study of the effect of the feedstock quality on FCC operation was based on a coupled kinetic−hydrodynamic model previously developed at CPERI and described in detail elsewhere.[26] The complete model for the steady-state simulation of the FCC riser reactor was assumed to be the product of the functions describing the influence of operating conditions, feed properties, and catalyst type on the cracking reactions. The general form of the final correlation for the prediction of the conversion (x, wt %) assumes riser reactor conditions with concurrent plug flow of the gas and solids phases and second-order kinetics for the total cracking reaction,[27,28] as presented in eq 1

$$\frac{x}{100 - x}\text{WHSV} = kC(\text{catalyst type})$$
$$F(\text{feed crackability}) \exp\left(-\frac{E}{RT}\right)t_c^{\ n} \quad (1)$$

The left-hand side of eq 1 is a linear function of the catalyst residence time (t_c) (when expressed on a log−log graph) for a given catalyst and feed and at constant temperature. The slope of this linear dependence is n, the catalyst decay exponent.[26] The same form of correlation was assumed to apply for the catalytic coke yield (u_x, wt %) for a zeroth-order reaction,[26] as presented in eq 2

$$u_x\text{WHSV} = k_u C_u(\text{catalyst type})$$
$$F_u(\text{feed coking tendency}) \exp\left(-\frac{E_u}{RT}\right)t_c^{\ n_u} \quad (2)$$

The so-called "operating conditions functions" were developed from experiments in the pilot unit using constant feed and catalyst. The values of the preexponential factors (k, k_u), activation energies (E, E_u), and decay exponents (n, n_u) were calculated through a linear regression of the experimental data.[26] For the calculation of the weight hourly space velocity (WHSV), a hydrodynamic model was developed in which the slip between the gas and solids phases was taken into account and shown to play an important role in small-diameter FCC risers.[26]

Feedstocks Database. The prediction accuracy of the operating conditions functions lies within 2% in terms of the average relative error (ARE) for the conversion (wt %) and 5% ARE for the coke yield (wt %).[26] These prediction errors are of the same magnitude as the experimental error for the measurements of weight percentage conversion and coke yield in the pilot plant, which supported the idea of using eqs 1 and 2 as prior knowledge to isolate the effects of feedstock properties. For that reason, experiments were performed with various feedstocks and constant catalyst, and a "feed index" was assigned to each different feedstock. This feed index is actually the best-fit multiplier to the predicted values of the operating conditions functions for the conversion and coke yield to equal the observed values for the constant-catalyst experimental series. For each set of experiments with constant feedstock and catalyst, the feed indices for conversion (named crackability) and coke yield (named coking tendency) were calculated with linear regressions.

Feed 4, presented in Table 1, was the base feed used for the development of the operating conditions functions,[26] so its respective feed indices were unity. As shown in Table 1, the quality of the feedstocks used ranged from highly paraffinic (feed 16) to highly aromatic (feed 17). Moreover, a hydrotreated feed (feed 12) was included in the training database, because the hydrotreatment of an FCC feedstock affects not only its sulfur and nitrogen contents, but also its general chemical structure. Finally, a light vacuum gas-oil (feed 15) was also included in the training dataset to examine the effects of boiling point and molecular weight on cracking reactions.

Average Hydrocarbon Structure Approach. The first step in the bulk molecular characterization approach proposed in this paper was to translate the knowledge presented in the literature into manageable parameters or functions that describe the crackability and coking tendency of an FCC feedstock. In this way, simple and easily measured bulk properties can be transformed into independent groups that monotonically influence the catalytic reactions in a certain way. Using the concept of Van Nes and Van Westen[11] in the development of the ndM method, the total hydrocarbon fraction can be represented by a hypothetical average molecular structure with properties equal to those of the total feedstock. Thus, one can actually simplify the very complex problem of thousands of different structures in an FCC feed into an average hypothetical molecule that is expected to represent the cracking behavior of the total feed. The latter is enhanced by the fact that the majority of the catalytic reactions in the FCC operation are governed by the same clear trends that are determined by the general theory of catalytic cracking.

Table 1. Bulk Properties of the Feedstocks Examined (Training Set)

property	code name									
	4	5	6	7	12	13	14	15	16	17
gravity, API	25.2	22.4	26.4	20.4	24.8	23.4	22.0	26.3	30.9	9.6
sulfur (wt %)	1.82	2.13	1.31	2.98	0.18	2.04	2.72	2.51	0.80	4.69
nitrogen (wt %)	0.096	0.101	0.080	0.086	0.116	0.092	0.086	0.037	0.007	0.178
CCR (wt %)	0.07	0.69	0.38	0.41	0.20	0.37	0.56	0.01	0.08	3.20
RI, 20 °C	1.5016	1.5101	1.4980	1.5162	1.4993	1.5086	1.5134	1.4996	1.4782	1.5689
TBP (°F)										
IBP	338.5	360.7	339.9	483.8	540.1	340.2	388.4	263.1	300.0	644.7
10%	605.5	646.6	650.6	815.1	724.9	626.8	612.8	578.3	752.7	744.1
30%	725.9	776.5	781.9	853.1	807.9	755.0	748.0	637.5	827.7	813.5
50%	797.4	856.0	844.5	879.3	871.2	832.8	820.2	676.4	879.4	868.6
70%	847.2	918.9	889.3	904.1	928.1	885.6	875.3	710.4	935.3	922.8
90%	905.7	1014.1	967.3	934.0	1008.9	962.6	961.5	770.5	1024.7	1014.8
FBP	948.9	1070.6	1028.7	970.0	1080.2	1026.9	1020.9	842.2	1043.8	1042.5
MW	345.8	381.5	384.5	414.5	423.3	365.5	358.0	283.1	437.7	381.5
C_A, ndM[a]	18.7	19.5	16.6	20.2	12.9	20.9	22.8	21.5	2.4	37.1
C_N, ndM[a]	19.9	21.6	18.5	20.8	30.0	18.0	17.0	18.4	29.1	11.0
C_P, ndM[a]	61.4	58.8	64.9	59.1	57.1	61.0	60.2	60.2	68.5	52.0
C (wt %)	85.4	85.3	86.3	85.1	86.7	85.0	85.4	85.0	85.9	85.3

[a] Aromatic, naphthenic, and paraffinic carbons estimated via the ndM method.

1. Prediction of Crackability. What is clear from the literature is that aromatic feeds give poorer FCC yields. Nace et al.[2] combined mass spectroscopy measurements for the molecular characterization of FCC feedstocks with the aromatic carbon content calculated with the ndM method and classified the aromatic molecules into aromatic carbon atoms and substituent groups attached to the aromatic rings. In other words, what Nace et al.[2] proposed to be of crucial importance in describing the crackability of an FCC feedstock is the "aromaticity of the average aromatic molecule". That is in perfect agreement with the experimental measurements of Lerner and Himpsl,[21] who observed that the degree of condensation of the aromatics plays an important role in the crackability of the feedstock. However, in this approach, the size of the average molecule is not taken into account, and some function of the boiling point or the molecular weight of the feedstock should be incorporated into the final correlation.[4] Furthermore, in a related paper, Voltz et al.[22] observed that the gas-oil cracking rate constant is better related to the ratio of aromatics to naphthenes. On the basis of this conclusion, Ancheyta-Juarez et al.[3] developed correlations for gasoline selectivity and catalyst deactivation using the structural characterization of the ndM method, instead of the molecular characterization provided by mass spectroscopy, and thus, their set of correlations was invariant to complex experimental measurements.

Taking into account all of the above findings, the parameters that were expected to describe the effect of the average hydrocarbon structure of an FCC feedstock on its crackability were the carbon number (N_C) of the hypothetical average molecule and the aromatic carbon content (C_A). The carbon number was calculated from the average molecular weight (MW) and the average carbon content (C%) via eq 3, while the aromatic carbon content was estimated via the ndM method.

$$N_C = (C\%/100)(MW/12) \qquad (3)$$

The inverse relation between aromaticity and crackability for the experimental dataset of CPERI is clear in Figure 2, although some scattering of feedstocks with similar aromatic carbon contents is evident. In Figure 3, the positive effect of the average carbon number on
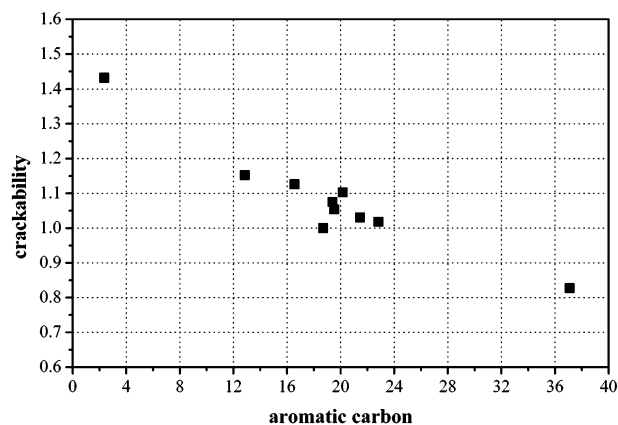

Figure 2. Effect of aromatic carbon (estimated with the ndM method) on crackability (set of model-development experiments).
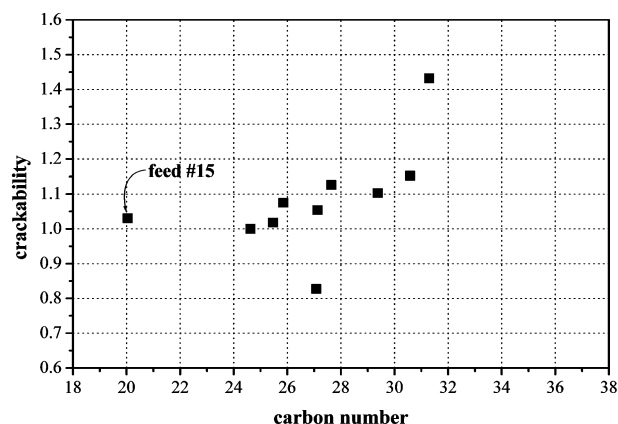

Figure 3. Effect of carbon number (estimated from eq 3) on crackability (set of model-development experiments).

crackability is shown. These oppositional effects were coupled into the functional group ($N_C - N_C C_A$). This functional group is called "*crackable carbon atoms*" and appears to be a good indicator of the effect of the hydrocarbon distribution in an FCC feedstock on its crackability, as shown in Figure 4. A simple translation of the proposed functional group is that the most important for the crackability of an FCC feedstock is the number of the crackable carbon atoms of the hypothetical average hydrocarbon molecule. In other words, the carbon atoms that are not aromatic are
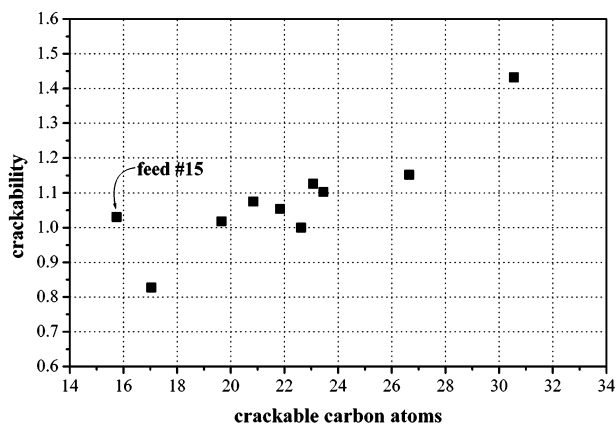
Figure 4. Relation between the crackable carbon atoms ($N_C - N_C C_A$) and crackability (set of model-development experiments).
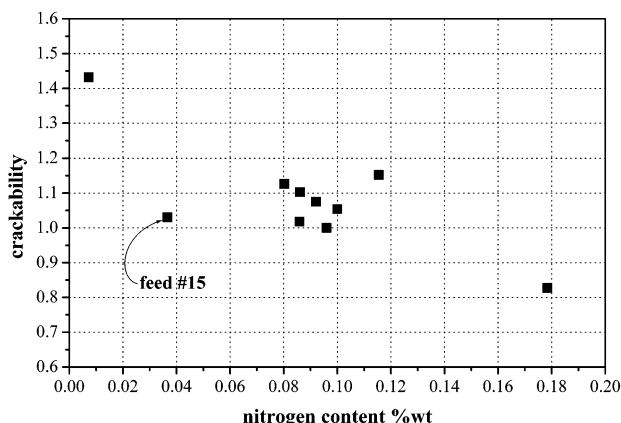

Figure 5. Effect of total nitrogen content (wt %) on crackability (set of model-development experiments).

supposed to be more likely to crack, when the heteroatoms are not taken into account.

Finally, the effect of catalyst deactivation due to nitrogen poisoning has been incorporated into the feed effect function by the addition of a catalyst deactivation term related to nitrogen adsorption. The negative effect of the total nitrogen content on crackability can be observed in Figure 5. The light VGO (feed 15), which did not accurately follow the relation of crackability with carbon number (Figure 3) and crackable carbon atoms (Figure 4), was easily explained by its low nitrogen content, as clearly shown in Figure 5. The functional group that was drawn for catalyst poisoning due to nitrogen was $N_N = (NT\%/100)(MW/14)$, where NT% is the total nitrogen content (wt %), N_N represents the number of nitrogen atoms present in the average hydrocarbon structure of weight equal to MW, and 14 is the atomic weight of nitrogen. The proposed functional groups, namely, the crackable carbon atoms and the nitrogen poisoning term, were assumed to fully describe the crackability of an FCC feedstock and were combined in eq 4, were w_1-w_3 are weighting factors calculated via linear regression of the experimental data

$$\text{crackability} = w_1(N_C - N_C C_A) + w_2(N_N) + w_3 \quad (4)$$

2. Prediction of Coking Tendency. The ability to predict coke formation during FCC operation is of crucial importance, because it impacts the overall heat balance of the FCC unit by determining the heat production by coke combustion in the regenerator and, thus, the catalyst circulation rate in the unit. FCC coke
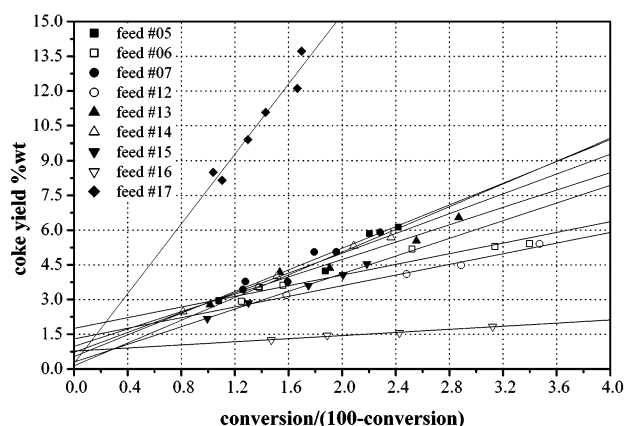

Figure 6. Linear dependence of catalytic coke on conversion for various feedstocks, for the experimental set with constant catalyst and temperature.

can be subdivided according to origin into four types: catalytic coke formed as a byproduct of catalytic cracking (u_x), carbon residue coke formed via thermal (noncatalytic) reactions (u_r), contaminant coke formed as a result of catalyst poisoning (u_c), and catalyst-to-oil coke yielded by incomplete stripping ($u_{C/O}$). Considering that the coke yield due to incomplete stripping is negligible, the total coke yield can be predicted by adding the noncatalytic coke (residue and contaminant) to the catalytic coke, as described in eq 5

$$u = u_r + u_c + u_x \quad (5)$$

In eq 5, u_x is the catalytic coke yield as described by eq 2, which includes the coking tendency of the feedstock used. Assuming that the overall catalyst deactivation parallels its deactivation for coke production, Krambeck[29] suggested a linear dependence of coke yield on kinetic conversion [$x/(100 - x)$] for constant feed, catalyst, and temperature. Figure 6 shows the good agreement of this linear dependence for the feedstocks examined in pilot experiments with constant catalyst and at constant reactor temperature. The intercept of each linear trend in Figure 6 is an estimate of the coke produced for zero conversion; in other words, it is a measure of the noncatalytic coke yield, and the slope stands as an estimate of the coke-conversion selectivity of each feedstock, which is a function of the catalyst and feedstock properties.

The noncatalytic coke yield was approximated by Sapre and Leib[30] as being equal to the Conradson carbon residue of the feedstock. Fisher[31] investigated the formation of residue coke in fluid catalytic cracking and concluded that it is independent of FCC conditions. In the latter work, the Conradson carbon percentage was found to strongly influence the residue coke, while making a much smaller contribution to catalytic coke. Furthermore, Green et al.[23] studied the effect of nitrogen on contaminant coke formation and suggested eq 6 to describe the contribution of basic nitrogen (NB%) compounds to contaminant coke (u_c) formation as a result of their adsorption onto the catalyst surface

$$u_c = NB\% \frac{MW_{NHC}}{14} \exp\left(-\frac{NB\%}{NB\% + 0.437S\%}\right) \quad (6)$$

The exponential term in eq 6 describes the synergistic effect of sulfur compounds toward enhancing catalyst poisoning by nitrogen.[23] For low-sulfur feeds, approxi-
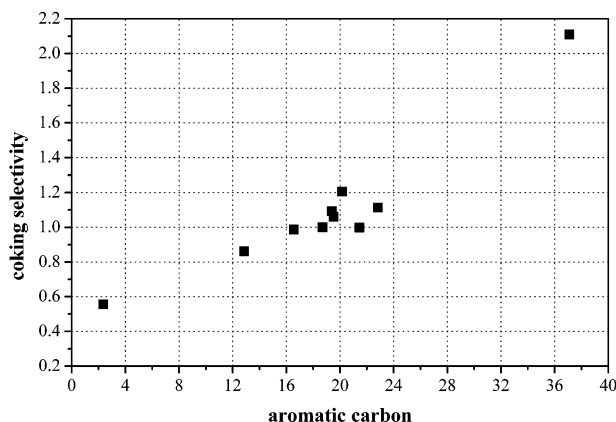
Figure 7. Effect of aromatic carbon (estimated with the ndM method) on coke-conversion selectivity (set of model-development experiments).

Figure 8. Effect of hydrogen content (wt %) on coke-conversion selectivity (set of model-development experiments).

mately one-third of the nitrogen compounds end up as coke, as the exponent of eq 6 receives the value of -1.[23] In eq 6, MW_{NHC} is the molecular weight of the average nitrogen compound and was assumed to equal the molecular weight of the average hydrocarbon structure (MW). Service[24] proposed that coke formation due to basic nitrogen deposition should be a function of the basic or total nitrogen with an expression of molecular weight and sulfur content for the estimation of the adsorption coefficient, which fully agrees with the form of eq 6. As discussed in the Introduction, the basicity of nitrogen compounds can vary widely at cracking conditions;[24,25] thus, in eq 6, the basic nitrogen term (NB%) was replaced by the total nitrogen content (NT%), which is believed to better represent the poisoning of the catalyst due to basic nitrogen compounds.[24]

Taking into account all of the above information and neglecting the catalyst-to-oil coke and the effect of metals (considering that metals are not removed during catalyst regeneration and their effect is cumulative over several catalyst cycles and thus can be ascribed as a property of the catalyst), the two major noncatalytic coke precursors, the nitrogen adsorption and the Conradson carbon residue (CCR) were coupled for the estimation of the noncatalytic coke yield, as shown in eq 5. Typically, less than 100% of the feed CCR goes to coke,[30] and the use of the total nitrogen content (NT%) instead of the basic nitrogen content (NB%) in eq 6 corresponds to a standard overprediction of the contaminant coke formation; thus, the weighting factors k_{CCR} and k_N were applied to eqs 7 and 8

$$u_r = k_{CCR}CCR \quad (7)$$

$$u_c = k_N NT\% \frac{MW}{14} \exp\left(-\frac{NT\%}{NT\% + 0.437S\%}\right) \quad (8)$$

The prediction of the coking tendency of an FCC feedstock (eq 5) requires the estimation of the coke-conversion selectivity, which expresses the effect of the average hydrocarbon structure on the catalytic coke formation. The coke-conversion selectivity[30] is defined as the tendency of a feedstock or a catalyst to produce catalytic coke for constant conversion, as expressed in eq 9

$$coking\ selectivity = \frac{coking\ tendency}{crackability} \quad (9)$$

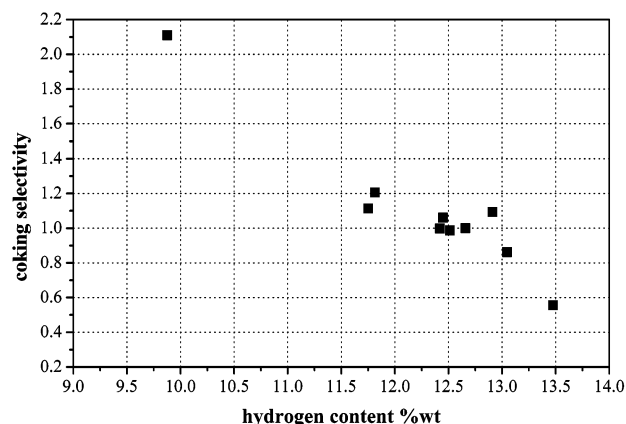The effect of the hydrocarbon structure on the coke selectivity is quite different from its impact on crackability. The major difference is that, whereas large hydrocarbon structures enhance cracking, coke formation is relatively independent of the size of the average molecule. As definite coke precursors are usually cited the large and condensed hydrocarbon structures.[32] Thus, the aromatic carbon content and the hydrogen content of the feed are good indicators of the coking selectivity, as shown in Figures 7 and 8. Generally, large and condensed molecules, primarily the heavy aromatics, are considered as coke precursors. Thus, the second-order dependence of coke selectivity on aromatic carbon observed in Figure 7 was depicted in the functional group $(1 + k_A C_A)^2$. The combination of the correlations for crackability and coke selectivity gives the final correlation for the estimation of the coking tendency of an FCC feedstock presented in eq 10

$$coking\ tendency = [w_1(N_C - N_C C_A) +$$
$$w_2(N_N) + w_3][(w_4 + w_5 C_A)^2] \quad (10)$$

Pseudocomponents Breakdown Approach. Jacob et al.[5] proposed that splitting the total FCC feed into two fractions, a light fraction of boiling point up to 650 °F and a heavy fraction with greater boiling point, describes the cracking behavior of the feedstock with much greater accuracy. This assumption was based on the fact that the two fractions impact the catalytic reaction in different ways, especially in tems of the behavior of the aromatics. In accordance with this concept, each feedstock of the database of CPERI was split into an appropriate number of pseudocomponents that can reproduce the properties of the total fraction. These pseudocomponents were then lumped into to a heavy and a light fraction according to the criterion of Jacob et al.[5] The splitting procedure was based on the constant Watson's factor method of Whitson[16] as described in Appendix A. The distributions of aromatics and carbon numbers with boiling point were estimated for the feedstocks examined; thus, it was possible to determine the carbon atoms belonging to aromatics rings for the heavy and the light fraction. Finally, the crackable carbon atoms were determined for each fraction.

Each fraction was assumed to contribute to the catalytic reaction in the same way as it contributes the total FCC feed. What was expected to make the differ-
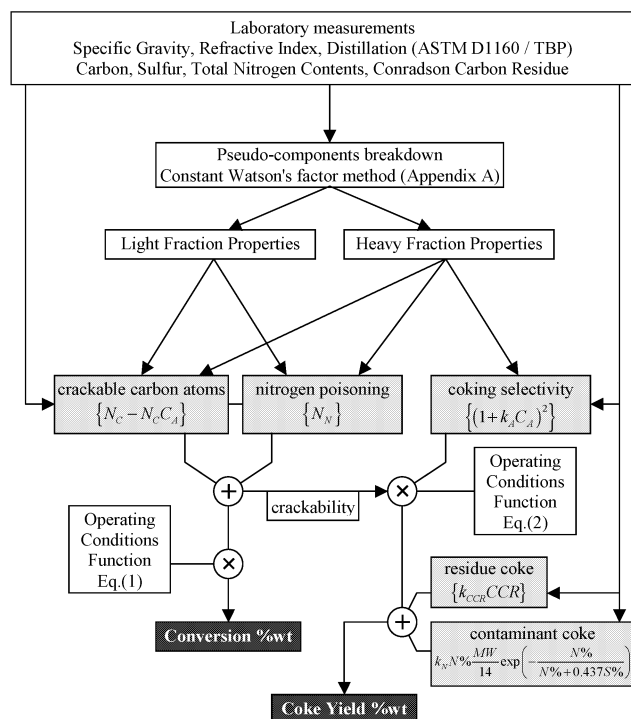
Figure 9. Logical scheme of the proposed method for the simulation of the effect of feed properties and operating conditions on the conversion and coke yield of the FCC process.

Table 2. Bulk Properties of the Feedstocks Examined (Validation Set)

property	code name		
	11	22	25
gravity, API	21.82	19.68	13.56
sulfur (wt %)	0.66	2.29	0.69
nitrogen (wt %)	0.105	0.140	0.280
CCR (wt %)	1.09	0.36	0.72
RI, 20 °C	1.5157	1.5182	1.5182
TBP (°F)			
IBP	357.2	556.0	577.8
10%	523.0	664.2	682.1
30%	721.8	737.9	747.7
50%	820.8	806.4	814.5
70%	890.4	860.0	880.5
90%	1013.9	940.1	977.2
FBP	1046.9	1008.3	1048.7
MW	342.8	359.9	355.7
C_A, ndM[a]	25.2	21.8	38.3
C_N, ndM[a]	20.9	26.5	10.4
C_P, ndM[a]	53.8	51.7	51.3
C (wt %)	86.6	85.6	88.3

[a] Aromatic, naphthenic, and paraffinic carbons estimated via the ndM method.

The proposed functional groups of Figure 9 can be transformed into complete equations for the prediction of conversion and noncatalytic and catalytic coke yields under different operating conditions and feedstock properties calculated as shown in eqs 13 and 14

$$\frac{x}{100 - x} = [w_1(N_C - N_C C_A) + w_2(N_N) + w_3] \exp\left(\frac{-E}{RT}\right) \cdot \frac{t_c^n}{\text{WHSV}} \quad (13)$$

$$u = k_{CCR}\text{CCR} + k_N \text{NT\%} \frac{\text{MW}}{14} \exp\left(-\frac{\text{NT\%}}{\text{NT\%} + 0.437\text{S\%}}\right) + [w_1(N_C - N_C C_A) + w_2(N_N) + w_3][(w_4 + w_5 C_A)^2] \exp\left(\frac{-E_u}{RT}\right) \cdot \frac{t_c^{n_u}}{\text{WHSV}} \quad (14)$$

The weighting factors $w_1 - w_5$ and $k_{CCR} - k_N$, as well as the form of the proposed functions, were developed using data on the 10 feeds presented in Table 1 and validated against the feedstocks of Table 2. Furthermore, for all feedstocks examined here, the procedure of Appendix A was applied to generate the light and heavy lumps and to estimate their respective properties.

The application of eq 13 for the total feedstock fractions is presented in Figure 10, where the calculated crackabilities of each feedstock are plotted against their predicted values. The prediction accuracy for the conversion prediction is excellent, with the diagonal correlation coefficient (r^2) receiving the value of 0.993. The prediction of coking tendency, however, is much lower in accuracy, with the r^2 value being 0.912. This was expected, because the coking tendency is strongly influenced by the heavy fraction portion. When the splitting and lumping method of Appendix A was applied, the prediction accuracy of crackability was not significantly improved, because the prediction when the properties of the total feeds were used was already precise. What was substantially improved was the accuracy of the model for coking tendency. In Figure 11, the coking tendency of only the heavy fraction is presented. The correlation factor r^2 is raised to 0.986,
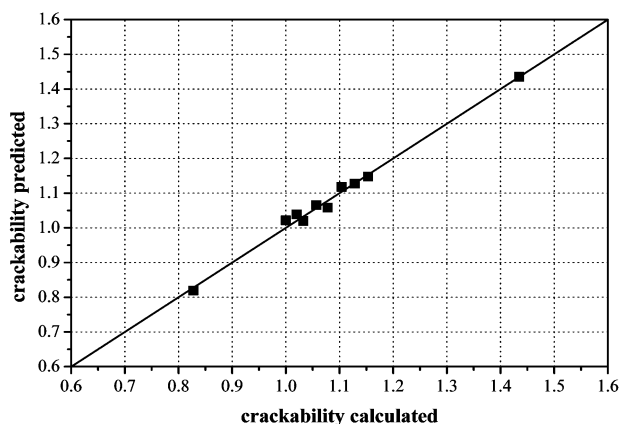
ence was the relative extent of each fraction's contribution. As shown in the 10-lump model of Mobil,[5] the cracking of heavy aromatics leads to aromatics in the light fraction and coke. This assumption appears to be in good agreement with the theory of crackable atoms, in the sense that aromatic ring structures are not expected to crack to a significant extent of the production of FCC products other than coke. Moreover, what is most important in both models is the aromatic carbon content, particularly that of the heavy fraction. Implementing the idea of different extents of contribution of the heavy and light fractions to the feed crackability and its coking tendency leads to eqs 11 and 12

$$\text{crackability}_{\text{FEED}} = f_1 \text{crackability}_{\text{LFO}} + f_2 \text{crackability}_{\text{HFO}} \quad (11)$$

$$\text{coking} - \text{tendency}_{\text{FEED}} = c_1 \text{coking} - \text{tendency}_{\text{LFO}} + c_2 \text{coking} - \text{tendency}_{\text{HFO}} \quad (12)$$

Model Application

Figure 9 presents the logical scheme of the proposed method for simulating the effects of feed properties and operating conditions in an FCC unit. Five functional groups are proposed to fully describe the crackability and coking tendency of an FCC feedstock: one for the prediction of the catalyst poisoning, one for the estimation of the extent of cracking, one for the estimation of coke-conversion selectivity, and two coking precursors for contaminant and residue coke formation. Moreover, a methodology is presented for the breakdown of an FCC feedstock into pseudocomponents and for the estimation of the properties of the light and heavy fractions separately. In this section, the applicability of this scheme to 13 different FCC feedstocks is presented and analyzed.

Figure 10. Predicted vs calculated crackabilities of the feedstocks of Table 1 (development dataset).
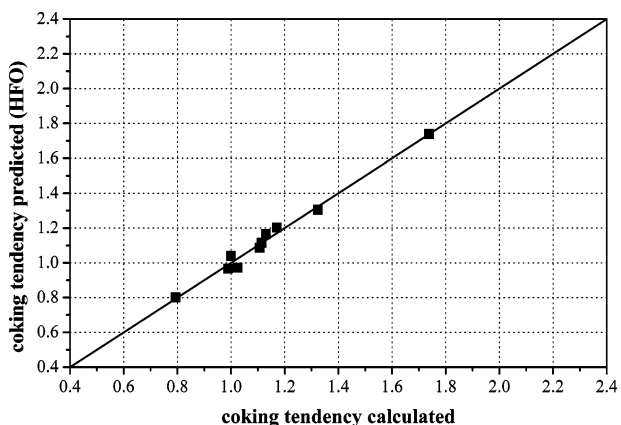

Figure 11. Predicted vs calculated coking tendencies of the feedstocks of Table 1 (development dataset). The properties of only the heavy fraction (HFO) (aromatic carbons in the heavy fraction) were used for the estimation of the coke-conversion selectivity of each feedstock.
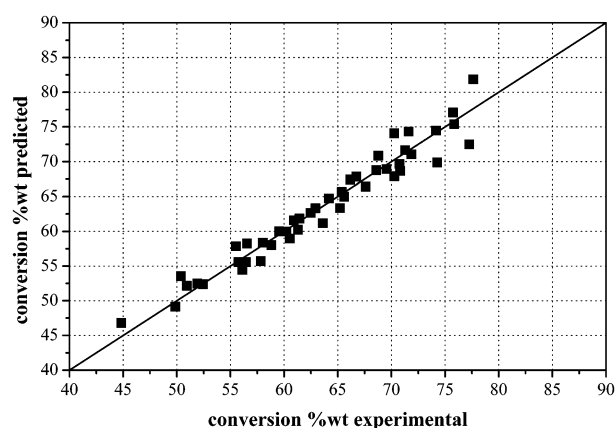

Figure 12. Conversion (wt %) prediction parity plot for the feedstocks of Table 1 (development dataset).

which means that the portion of heavy aromatics is the dominant factor for catalytic coke formation. The parity plots of conversion and coke formation for the feeds of Table 1 are presented in Figures 12 and 13, respectively. The average relative error of both conversion and coke yield was maintained at the same levels as those of the operating conditions models (eqs 1 and 2), namely, 2.3% for the conversion and 5.3% for the coke yield.

Finally, the overall efficiency of eqs 13 and 14 was tested. For this test, all kinds of variables of the pilot
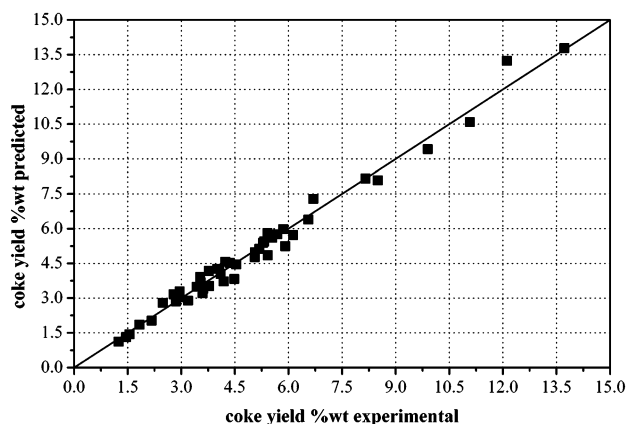

Figure 13. Coke yield (wt %) prediction parity plot for the feedstocks of Table 1 (development dataset).
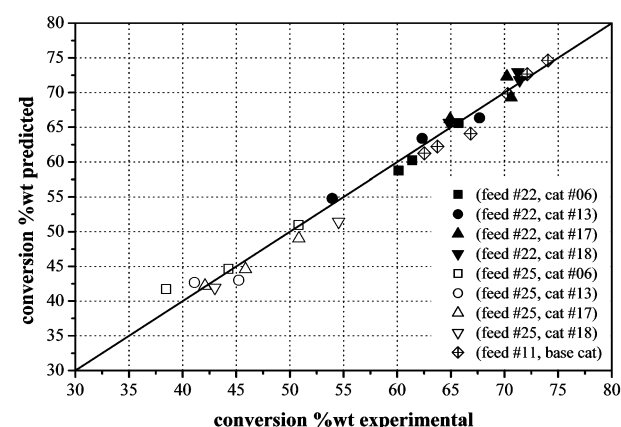

Figure 14. Conversion (wt %) prediction parity plot for the feedstocks of Table 2 (validation dataset). Experiments for feed 11 were performed with the base catalyst; feeds 22 and 25 were examined in experiments with four different catalysts each.

unit were altered: the operating conditions, the feed properties, and the catalyst supply. In Table 2, the properties of the feedstocks used in the validation set of experiments are presented. Feed 11 was cracked with the base catalyst (the one used for the development of eqs 13 and 14), whereas feeds 22 and 25 were tested with four different catalysts. The effect of the catalyst properties on cracking was included in a catalyst index that is a multiplier to the product of operating and feed effect functions. The reason for using a simple multiplier to characterize the effect of the catalyst on the cracking reactions is that the development of a predictive catalyst function appears quite complex and, generally, it is considered to be the limit in any FCC modeling approach. Moreover, the concept of describing catalyst activity and selectivity with a catalyst index is a common industrial strategy for the validation of catalyst performance. As shown in Figures 14 and 15, the average relative errors in the prediction of conversion and coke for these experiments remain at the same levels, namely, 2.4% and 5.0%, respectively. Some prediction errors are evident for very low conversions and very high coke yields, which are probably generated by the operating conditions functions. However, in the great range of 36−75 wt % for conversion and 3−12 wt % for coke yield, the predictive accuracy of the model is quite satisfactory. In Appendix B, a practical example of the feed characterization procedure is demonstrated for feed 11.
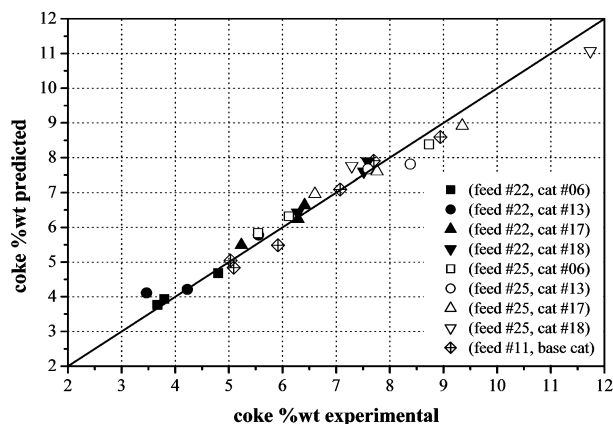
Figure 15. Coke yield (wt %) prediction parity plot for the feedstocks of Table 2 (validation dataset). Experiments for feed 11 were performed with the base catalyst; feeds 22 and 25 were examined in experiments with four different catalysts each.

Conclusions

A bulk molecular characterization approach was presented for the simulation of FCC feedstocks regarding their relative (compared to a reference feedstock) potential to enhance catalytic cracking (crackability) and coke formation (coking tendency). The final models for the prediction of crackability and coking tendency incorporate the specific gravity, the refractive index, and the TBP (or ASTM) distillation of the feedstock, along with the sulfur, nitrogen, and carbon contents. These properties were combined properly to derive five functional groups that accurately characterize the behavior of FCC feedstocks at cracking conditions. The impact of the average hydrocarbon structure on catalytic cracking was expressed via the functional group called crackable carbon atoms, which describes the effect of the average molecular structure and size of the feedstock on its crackability. The total nitrogen content was considered as a major contributor to catalyst deactivation and contaminant coke formation and was involved in two functional groups. The aromaticity of the feedstock was proposed to satisfactorily describe the feed's tendency to produce catalytic coke, and a functional group of the aromatic carbon content was devised to express the coke-conversion selectivity. Finally, a splitting and lumping scheme for the total feed fraction was applied to explore the different extents of contribution to catalytic cracking for the heavy and light fractions. The results demonstrated the ability of the proposed functional groups to explain the results of fluid catalytic cracking. The aromaticity and size of the average hydrocarbon were shown to dominantly impact the crackability, whereas the total nitrogen content was verified to be the major catalyst inhibitor. Finally, the splitting and lumping approach revealed the strong relation between coke formation and the heavy components of an FCC feedstock.

Appendix A: Characterization of Petroleum Fractions According to a Pseudocomponent Breakdown

The total FCC feed can be split into a number of pseudocomponents by using its true boiling point distribution and its bulk properties following an appropriate distribution function. The three-parameter γ-distribution model[17] or the two-parameter distribution function[20] are more appropriate for describing distributions for total fractions of petroleum; however, for the small area of FCC feeds (vacuum gas-oils, residua, etc.), the assumptions of a constant Watson's characterization factor method[16] are quite accurate. The characterization method involves the following calculation procedure:

1. Convert ASTM D-1160 distillation data to TBPs using the method proposed in the *API Technical Data Book—Petroleum Refining* of the American Petroleum Institute.[33]

2. Interpolate the TBP distillation curve with an appropriate probability or Lagrangian method.

3. Estimate the Watson factor (K_W) using the 50% TBP as the starting value for the mean average boiling point (MeABP).

4. Using K_W, create the specific gravity distribution of the fraction; use the density to convert volume fractions to weight fractions (for very wide boiling range fractions, one could use the reduced two-parameter γ-distribution model for more accurate specific gravity distributions).

5. Calculate the molecular weight of each pseudocomponent using the correlation of Riazi;[20] convert weights to molar fractions.

6. Calculate volume-, cubic-, molar-, and mean-average boiling points of the total fraction

7. If the absolute difference between the MeABP values of steps 6 and 3 is greater than 0.1, assign the new value to MeABP and go to step 3; on convergence, proceed to step 8.

8. Assign a pseudocomponent to every 25 °C of the TBP curve;[34] calculate the boiling point, molecular weight, density, volume, and weight and molar concentrations of each pseudocomponent.

9. Use the correlation proposed by Goossens[35] ($n_i = 0.9365 + sd_i$) to estimate the refractive index of each pseudocomponent. The slope (s), which is an indicator of the aromaticity of the pseudocomponent, is calculated from

$$s = \frac{\sum d_i - 0.9365}{n_{tot}}$$

so the refractive index distribution is calculated and the refractive index convergence is this way established.

10. Use the correlation proposed by Goossens[35] to estimate the hydrogen and carbon content of each pseudocomponent (H%$_i$ = 30.346 − 65.342n_i/d_i + 82.952/d_i − 306/MW$_i$); calculate the carbon number (N_{Ci}) of each component.

11. Use the ndM method to calculate the aromatic carbon content (C_{Ai}) of each pseudocomponent.

12. Gather the pseudocomponents into two fractions, the light fraction (IBP < 650 °C) and the heavy fraction (650 °C < FBP). Calculate the molar fraction, carbon number, and aromatic carbon content for the light and heavy fractions.

The accuracy of the method is subject to the accuracy of the empirical correlations applied and the correctness of the constant K_W method. The integration of the

pseudocomponents into the total fraction reproduces the average values for molecular weight, carbon number, and aromatic carbon content within an average relative error of 1%.

Appendix B: Demonstration of the Application of the Bulk Molecular Characterization Approach

In this appendix, we demonstrate the applicability of the proposed procedure using the case of feed 11 as an example. The bulk properties known for the feedstock examined were its ASTM D1160 distillation (at 1 atm); its sulfur (S%), carbon (C%), total nitrogen (NT%), and Conradson carbon residue (CCR) contents; its gravity (API); and its refractive index (RI), all measured with the ASTM methods described in the Experimental Setup section. The bulk feed properties, as well as the operating conditions of the five experiments performed with feed 11 and the base catalyst, are given in Table 3. The application of steps 1−7 of Appendix A led to the calculation of the molecular weight of the total fraction. With the molecular weight and the carbon content of the total fraction known, the carbon number of the average hydrocarbon molecule (N_C) was then calculated using eq 3. The number of nitrogen atoms in the average hydrocarbon molecule (N_N) was calculated using the respective equation [$N_N = (NT\%/100)(MW/14)$]. The percent of carbon atoms that belong to aromatic rings (C_A) was calculated using the ndM method. The application of steps 8−11 of Appendix A led to the calculation of the aromatic carbons of the heavy fraction ($C_{A,HFO}$), which was used for the estimation of the characteristic coking selectivity (eq 9) of the heavy fraction of feed 11. Using eqs 13 and 14, the conversion and coke yield were predicted with average absolute relative errors of 1.5% and 3.2%, respectively, as reported in Table 3.

Table 3. Demonstration of the Proposed Procedure for the Prediction of Conversion and Coke Yield[a]

measured feed properties		calculated feed properties	
ASTM D1160 (°F)		TBP (°F)	
IBP	405.0	IBP	357.2
10%	553.3	10%	523.0
30%	737.6	30%	721.8
50%	820.9	50%	820.8
70%	890.4	70%	890.4
90%	1013.9	90%	1013.9
FBP	1046.9	FBP	1046.9
gravity, API	21.82	MW	342.8
RI, 20 °C	1.5157	N_C	24.7
sulfur (wt %)	0.66	N_N	0.026
nitrogen (wt %)	0.105	C_A (ndM)	25.2
C (wt %)	86.6	$C_{A,HFO}$	29.6
CCR (wt %)	1.09		

operating data	test 1	test 2	test 3	test 4	test 5
TRX (°F)	978.7	972.1	976.3	968.0	970.7
t_c (s)	3.3	2.8	3.0	3.9	4.2
WHSV (h⁻¹)	53.8	78.0	63.6	75.8	79.2
conversion (wt %)	74.1	70.3	72.1	66.8	63.7
predicted conversion (wt %)	75.0	70.3	73.1	64.6	62.8
absolute relative error (%)	1.3	0.0	1.3	3.3	1.5
coke yield (wt %)	8.9	7.1	7.7	5.9	5.0
predicted coke yield (wt %)	8.6	7.1	7.9	5.5	5.0
absolute relative error (%)	3.9	0.3	2.7	7.3	0.3

[a] Validation set: feed 11, base catalyst.

Nomenclature

C_A = aromatic carbon content calculated with the ndM method
C% = carbon content (wt %)
CCR = Conradson carbon residue (wt %)
d = density at 20 °C
n = refractive index at 20 °C
N_N = number of nitrogen atoms in the average hydrocarbon molecule
N_C = carbon number of the average hydrocarbon molecule
NB% = basic nitrogen content (wt %)
NT% = total nitrogen content (wt %)
S% = total sulfur content (wt %)
t_c = catalyst residence time (s)
u = coke yield (wt %)
u_c = contaminant coke yield (wt %)
u_r = residue coke yield (wt %)
u_x = catalytic coke yield (wt %)
WHSV = weight hourly space velocity (h⁻¹)
x = reaction conversion (wt %)

Definitions

crackability = relative tendency of an FCC feedstock to enhance catalytic cracking reactions, compared to the base feedstock used for the development of the function describing the effect of the operating conditions on the reaction conversion (feed 4, for which the crackability was assumed equal to unity)
coking tendency = relative tendency of an FCC feedstock to produce catalytic coke, compared to the base feedstock used for the development of the function describing the effect of the operating conditions on the coke yield (feed 4, for which the coking tendency was assumed equal to unity)
coking selectivity = propensity of an FCC feedstock to produce catalytic coke for constant conversion
catalytic coke = coke produced as a byproduct of the catalytic reactions.
carbon residue coke = coke formed via thermal noncatalytic reactions.
contaminant coke = coke formed as result of catalyst poisoning.
catalyst-to-oil coke = amount of FCC products that is not stripped from the catalyst surface, due to incomplete stripping, and is considered as coke
base feed = feed 4 (properties listed in Table 1), feed for which the operating conditions functions were developed

Literature Cited

(1) Altgelt, K. H.; Boduszynski, M. M. *Composition and Analysis of Heavy Petroleum Fractions*, 1st ed.; Marcel Dekker: New York, 1994.
(2) Nace, D. M.; Voltz, S. E.; Weekman, V. W. Application of a Kinetic Model for Catalytic Cracking—Effects of Charge Stocks. *Ind. Eng. Chem. Process Des. Dev.* **1971**, *10* (4), 530.
(3) Ancheyta-Juarez, J.; Lopez-Isunza, F.; Aguilar-Rodriguez, E. Correlations for predicting the effect of feedstock properties on catalytic cracking kinetic parameters. *Ind. Eng. Chem. Res.* **1998**, *37* (12), 4637.
(4) Castiglioni, B. P. How to Predict FCC Yields. *Hydrocarbon Process.* **1983**, *62* (2), 35.
(5) Jacob, S. M.; Gross, B.; Voltz, S. E.; Weekman, V. W. Lumping and Reaction Scheme for Catalytic Cracking. *AIChE J.* **1976**, *22* (4), 701.
(6) Lappas, A. A.; Patiaka, D.; Ikonomou, D.; Vasalos, I. A. Separation and characterization of paraffins and naphthenes from FCC feedstocks. *Ind. Eng. Chem. Res.* **1997**, *36* (8), 3110.
(7) Arbel, A.; Huang, Z. P.; Rinard, I. H.; Shinnar, R.; Sapre, A. V. Dynamic and Control of Fluidized Catalytic Crackers. 1. Modeling of the Current Generation of FCCs. *Ind. Eng. Chem. Res.* **1995**, *34* (4), 1228.

(8) Dewachtere, N. V.; Froment, G. F.; Vasalos, I.; Markatos, N.; Skandalis, N. Advanced modeling of riser-type catalytic cracking reactors. *Appl. Therm. Eng.* **1997**, *17* (8−10), 837.

(9) Dewachtere, N. V.; Santaella, F.; Froment, G. F. Application of a single-event kinetic model in the simulation of an industrial riser reactor for the catalytic cracking of vacuum gas oil. *Chem. Eng. Sci.* **1999**, *54* (15−16), 3653.

(10) Bollas, G. M.; Papadokonstadakis, S.; Michalopoulos, J.; Arampatzis, G.; Lappas, A. A.; Vasalos, I. A.; Lygeros, A. Using hybrid neural networks in scaling up an FCC model from a pilot plant to an industrial unit. *Chem. Eng. Process.* **2003**, *42* (8−9), 697.

(11) Van Nes, K.; Van Westen, H. A. *Aspects of the Constitution of Mineral Oils*; Elsevier Publishing Co.: New York, 1951.

(12) Riazi, M. R.; Daubert, T. E. Prediction of Molecular-Type Analysis of Petroleum Fractions and Coal Liquids. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25* (4), 1009.

(13) Dhulesia, H. New Correlations Predict Fcc Feed Characterizing Parameters. *Oil Gas J.* **1986**, *84* (2), 51.

(14) Guilyazetdinov, L. P. Structural Group Composition and Thermodynamic Properties of Petroleum and Coal-Tar Fractions. *Ind. Eng. Chem. Res.* **1995**, *34* (4), 1352.

(15) Korsten, H. Characterization of hydrocarbon systems by DBE concept. *AIChE J.* **1997**, *43* (6), 1559.

(16) Whitson, C. H. Characterizing Hydrocarbon Plus Fractions. *Soc. Pet. Eng. J.* **1983**, *23* (4), 683.

(17) Whitson, C. H. Effect of C-7+ Properties on Equation-of-State Predictions. *Soc. Pet. Eng. J.* **1984**, *24* (6), 685.

(18) Ahmed, T. *Hydrocarbon Phase Behavior*; Gulf Publishing Co.: Houston,TX, 1989.

(19) Pedersen, K. S.; Blilie, A. L.; Meisingset, K. K. *PVT Calculations on Petroleum Reservoir Fluids Using Measured and Estimated Compositional Data for the Plus Fraction. *Ind. Eng. Chem. Res.* **1992**, *31* (5), 1378.

(20) Riazi, M. R. A continuous model for C7+ fraction characterization of petroleum fluids. *Ind. Eng. Chem. Res.* **1997**, *36* (10), 4299.

(21) Lerner, B. A.; Himpsl, F. L. Feed molecular properties explain cracking results. *Oil Gas J.* **1997**, *95* (48), 61.

(22) Voltz, S. E.; Nace, D. M.; Weekman, V. W. Application of a Kinetic Model for Catalytic Cracking—Some Correlations of Rate Constants. *Ind. Eng. Chem. Process Des. Dev.* **1971**, *10* (4), 538.

(23) Green, J. B.; Green, J. A.; Young, L. L. Correlating coke yield with feedstock properties in FCC. *Abstr. Pap. Am. Chem. Soc.* **1998**, *216*, 034 PETR.

(24) Service, W. J. Catalytic Cracking Feed Stocks. *Pet. Chem. Eng.* **1960**, *32*, C31.

(25) Plank, C. J.; Nace, D. M. Coke Formation and Its Relationship to Cumene Cracking. *Ind. Eng. Chem.* **1955**, *47* (11), 2374.

(26) Bollas, G. M.; Vasalos, I. A.; Lappas, A. A.; Iatridis, D. Modeling small-diameter FCC riser reactors. A hydrodynamic and kinetic approach. *Ind. Eng. Chem. Res.* **2002**, *41* (22), 5410.

(27) Corella, J.; Frances, E. Analysis of the Riser Reactor of a Fluid Cracking Unit—Model Based on Kinetics of Cracking and Deactivation from Laboratory Tests. *ACS Symp. Ser.* **1991**, *452*, 165.

(28) Blanding, F. H. Reaction rates in the catalytic cracking of petroleum. *Ind. Eng. Chem.* **1953**, *45*, 1186.

(29) Krambeck, F. J. Continuous Mixtures in Fluid Catalytic Cracking and Extensions. In *Mobil Workshop on Chemical Reaction in Complex Mixtures*; Van Nostrand Reinhold: New York, 1991.

(30) Sapre, A. V.; Leib, T. M. Translation of Laboratory Fluid Cracking Catalyst Characterization Tests to Riser Reactors. *ACS Symp. Ser.* **1991**, *452*, 144.

(31) Fisher, I. P. Residuum Catalytic Cracking—Influence of Diluents on the Yield of Coke. *Fuel* **1986**, *65* (4), 473.

(32) Sheppard, C. M.; Green, J. B.; Vanderveen, J. W. Relating feedstock composition to product slate and composition in catalytic cracking. 4. An extended pendant−core model for gasoline composition. *Energy Fuels* **1998**, *12* (2), 320.

(33) *API Technical Data Book−Petroleum Refining*, 5th ed.; American Petroleum Institute (API): Washington, DC, 1992.

(34) Miquel, J.; Castells, F. Easy Characterization of Petroleum Fractions. 1. *Hydrocarbon Process.* **1993**, *72* (12), 101.

(35) Goossens, A. G. Prediction of the hydrogen content of petroleum fractions. *Ind. Eng. Chem. Res.* **1997**, *36* (6), 2500.