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A Lumping and Reaction Scheme for Catalytic Cracking

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A predictive kinetic model has been developed for fluid catalytic cracking (FCC). The kinetic scheme involves lumped species consisting of paraffins, naphthenes, aromatic rings, and aromatic substituent groups in light and heavy fuel oil fractions. The kinetic model also incorporates the effect of nitrogen poisoning, aromatic ring adsorption, and time dependent catalyst decay. The rate constants for these lumped species are invariant with respect to charge stock composition. The predictive capabilities of the model have been verified for wide ranges of charge stocks and process conditions.

SCOPE

The purpose of this work was to develop a predictive kinetic description of fluid catalytic cracking (FCC) for incorporation into an integrated FCC process model. Process models are useful for the design, optimization, and control of commercial plants. In addition, they provide guidance in the development of a new process and can reduce both time and capital requirements. The utility of a process model depends strongly on its predictive capabilities. The predictions should be reliable over wide ranges of charge stock compositions and process conditions. Catalytic cracking has been an important petroleum refining process for over 30 yr, and considerable research has been conducted with both pure hydrocarbons and gas oils over many different types of cracking catalysts. The results have provided an understanding of the chemical reactions involved and led to the development of improved cracking catalysts and processes. Previously published models generally utilize this knowledge through empirical correlations relating conversion or product selectivity to charge stock properties and process variables. The identification of lumped species whose reaction rate constants are invariant with feedstock composition and source provides a more fundamental basis for predicting charge stock and process variable effects.

In this work, a wide variety of charge stocks were cracked in a fluidized dense-bed reactor. Detailed analysis of the molecular compositions of the charge stocks and products provided the necessary data to develop a predictive kinetic model. Rate constants and activation energies were calculated for lumped species including paraffins, naphthenes, aromatic rings, and aromatic substituent groups. The reliability of the kinetic predictions for various charge stocks over a wide range of process conditions has been shown.

CONCLUSIONS AND SIGNIFICANCE

The reaction kinetics of catalytic cracking is presented, based on a reaction scheme that includes paraffins, naphthenes, aromatic rings, and aromatic substituent groups in light and heavy fuel oil fractions. The kinetic model also accounts for nitrogen poisoning, aromatic adsorption, and time dependent catalyst decay. The conversion of these lumped species to gasoline, light products, coke, heavy fuel oil, and light fuel oil can be readily calculated by these kinetics. In addition, the detailed composition of the heavy and light fuel oil fractions can be tracked, increasing the utility of the model for predicting recycle behavior and physical properties of the products. The invariant kinetic parameters (rate constants and activation energies) allow the conversion and product selectiv-

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ities to be calculated for the cracking of any charge stock for which the requisite molecular compositions have been determined.

The effects of space velocity, temperature, pressure, and catalyst residence time on conversion and product *selectivities* are included in the kinetic model. The predictive capabilities have been substantiated over wide ranges of charge stock compositions and process variables. In addition, the kinetic scheme has been incorporated into an integrated FCC process model (not reported here) with complete heat and mass balances for reactor and regenerator. This has been used successfully in many commercial applications.

The use of lumped species and invariant kinetic parameters increases the predictive capabilities of the process model and represents a significant improvement over previous correlative models. When the catalyst composition or physical properties are changed, the rate constants must be reidentified; however, the kinetic framework presented makes it possible to minimize the required experimental work.

By any standard, be it total capacity, catalyst cost, or product value, catalytic cracking remains the largest catalytic process in the world. It is not surprising, therefore, that considerable effort has been devoted to understanding the complex chemical reactions, kinetics, and effects of process variables on the operation of this key process. The present research effort, which has resulted in the development of the process kinetics given in this paper, has been built upon previous work in several areas, including kinetics, catalyst decay, compositional analysis of petroleum fractions, and subsequent chemical kinetic lumping. These kinetics have been incorporated into an integrated reactor-regenerator process model, which can be used to predict the performance of commercial FCC units. Only the kinetics are discussed in this paper.

Some of the earliest work in the kinetics of coke formation and cracking conversion was published by Voorhies (1945). This simple rate law has played a vital role in the design of most commercial catalytic cracking units during the past 30 yr. Voorhies showed, for a given catalyst and charge stock, that coke formation was primarily dependent on the catalyst-to-oil contact time and the reaction temperature. Since catalyst decay is largely a result of the carbon formation, it is strongly related to catalyst-to-oil contact time. Voorhies' basic conclusions were subsequently verified by Rudershausen and Watson (1954) and Prater and Lago (1956) in studies of cyclohexane and cumene cracking, respectively. Appelby (1962) studied the chemistry of coke formation for a variety of aromatic, naphthenic, and paraffinic hydrocarbons and showed that carbon formation resulted primarily from aromatic condensation and hydrogen elimination reactions. These reactions ultimately lead to a graphitic-like deposit as observed by Haldeman and Botty (1959). Eberly (1966) and Ozawa and Bischoff (1968) disagreed somewhat with Voorhies' original conclusions. Eberly used a much greater range of space velocity than originally reported by Voorhies and observed an independent space velocity effect on coke formation. Ozawa et al. noted a tendency for higher initial coking rates than the Voorhies rate law would predict. More recent work by Voltz et al. (1971) has verified Voorhies' law and shown it to be adequate for a wide variety of charge stocks with a zeolite catalyst.

Blanding (1953) used implicit second-order kinetics to explain gas oil conversion behavior. Andrews (1959) subsequently extended the work of Blanding and Voorhies and developed expressions to predict coke and conversion in various reactor configurations. None of these earlier studies made any effort to incorporate catalyst decay directly into the kinetic rate expressions. One of the first studies relating the distribution of catalyst activity to the overall reactor performance was that of Anderson and Whitehouse (1961). Froment and Bischoff (1961) made the first comprehensive study on the effect of catalyst decay and reactor performance. They showed that when carbon is produced from both products and reactants, a Voorhies type of law holds over certain operating ranges. This probably explains the almost universal applicability of the Voorhies correlation.

Weekman (1968) compared performance of fixed-, moving-, and fluid-bed reactors with decaying catalyst activity for the case of second-order reaction coupled with time-dependent decay. His analysis adequately explained a wide range of experimental catalytic cracking conversions and was later extended (Weekman and Nace, 1970) to gasoline selectivity. Sadana and Doraiswamy (1971) extended this approach to general-order reactions, and later Prasad and Doraiswamy (1974) experimentally studied such decaying catalyst systems. Gustafson (1972) utilized the second-order-reaction–first-order-decay approach to develop a catalyst test procedure and successfully compared it with experimental cracking results. This same kinetic-decay approach has also been incorporated into process models of catalytic cracking that have proven useful in explaining the effect of process variables on performance (Buckner, Kelly, Reduto, Tayyabkhan, and Weekman, 1967; Wollaston, Haflin, Ford, and D'Souza, 1975; Paraskos, Shah, McKinney, and Carr, 1976).

Szepe and Levenspiel (1971) have shown that many of the rate laws, proposed by previous workers, can be readily derived by assuming that the rate of decay is a function of the number of active sites. Wojciechowski (1968, 1969) and Campbell and Wojciechowski (1971) have developed criteria for distinguishing between different types of time-dependent catalyst decay. Recently, Butt (1972) has presented a very comprehensive review of the important work in catalyst deactivation.

Catalytic cracking feedstocks normally have initial boiling points around 430°F (221°C) with end points about 1,000°F (538°C) or even higher. American Petroleum Institute studies (Sachanen, 1945) have shown that literally tens of thousands of individual molecular species may be present in such a broad boiling range gas oil. Long before lumping analysis became popular in reaction engineering, it was common in the petroleum industry to lump large numbers of molecular species together, depending on the type of chemical or physical analysis employed. For example, with physical measurements such as density, molecular weight, and refractive index, Van Nes and Van Westen (1951) developed a correlation which predicted the weight fraction of carbon atoms present in paraffinic, naphthenic, and aromatic species.

A more detailed analytical procedure was recently reported by Fitzgerald et al. (1970); it included distillation, separation by molecular sieves, mass spectrometry, and ultraviolet spectroscopy. Crocoll and Jaquay (1960) described the relative cracking rates of saturates (paraffins and naphthenes) and unsaturates based on differences in the cracking behavior of major hydrocarbon types. In the same year, Service (1960) discussed the detailed characterization of feedstocks for catalytic cracking including correlation methods to determine carbon atom distributions. Reif et al. (1961), in a similar approach, developed yield correlations based on the detailed characterization of a wide variety of catalytic cracking feedstocks. Their equations were based, to a large degree, on the carbon atom distribution in the feedstock. White (1968) developed a regression correlation model to predict product yields utilizing nine different hydrocarbon feedstock types; his scheme was based on the subsequently published method of Fitzgerald et al. (1970).

Lumping of many constituents together has always been a necessity in the petroleum industry where, as mentioned earlier, thousands of individual molecular species are present in even relatively narrow boiling range cuts. For example, all of the previously mentioned work in kinetics of catalytic cracking have dealt with lumped species. One of the first formal efforts to analyze lumped kinetics was by Aris and Gavalas (1966) and Aris (1968). They found that when all reactions are first order, the initial distributions of components can determine the functional form of the rate expression. Weekman (1968) and Weekman and Nace (1970) have shown that a second-order reaction form could result from a difference in charge stock crackability. The distribution of fast and slow reacting species leads to an apparent reaction order higher than one, since the reaction tends to slow down as the more refractory species remain to be cracked. This is in agreement with the work of Luss and Hutchinson (1971) and Hutchinson and Luss (1970); they showed theoretically that lumping of first-order parallel reactions leads to reaction orders greater than one. Using a fitted refractivity function, Kemp and Wojciechowski (1974) have proposed a method to correlate the effects of varying feedstock composition. In a comprehensive study of complex monomolecular systems, Wei and Kuo (1969) have given criteria for lumping species together so as to preserve the important characteristics of the reaction system. They have also shown the error involved in lumping systems which are not exactly lumpable in terms of overall system behavior. In an extension of this work, Ozawa (1973) has given criteria on which species should be lumped in the absence of complete information on the system rate constants. For catalytic reforming, Kmak (1971) has described the kinetic behavior in terms of thirteen lumps composed of paraffins, naphthenes, and aromatics in the C_6, C_7, C_8, and C_9^+ boiling ranges.

Weekman and Nace (1970) showed that a three-lump system could adequately describe gasoline selectivity behavior in catalytic cracking. Subsequent work by Nace et al. (1971) and Voltz et al. (1971) showed that the rate constants for this three-lump system changed with charge composition but could be correlated to the paraffin, naphthene, and aromatic compositions of the charge stock. While these rate constant correlations were adequate for the range of charge stocks investigated, they could not be extrapolated, with any confidence, to unknown charge stocks outside the range of the correlation.

In this paper, we present a kinetic scheme that identifies lumps whose rate constants are independent of the initial composition of the charge stock (that is, invariant with charge stock). Unfortunately, at the time the study was initiated, lumping theory was not far enough advanced to give useful guidelines as to which lumps to choose. One can, however, use a heuristic approach, based on known chemical principles, to formulate schemes with lumps that can be readily identified by available analytical techniques. Silica gel separation and mass spectrometry were employed to define paraffinic, naphthenic, and aromatic lumps with cracking rate constants which were indeed independent of the initial charge composition. Further improvements in the lumpability were obtained by splitting the aromatic lump into weight fractions of side chains and the bare rings. The bare ring aromatic lumps also play a key role in determining the adsorption behavior of the catalyst. By incorporating a variation of the previously developed time-dependent decay, it was then possible to describe the kinetic cracking behavior over a broad range of feedstock compositions for a wide range of reaction conditions.

EXPERIMENTAL METHODS

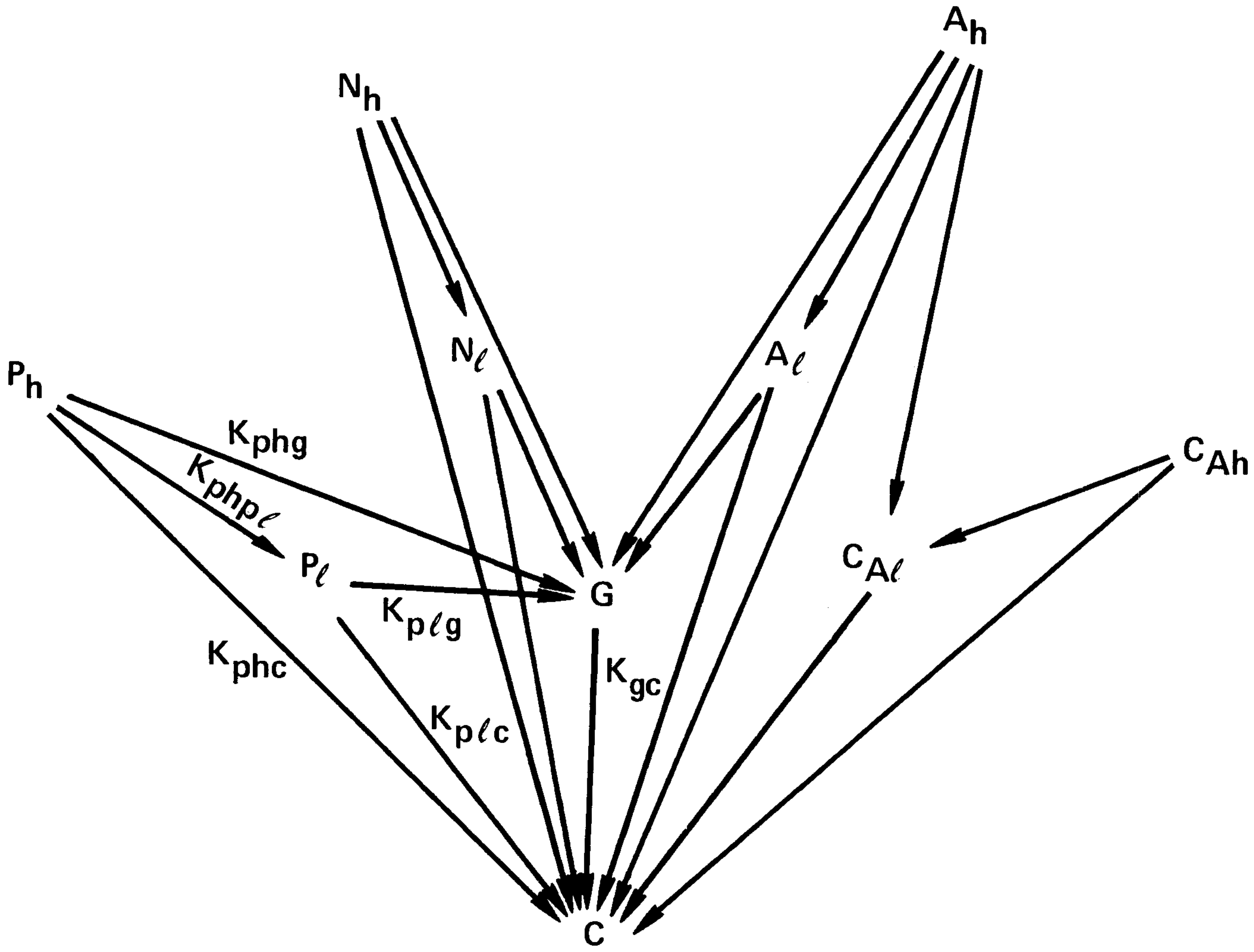
Over a dozen charge stocks, covering wide ranges of properties and molecular compositions, were used to provide data for the development of the kinetic model. Selected fractions of refinery stocks were blended together to give the desired ranges of boiling points and relative concentrations of paraffins, naphthenes, and aromatics. The properties and compositions of most of these charge stocks were described previously (Nace et al., 1971); therefore, only the ranges are summarized in Table 1.

The molecular compositions were primarily determined by using distillation and liquid chromatography for physical separations followed by mass spectrometric analysis of each fraction. The correlative n-d-M technique (based on refractive index, density, molecular weight, and sulfur content) was also employed.

The catalytic cracking experiments were made in a fluidized dense-bed reactor. Details of the reactor, operating procedures, and product analyses were also described previously (Nace et al., 1971). Most of the experiments were conducted at catalyst residence times of 1.25 and 5.0 min, catalyst/oil ratios of 1.25 to 6.0 (g/g), atmosphere pressure, 10 mole % nitrogen dilution, and 900°F (482°C). A limited number of the charge stocks were also cracked at different temperatures and other operating variables (that is, residence times).

TABLE 1. RANGES OF PROPERTIES AND MOLECULAR COMPOSITIONS OF CHARGE STOCKS

ASTM distillation	
5%	443-723°F (228-384°C)
95%	650-959°F (343-515°C)
Average molecular wt	206-402
Sulfur	0.01-3.77 wt %
Nitrogen	0.001-0.14 wt %
Hydrogen	10.87-13.85 wt %
Conradson carbon	0.01-0.73 wt %
Bromine number	0.0-5.3
Molecular composition	
Mass spectrometry	
Paraffins	8.6-51.9 wt %
Naphthenes	14.2-68.8 wt %
Aromatics	14.4-74.8 wt %
n-d-M method	
C_P	40.1-69.9 wt %
C_N	6.1-53.8 wt %
C_A	6.1-35.1 wt %



P_ℓ = Wt. % paraffinic molecules, (mass spec analysis), 430° - 650° F

N_ℓ = Wt. % naphthenic molecules, (mass spec analysis), 430° - 650° F

$C_{A\ell}$ = Wt. % carbon atoms among aromatic rings, (n-d-M method), 430° - 650° F

A_ℓ = Wt. % aromatic substituent groups (430° - 650° F)

P_h = Wt. % paraffinic molecules, (mass spec analysis), 650° F^+

N_h = Wt. % naphthenic molecules, (mass spec analysis), 650° F^+

C_{Ah} = Wt. % carbon atoms among aromatic rings, n-d-M method, 650° F^+

A_h = Wt. % aromatic substituent groups (650° F^+)

G = G lump (C_5 - 430° F)

C = C lump (C_1 to C_4 + COKE)

$C_{A\ell} + P_\ell + N_\ell + A_\ell$ = LFO (430° - 650° F)

$C_{Ah} + P_h + N_h + A_h$ = HFO (650° F^+)

Adapted Nomenclature for rate constants is detailed in the above Figure for the paraffinic molecules. Similar rules apply for the other reaction steps.

Fig. 1. Lumped kinetic scheme.

DESCRIPTION OF MODEL

Lumping and Reaction Scheme for Catalytic Cracking

The lumping and reaction schemes are based on the concentrations of paraffins, naphthenes, aromatic rings, and aromatic substituent groups (paraffinic and naphthenic groups attached to aromatic rings) in both the heavy and light fractions of the charge stock. Much of the work on the cracking of pure hydrocarbon (Haensel, 1951) and petroleum feedstocks (Shankland, 1954) suggested that these hydrocarbon types and boiling ranges were reasonable to use as the basic lumps of a kinetic model.

The kinetic model for fluid catalytic cracking consists of the kinetic scheme shown in Figure 1. Ten lumps are necessary to follow the cracking of virgin gas oils and recycle charge stocks. This lumping scheme successfully treats gasoline (G lump, C_5^+ to 430°F), C lump (H_2, H_2S, $C_1 - C_4$ + coke), and light fuel oil (430° to 650°F) yields resulting from gas oil cracking. The total conversion (weight percent) is the sum of the G and C lumps. Detailed composition changes resulting in the LFO (430° to 650°F) and HFO (650°F^+) are obtained by following the concentrations of paraffinic, naphthenic, aromatic rings, and aromatic substituent groups as the gas oil cracking proceeds.

The kinetic scheme (Figure 1) shows that a paraffinic molecule in HFO will form paraffinic molecules in LFO

$$
\begin{array}{c|cccccccccc|}
 & P_h & N_h & A_h & C_{Ah} & P_\ell & N_\ell & A_\ell & C_{A\ell} & G & C \\
P_h & -(K_{php\ell}+K_{phg}+K_{phc}) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
N_h & 0 & -(K_{nhn\ell}+K_{nhg}+K_{nhc}) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
A_h & 0 & 0 & -(K_{aha\ell}+K_{ahg}+K_{ahc}+K_{ahca\ell}) & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
C_{Ah} & 0 & 0 & 0 & -(K_{cahca\ell}+K_{cahc}) & 0 & 0 & 0 & 0 & 0 & 0 \\
P_\ell & \nu_{h\ell}\,K_{php\ell} & 0 & 0 & 0 & -(K_{p\ell g}+K_{p\ell c}) & 0 & 0 & 0 & 0 & 0 \\
N_\ell & 0 & \nu_{h\ell}\,K_{nhn\ell} & 0 & 0 & 0 & -(K_{n\ell g}+K_{n\ell c}) & 0 & 0 & 0 & 0 \\
A_\ell & 0 & 0 & \nu_{h\ell}\,K_{aha\ell} & 0 & 0 & 0 & -(K_{a\ell g}+K_{a\ell c}) & 0 & 0 & 0 \\
C_{A\ell} & 0 & 0 & \nu_{h\ell}\,K_{ahca\ell} & \nu_{h\ell}\,K_{cahca\ell} & 0 & 0 & 0 & -K_{ca\ell c} & 0 & 0 \\
G & \nu_{hg}\,K_{phg} & \nu_{hg}\,K_{nhg} & \nu_{hg}\,K_{ahg} & 0 & \nu_{\ell g}\,K_{p\ell g} & \nu_{\ell g}\,K_{n\ell g} & \nu_{\ell g}\,K_{a\ell g} & 0 & -K_{gc} & 0 \\
C & \nu_{hc}\,K_{phc} & \nu_{hc}\,K_{nhc} & \nu_{hc}\,K_{ahc} & \nu_{hc}\,K_{cahc} & \nu_{\ell c}\,K_{p\ell c} & \nu_{\ell c}\,K_{n\ell c} & \nu_{\ell c}\,K_{a\ell c} & \nu_{\ell c}\,K_{ca\ell c} & \nu_{gc}\,K_{gc} & 0
\end{array}
$$

where,

$\nu_{h\ell}$ = Stoichiometric coefficient (Mol. Wt. of heavy fuel oil / Mol. Wt. of light fuel oil)
ν_{hg} = Stoichiometric coefficient (Mol. Wt. of heavy fuel oil / Mol. Wt. of gasoline)
ν_{hc} = Stoichiometric coefficient (Mol. Wt. of heavy fuel oil / Mol. Wt. of C lump)
$\nu_{\ell g}$ = Stoichiometric coefficient (Mol. Wt. of light fuel oil / Mol. Wt. of gasoline)
ν_{c} = Stoichiometric coefficient (Mol. Wt. of light fuel oil / Mol. Wt. of C lump)
ν_{gc} = Stoichiometric coefficient (Mol. Wt. of gasoline / Mol. Wt. of C lump)

Fig. 2. Matrix of rate constants *K*.

($P_h \rightarrow P_l$) and molecules in G lump ($P_h \rightarrow G$) and C lump ($P_h \rightarrow C$). Paraffinic molecules in LFO can only crack to molecules in G lump ($P_l \rightarrow G$) and in C lump ($P_l \rightarrow C$). Likewise, a naphthenic molecule in HFO can form a naphthenic molecule in LFO and molecules in the G and C lumps. This is popularly designated as saying there is no interaction between the paraffinic, naphthenic, and aromatic groups. Various kinetic schemes with interactions were investigated, but they did not improve the predictive capabilities of the model.

The side chains and naphthenic rings attached to the aromatic rings react similarly except for a single interaction step which allows $A_h \rightarrow C_{Al}$. This is the only interaction reaction step in the model and is designated by the rate constant K_{ahcal} in the matrix of rate constants (Figure 2). The aromatic rings in the HFO (C_{Ah}) and LFO (C_{Al}) do not form gasoline but result in the formation of the C lump and are primarily manifested as the coke contribution to the C lump. At this point, explanation is necessary to clarify the aromatic reaction rate.

Bare aromatic rings in LFO cannot form gasoline. However, an aromatic ring with an attached substituent group could undergo reaction such that the substituent group reacts to give molecules in G lump or C lump. In this case, the associated aromatic ring could then drop into the gasoline fraction (due to the resultant lowering of boiling point). In the kinetic model, this entire effect is included in the rate constant of the substituent group. The rate constant for $C_{Al} \rightarrow G$ is still maintained as zero. This treatment, therefore, recognizes that aromatic rings by themselves cannot form gasoline, but they can form gasoline if an associated substituent group is removed.

No distinction is made between P, N, A molecules in the gasoline fraction; consequently, all the gasoline molecules are lumped together with a single cracking rate. (In order to predict gasoline composition and quality, it is necessary to further subdivide the gasoline lump. By using this approach, it was found that a rather complex kinetic scheme is required to successfully describe composition changes within the gasoline fraction. This more detailed approach to gasoline delumping is not described in this paper.)

The matrix of rate constants (Figure 2) is lower triangular and is a consequence of the irreversible nature of the postulated cracking network. Irreversible reactions lend themselves quite naturally to stepwise solution, and considerable advantage is derived from the fact that many of the rate constants can be determined independently. Coke is predicted by using a separate kinetic calculation which is discussed later.

In addition to the lumping scheme, other factors have been incorporated into the model to account for process variable effects and other related phenomena. A catalyst decay term is needed to account for the rapid deactivation of the catalyst which occurs during the catalytic cracking of gas oils. Other features are an adsorption term for nitrogen poisoning, activation energies, molar expansion, and oil partial pressure. These factors arise naturally in the development of the reactor model.

It is important to note that the scheme with the set of rate constants obtained from a fixed fluidized dense-bed reactor has proven sufficient in representing the selectivity and conversion behavior in laboratory risers and commercial FCC units.

Derivation of Equations

The laboratory units can be described by the continuity equation for an isothermal, vapor phase, plug flow reactor with negligible interparticle diffusion and a time-decaying catalyst:

$$\left(\frac{\partial \rho a_j}{\partial t}\right)_x + G_v\left(\frac{\partial a_j}{\partial x}\right)_t = r_j \tag{1}$$

We have assumed that the reactor cross section and the void fraction are uniform and that the mass flow rate is steady; that is

$$G_v = \rho U = \text{constant} \tag{2}$$

For steady state moving and fluid-bed reactors, the time partial derivative is, of course, zero. For fixed beds and fixed fluidized beds, the full partial differential equation is necessary to describe them.

The rate of disappearance of a chemical species j in a single reaction is assumed to be proportional to the molar concentration of species j (that is, ρa_j) and the mass density of catalyst relative to the gas volume (that is, ρ_c/ϵ). (Note: ρ_c is defined as gram catalyst per cubic centimeter bed; ϵ is bed void fraction). The adsorption of heavy, inert aromatic rings on the catalyst surface influences the availability of active sites and consequently the rate of reaction; thus

$$r_j = -k_j'(\rho a_j)\left(\frac{\rho_c}{\epsilon}\right)\frac{1}{1 + K_h C_{Ah}} \qquad (3)$$

The rate constant k_j' has units of (gram catalyst/cubic centimeters)$^{-1}$ (hour)$^{-1}$. Combining the rate and material balance equation, we get

$$\left(\frac{\partial \rho a_j}{\partial t}\right)_x + G_v\left(\frac{\partial a_j}{\partial x}\right)_t = -k_j'\rho a_j \frac{\rho_c}{\epsilon}\frac{1}{1 + K_h C_{Ah}} \qquad (4)$$

The rate constant need not be constant, but it can decay with time.

Equation (4) may be recast by defining a normalized distance based on overall reactor length and a true weight hourly space velocity which includes the effect of inerts (usually less than 10 mole % in the gas oil feed). Thus

$X = x/L$ dimensionless distance into bed

S_{WH} = gram feed (oil + inerts)/(hour) (gram catalyst)

From the definitions of G_v and S_{WH}, we get

$$G_v = \frac{S_{WH}\rho_c L}{\epsilon} \qquad (5)$$

If the rate of concentration change with time $(\partial \rho a_j/\partial t)_x$ is small relative to the rate of change with position [in a fixed fluidized dense bed this is tantamount to the oil molecules traversing the bed so fast, relative to catalyst decay, that they are exposed to catalyst of essentially uniform age (or activity)], then the model becomes

$$\frac{da_j}{dX} = -\frac{1}{1 + K_h C_{Ah}}\frac{k_j' a_j}{S_{WH}} \qquad (6)$$

As mentioned previously, Voorhies showed that coke formation and catalyst decay are strongly related to catalyst contact time. Also, since the same type of catalyst sites would be expected to crack both gas oil molecules and gasoline range molecules, the catalyst decay can be represented as nonselective. This was found to be a reasonable assumption (Weekman and Nace, 1970). Thus, the matrix of rate constants becomes

$$k_j' = k_j \Phi(t_c) \qquad (7)$$

where k_j are invariant rate constants. With the ideal gas assumption

$$\rho = \frac{P\,\overline{MW}}{RT} \qquad (8)$$

Equation (6) becomes

$$\frac{da_j}{dX} = -\frac{1}{1 + K_h C_{Ah}}\frac{\Phi(t_c) P\,\overline{MW}\, k_j a_j}{S_{WH} RT} \qquad (9)$$

In matrix notation

$$\frac{d\mathbf{a}}{dX} = \frac{1}{1 + K_h C_{Ah}}\frac{P\,\overline{MW}\,\Phi(t_c)}{S_{WH} RT}\mathbf{K}\mathbf{a} \qquad (10)$$

In this expression, the $\overline{MW}$ is not constant but changes with distance into the bed. Note that

$$\overline{MW} = \frac{\Sigma a_j M_j}{\Sigma a_j} = \frac{1}{\Sigma a_j} \qquad (11)$$

since the units for a_j are moles j per gram of gas.

Thus, an increase in the total pressure will increase the concentration of gas oil molecules and enhance their rate of reaction. However, at higher pressure the catalyst cokes faster and deactivates more rapidly. This is reflected in the deactivation function for the catalyst:

$$\Phi(t_c) = \frac{\alpha}{(\bar{p})^m(1 + \beta t_c{}^{\gamma})}$$

This form was chosen because it represented experimental decay rates adequately.

The oil partial pressure effect was not necessary in analyzing the fixed fluidized-bed results which were all run at atmospheric pressure. It must be used, however, for riser pilot plants and commercial FCC units.

Nitrogen Poisoning

Basic nitrogen compounds are known to poison acidic cracking catalysts. Considerable research has been done on the effects of nitrogen poisoning on the cracking of pure hydrocarbons and gas oils (Mills et al., 1950; Plank and Nace, 1955; Service, 1960; Reif et al., 1961; Schneider et al., 1969). Some simple kinetic models have been developed to quantitatively describe the results, especially in the case of pure hydrocarbons. Recent work of Voltz et al. (1972) has shown that quinoline added to a wide-cut, Mid-Continent gas oil (WCMCGO) gives the same effects on conversion and selectivity as the natural occurring nitrogen bases in a typical FCC feedstock.

The effects of nitrogen poisoning have been incorporated into the model by the addition of a catalyst deactivation term related to nitrogen adsorption and the use of a scalar quantity on the gasoline formation rate constants.

Nitrogen deactivation is accounted for by a deactivation function $f(N)$ given by

$$f(N) = \frac{1}{1 + K_n N/\text{grams of catalyst}}$$

$$= \frac{1}{1 + \dfrac{K_n}{100}\dfrac{\text{weight percent basic } N \text{ in charge}}{\text{CAT/OIL}}\theta} \qquad (12)$$

where N = grams of basic nitrogen to which the catalyst has been exposed at catalyst residence time t_c. At high catalyst/oil ratios, there are small quantities of basic nitrogen per cracking site, and the deactivation is insignificant. θ is the normalized catalyst residence time. $f(N)$ is a scalar multiplier on the rate constant matrix.

A scalar increase of all gasoline formation reactions accounts for the slight increase in selectivity observed.

Time Averaging for Fixed and Fluidized Dense Beds

Experimental runs with fluid and fixed beds often obtain products collected over the duration of a run. If catalyst decay is present, then this collected material represents the mixed average reactor effluent. To account for time averaging, it is necessary to integrate the model equations from bed inlet to outlet ($X = 0$ to $X = 1$) and then to integrate the reactor effluent over the duration of the run ($t_c = 0$ to $t_c = t_{\text{run}}$).

The following coordinate transformation greatly simplified the calculation procedures:

$$dW = \frac{\Phi(t_c)P}{S_{WH}RT}dX \qquad (13)$$

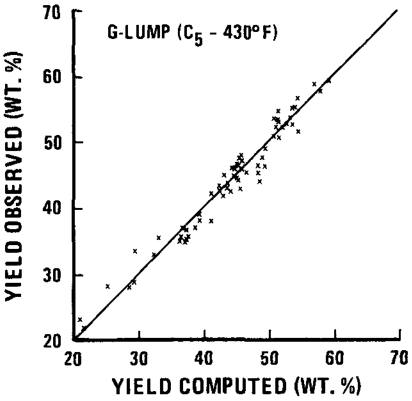


Fig. 3a. Computed vs. observed time-averaged gasoline yields.

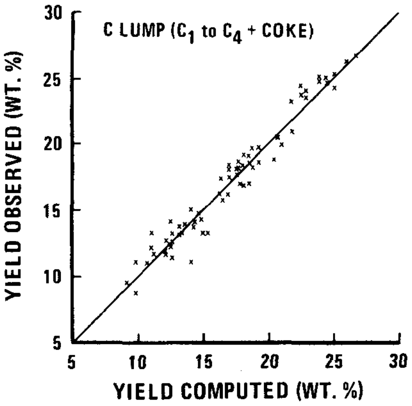


Fig. 3b. Computed vs. observed time averaged C lump yields.

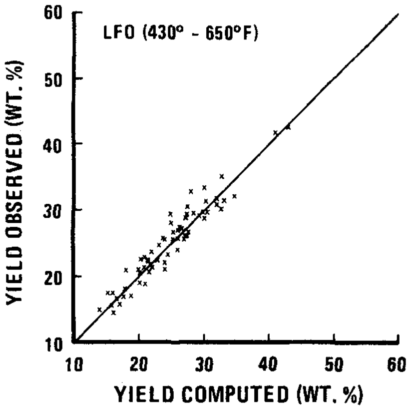


Fig. 3c. Computed vs. observed time averaged LFO yields.

This transformation of the reaction coordinate X yields a crazy clock time W which incorporates into its definition the effect of S_{WH} and t_c and is given by

$$W = \frac{\Phi(t_c)P}{S_{WH}RT} X \tag{14}$$

Note that this transformation holds only for fixed or fluidized dense beds [for a riser and moving bed $\Phi(t_c) = f(X)$]. Our model becomes simply

$$\frac{da}{dW} = \frac{1}{1 + K_h C_{Ah}} \frac{Ka}{\sum_j a_j} \tag{15}$$

The utility of this result can be demonstrated by determining the mixed average concentration for a particular run. From the initial conditions (the specific feedstock), the model equation is integrated to give a as a function of W. Next, W is evaluated for $X = 1$ (reactor outlet)

$$W = \frac{\Phi(t_c)P}{S_{WH}RT} \tag{16}$$

where P, R, T, and S_{WH} are known from the run. Six times from 0 to t_c are then chosen according to the six-point Gaussian quadrature integration formula. From the above equation, this specifies the six transformed coordinate values at which $a(W)$ is evaluated and supplied to the Gaussian formula. This together with the appropriate weighting factors gives the time averaged composition.

For any given feed composition, only one evaluation of a_j vs. W is required; thus computation time is substantially reduced. Furthermore, with one set of solutions a vs. W, we know the instantaneous reactor effluent for all S_{WH}, and t_c for both fixed and fluid beds is known.

Determination of Rate Constants

An improved version of a technique for least-squares estimation of nonlinear parameters was used to determine the rate constants k_j from the data obtained in a fluidized dense bed with a commercial FCC catalyst. The ranges of process variables and resulting yields are given in Table 1. It should be noted that all the experimental data in the fixed fluidized bed are time-averaged data.

A fitting function that attached more importance to the G and C lumps vs. LFO (for data reliability reasons) was used. Standard errors defined as $\sqrt{\sigma^2/(N_D - N_P)}$ where N_D is the number of data points and N_P the number of rate constants, were comparable with the accuracy of the data. The standard errors were 1.78, 0.95, and 1.90%, respectively, for gasoline, light ends (H_2, H_2S, $C_1 - C_4$) + coke, and light fuel oil. The plots of observed vs. computed yields of gasoline, C lump, and LFO are shown in Figure 3.

RESULTS

The kinetic framework thus developed is capable of predicting time-averaged conversion, gasoline, light fuel oil, and light ends (H_2, H_2S, $C_1 - C_4$) yields for a wide range of virgin and recycled gas oils as a function of catalyst residence time, space velocity, and other process variables. In addition, the LFO and HFO compositions are accurately traced as conversion proceeds. The individual light end compositions are also predicted with a pseudo kinetic scheme (not given here).

It is interesting to compare some ratios of the various rate constants with the known cracking behavior of pure hydrocarbons and petroleum feedstocks (that is, Haensel, 1951; Hansford, 1952; Oblad et al., 1951; and Shankland, 1954). The rate constants for the cracking of the heavy fuel oil fractions of the P, N, and A lumps to gasoline are greater than the respective ones for the light fuel oil fractions. The ratio is 2.31 for K_{phg}/K_{plg}, for example. This is quite reasonable, as the cracking rates of most paraffins and naphthenes increase with increasing molecular weight.

The aromatic substituent groups in heavy fuel oil (A_h) have the highest rate constant (K_{ahc}) for C lump formation. The ratio of K_{ahc} to K_{nhc}, for instance, is 2.29, indicating that aromatic substituent groups form light ends and coke much faster than naphthenic heavy compounds. This is consistent with the high cracking rate of side chain alkyl groups, particularly C_3 and C_4, and the high coking tendency of three and four membered ring aromatic compounds.

The refractory aromatic rings in LFO (C_{Al}), exhibit smaller coke forming and cracking tendencies (K_{calc}) compared to the higher boiling aromatic fractions.

The ratios of the respective rate constants for gasoline formation to the corresponding ones for C lump formation are an approximate measure of the selectivity of each lump for gasoline formation. The selectivity of paraffins and naphthenic groups are approximately the same, $K_{nhg}/K_{nhc} = 5.69$ and $K_{phg}/K_{phc} = 5.82$. Also noteworthy is the high reactivity of naphthenic compounds relative to paraffinic compounds for both the high and low boiling ranges; that is, $K_{nlg}/K_{plg} = 2.77$. The cracking of gaso-

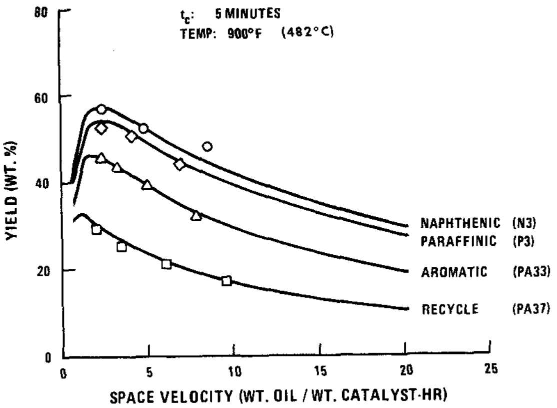


Fig. 4a. Observed vs. computed time averaged gasoline yields as a function of charge stock.

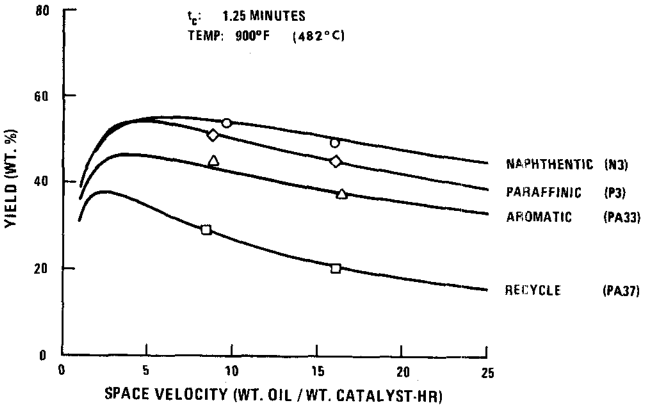


Fig. 4b. Observed vs. computed time averaged gasoline yields as a function of charge stock.

line to C lump (K_{gc}) is considerably smaller than the rate constants for gasoline formation, as would be expected. The ratio, for example, of K_{ahg}/K_{gc} is 14.3.

Further significance of these rate constants will become evident as predicted and experimental yields are discussed for paraffinic, naphthenic, aromatic, and recycle charge stocks.

Compositional Effects

Plots of gasoline yields vs. space velocity are given for four different charge stocks in Figures 4*a* and *b*. The catalyst residence times are 5.0 and 1.25 min, respectively, in these plots. The points are the experimental data for each charge stock, and the solid curves were calculated from the model. N3 is a highly naphthenic charge stock and gives the greatest yields of gasoline. The highly paraffinic charge stock, P3, gives gasoline yields only slightly lower than N3.

The highly aromatic stock, PA33, prepared by blending P3 with 30% of an aromatic extract gives lower gasoline yields, while the recycle stock, PA37, yielded significantly lower gasoline. The side chains on aromatic rings crack quite readily, but aromatic rings are very stable and are extremely resistant to cracking reactions. Recycle charge stocks consist largely of refractory aromatic molecules and give very low yields of cracked products.

The four stocks, P3, N3, PA33, and PA37, represented a wide range of paraffinic, naphthenic, and aromatic concentrations, with a corresponding divergence in selectivity and conversion behavior. As Figures 4*a* and *b* show, the kinetic scheme accurately reflects this behavior. Selectivity curves for P3 vs. space velocity and conversion indicate that the model not only fits the experimental data well but also predicts the proper trends over the entire range of conversion (Figures 5 and 6).

Some of the stocks (that is, P1 and N1) correspond to light fuel oil fractions, while others, P2 and N2, correspond to heavy fuel oil boiling ranges. The model accurately predicts the behavior of these stocks as shown in Figure 7 for N1 and N2.

Effects of time averaging are also noteworthy, as shown in Figure 4*a* at 5 min and Figure 4*b* for 1.25 min. The time-averaged yield is higher at 1.25 min than at 5 min residence time. This is expected behavior with a time-decaying catalyst and shows that the deactivation function accurately follows the catalyst decay.

Compositional Changes During Reaction

Most importantly, it has been demonstrated that with the model parameters (that is, rate constants) the HFO and LFO compositions are accurately traced as conver-

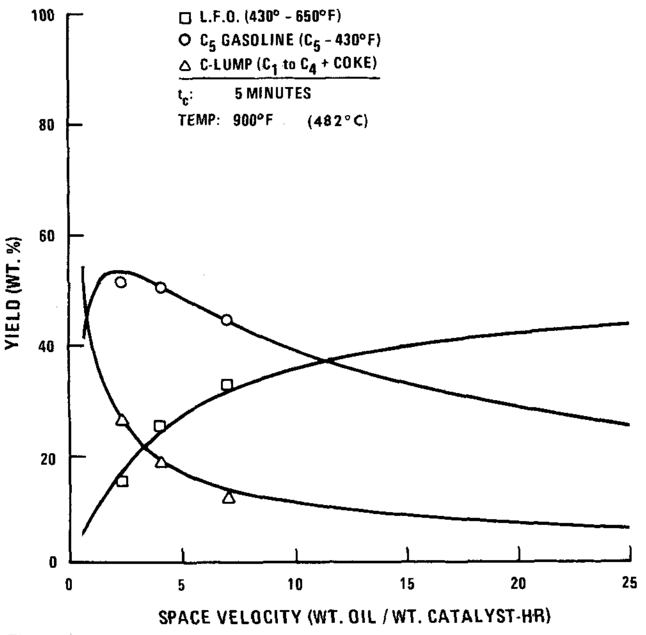


Fig. 5. Experimental cracking yields vs. computed yield for a paraffinic charge stock (P3) as a function of space velocity.

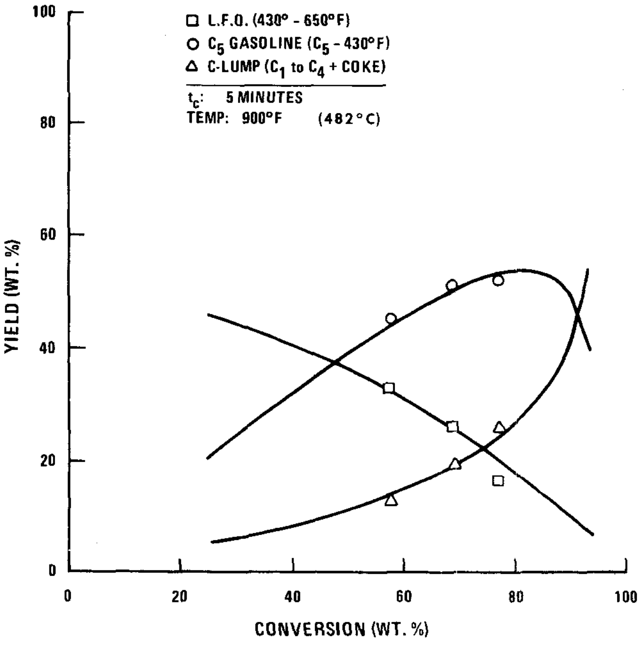


Fig. 6. Model selectivity plots vs. experimental cracking selectivity for a paraffinic charge stock (P3).

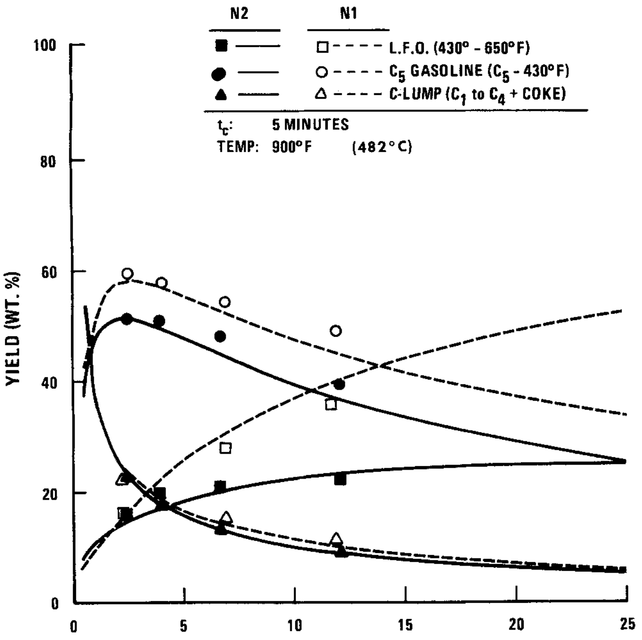


Fig. 7. Experimental cracking yields vs. computed yields for a heavy (N2) and light (N1) naphthenic charge stock as a function of space velocity.

sion proceeds. It must be remembered that these compositional changes were not used in determining the model parameters. Rather, the computed compositional changes result (as a pure prediction) from fitting the model to the G lump, C lump, and LFO and provide considerable support for the validity of the kinetic scheme.

Detailed experimental analysis of the LFO and HFO are shown for a single charge stock, PA33, in Figures 8 and 9 as a function of conversion. The solid lines represent the kinetic paths traced by the model for each of the compositional lumps. The model accurately follows the increase and subsequent decrease of the kinetic lumps in LFO and follows the decrease of the kinetic lumps in HFO.

It is especially important, from the viewpoint of recycle, to be able to predict the polynuclear aromatic rings in the HFO (percent C_{Ah}). This lump primarily determines the increased coke production from recycle charge stocks and also reflects its cracking characteristics. At high conversion (60 to 70 wt %), the HFO is almost solely composed of polynuclear aromatic rings. Since the lumped composition of these fractions is accurately predicted, recycle situations (recycling HFO or LFO, or both) may be treated with confidence.

Coke Yields

Carbon on catalyst is treated by using the classic coking relation of Voorhies (1945):

$$C = at_c{}^n \tag{17}$$

where

C = wt % carbon on catalyst
a = a function of charge stock
t_c = the catalyst residence time
n = an exponent which is a function of catalyst

Approximately 95 sets of coke data at 900°F (482°C) and catalyst residence times of 1.25, 5.0, and 10.0 min were used to develop a relation that would be charge stock independent. The results of this fit gave the equation below with a standard error of 0.25 (absolute weight percent) for coke (weight percent) produced on charge. Computed coke yields are generally within 6% or less of the observed values:

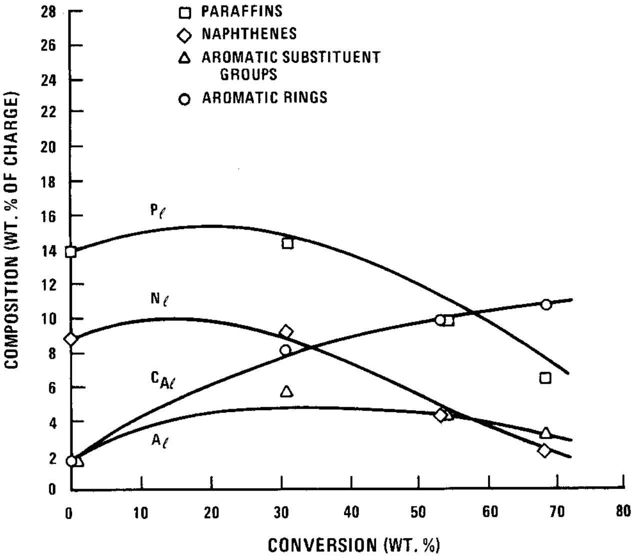


Fig. 8. Light fuel oil (430° to 650°F) composition-model predictions (lines) vs. experimental data (points).

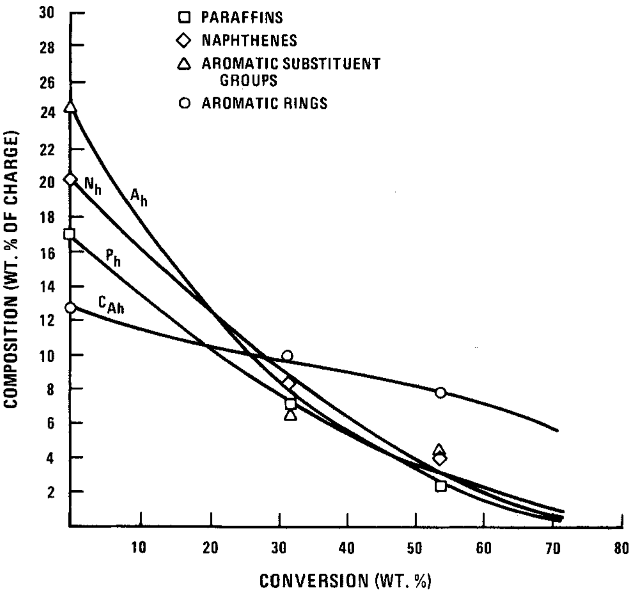


Fig. 9. Heavy fuel oil (650°F+) composition-model predictions (lines) vs. experimental data (points).

$$C = \frac{a}{100}\left(\frac{t_c}{5.0}\right)^{0.2} \tag{18}$$

where

$a = \Psi(P_{lo}, N_{lo}, A_{lo}, C_{Alo}, P_{ho}, N_{ho}, A_{ho}, C_{Aho})$
t_c = catalyst residence time in minutes
P_{lo}, N_{lo}, A_{lo}, C_{Alo} = weight percent paraffins, naphthenes, aromatic substituent groups, and aromatic rings in LFO of charge
P_{ho}, N_{ho}, A_{ho}, C_{Aho} = weight percent paraffins, naphthenes, aromatic substituent groups, and aromatic rings in HFO of charge

a thus represents a compilation of the coking tendencies of the various species. For example, the coking tendency of a stock high in heavy aromatic rings is greater than that of a stock that contains a preponderance of naphthenic species. The coke yield (weight percent) may then be calculated from

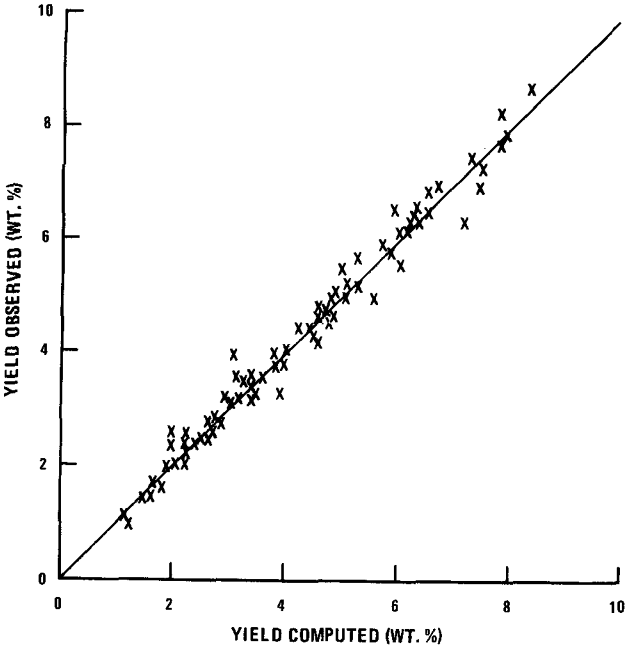


Fig. 10. Computed vs. observed light ends yields—ISOC4.

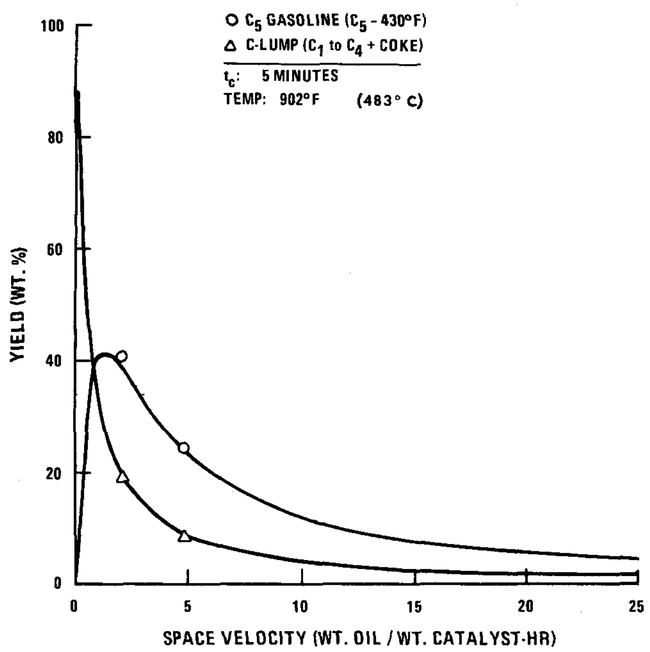


Fig. 12. Predicted vs. experimental yields for a California charge stock with 0.096 wt % basic N.

$$\text{coke yield (wt \%)} = 1.1\,C\ (\text{cat/oil})$$

where the factor 1.1 accounts for the carbon hydrogen ratio in the coke.

Light Ends Yields

Correlations to predict the yields of light ends from catalytic cracking have been developed at 900°F (482°C) on widely different charge stocks. The correlation is based on gasoline and C lump yield and the lumped composition of the charge stock.

Typical results for iso C_4 yields are shown in Figure 10. Computed yields for C_1-C_4 are generally within 10% or less of the observed values.

Nitrogen Poisoning

The nitrogen poisoning function was presented earlier. The deactivation function is such that at the end of an experimental run ($\theta = 1$), where the catalyst/oil = 2.0 and the basic nitrogen in the feedstock is 0.1 wt %, the catalyst activity is reduced by over one third.

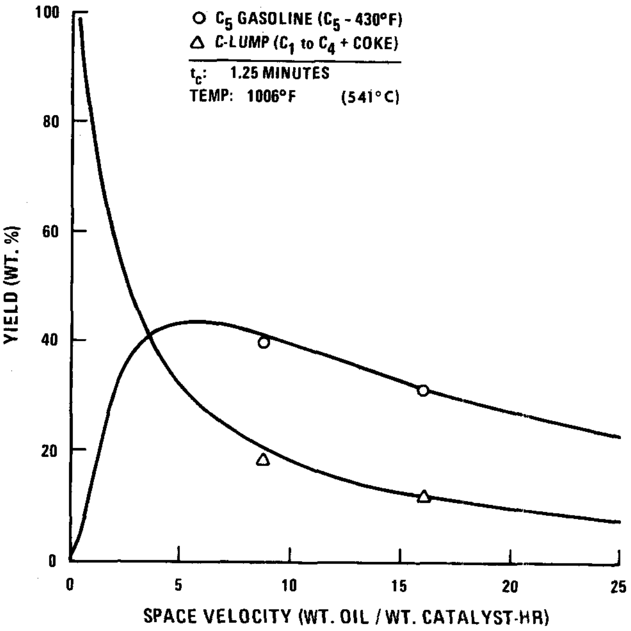


Fig. 11. Experimental cracking yields vs. computed yields for WCMCGO with 0.2 wt % addition basic N as quinoline.

Results for WCMCGO with 0.2 wt % addition of quinoline at 1,000°F (538°C) are indicated in Figure 11.

The model has been successfully tested on a California gas oil (TK520) with 0.096% basic nitrogen. The result, Figure 12, is encouraging; it provides a simultaneous test of lumping scheme and basic nitrogen poison term.

Temperature

Temperature effects in the lumped kinetic model are accounted for by assigning activation energies to groups of reactions. The model has six activation energies derived from temperature data at 900° (482°C), 950° (510°C), and approximately 1,000°F (538°C) on several charge stocks. Comparison of the predicted yields with the experimental data from these activation energies is shown in Figure 13 for Amal (P3) at 1,010°F (543°C). P3 at 900°F (482°C) is shown for comparison. The activation energy groupings include:

1. Gasoline (G lump) formation reactions from paraffins and naphthenes.
2. C lump formation reactions from paraffins and naphthenes.
3. Gasoline (G lump) formation reactions from A_h, A_l.
4. C lump formation reactions from A_h, A_l, C_{Ah}, C_{Al}.
5. C lump formation reactions from gasoline.
6. LFO formation reactions from paraffins, naphthenes, and aromatics.

The activation energy for C lump formation from gasoline is 20 kcal/mole. Activation energies for group 3 and group 4 reactions are much greater (14 to 18 kcal/mole) than the activation energy for group 1 and group 2 reactions (5 to 9 kcal/mole). At the same conversion level, an increase in temperature results in a lower gasoline yield since the gasoline cracking rate increases faster than the gasoline formation rate.

Temperature effects have also been included in the coke and light end correlations.

Some Predictive Capabilities of the Model

The model has been used to successfully predict G lump (C_5^+ to 430°F gasoline), C lump (H_2, H_2S, C_1 — C_4, coke), and LFO (430° to 650°F) yields for charge stocks not used in determining the rate constants. The

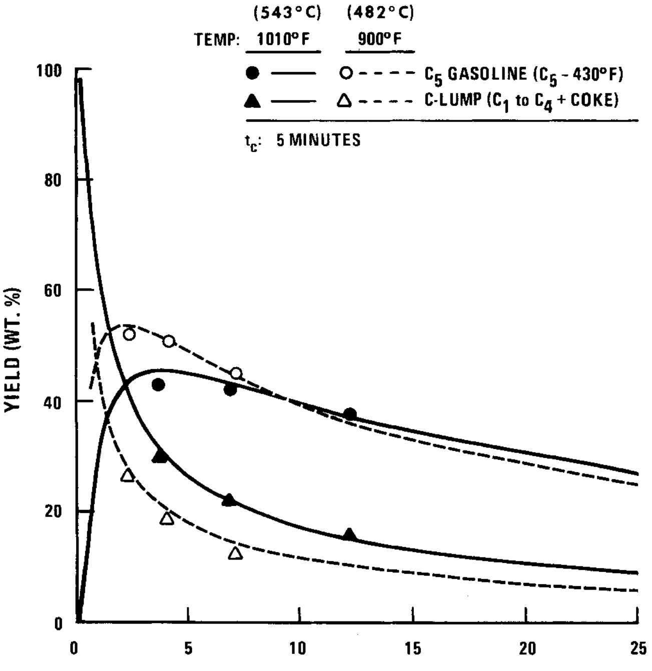


Fig. 13. Temperature effect on yields of charge stock (P3).

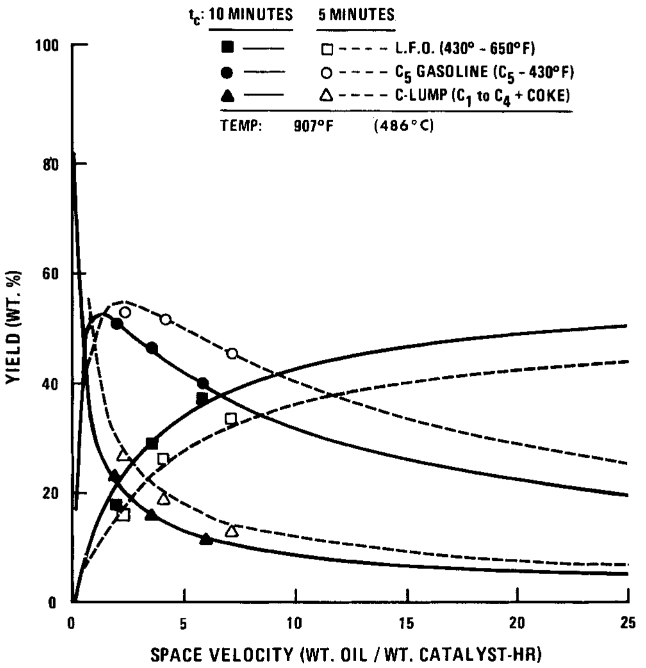


Fig. 14. Catalyst residence time effect on yields of charge stock (P3).

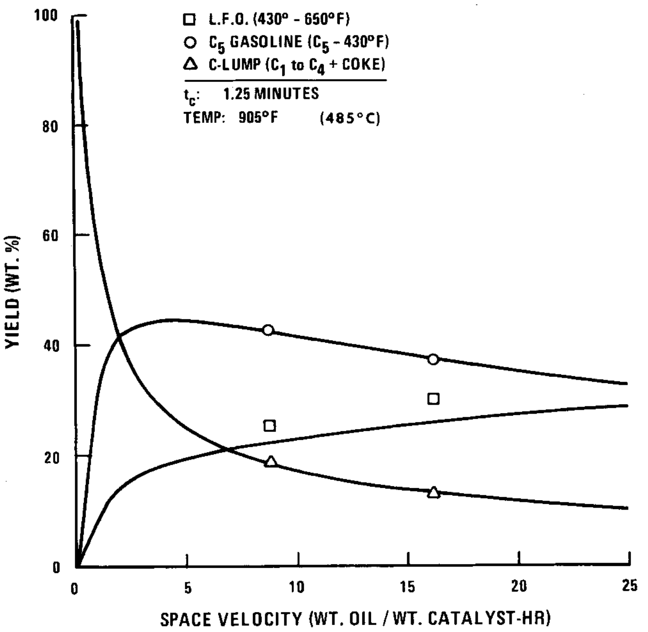


Fig. 15. Predicted vs. experimental cracking yields for a charge stock with high boiling aromatics (PA38).

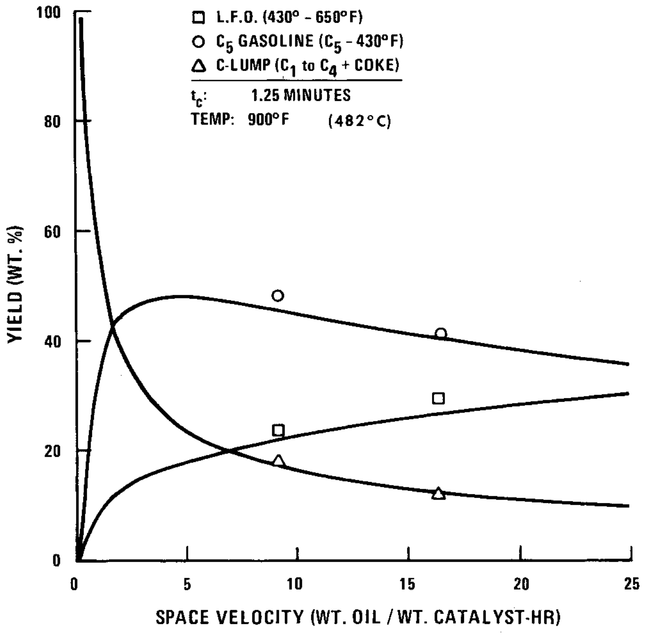


Fig. 16. Predicted vs. experimental cracking yields for WCMCGO.

average and standard errors of the predictions are similar to those obtained when the model was fitted to the original data. The model appears to have good prediction capability as demonstrated by the following examples:

1. Amal gas oil (P3) was run at a catalyst residence time of 10 min to test the validity of extrapolating the catalyst residence times. The catalyst deactivation function was previously computed from the cracking results of fifteen charge stocks at 1.25 and 5 min onstream periods. Figure 14 shows that the deactivation function adequately predicts the cracking yields of gasoline, C lump, and LFO at longer catalyst residence times ($t_c = 10$ min).

2. Figure 15 is a plot of the yields of gasoline, C lump, and light fuel oil vs. space velocity for PA38. This charge stock was not used in the determination of the rate constants. The agreement between the experimental data and the predicted curves is excellent.

3. A similar plot is shown for WCMCGO, a charge stock not previously used in the model (Figure 16), and again the agreement is very good.

CONCLUSIONS

A kinetic lumping and reaction scheme has been developed for catalytic cracking. The model is capable of predicting catalytic cracking behavior for a wide variety of feedstock compositions over a broad range of reaction conditions. The model successfully predicts conversion, gasoline selectivity, light fuel yields, light ends distribution, effects of nitrogen poisoning, effects of aromatic adsorption, temperature effects, and also traces HFO and LFO compositions as conversion proceeds.

The scheme with the set of rate constants obtained from a fixed fluidized dense-bed reactor has also proved successful in representing selectivity and conversion behavior in instantaneous pilot plant and commercial riser reactors, without alteration of the intrinsic rate constant matrix. It has been incorporated into an integrated reactor-regenerator process model, which can make detailed predictions of FCC commercial behavior for different feedstock compositions and process variable conditions.

NOTATION

a = coking constant for Voorhies equation, $C = at_c^n$
$\mathbf{a}$ = composition vector consisting of j lumped species (a_j = moles j/g gas)
a_j = concentration lump j (moles j/g gas)
A_h = wt % aromatic substituent groups in HFO (650°F$^+$)
A_{ho} = wt % aromatic substituent groups in HFO of charge
A_l = wt % aromatic substituent groups in LFO (430° to 650°F)
A_{lo} = wt % aromatic substituent groups in LFO of charge
C = C lump, wt % H_2, H_2S, C_1-C_4 + coke
C_{Ah} = wt % aromatic rings in HFO (650°F$^+$)
C_{Aho} = wt % aromatic rings in HFO of charge
C_{Al} = wt % aromatic rings in LFO (430° to 650°F)
C_{Alo} = wt % aromatic rings in LFO of charge
G_c = superficial mass flow rate of catalyst (g/cm^2 cross section, s)
G_v = superficial mass flow rate of vapor (g/cm^2 cross section, hr)
G = G lump, wt % gasoline (C_5^+ – 430°F)
$\mathbf{K}$ = rate constant matrix (See Figure 2.)
K_h = heavy aromatic ring adsorption coefficient (wt % C_{Ah})$^{-1}$
K_j = rate constant of j^{th} lump (gm cat/cm^3)$^{-1}$ (hr^{-1})
K_n = basic nitrogen adsorption coefficient (g basic N/g catalyst)$^{-1}$
L = total length of riser and conical section
$\overline{MW}$ = mean molecular weight of gas mixture = $1 \Big/ \sum_j a_j$
N_D = number of data points
N_h = wt % naphthenic molecules in HFO (650°F$^+$)
N_{ho} wt % naphthenic molecules in HFO of charge
N_l = wt % naphthenic molecules in LFO (430° to 650°F)
N_{lo} = wt % naphthenic molecules in LFO of charge
N_P = number of parameters
$\bar{p}$ = oil partial pressure at inlet (atm)
P = absolute pressure (atm)
P_h = wt % paraffin molecules in HFO (650°F$^+$)
P_{ho} = wt % paraffin molecules in HFO of charge
P_l = wt % paraffin molecules in LFO (430° to 650°F)
P_{lo} = wt % paraffin molecules in LFO of charge
R = gas constant (82.05 atm cm^3/g-mole °K)
r_i = rate of formation of kinetic lump i (lb/hr)
S_{WH} = true weight hourly space velocity (g feed/g catalyst-hr)
t_c = catalyst residence time, hr
T = temperature (°K)
U = gas velocity in bed, cm/hr

Greek Letters

α = catalyst deactivation constant
β = catalyst deactivation constant
γ = catalyst deactivation constant
$\Phi(t_c)$ = catalyst decay as a function of catalyst residence time, $\alpha/\text{OPP}^m(1 + \beta\, t_c^\gamma)$, (dimensionless)
σ_C^2 = sum of the square of the deviations for C lump
σ_G^2 = sum of the square of the deviations for G lump
σ_L^2 = sum of the square of the deviations for LFO
ϵ = void fraction
ρ_c = catalyst density, g catalyst/cm^3 of bed
η = fraction of available cracking sites
Ψ = coke formation function

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Basic Concepts of Spray Dryer Design

The major parameters in the design of spray dryers are discussed. A Lagrangian approach, combining experimental data with theoretical concepts, is proposed to develop design methods. Vortex flow patterns, obtained experimentally in a laboratory size chamber, are correlated and presented.

Based on this design methodology, computational methods are given to calculate droplet trajectories and hence to predict the optimum chamber dimensions and operating conditions for maximum thermal efficiency and/or minimum operating cost. Application of these basic principles is illustrated by the design of an industrial size, spray drying chamber for a specific feed solution and production rate.

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The growing importance of spray drying is abundantly evident from the ever increasing number of industrial applications in the production of pharmaceuticals, detergents, food products, pigments, ceramics, and a large number of organic and inorganic chemical compounds. In spite of these impressive developments and of the large number of fragmented experimental studies which have appeared in the technical literature during the past three decades, the design of spray dryers has remained largely empirical; it is still mainly based on the extensive experience and the vast body of operating data which the manufacturers have acquired over the years.

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