Sensitivity of Octane Number to Catalytic Cracking Rates and Feedstock Structure

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Many studies have examined the catalytic cracking reactions of petroleum feedstocks (Voorhies, 1945; Greensfelder et al., 1949; Weekman, 1968; Jacob et al., 1976; Liguras and Allen, 1989a,b), and an immense literature has been developed on estimating the physical, chemical and thermodynamic properties of petroleum components. Unfortunately, these two fields of research have not been coupled. In the kinetic models, oils have traditionally been characterized by compound classes (kinetic lumps), and the concentrations of these compound classes are not generally sufficient to yield predictions of important distillate properties such as vapor pressure or octane number.

This situation has changed, however, with the introduction of a new, structurally based approach to modeling the catalytic cracking of petroleum (Liguras and Allen, 1989a,b). In this approach, the oil is modeled by several hundred pseudocomponents, which are selected on the basis of analytical data typically available on petroleum feedstocks (Allen and Liguras, 1990). The reaction rates and product distributions for these pseudocomponents simulate the reactions of the petroleum feedstock. The rate parameters for the hundreds of pseudocomponents are estimated using group contribution parameters developed in independent model compound experiments. The modeling methodology and its application to cracking over an amorphous silica alumina catalyst have been described in detail by Liguras and Allen (1989a,b).

This work will describe how the structural model of cracking kinetics can be interfaced directly with property estimation methods. The output of the kinetic model will be used to estimate gasoline range research octane number (RON) and gasoline range motor octane number (MON). The sensitivity of RON, MON and gasoline yield to changes in the values of rate parameters will be examined quantitatively. We begin with a brief overview of the kinetic modeling methodology. We then describe the interface between the kinetic model and property estimation methods for RON and MON (Cotterman and Plumlee, 1989). Finally, we perform a few simple sensitivity calculations which demonstrate the use of the integrated kinetic/property prediction model.

Overview of Structural Models of Catalytic Cracking Kinetics

There are two basic elements in a structural model of catalytic cracking kinetics. The first element is the characterization of the petroleum feedstock in terms of a reasonable number of molecular structures. While the real feedstock contains on the order of 10^4 components, it is represented in the model by several hundred molecular structures (pseudocomponents). These pseudocomponents are selected based on analytical data typically available on petroleum feedstocks: compound class analyses, NMR spectra, and mass spectra. These analytical data yield between a few score and a few hundred independent pieces of structural information, depending on the degree to which one is willing to interpret the NMR and mass spectra. Methods for determining the structure and concentrations of the pseudocomponents have been described in detail by Allen and Liguras (1990). Once the pseudocomponents are chosen, the second element of the structural kinetic model is implemented. This part of the model uses a group contribution approach to estimate the rates and product distributions of the pseudocomponent reactions. A detailed description of the group contribution approach is available elsewhere (Liguras and Allen, 1989a). In this note we will merely summarize the number and type of adjustable parameters in the model.

Group contributions were determined for each of the major pathways (cracking, isomerization, cyclization, dehydrogenation, ring opening, dealkylation and coke formation) and for each of the major compound classes (*n*-paraffins, isoparaffins, olefins, naphthenes, and aromatics). As a simple example, consider the group contributions for cracking of an *n*-paraffin. The overall cracking rate for several *n*-paraffins were observed

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in model compound studies. These data indicate that overall cracking rate is a quadratic function of carbon number. Overall rates of *n*-paraffin cracking can be obtained for all carbon numbers by fitting a quadratic equation to the available data (three adjustable parameters). Product distributions were calculated by assuming that carbenium ions reach their equilibrium distribution and that the cracking position depends on the relative stability of the carbenium ions formed as products. This yields two more adjustable model parameters if we assume that relative carbenium ion stabilities are known and invariant. Thus, we build the entire model of *n*-paraffin cracking based on five adjustable parameters. The isoparaffin cracking model utilizes our knowledge of *n*-paraffin cracking; however, it must account for the enhanced overall rate of cracking due to the presence of tertiary carbon centers. This yields three more adjustable parameters (Liguras and Allen, 1989a), bringing our total to eight for isoparaffin and *n*-paraffin cracking. If one considers all of the compound classes and all of the reaction pathways, the model has roughly 20 adjustable parameters. The values of these parameters were determined from the product distributions observed in approximately 25 isothermal (500°C) model compound experiments (well over 100 independent pieces of data).

Once the rate parameters are estimated using the group contribution approach, the kinetic model can be integrated to yield the concentrations of roughly a thousand molecular structures as a function of reaction time. Note that the number of molecular structures increases with time as new reaction products are created.

Integrating the Structural Kinetic Model with Property Estimation Methods

Since the structural kinetic model predicts the concentrations of roughly a thousand molecular structures, it is computationally intensive but completely straightforward to estimate chemical, physical and thermodynamic properties of the products. We merely use the group contribution methods developed over the past several decades by the thermodynamics community (see, for example, Benson, 1976; Fredenslund et al, 1975). To demonstrate this concept we will estimate the research and motor octane numbers of gasoline range products using a group contribution method developed by Cotterman and Plumlee (1989). This method requires as input the carbon number distribution of *n*-paraffins, isoparaffins, olefins, naphthenes, and aromatics in the C_3 and C_{12} range. The research and motor octane numbers for the gasoline range are calculated using a transformation method (Rusin, 1975), where the group octane numbers are taken from values reported in API Project 45 (1958). Cotterman and Plumlee (1989) report that this method predicted 80 octane numbers determined in engine tests with a standard deviation of 0.64 and negligible bias. The structural information required as input data for the methods can be obtained directly from the molecular concentrations generated by the structural kinetic model. Typical summaries of product structures predicted by the kinetic model are given in Figure 1.

Using our integrated kinetic and RON/MON estimation model, we examined the sensitivity of gasoline yield and gasoline range RON and MON to various model rate parameters. The results of the sensitivity analysis are reported in Tables 1 and 2. In performing this sensitivity analysis, we used a molecular definition of gasoline, rather than a volatility-based definition. Specifically, we assumed that gasoline consists of all components with carbon numbers between 5 and 12. Clearly, this molecular definition is not entirely consistent with a volatility-based definition, and ignoring the C_3 and C_4 components may lead to low estimates of octane number. Despite these limitations, the qualitative features of the sensitivity study should be valid. Two types of model parameters were varied in the calculations. In the first type of calculation in Table 1, the rate constants for major reaction pathways were perturbed. In the second type of calculation reported in Table 2, the structure of the initial feedstock was perturbed.

Consider first the effect of varying the rates of major reaction pathways. In these sensitivity studies, the rate for a particular reaction pathway (e.g., isomerization) was changed for all compounds undergoing that reaction by the same percentage. The reactions considered were the cracking of paraffins to form carbenium ions and olefins (primary paraffin cracking), the cracking of carbenium ions to form carbenium ions and olefins (secondary paraffin cracking), the cracking of olefins, the isomerization of olefins and the dehydrocyclization of paraffins (aromatization). Examination of Table 1 reveals that the effect of the reaction rates on the absolute magnitude of gasoline yield (C_5–C_{12}) exhibits the following order:

$$\begin{matrix}\text{primary}\\ \text{paraffin}\\ \text{cracking}\end{matrix} \gg \text{aromatization} > \begin{matrix}\text{secondary}\\ \text{paraffin}\\ \text{cracking}\end{matrix} \cong \begin{matrix}\text{olefin}\\ \text{cracking}\end{matrix} > \begin{matrix}\text{olefin}\\ \text{isomerization}\end{matrix}$$

That is, the effect of a change in primary paraffin cracking rate far exceeds the effect of a change in aromatization rate, which in turn exceeds the effects of secondary paraffin cracking, olefin cracking and olefin isomerization. For octane number, all pathways are of comparable importance, but the following minor differences were observed:

$$\text{aromatization} > \begin{matrix}\text{olefin}\\ \text{isomerization}\end{matrix} > \begin{matrix}\text{primary}\\ \text{paraffin}\\ \text{cracking}\end{matrix} > \begin{matrix}\text{secondary}\\ \text{paraffin}\\ \text{cracking}\end{matrix} \approx \begin{matrix}\text{olefin}\\ \text{cracking}\end{matrix}$$

Finally, for the octane-barrel yield (gasoline yield multiplied by MON), we observe the following ordering:

$$\begin{matrix}\text{primary}\\ \text{paraffin}\\ \text{cracking}\end{matrix} \gg \text{aromatization} > \begin{matrix}\text{secondary}\\ \text{paraffin}\\ \text{cracking}\end{matrix} \cong \begin{matrix}\text{olefin}\\ \text{cracking}\end{matrix} \cong \begin{matrix}\text{olefin}\\ \text{isomerization}\end{matrix}$$

While this sensitivity analysis is somewhat simplistic in that it assumes that each compound's reaction rate can be altered by the same factor, it does reveal that the two most important reaction pathways in catalytic cracking are formation of the initial carbenium ion on paraffins and aromatization. This conclusion is generally consistent with previous studies of octane number enhancement. Existing strategies (Cotterman and Plumlee, 1989) emphasize, in decreasing order of importance, aroma-

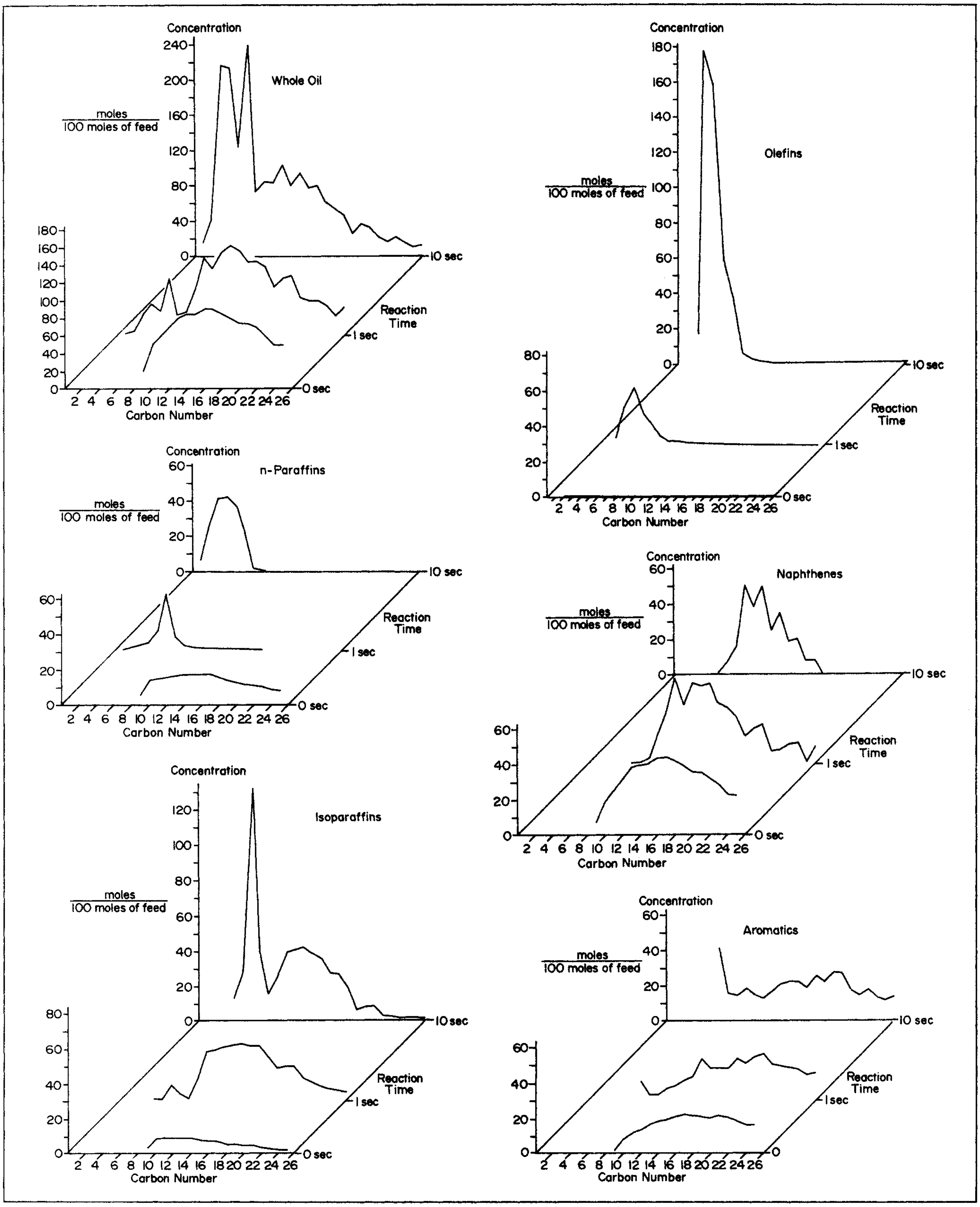

Figure 1. Evolution of carbon number distributions in the base case as a function of time.

Details of the kinetic modeling methodology are given by Liguras and Allen (1989a,b).

Table 1. Sensitivity of Gasoline Yield and Octane Number to Kinetic Model Parameters

Case Study	Gasoline Yield (wt %)	% Change from Base Case	RON	% Change from Base Case	MON	% Change from Base Case	Gasoline Yield × MON	% Change from Base Case
Base Case								
Reaction time, 1 s	24.04	—	66.60	—	65.62	—	1,578	—
Reaction time, 10 s	39.75	—	75.02	—	72.43	—	2,879	—
Primary Paraffin Cracking Rate Increased by 50%								
Reaction time, 1 s	26.65	+10.9	65.76	−1.3	64.70	−1.4	1,724	+9.3
Reaction time, 10 s	42.07	+5.8	74.98	−0.1	72.24	−0.3	3,039	+5.5
Primary Paraffin Cracking Rate Decreased by 50%								
Reaction time, 1 s	19.35	−19.5	66.90	+0.5	66.48	+1.3	1,286	−18.5
Reaction time, 10 s	33.56	−15.6	76.34	+1.7	73.51	+1.5	2,467	−14.3
Secondary Paraffin Cracking Rate Increased by 50%								
Reaction time, 1 s	24.08	+0.2	67.04	+0.7	65.86	+0.4	1,586	+0.5
Reaction time, 10 s	39.78	+0.1	75.04	0.0	72.18	−0.4	2,871	−0.3
Secondary Paraffin Cracking Rate Decreased by 50%								
Reaction time, 1 s	23.87	−0.7	66.05	−0.8	65.38	−0.4	1,561	−1.1
Reaction time, 10 s	40.37	+1.5	74.86	−0.2	72.29	−0.2	2,918	+1.3
Olefin Cracking Rate Increased by 50%								
Reaction time, 1 s	23.99	−0.2	66.27	−0.5	65.43	−0.3	1,569	−0.6
Reaction time, 10 s	39.56	−0.5	74.54	−0.6	72.23	−0.3	2,857	−0.8
Olefin Cracking Rate Decreased by 50%								
Reaction time, 1 s	24.11	+0.3	67.09	+0.7	65.92	+0.5	1,589	+0.7
Reaction time, 10 s	39.85	+0.3	76.18	+1.5	72.91	+0.7	2,905	+0.9
Aromatization Rate Increased by 50%								
Reaction time, 1 s	23.14	−3.7	67.12	+0.8	66.05	+0.7	1,528	−3.2
Reaction time, 10 s	37.63	−5.3	76.62	+2.1	73.51	+1.5	2,766	−3.9
Aromatization Rate Decreased by 50%								
Reaction time, 1 s	24.69	+2.7	65.97	−0.9	65.12	−0.8	1,608	+1.9
Reaction time, 10 s	41.29	+3.9	73.74	−1.7	71.49	−1.3	2,952	+2.5
Olefin Isomerization Rate Increased by 50%								
Reaction time, 1 s	24.07	+0.1	67.68	+1.0	66.78	+1.8	1,607	+1.8
Reaction time, 10 s	39.77	+0.1	75.74	+1.0	73.09	+0.9	2,906	+0.9

tization, increased branching of isoparaffins, conversion of *n*-paraffins to olefins and conversion of *n*-paraffins to isoparaffins. A major limitation of previous studies on octane number enhancement has been the absence of kinetic pathway constraints. For example, if the chosen strategy is to convert *n*-paraffins to isoparaffins, we should know that isomerization rates for olefins can be orders of magnitude higher than those for paraffins (Liguras and Allen, 1989a). Thus, the most effective reaction pathway for converting *n*-paraffins to isoparaffins may be through an olefin intermediate. Thus, the strategies of converting *n*-paraffins to isoparaffins and *n*-paraffins to olefins may be inseparable. The results given in Table 1 focus on octane number enhancement strategies that are consistent with reaction pathway constraints.

Table 2. Sensitivity of Gasoline Yield and Octane Number to Feedstock Structure

Case Study	Gasoline Yield (wt %)	% Change from Base Case	RON	% Change from Base Case	MON	% Change from Base Case	Gasoline Yield × MON	% Change from Base Case
*Feedstock Made More Paraffinic**								
Reaction time, 1 s	22.16	−7.8	66.31	−0.4	65.13	−0.7	1,443	−8.6
Reaction time, 10 s	38.22	−3.8	76.67	+1.9	72.94	+0.7	2,788	−3.2
*Feedstock Made More Aromatic**								
Reaction time, 1 s	23.11	−3.9	68.24	+2.5	66.83	+1.8	1,544	−2.2
Reaction time, 10 s	38.78	−2.4	76.42	+1.9	73.38	+1.3	2,845	−1.2

*See text for description.

Table 3. Sensitivity of Gasoline Yield and Octane Number to Elimination of Olefin Isomerization Pathways

Case Study	Gasoline Yield (wt %)	% Change from Base Case	RON	% Change from Base Case	MON	% Change from Base Case	Gasoline Yield × MON	% Change from Base Case
Olefin Isomerization Rate Decreased by a Factor of 10^6								
Reaction time, 1 s	24.07	+0.1	50.18	−24.7	47.53	−27.6	1,144	−27.5
Reaction time, 10 s	39.77	+0.1	61.25	−18.4	58.12	−14.3	2,311	−19.7
Olefin Isomerization Rate Decreased by a Factor of 5×10^{-3}								
Reaction time, 1 s	24.07	+0.1	50.62	−24.0	48.00	−26.9	1,155	−26.8
Reaction time, 10 s	39.77	+0.1	65.29	−13.0	62.52	−13.7	2,486	−13.7

The results given in Table 1 are for a particular feedstock, described by Liguras and Allen (1989b). These results will of course depend on the nature of the feedstock, since primary paraffin cracking clearly cannot be of great importance in a feedstock with no paraffins. To examine the importance of feedstock variations relative to rate constant variations, several sensitivity calculations were performed. The results of these calculations are reported in Table 2. In one study, 10% of the cyclic fraction (roughly 1% of the oil) in the feedstock was changed to aromatics of the same carbon number. This had a minor overall effect when compared to changes in reaction rate constant. In a second set of calculations, 30% of the cyclic fraction (roughly 3% of the oil) in the feedstock was changed to *n*-paraffins and isoparaffins of the same carbon number (2 moles of *n*-paraffin per mole of isoparaffin). This change in feedstock structure had a major impact on gasoline yield and a moderate impact on octane number.

The sensitivity results in Tables 1 and 2 assess the impact of incremental changes in rate constants and feedstock composition on model predictions. Additional sensitivity calculations were performed to address the issue of eliminating reaction pathways from the model. Reaction pathways could be eliminated for the sake of model simplification or because of the shape selectivity of nonamorphous catalysts (e.g., dehydrocyclization reactions might be eliminated for paraffins cracking in a ZSM-5 zeolite). Table 3 shows the effect of greatly reducing or eliminating olefin isomerization reactions. Gasoline yield is not impacted; however, octane number yields are dramatically reduced. In general it was found that none of the reaction pathways in Table 1 could be eliminated from the model without sacrificing the quality of the model's predictions.

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