

# Molecule-Based Modeling of Gasoil Fluid Catalytic Cracking

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## INTRODUCTION

Fluid Catalytic Cracking (FCC) is a major refinery process designed to upgrade heavy and less valuable petroleum products to gasoline and lighter products. The feedstock for the FCC process ranges from light gas oils to heavy hydro-treated resids. The complexity of the feedstock, and the associated analytical chemistry and computational obstacles, helped shape early FCC modeling approaches (2,3,7). The traditional need for easily deployed reaction models led to the formulation of simple, lumped kinetic models. Lumped models often fail to capture the complex FCC chemistry and as a result are specific to the feedstock, the catalyst used and the operating conditions. Additionally, lumped models do not give the detailed product distribution required for process design and optimization.

The new paradigm is to track each molecule in the feed and product through the process and to move towards models having fundamental kinetic information. This has led to the modeling of the chemistry at the mechanistic level (5,6). These mechanistic models have a large number of gaseous and surface species and, hence, are very CPU intensive. Thus, on the one hand, the need for a detailed molecular representation and fundamental kinetic information make the use of mechanistic models attractive, but, on the other hand, the large solution time renders them of limited use in practice. This motivates the development of pathways-level models. Pathways-level models are not as large and complex as the mechanistic models because of the exclusion of reactive intermediaries, e.g., surface species. They also offer the advantage of being solved in a reasonable amount of time. They offer the opportunity to incorporate detailed kinetic information by the inclusion of all important observable molecules explicitly, and hence have the predictive capability lacking in the lumped models.

Developing such molecularly explicit models for gasoil fluid catalytic cracking is now possible because of two enabling advances. First, recent developments in analytical chemistry now allow a molecularly explicit stochastic description of gasoils. Second, the explosion in computational power makes possible the necessary bookkeeping to generate and solve reaction networks with a large number ( $O(10^3)$ ) of molecules. The aim of this work is to develop an automated capability for building pathways-level FCC models for heavy hydrocarbons (e.g. gasoils). In the following sections, we will briefly discuss the methodology used for determining a molecular description of the feedstock and then also outline the strategy used for computer-generation of gasoil FCC pathways-level kinetic model.

## FEEDSTOCK CHARACTERIZATION

The ability of a reaction model to describe the product distribution depends to a large extent on the initial conditions i.e., the structure and the mole fractions of the molecules in the feedstock. Such detailed characterization for the heavier feedstock, such as gasoils, is seldom available. Even modern analytical techniques reveal only structural attributes (i.e. the number of aromatic rings, number of saturated rings, number of sidechains, etc.) rather than the detailed individual molecular structures. The first challenge, then, is to determine a set of molecules and associated mole fractions characteristic of the feed from routinely available analytical data, such as true boiling point distribution, average molecular weight, elemental analysis, NMR data and GC/MS lumps. This can be done using the *MoleGen* technique (4).

In this technique, molecules are represented in terms of a collection of molecular attribute building blocks ( e.g. number of aromatic rings, number of naphthenic rings, number and length of sidechains, etc.). Each attribute is represented by a probability density function. Monte Carlo sampling of the set of probability density functions provides a large ensemble of molecules ( $O(10^3)$ ). The properties of this ensemble of molecules are compared to experimentally obtained analytical data to obtain an optimal set of probability density functions. These optimized probability density functions contain the statistical description of the feedstock and can be easily transformed into a set of molecular structures and their associated mole fractions.

## MODEL BUILDING

Pathways models for complex feedstocks, such as gasoils, can have a large number of molecules and their reactions. It can be quite tedious and time-consuming to build such models by hand. This motivates the automation of the model building process.

To automate the process of reaction network building use is made of graph theoretic concepts. In this approach, a molecule is represented by a graph, the atoms being the nodes of the graph and the bonds being the edges of the graph. For all the reactions in FCC, the connectivities of only a few of the atoms in the involved molecules change. This means that a reaction can be represented by the change in the connectivity of only a few anodes in the graph. The connectivity matrices of the reactants are combined into an augmented reactant matrix, which, after permutation gives the reduced matrix for the reactants, containing the connectivities of only those atoms whose connectivity changes in the reaction process. The bond breaking and forming (i.e., the reaction) is then carried out by simple matrix addition operations (1).

The chemistry is represented through the implementation of reaction rules. These rules rely on theoretical and experience-based kinetic approximations and are useful tools in keeping the size of the model realistic without significantly effecting the product distribution. The reaction network is then converted to a set of differential equations using the *OdeGen* parsing code (1). Conceptually, the resulting mathematical model can then be solved with appropriate initial conditions and rate constants. However, during the developmental stage, the rate constants for most of the reactions are usually not known *a priori* and the model has to be solved within an optimization framework to determine the rate constants.

This requires that the number of rate parameters must be kept to a reasonable number to obtain true rate constant information from optimization to the experimental data. Even with the use of reaction rules for the complex FCC chemistry the detailed reaction model can have a large number of reactions and their associated rate constants ( $O(10^3)$ ). Clearly, some organizational or "lumping" scheme that does not sacrifice the basic chemistry is in order. To this end, it is useful to realize that much of the complexity is statistical or combinatorial, and that the large number of reactions and rate parameters in the pathways-level model can be handled by lumping the reactions involving similar mechanistic steps into one reaction family. The kinetics of all the reactions within the same reaction family are described by a common set of parameters. Differences in the reactivity within the same reaction family can be traced to differences in the heat of the reaction.

## RESULTS AND MODEL DIAGNOSTICS

These ideas of feedstock characterization and automated model building were applied to gasoil FCC reaction modeling. The analytical data available for gasoil included boiling point distribution, average molecular weight, Clay Gel analysis, MS lumps and average parameters from NMR analysis. These analytical data were used to determine a stochastic molecular representation of the feed using the *MolGen* technique. The feed was described in terms of 222 representative molecules and their mole fractions.

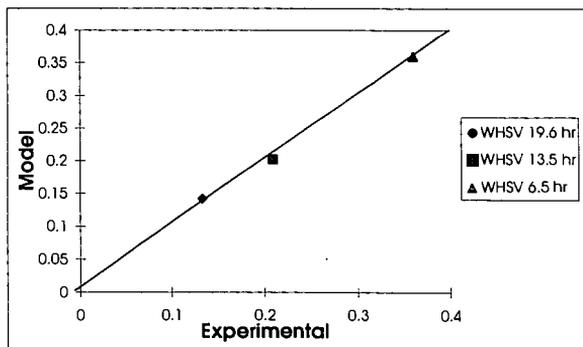
The feed was then grouped into a few compound classes ( paraffins, iso-paraffins, naphthenes and aromatics), which, in turn, were allowed to react through a limited

number of reaction families (cracking, isomerization, dehydrogenation, hydrogenation, and aromatization). This allowed the division of all the reactions into a small number of reaction families with associated rate parameters. Table 1 shows the model diagnostics for the final model. The use of reaction family concept allowed the description of all the rate constants for 3293 reactions in terms of about 30 rate parameters.

|                                  |            |
|----------------------------------|------------|
| Feed Molecules                   | 222        |
| Total number of molecules        | 823        |
| Paraffin Cracking Reactions      | 574        |
| Paraffin Isomerization Reactions | 206        |
| Olefin Cracking Reactions        | 131        |
| Naphthenic Cracking Reactions    | 138        |
| Aromatic Cracking Reactions      | 435        |
| Hydrogenation Reactions          | 274        |
| Dehydrogenation Reactions        | 221        |
| Model Generation Time            | 433s       |
| Model Solution Time              | < 1 minute |

**Table 1. Gasoil Fluid Catalytic Cracking Model Diagnostics**

To develop the optimal reaction network and to determine the rate constants the model predictions were constrained to match the pure components as well as gasoil experimental data. As an example of the quality of fit between model and experimental values Figure 1 shows the results for n-heptane cracking.



**Figure 1a. Parity Plot for Heptane Conversion at different weight hourly space velocity (WHSV).**

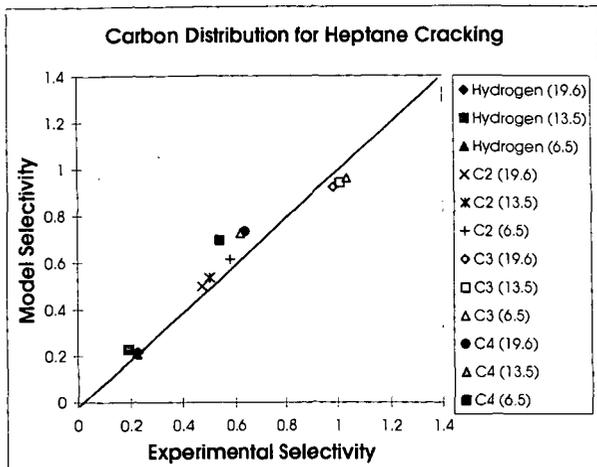


Figure 1b. Parity Plot of Selectivity by Carbon number for n-heptane cracking. Values in brackets are the WHSV.

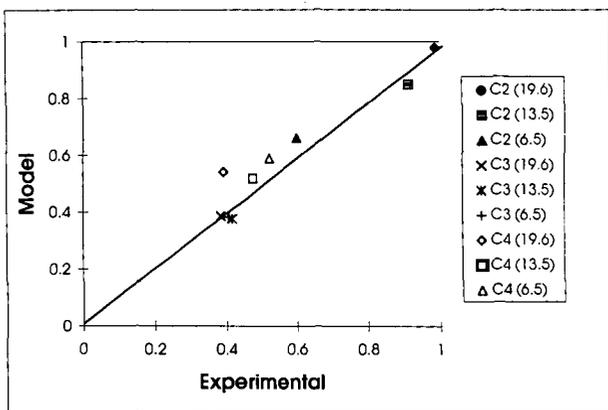


Figure 1c. Parity Plot of Paraffin / Olefin ratio for n-heptane cracking. Values in brackets are the WHSV.

### CONCLUSIONS :

1. Graph theory was successfully used to generate a molecularly explicit gas oil FCC model containing 823 species and 3293 reactions.
2. The parity of the predicted results was reasonably good with the experiments. This suggests that the stochastic approach for generation of the feedstock and the reaction family concept for expressing the rate constants are very good tools for predicting the reactivity of a complex mixture.
3. This approach to automated pathways-level model building can be easily extended to other feedstocks and catalyst systems in order to obtain kinetics information.

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