

## Toward a New Generation of Hydrocarbon Reaction Models

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### ABSTRACT

Significant advances in several independent areas are enabling the development of new modeling tools well beyond those capable a short time ago. These significant advances include improvements in experimental kinetics, a priori prediction of molecular energetics and rates, instrumental approaches to the composition of complex mixtures, computational conversion of compositional information to molecular structure determination, and automated generation of reaction networks and modeling software. In this presentation, we will examine the state of development of these tools and their incorporation into online molecular optimization of conversion processes.

### INTRODUCTION

The current business environment in the chemical process industry has resulted in an emphasis on improving performance of existing operations to maximize profitability of existing capital equipment. One strategy to achieve this objective is an increase in process monitoring, automation, control and optimization. For process equipment involved in chemical conversion, an essential step in reaching the on-line optimization objective is the creation of detailed reaction models capable of simulating a multitude of simultaneous reactions.

Much work has been done in moving chemical process models from the early linear programming correlative tools to a new generation of models based on actual reaction kinetics. Workers at Mobil introduced models based on molecular structural characteristics of the feed (Quann and Jaffe). This pioneering work demonstrated the practicality of construction of kinetic models for even the most complex feedstocks and processes.

Recent advances in many fields are enabling the construction of ever more detailed chemical reaction models. Although it is still not possible to identify and provide detailed kinetics of every reaction in a mixture as complex as a petroleum vacuum gas oil, significant improvements are now possible which will create a new generation of reaction models capable of controlling processes at the molecular level. This paper will discuss these advances and how they may be incorporated to improve the existing generation of modeling tools.

### ADVANCES IN RELATED FIELDS

#### I. Analytical approaches - identifying the molecules

For years, gas chromatography has been the workhorse of detailed analysis. However, the use of gas chromatography for mixtures boiling above the light distillates range is greatly limited by the presence of a myriad of possible components at similar or equal retention times. Methods such as GCMS and separation-analysis approaches such as employed by Boduzsynski enable identification of some of the overlapping areas, but are too tedious or expensive to apply to online applications.

The use of simulated distillation methods and their extension to high boiling ranges, while not providing molecular detail, significantly expanded the range of chromatographic approaches. Petroleum-derived feeds boiling up to 1200 F and higher could be characterized in terms of the mass of materials boiling in very narrow boiling range fractions, with high precision. Workers began to develop additional methods to allow additional characterization of these narrow fractions, for instance by using chemiluminescence detectors (Chawla). Recent work employing Atomic Emissions Detection has made elemental determination practical for many elements including of carbon, hydrogen, nitrogen, sulfur, nickel, vanadium, and iron (Quimby et al). Use of additional detectors permit other molecular characteristics to be determined for the

narrow fractions such as mass distribution (GC-FIMS, Malhotra et al), and molecular type (using fragmentation MS detection). While still short of the objective of individual component determination, the capability exists for providing far greater detail than was previously available via methods that provided similar information across far wider boiling ranges.

The detailed information on composition of the narrow fractions must now be converted to an accurate quantitative representation of the distribution of molecular species in the sample. The work of Wilcox and Faulon have shown that this may be accomplished through optimization of selection of molecules from a library of possible species representing the possible components in a given boiling range. The development of the Signature algorithm by Faulon permits automated construction of molecular structures from analysis information. Application of Signature with expert knowledge of the molecular types present in petroleum fractions enables the construction of a library of possible molecular species for each boiling range fraction. The process of providing detailed molecular type distributions for a given feed then becomes an optimization problem of choosing the best possible match for the characteristics of each narrow fraction with the available library species. The analytical information is converted to a set of molecules representing in the greatest detail available the distribution of molecular types within the feed. Figure 1 provides an example application of this approach for the prediction of the molecular species in a light gas oil fraction. A high level of accuracy is obtained in comparison to detailed GCMS identification. The remaining degeneracy is between species with similar reaction performance (e.g. paraffin isomers).

## II. Kinetics Advances – how do the molecules react?

With information on the distribution of molecular types in the feed, it is necessary to have kinetic information on their behavior in the mixture. Use of model compound reactions continues to be a key in defining the reaction pathways and rules that define the kinetics of specific reaction types (for example the work of Mochida and co-workers on desulfurization, Korre et al in aromatics hydrogenation, Souverijns et al in cycloparaffins isomerization). Additional information is required of the reactions of these species in complex mixtures as 'matrix effects' can cause variations in reactivity beyond those observed in pure feed studies. The analytical methods described above permit the examination of reactivities of individual species within complex mixtures. Recent revealing work by Shin and Mochida has shown the importance of these effects in HDN and HDS reactions.

## III. Computation and Modeling advances – building the reaction models.

A central problem in construction of complex kinetic models is known as the 'explosion of species', that is the number of possible molecular species increases dramatically with carbon number. This fundamental problem makes it difficult to represent the possible reactions completely, and renders measurement of the detailed kinetics of each species impossible. One needs a way to reduce the number of species considered and to provide rate information and reaction network information to describe the process performance of the complex mixture. Research developments in computational chemistry and its use to model kinetics are enabling significant advances in this arena.

Approaches to limit the number of species utilize the molecular characteristics of the molecules to form groups that are presumed to behave similarly, a technique known as 'lumping'. Early lumped models grouped all molecules in a single boiling range as equivalent. The advances of Quann et al have moved this approach to the molecular characteristics level. The ultimate lumped model would group molecules on a reaction kinetic behavior basis. This possibility is enhanced by the presence of the advanced analytical information described above.

Another 'explosion' problem results due to the expansion in the possible reactions of species as carbon number increases. Early kinetic models used hand-written reaction networks to describe the essential reactions which connect feed and product species. Advances by Michael Klein and coworkers has created the prospect of computer-generated reaction networks, employing chemically specific reaction rules to limit the explosion of reaction types. Recently, Hou et al have shown that these approaches can be successful in representing the reaction behavior of catalytic hydroprocessing, while producing a model small enough to be solved on a personal-computer platform in solve times of under one minute. The Klein et al approach also employs computational approaches to write the necessary set of differential equations to integrate them to solve

the reaction model and predict the products from a given set of feed molecules and conditions.

Klein has also demonstrated approaches for lumping the reaction behavior of molecular species according to kinetic behavior. The work of Korre et al demonstrated the use of the relationship between linear free energy of formation and reaction rate for similar species to permit the calculation of the kinetics of many similar molecules without measuring the kinetics of each member. This approach has been demonstrated to be very effective even for complex reactions of molecular groups such as polynuclear aromatic hydrocarbons.

Advances in computational chemistry allow rate predictions for groups of molecules from first principles calculations. A first level approach allows computation of the free energies of reactants and intermediates to construct plausible reaction pathways and form the abscissa for the Linear Free Energy-Rate relationships developed by Klein. Perry and Goddard demonstrated the effectiveness of this approach even for catalytic systems by showing that the kinetic performance of catalytic reforming could be predicted using gas-phase molecular energetics with a very limited set of parameters to represent the interactions of various molecular types with the surface catalytic functions. More recent work involves the development of high-level group additivity relationships, based on detailed quantum mechanical calculations, to permit the rapid determination of the energetics of millions of molecules in a mixture. This information also facilitates the grouping of these molecules into species that have similar bonding energetics – a key to lumping based on reaction performance.

### CONNECTING THE PIECES

The challenge for the modeler is to utilize the advances collectively to produce more accurate predictive tools based upon detailed reaction chemistry. Figure 2 provides a schematic representation of this approach. Analytical information is passed to the structure generator module providing detailed information on the composition of the feed (or products). The molecular information is passed to model, constructed on the basis of the process information using the automated reaction network generator, reaction-property information, and a model solver. QM calculations provide a basis for reaction rate information for similar molecules. The output molecules are then utilized with additional Quantitative Structure Property Relationship information (made possible by employing the detailed analysis approach on a broad range of products).

An additional critical step involves the use of database technology to sample the performance of pilot plant and commercial operations and determine the relationship between feed composition, controllable process parameters, and product composition. These commercial data sources are essential in validating and adjusting the model performance in a feedback loop that includes the kinetic model reconstruction (adjustments in reaction rules, molecular family kinetics, etc).

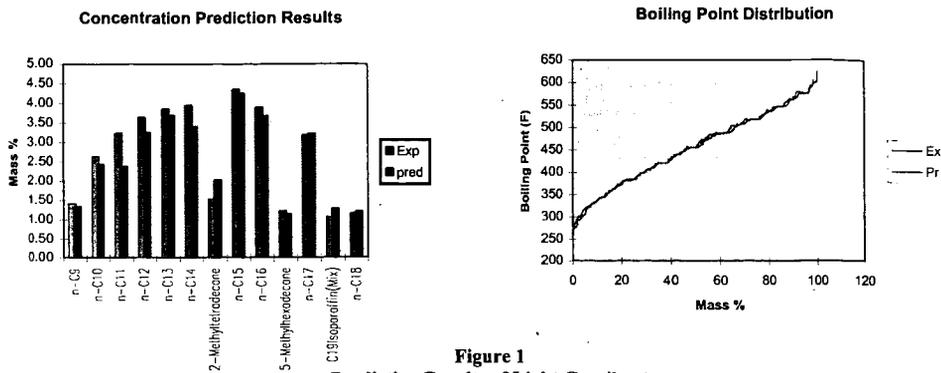
The ultimate use of these kinetic models comes in integration with the process itself. The analysis approaches described above are specifically developed for their capability to be utilized on-line. Computational network generation allows adjustment of the model itself as part of the validation process. Combination of the analysis information, 'living' kinetic models, and advanced monitoring and control information will permit a level of sophistication of process tuning we term 'molecular optimization'.

### ACKNOWLEDGEMENTS

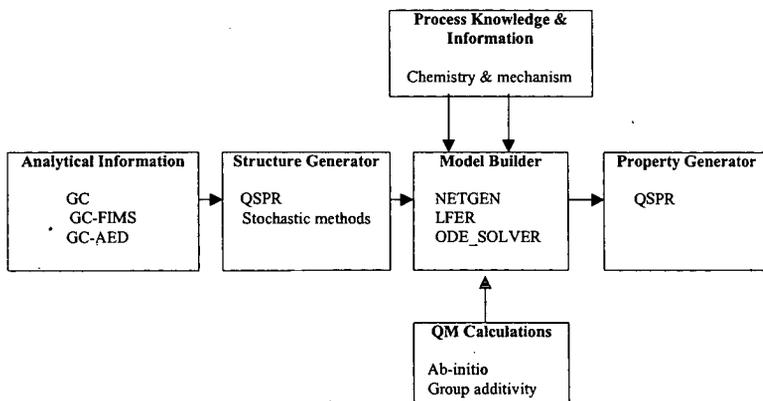
This work would not be possible without the ingenuity of leading research groups from around the world. Collaborations of this type are essential to create the prospects of significant advances in kinetic models – it is unlikely that any single research organization would have the combined capability to provide these advances. We are greatly indebted to and grateful for the work of Professor William A. Goddard of California Institute of Technology, Professor Michael T. Klein of Rutgers University, Professor Isao Mochida of Kyushu University, Dr. D. Duayne Whitehurst (consultant), Dr. Jason K. Perry of First Principles Inc., Dr. Jean Loup Faulon and R. Wilcox of Sandia National Laboratory, and Chevron colleagues Dr. David A. Grudowski, Dr. Ram Ramamoorthy, and Dr. Michael A. Shippey.

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**Figure 1**  
Prediction Results of Light Gasoil cut



**Figure 2**  
New Generation Models - Connecting the Pieces