

Visualization of Complex Hydrocarbon Reaction Systems

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Abstract

Many hydrocarbon reactions of interest involve either poorly characterized reactants and products and/or large numbers of simultaneous reactions. An important step in understanding the behavior of such systems is to develop quantitative pictures of the feeds and products and the transformations which connect them. The processes for constructing these reaction visualizations is illustrated by examining the construction of a molecular model for coal liquefaction and subsequent conversion to distillate products, and the construction of a video simulation of catalytic petroleum naphtha reforming. New techniques which are permitting advances in these visualizations are discussed.

Introduction

When studying feedstocks such as coal or reactions such as those used in converting petroleum to commercial products one must confront an overabundance of information concerning chemical composition and molecular transformations. The essential features which govern the behavior of a material or process may be lost in the detail. In such cases, the production of a simple picture, or visualization can be important.

Visualizations can have many values including:

- identifying major deficiencies in knowledge**
- highlighting the most important aspects of the structure or reaction system** which control reaction behavior, and those which are of relatively minor importance
- setting the stage for more quantitative tools** such as predictive kinetic models used in process optimization and control
- training**
- as a basis of comparison** between the composition of similar materials or the reactions of similar feedstocks
- to stimulate discussion** creating focus on controversial aspects of the knowledge.

Over the past 15 years, we have been utilizing visualizations to examine several complex reactions systems. In this paper, we provide a review of the process of creating quantitative reaction visualizations and review their use. We will use as examples the construction of models of coal and coal liquefaction and in a video model of catalytic naphtha reforming.

Making a Quantitative Visual Model - Model of Coal and Coal Liquefaction

The first step in assembling a visual model is to collect available information on composition and reactivity. In the case of coal structure, such information includes the proper distribution of elements, element groups, aliphatic and aromatic carbon species, functional groups (oxygen, sulfur and nitrogen), and reactive crosslinks. Knowledge of the reaction chemistry is critical in providing the glue which binds the structures together in a manner which may be used to simulate reaction behavior.

Quantitative reaction models require information on product yields and quality at many stages of reaction, so that the progressive steps in conversion can be illustrated. By assembling composition information on the feedstock and each of the intermediate products, one constructs structures which are consistent with this information at each severity level. The product distribution at the most mild reaction conditions may be used in conjunction with knowledge of the important reaction processes to feedback information to the necessary structures which must be present in the feed to explain the appearance of the products. In the case of mild coal liquefaction, the processes of aliphatic and etheric crosslink cleavage between aromatic centers, the hydrogenation/dehydrogenation and associated hydrogen transfer reactions, and functional group distribution changes (particularly disappearance of reactive oxygen functional groups) have long be attributed to as the primary important reaction paths. A likely representation assumes that the original coal structure contains components similar to those in the products of

mild liquefaction, modified by hydrogen transfer and defunctionalization, and joined by certain reactive crosslinks. In a similar manner, the products and reactions from somewhat more severe processing may be used to imply the structures of the less severe products forming an iterative chain connecting the products of most severe treatment with the structure of the original feed.

To maintain a quantitative picture, the molar quantities of elements, functional groups, aromatics and aliphatics and the like are continuously accounted for throughout the transformation. Choosing the molecular size of the model is also critical - for coal the size of 10000 daltons proved a good compromise. This provided us with a model which was both large enough to represent the variations in product composition which are observed and to include sufficient quantities of crosslinks and functional groups to characterize the feed properly. Larger models required a far more complex task of construction and resulted in a loss of detail in the overall mass. Smaller models would not permit incorporation of product distribution detail and reactivity which are important in liquefaction behavior.

Figures 1 and 2 show models of a subbituminous and a bituminous coal produced in the manner described above. The models are quantitative in terms of the elemental distributions, aromatic and aliphatic components and functional groups as collected from composition and reaction data. The visualizations allow for a quick comparison between the two coals highlighting similarities and differences. Both illustrate a relatively low degree of aromatics condensation (in comparison to heavy crude oils, for instance) and although differences in the distribution of aromatics exist between the two, these features are relatively minor. The role of oxygen in the chemistry of both is apparent: oxygen is prevalent throughout the structure as crosslinks and ring substituents and multiple opportunities for hydrogen bond formation are seen, especially in the bituminous coal. Clearly any consideration of the reactions of these coals without including oxygen would be insufficient. At the time that these models were constructed, very little information was available on the detailed distribution of much of the oxygen, particularly the ether oxygen. Thus the percentage of ether oxygen present in important structural crosslinks, and the nature of non-crosslink ethers is seen as an important uncertainty in coal structure. For both of these coals, sulfur and nitrogen are seen to play relatively unimportant roles (with only a handful of each element in the 10000 dalton model), at least so far as their importance in the overall structure is concerned.

These models are presented in planar form with the intention of allowing for better visualization of the chemical connectivity. In reality, coal is a three-dimensional structure. Recent advances have allowed construction of more sophisticated models utilizing molecular dynamics to provide energy minimized three dimensional structures. Such models are far superior in representing the constraints imposed by spatial and energetic considerations and provide better tools for examination of three dimensional properties such as density and porosity.

Figures 3 and 4 show the progressive conversion of the bituminous coal via donor solvent liquefaction. The reactive crosslinks are disrupted and products of various functionalities, aromaticities and molecular sizes are generated. With more severe processing, both forward and reverse reactions occur leading to both smaller and larger products. Even at relatively severe conditions, these liquefaction products are substantial in molecular size and contain a significant amounts of heteroatom species (particularly oxygen). Figure 5 shows the products from two-stage liquefaction employing a thermal donor solvent stage and a catalytic hydrotreating stage in close sequence. The comparison of figures 4 and 5 provides a rapid visual sense of the advantages of two-stage technology. In contrast to the solvent products, the two-stage products are of far reduced molecular size and dramatically reduced heteroatom content.

Construction of a Model of Catalytic Naphtha Reforming

The process of catalytic naphtha reforming is an essential feature of the production of high quality gasoline components from crude oil. In reforming, a feedstock consisting entirely of hydrocarbons (no heteroatoms) of carbon numbers typically between C6 and C12 are processed over a catalyst (platinum-rhenium on alumina, for instance) to convert species having a low gasoline octane rating to species with improved octane values. The principal desired reactions involve the dehydrogenation of naphthenes and the dehydrocyclization of paraffins to produce aromatic species. Side reactions of cracking, hydrocracking, and isomerization occur with the desired reactions.

Modeling reforming reactions is complex because many species are reacting simultaneously via many potential reaction paths. Unlike liquefaction, the individual species in reforming can be largely identified using relatively straightforward techniques. The difficulty lies in understanding the balance of reactions occurring for each species, the relative contributions of the reactions for the different feed molecules, and in understanding how to control the reaction to provide the highest yields of desired products.

The process of producing a visualization of the reforming reactions involves many of the steps outlined in construction of the coal models: Namely, collecting detailed information on product composition at various levels of reaction severity and iterating back to the prior composition and reaction changes via information on the reaction matrix allow the transformation model to be constructed. Figures 6 and 7 show a quantitative representation of the feed and products from the reforming of an Arabian naphtha. Even for the relatively mild reforming to a product octane of 81, there has been considerable production of aromatic species and conversion of most of the naphthenes. Heavy paraffins have also been converted, substantial hydrogen has been produced and some of the product has been converted to undesired light gases. Relatively few reactions are needed to explain the product distribution shifts, beyond the dominant roles of dehydrogenation, dehydrocyclization and cracking.

For the reforming visualization, we were interested in producing a tool to enhance the training of new operators and engineers involved in commercial reformer operation. We extended our visualization by creating individual 'snapshots' of the composition at various ranges of severity, taking the reactions one group at a time. These snapshots were then assembled using computer drawings and video tape and assembled into a video depicting the entire sequence of reactions. We have found this video visualization can provide an excellent overall feel for the process of reforming in a very short period of time.

Visualizing - the Future.

A number of emerging tools are permitting visualizations to be created with greater ease, high detail, greater accuracy, and with better ability to serve the valuable roles of visualizations outlined above. These tools include:

- Computational tools for representing molecular connectivity permitting construction of models on a computer platform.
- Use of molecular dynamics software to produce energy-minimized three-dimensional structures.
- Use of quantum mechanical simulations to predict reaction pathways from molecular energetics, reducing the need for experimental determinations of reaction paths and rates.
- Monte-Carlo approaches to assembling possible structures from component pieces and for displaying a full range of potential structures from multiple possibilities.
- Advances in compositional capability permitting models of greater molecular detail.

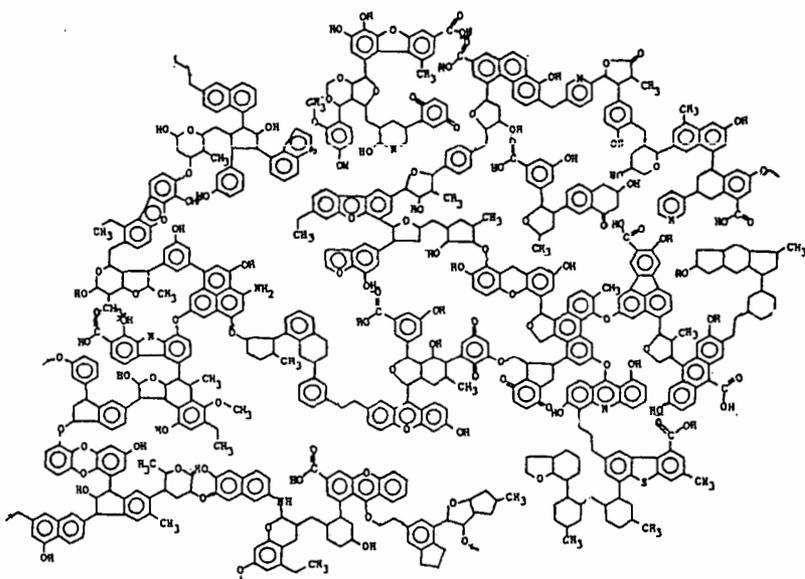


Figure 1. Model of Subbituminous Coal Structure

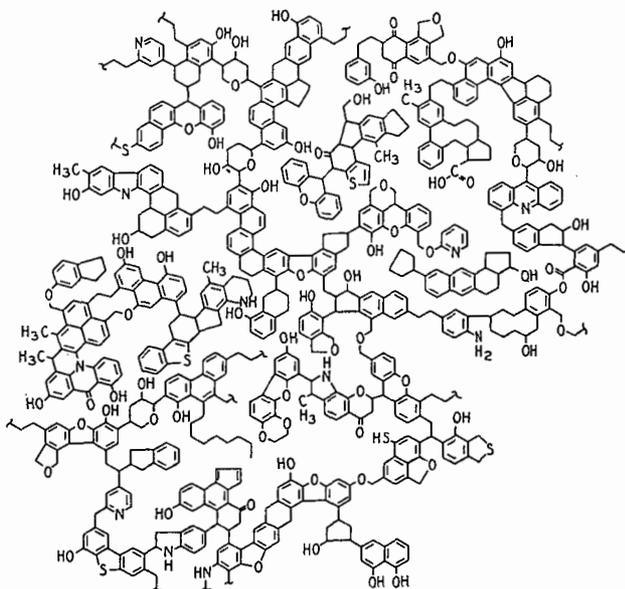


Figure 2. Model of Bituminous Coal Structure.

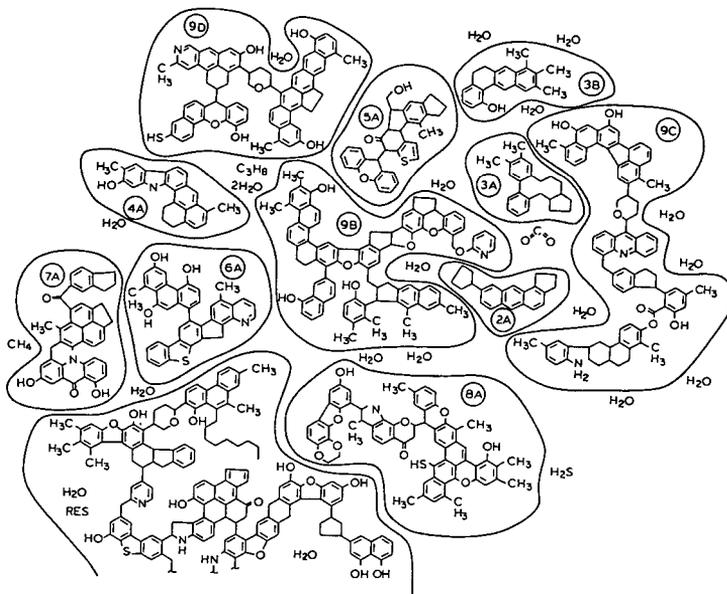


Figure 3. Model of Products from Mild Donor Solvent Liquefaction of Bituminous Coal

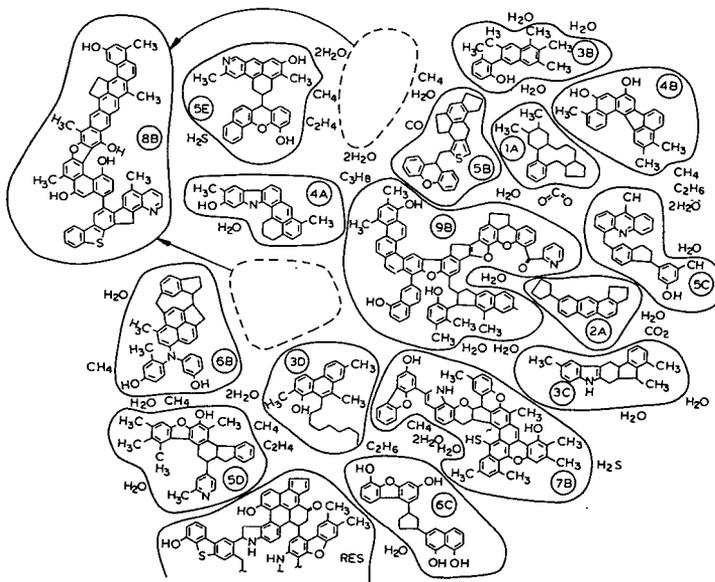


Figure 4. Model of Products from Severe Donor Solvent Liquefaction of Bituminous Coal

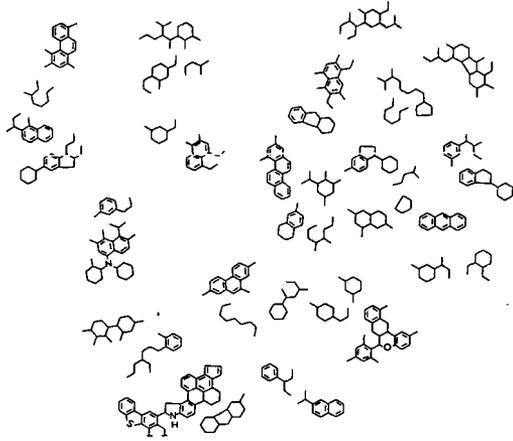
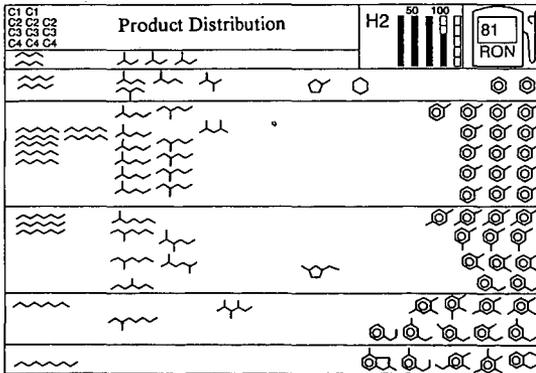
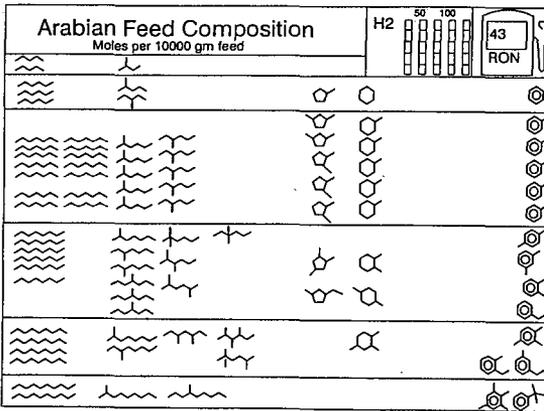


Figure 5. Model of Products from Two-Stage Liquefaction of Bituminous Coal



Figures 6 and 7. Feed and Products from Mild Reforming of an Arabian Naphtha.