Modeling the chemistry in combustion processes of large hydrocarbons and biofuels

In my academic journey from computational chemistry in my graduate studies to computer aided organic synthesis to quality control studies in industrial processes to the study of the chemical processes of combustion of large hydrocarbon and biofuels, I have accumulated a multidisciplinary toolset of mathematical and artificial intelligence techniques and used them to solve the modeling problem at hand. In this journey, these techniques have been encapsulated in a hierarchy of software technical tools: ANALYSIS++, for the use of artificial intelligence, machine learning and statistics, in manipulating data, REACTION, for the automatic generation of hundreds to thousands of reactions in a combustion process and JTHERGAS2, for the fast estimation of thermodynamic constants for use in combustion.

Both REACTION and JTHERGAS have large databases of chemical knowledge as their base. In this talk I will discuss this journey with emphasis on my current work in combustion. One purpose of the talk is to provide a foundation for which discussion can be made for interdepartmental cooperation.

An important determinant in increasing the efficiency and reducing the pollutants in combustion processes, whether within the fields of transport or energy production, is to understand the complex chemical processes that occur from the initial ignition of the fuel to the final products. The combustion process is highly dependent on not only the conditions of the combustion process itself, but also on the structural nature of the fuel molecule(s). With the increasing tendency to reduce the dependence on hydrocarbon fossil fuels by using 'alternative' fuels, such as 'biofuels', comes and increasing complexity of the combustion modeling process. A major goal of what my research entails is the efficient setting up of combustion models to be able to take into account the variety of chemical structures, both in the fuels and in the intermediates, found in the combustion process.

Detailed combustion mechanisms map the chemical evolution of the individual molecules, including radicals, through a model consisting of a set of temperature dependent reactions. These models can range from a single global reaction to a complex set of interacting reactions consisting of tens to hundreds to thousands of molecules and reactions. The number of reactions to be used within the model is due to limitation of computational power of computers. To model the combustion process within a piston engine most of the computational effort needs to be allocated to the complex physical processes in CFD (computational fluid dynamic) modeling and only very simple global reactions are viable. However, in simulating the time dependent molecular species and temperature evolution under the simple physical conditions of a constant pressure (or volume) homogeneous combustor, large sets of reactions and molecule species can be used to study in detail the chemical behavior. Complex combustion mechanisms of large species, having up to 16 carbons, have been modeled by automatically, simulating and generating all the interactions of the intermediate species in a complete combustion process.

In order to set up these reactions, two important sets of information are required: the temperature dependent thermodynamics (enthalpy, entropy and heat capacity) and reaction kinetic constants (usually represented by the Arrhenius equation). The origins of the constants range can be from chemical intuition, optimization, general chemical/physical principles, computations (quantum mechanical, semi-empirical, statistical mechanical, etc.), experimental results or, most often, a complex combination of these methods. Whatever the source of the information, especially with the continual introduction of new fuel structures and complexities, all the thermodynamic and kinetic constants are not necessarily available. This is especially true if the mechanisms are automatically generated. For this reason simple methods for the fast estimation of arbitrary species are needed. A key concept in one class of estimation procedures is that of the functional group represented as Lewis structures with in a graph theoretical framework. In estimating rate constants, functional groups are represented as reaction classes, with each class representing a certain type of reactivity. A reaction class 'applied' to a molecule specifies how that molecule can react. In estimating thermodynamics, the presence of functional groups, represented as molecular classes, contributes (in the first approximation) additively the molecule's thermodynamics.

The concepts of reaction and molecular classes have been incorporated in the databases of the complex software systems which I have continually developed, REACTION and JTHERGAS2 for the generation of combustion mechanisms. At the base of these systems is a wide range of mathematical, graph theoretical, artificial intelligence, machine learning, statistical and database techniques (in the form of the ANALYSIS++) system. These systems provide the foundation for encapsulating the necessary chemical modeling information, however, the source of this information comes from other sources, one of which is computational chemistry. In addition, these software systems are quite general and can be, within limits, applied to 'similar' modeling problems.

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