Graph Based Database Development for Gasoil Reactive Systems

AIChE Abstract
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Sessions:

- 10A03 Product and Molecular Design

In the petroleum refining industry, the accurate design and optimization of hydrocarbon conversion processes for gasoil feedstocks demand a growing effort in developing rigorous and reliable kinetic models (Van Geem *et al.*, 2002). Existing techniques rely on the approximation of gasoil stream compositions using a set of pseudo-components called “oil cuts” characterized by a set of lumped kinetic models. Although the lumped models are easy to construct and implement, they lack molecular information which makes them feedstock dependent and of limited use in process simulation and design. Developments by Neurock *et al.* (1994), Trauth *et al.* (1994), and Stark *et al.* (1995) address this limitation using molecular reconstruction techniques to approximate the individual components of the gasoil streams via stochastic optimization methods coupled with Monte Carlo kinetic models. The application of stochastic methods is, however, limited by the computational intensity imposed by the large sampling frequency needed to achieve statistical significance (Van Geem 2007). For specific classes of gasoils, Hudebine and Verstraete (2011) utilize a hybrid stochastic method that maximizes an entropy function with Lagrangian parameters associated with analytical constraints in order to reduce the computational burden. However, the method strongly depends on the initial set of molecules which must be chosen and built in relation to the type of gasoil studied.

An alternative, deterministic approach to molecular reconstruction has been developed by Bryan Research & Engineering (BRE) for the process simulator, ProMax®. The approach replaces the stochastic methods with a parallelized SQL call to a molecular database that contains all chemical constituents important to gasoil products and streams. The method is dependent on two competing factors, the completeness of the database and the size of the database. Unfortunately, most gasoil reconstructions require representations of chemical constituents of up to 40 atoms in a hydrogen suppressed, molecular graph. Enumerating all chemical constituents up to this size is cumbersome for even state-of-the-art graph generation algorithms and would result in a database too large to be efficiently searched (Peironcely *et al.,* 2012).

To address these limitations, a hybrid method is proposed that limits the size of the graph database using a set of constraints provided by molecular group and point group theory. In the first step of the method, a modified set of molecular functional groups described by Joback and Reid (1987) are used as building blocks to construct a complete set of vertex subgraphs that contain all double bonds, aromatic ring structures, and non-aromatic ring structures necessary to model gasoil systems. Next, these vertices are perturbed using point group symmetry operations to create a set of isomeric vertex graphs. Of these graphs, constitutional isomeric vertices are selected and separated into terminal and internal vertex sets. The internal vertices are constructed using graph generation algorithms and the terminal vertices are added at the final step to create complete molecular graphs. By utilizing coarse-grained sub-graphs of vertices, specific isomer classes common to gasoil systems can be created, without overloading the database, thus ensuring the capability of the SQL call to search the database in a timely manner. In addition, the database generation routing is constructed such that it is expandable by toggling various stereoisomer point groups and vertex rotations. The molecular library will be utilized to illustrate the database generation method as it is applied to a diesel hydrotreater case study.

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