

# USING CHEMISTRY-ORIENTED LUMPING TO MODEL HEAVY OIL HYDROPROCESSING

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## Abstract

Building on the principles of *structure-oriented lumping* (SOL), *chemistry-oriented lumping* methods have been developed to describe the composition in tandem with the hydro-processing chemistry of heavy oils such as vacuum residue, de-asphalted oil, tar and bitumen. Recent advances in analytical chemistry have provided the necessary fundamental insights that are required to develop such models. While all aspects of the original SOL modeling approach are applicable to heavy oil; a much higher degree of lumping as well as additional strategies to keep the number of components in the kinetic model manageable are required. Chemistry-oriented lumping methods are used to define a practicable model of heavy oil composition that is chemistry consistent.

## Keywords

Compositional modeling, refining, heavy oil, hydrotreating, kinetic modeling.

## Introduction

Crude oil refining heavily relies on process models for a wide variety of applications; including raw material valuation, planning, real-time optimization, process health monitoring, opportunity studies and process design.

Only detailed compositional process models possess the necessary flexibility and rigor required by present-day refineries. These compositional models incorporate a fundamental understanding of crude oil composition, chemistry, thermodynamics, and kinetics. As such, they allow meaningful inter- and extrapolation in the multidimensional space of feed composition, process conditions and catalysts.

## From Naphtha, Distillate and VGO ...

Structure-oriented lumping (SOL), developed by Quann et al. (1992, 1996, 1998), is a systematic method for describing the detailed composition and chemistry of crude oil. The SOL modeling approach was initially

developed for naphtha, distillate and gas oil range material, i.e. crude oil fractions and products that boil below ~1050 °F. In this boiling range molecules can be organized in terms of homologous series of single-core components; where each component represents (or lumps together) numerous structural isomers (e.g. the homologous series of benzene shown in Figure 1).

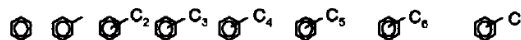


Figure 1. Homologous series of benzene and alkylated benzenes (Quann and Jaffe, 1992)

The approach uses SOL vectors to represent molecular components. This vector representation enables a concise description of crude oil composition. It also allows predicting bulk physical properties, generating large reaction networks, and defining kinetic rate expressions.

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### ... To Residues and Heavy Oils

Analyzing and describing the composition and chemistry of the heaviest crude oil fractions (e.g. vacuum residues and de-asphalted oils) as well as heavy intermediates (e.g. FCC bottoms and steam cracker tar) has remained a challenge.

However, thanks to recent advances in analytical chemistry it is now possible to characterize these fractions with an unprecedented level of detail. Advanced analytical techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), field desorption mass spectroscopy (FD-MS) and collision induced dissociation (CID) have revealed the importance of multi-core molecular components in heavy oils. Moreover, Qian et al. (2012) showed that the building blocks that make up these multi-core structures (e.g. Figure 2) are similar to the single-core structures that can be found in naphtha, distillate and VGO.

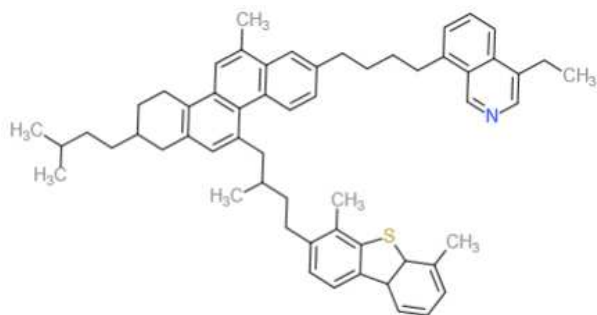


Figure 2. Example of a multi-core molecule composed of typical gas oil range single-core molecules

The analytical techniques mentioned above have provided the necessary fundamental insights required to model heavy oil composition and chemistry using SOL concepts.

Lumping of structural isomers in homologous series of components (i.e. one of the basic principles of the SOL modeling approach) is a powerful strategy to organize molecules. Nevertheless, the vast compositional complexity observed in heavy oils requires a much higher degree of lumping and additional strategies to keep the number of components (and therefore the number of differential equations in a process model) manageable.

Chemistry-oriented lumping methods have been developed to lump together numerous multi-core molecules with similar carbon number and hydrogen deficiency in a tractable number of components. The developed lumping strategies ensure that the resulting *model of composition* (i) remains detailed enough so it can capture key compositional differences between heavy oils; and (ii) is chemistry consistent.

The latter is achieved by using clusters of ‘chemistry-related’ components to define a practicable model of heavy

oil composition. For example, all multi-core hetero-atom components included in the model are defined as chemistry-related children of a parent hydrocarbon. By doing so, automatic generation of the reaction network describing hydrotreating chemistry (e.g. HDS, HDN, HDO, etc.) becomes nearly trivial.

In addition, reaction network generation strategies to describe hydrocracking and thermal cracking chemistries, where multi-core components decompose in a multitude of products, have been developed as well.

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