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Simulating vacuum residue hydroconversion by means of Monte-Carlo techniques

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ABSTRACT

The present work focuses on the development of a novel methodology for the kinetic modeling of heavy oil conversion processes. The methodology models both the feedstock composition and the process reactions at a molecular level. The composition modeling consists of generating a set of molecules whose properties are close to those of the process feedstock analyses. This synthetic mixture of molecules is generated by a two-step molecular reconstruction algorithm. In its first step, an equimolar set of molecules is built by assembling structural blocks in a stochastic manner. In the second step, the mole fractions of the molecules are adjusted by maximizing an information entropy criterion. Once the composition of the feedstock is represented, the conversion process is simulated by applying, event by event, its main reactions to the set of molecules by means of a kinetic Monte Carlo (kMC) method. The methodology has been applied to hydroconversion of Ural vacuum residue and both the feed and the predicted effluents were favorably compared to the experimental yield pattern.

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1. Introduction

Over the last decade, the world demand for high-quality low-boiling products such as gasoline, jet fuel and diesel has continually increased, while at the same time the available crude oils have become increasingly heavier. Both trends boost the importance of refining processes that are able to convert heavy petroleum fractions, such as vacuum residues, into lighter and more valuable clean products [1–3]. Petroleum residue conversion processes, such as residue hydrocracking or residue fluid catalytic cracking (RFCC), are based on the degradation of the largest molecules by thermal and/or catalytic cracking reactions at high temperature. To accurately predict the process performances, reliable kinetic models are needed [4–6]. Kinetic models for heavy oil conversion processes have classically been based on a lumping strategy [7], in which molecular components are grouped into several chemical families, according to their global properties (boiling point, solubility, etc.). To improve the predictions of these lumped models, the number of lumps is generally increased, as exemplified by literature kinetic models for residue hydroprocessing [8–20]. Besides their feed dependence and lack of robustness, such models also seem to reach their limits due to very high number of reaction parameters (rate constants, adsorption parameters) that need to be identified when applied to the heavy oil conversion. The development of more detailed kinetic models containing molecule-based reaction pathways is therefore required [5,21] and has been ongoing over the last 2 to 3 decades for a wide variety of chemical processes, such as pyrolysis, steam cracking, catalytic cracking, hydrocracking, hydrotreating, catalytic reforming, alkylation, and many more [22]. Such models expect a molecular description of the feedstock, however. Unfortunately, even though the most advanced analytical techniques allow to identify a large number of compounds and classes of chemical families, the complete and quantitative molecular detail of heavy feedstocks still remains unknown [23–27]. Our work presents a novel two-step kinetic modeling methodology for heavy oil conversion processes that retains the molecular detail throughout the method (Fig. 1). In the proposed approach, the lack of molecular detail of the petroleum fractions is overcome by using a carefully selected synthetic mixture of representative molecules, the

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Abbreviations: AEBP, Atmospheric Equivalent Boiling Point; BT, benzothiophene; CME, chemical master equation; DBT, dibenzothiophene; GC, Gas Chromatography; GO, gas oil; HDA, hydrogenation of aromatic rings (hydrodearomatization); HDM, hydrodemetallization; HDN, hydrodenitrogenation; HDS, hydrodesulfurization; kMC, kinetic Monte Carlo; LAD, least absolute deviations; LCO, Light Cycle Oil; LFER, linear free energy relationships; LSQ, least squares; MS, mass spectrometry; MD, molecular discretization; NMR, nuclear magnetic resonance; PDF, probability distribution function; QS/RC, Quantitative Structure/Reactivity Correlation; REM, Reconstruction by Entropy Maximization; SARA, saturates–aromatics–resins–asphaltenes analysis; SR, stochastic reconstruction; SR-REM, coupled SR-REM method; SSA, Stochastic Simulation Algorithm; T, thiophene; VGO, vacuum gas oil; VR, vacuum residue.

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a_ν	Probability of reaction ν (s^{-1})
c_ν	Stochastic rate parameter of reaction ν
$c_{Dehydro}$	Stochastic rate parameter of a dehydrogenation reaction (s^{-1})
c_{Hydro}	Stochastic rate parameter of a hydrogenation reaction ($s^{-1}\,atm^{-n}$)
D_R	Normalized cumulative probability distribution for all possible reactions
$E(x_i)$	Shannon entropy criterion
E_a	Activation energy ($J\,mol^{-1}$)
$F_j()$	Mixing rule for analytical property j
F_{rep}	Replication factor
h_ν	Distinct combination of the reactant molecules of the reaction ν
J	Total number of analytical constraints in the REM method
K_{eq}	Equilibrium constant (–)
k_ν	Deterministic rate parameter of the reaction ν
M	Number of possible reactions
MW	Molecular weight ($g\,mol^{-1}$)
N	Number of molecules present in the predefined set of molecules
N_A	Number of analyses present in the objective function
$N_{M,i}$	Number of measurements of analysis i
N_{AR}	Number of aromatic rings
N_{SR}	Number of saturated rings
N_{TR}	Number of thiophenes fused to the aromatic ring
n_H	Reaction stoichiometry with respect to molecular hydrogen
OF	Objective function
p_{H_2}	Partial hydrogen pressure (atm)
P_j	Value of analytical property j
P_ν	Normalized probability of reaction ν
R	Ideal gas constant ($J\,K^{-1}\,mol^{-1}$)
RN_i	Random number i
x	Vector of mole fractions x_i
x_i	Mole fraction of molecule i (–)
$X_{i,j}^{exp}$	Experimental value of measure j of analysis i
$X_{i,j}^{calc}$	Calculated value of measure j of the analysis i
δ_i	Deviation between the calculated and experimental values of analysis i
ΔH_R^0	Heat of reaction at 25 °C ($J\,mol^{-1}$)
ΔH_R	Heat of reaction at reaction temperature ($J\,mol^{-1}$)

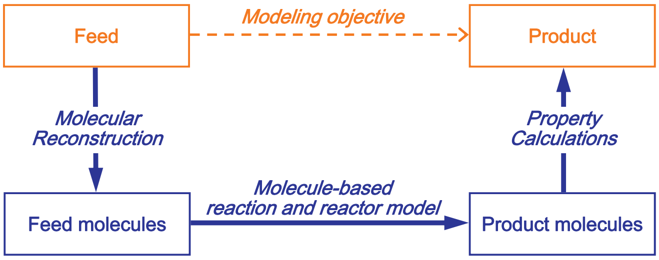

Fig. 1. Molecule-based process modeling methodology (after [6]).

properties of which correspond closely to the available feedstock analyses. The conversion process is then simulated by transforming each molecule of this set by means of a kinetic Monte Carlo (kMC) method.

2. Description of the methodology

As mentioned in the introduction, the proposed methodology comprises two main steps. In the first step of the methodology, the feedstock composition is modeled by means of a set of molecules whose mixture properties are close to the process feedstock analyses. The set of molecules is generated using the SR-REM molecular reconstruction algorithm [28,29]. This approach results from the coupling of two methods: Stochastic Reconstruction (SR) [28,30–33] and Reconstruction by Entropy Maximization (REM) [28,34–38]. The SR algorithm generates an equimolar set of molecules by assembling structural blocks in a stochastic manner, while the REM algorithm adjusts the mole fractions of the set of molecules by maximizing a Shannon information entropy criterion. During previous work, this algorithm was first developed and validated for Light Cycle Oils (LCO) [28,33,39] and for vacuum gas oils (VGO) [40,41]. The SR-REM algorithm was also applied to various petroleum vacuum residues by Verstraete et al. [42] and de Oliveira et al. [29]. In the present work, the reconstruction of an Ural vacuum residue (VR) will be illustrated.

In the second step of the methodology, the kinetics of the conversion process is modeled using a kinetic Monte Carlo (kMC) method, proposed by Gillespie [43] and termed Stochastic Simulation Algorithm (SSA). In this approach, the SSA identifies all possible reactions at each instant in time. For each reaction, its rate coefficient determines its reaction probability. Based on these probabilistic considerations, the algorithm then selects a reaction event, transforms the reactant molecule into its corresponding product, and increments the simulation time. The simulation proceeds event by event (reaction by reaction) until the final simulation time is reached, leading to the set of product molecules. In the present work, the hydroconversion of an Ural VR in a batch reactor will be simulated and compared to the experimental data.

2.1. Composition modeling

2.1.1. Stochastic reconstruction (SR) method

The goal of the SR method is to create a representative ensemble of probability distribution functions (PDF) for molecular structural attributes (e.g. type of molecule, number of cores, number of aromatic rings, number of side chains, etc.) from available analytical information of the given petroleum fraction. Once the PDFs have been created, they are sampled to generate an equimolar set of molecules whose mixture properties are close to those of the given petroleum fraction. The transformation of the analytical information into PDFs of molecular attributes is carried out via an iterative procedure shown in Fig. 2.

First, appropriate molecular attributes are chosen from the available analytical information (elemental analysis, ^{13}C NMR, GC–MS, etc.) of the feedstock and from expert knowledge. A PDF is selected to represent each molecular attribute. The PDFs employed may either be discrete, such as histograms, or continuous, such as normal distribution functions, gamma distribution functions, or exponential distribution functions. The choice of the type of PDF is based on its form, its flexibility and its number of parameters. A flexible PDF is desirable in order to easily pick up the correct form of the experimental observations, as well as a small number of parameters to characterize it.

After the appropriate PDFs are found for each molecular attribute, they are sampled via a Monte Carlo procedure to determine the functional and structural attributes of a molecule. The sequence of the PDF sampling steps is defined through a building diagram. The selected molecular attributes are randomly assembled, yet respecting chemical rules. These rules avoid the creation of impossible and improbable molecules on chemical, thermodynamic or probabilistic grounds.

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