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A molecular lump based model for simulation of industrial naphtha hydro treators

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ABSTRACT

A detailed, molecule-based kinetic model has been developed to simulate industrial naphtha hydro treators. A feed characterization module has been developed to calculate the composition of pre-defined *pure* molecules representing the feed quality without any detailed experimental component analysis. Feed naphtha is represented by a pre-defined set of 95 pure molecules, from carbon numbers C_5 to C_{11}, and the proportion of these components is calculated using an optimization algorithm so as to match the physico-chemical properties of the mixture with those of naphtha, as measured in the laboratory. The output from this optimization model is used as a direct input to a model of a hydro treating reactor. The main reactions occurring in the hydro treator, such as hydro desulfurization reactions and olefin saturation reactions, are modeled. The kinetic parameters for these reactions have been estimated from a comprehensive set of experimental pilot plant data spanning a wide range of process conditions. The kinetic model quantitatively predicts the exit composition, temperature rise and pressure drop in the catalyst bed for a range of conditions for two *industrial* refinery units.

1. Introduction

Sulfur compounds in combustion products are major pollutants in hydrocarbon fuels. Removal of sulfur is mandatory now to meet stringent environmental regulations on gasoline/distillate fuels. Almost all countries in the world have now adopted Euro-V specifications that mandate the gasoline fuels to have 10 ppm or less of elemental sulfur. A typical gasoline pool consists of a blend of different refinery process streams such as reformates, FCC naphtha, coker naphtha, vis-breaker naphtha, hydrocracker naphtha, etc. Cracked naphtha generally contains more sulfur, nitrogen and olefins. Moreover, these sulfur and nitrogen containing compounds are mostly aromatic in nature and are produced during catalytic cracking and thermal operations. These streams are required to be hydro treated before blending in the gasoline pool. Table 1 shows the relative amounts of different process streams in commercial gasoline and their relative contributions of sulfur to the gasoline pool. FCC naphtha in the gasoline pool is the largest source of sulfur. The important sulfur molecules in the above streams are thiophene (T) and its alkyl derivatives like C_1-T, C_2-T, benzothiophene (BT) and its alkyl derivatives like C_1-BT, C_2-BT, dibenzothiophene (DBT) and its alkyl derivatives, etc. Hydro treating is an important process not only for the removal of sulfur, but of nitrogen compounds as well. Additionally, some of the olefins get saturated. Olefin saturation reactions are important reactions in naphtha hydro desulfurization (HDS) as they are responsible for the octane loss during HDS. The important nitrogen molecules present in these streams include anilines, pyridine, pyrrole, quinolone [1].

The gasoline fraction has a broad boiling range and comprises of a very large number of individual molecules, each with its own boiling point (and other properties). It is not feasible to work with so many molecules. A laboratory assay provides only limited information on such compounds. Conventionally, petroleum refiners characterize petroleum fractions by their physical properties such as ASTM D1160/D86, TBP, specific gravity, API gravity, etc., using laboratory tests. Sophisticated analytical techniques, e.g., nuclear magnetic resonance (NMR) and gas chromatography (GC), can be used for these fractions to give further classification in terms of their molecular basis, e.g., contents of paraffins, olefins, naphthenes and aromatics (PONA).

So far, the hydro desulfurization of naphtha and gas oils has been studied in terms of kinetic lumps of sulfur components which are converted by first or second order reactions [2]. These models have limitations, as these do not reveal the underlying reaction mechanisms since the actual composition of the lumps in terms of molecular components may differ with changes in the kind of feed. Indeed, the performance of catalytic reactions is governed by molecular information rather than

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Nomenclature

A_i–D_i	Constants for spline-fitting
A	Aromatic content [wt%]
A	Cross sectional area of the reactor [m^2]
CCR	Conradson carbon number
C_p	Heat capacity [kJ/kmol-K]
C_A	Aromatic carbon atoms
C_P	Paraffinic carbon atoms
C_N	Naphthenic carbon atoms
d_p	Equivalent diameter of the catalyst particle [m]
E_i	Activation energy of reaction, i
F_{obj}	Objective function for optimization
F_{obj},1	First part of objective function, F_{obj}
F_{obj},2	Second part of objective function, F_{obj}
F_j	Molar flow rate of component, j
F_j^o	Inlet molar flow rate of component, j
f	Ergun friction factor
f_r	Relative reactive factor with respect to base component
F_j^{in}	Molar flow rate of pure component, j, in the stream entering bed-2 [kmol/h]
F_{1j}	Molar flow rate of species, j, in the outlet stream from bed-1[kmol/h]
F_j^{out}	Molar flow rate of species, j, in the effluent from bed-2 [kmol/h]
ΔH_i	Net heat of reaction, i [kJ/kmol]
$\Delta H_{f\,j}$	Heat of formation of component, j [kJ/kmol]
k_1–k_5	Rate constants [kmol/kgcat·h]
K_i	Adsorption constant of component, i [bar^{-1}]
K_{eq}	Equilibrium constant
$k_{i,o}$	Frequency factor [kmol/kgcat·h]
MW	Molecular weight
M	Number of reactions
n	Number of weight increments
N	Naphthenic content [wt%]
N_c	Number of components
O	Olefin content [wt%]
P	Paraffin content [wt%]
p_i	Partial pressure of component, i
P_t	Total pressure [Mpa]
P_o	Inlet pressure [Mpa]
RI	Refractive index of a petroleum fraction
R_j	Net rate of generation of species, j
R	Universal gas constant
R_R	Recycle ratio
RMSE	Root mean square error
R^2	Correlation coefficient
r_T,σ, $r_{BT,\sigma}$, $r_{HBT,\sigma}$	Rate of thiophene, benzothiophene, dihydrobenzothiophene desulfurization on σ sites [kmol/kgcat·h]
r_{BT},τ, $r_{Olefin,\tau}$	Rate of benzothiophene, olefin saturation on τ sites [kmol/kgcat·h]
SG	Specific gravity
S	Sulfur content [wt%]
TBP	True boiling point
T_b	Boiling point of any component [°C]
T	Reaction temperature [°C]
T_o	Inlet feed temperature [°C]
TMTPA	Thousand metric tons per annum
u_s	Superficial velocity [m^2]
W_0	Weighting factor for the first part of the objective function
W_1	Weighting factor for the second part of the objective function
x_w	Weight fraction of any component
x_w,A	Weight fraction of the aromatic molecule
x_w,N	Weight fraction of the naphthenic molecule
x_w,o	Weight fraction of the olefin molecule
x_w,p	Weight fraction of the paraffin molecule
x_w,S	Weight fraction of the sulfur molecule
x_i	Total weight fraction of paraffin/naphthene/olefin/sulfur content
Y_j	Global property of the petroleum fraction
z	Axial location in the reactor [m]

Greek symbols

α_{ij}	Stoichiometric coefficient of component, j, in reaction, i
θ	Average global physical property
ρ_B	Bulk density of the catalyst [kg/m^3]
σ	Sigma site for hydro desulfurization reactions
τ	Tau site for saturation reactions
Ω	Cumulative weight fraction

Subscripts

BT	benzothiophene
EB	ethyl benzene
HBT	dihydrobenzothiophene
H_2	hydrogen
H_2S	hydrogen sulfide
T	thiophene

information on lumps generated from the bulk properties of the feed. In the present model, the optimal composition of the *pure* components representing the feed is generated from a given TBP data and *a few* global properties of the feed. These pure compounds have boiling points in the range of the IBP (initial boiling point: ~35 °C) and the FBP (final boiling point: ~230 °C) of the naphtha feed. The composition of the pure compounds in the mixture is found by an optimization routine. Routinely measured properties of naphtha, e.g., ASTM distillation, specific gravity, bromine number, etc., are estimated by mixture rules for the model mixture and the error between the calculated and measured values is minimized in a least-squares sense, using the percent composition of the pure compounds as the decision/control variables. The reaction network for hydro desulphurization and olefin saturation reactions is incorporated in the reactor model. The model predicts the product composition in terms of paraffins/olefins/naphthenes/aromatics/sulfur. The model also predicts, quite accurately, the temperature rise in the two reactor beds. This is because the present model deals with *pure* molecules and so can utilize their specific heats and heats of formation without any approximation in the energy balance equation for the reactor. The model can be used as a quick tool for simulating the performance of industrial naphtha hydro treators without detailed experimental component analysis, predicting the molecular composition of the product.

Table 1
Typical sulfur content in commercial gasoline blending streams.

Gasoline blending component	Sulfur (ppm, wt)	Typical % vol in gasoline pool	% (wt.) contribution of sulfur
Reformate	0.1	30	0.1
FCC gasoline	100	36	99.6
Isomerate	0.3	34	0.3