KINETIC MODELING OF HYDROPROCESSING PROCESS

KUNCHE BABU SRINIVAS

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

KUNCHE BABU SRINIVAS

DEPARTMENT OF CHEMICAL ENGINEERING

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CERTIFICATE

This is to certify that the thesis entitled **"KINETIC MODELING OF HYDROPROCESSING PROCESS"** submitted by **Mr. Kunche Babu Srinivas** to the Indian Institute of Technology Delhi for the award of degree of **Doctor of Philosophy** is a record of original bonafide research work carried out by him under my guidance and supervision. The thesis has reached the standards of fulfilling the requirements of the regulations of Indian Institute of Technology Delhi for awarding the degree.

The research report and results presented in the thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

Date:

Dr. Kamal K.Pant
Professor and Head
Department of Chemical Engineering
Indian Institute of Technology Delhi, India

Dr. S. K. Gupta
Distinguished Professor
Department of Chemical Engineering, University of Petroleum and Energy Studies,
Dehradun, Uttarakhand, India

Dr. D. N. Saraf
Distinguished Professor
Department of Chemical Engineering, Dehradun Institute of Technology,
Dehradun, Uttarakhand, India

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ABSTRACT

Hydroprocessing has emerged as the key refining process equal in importance to distillation in the refinery. The goals for fuels with higher hydrogen, lower aromatics and with low hetro-atoms (e.g. Sulfur, Nitrogen, etc.,) have been a key factor for the development of new grass root refineries as well as for revamps. Almost all countries in the world have now adopted Euro-V specifications that mandate the gasoline/diesel fuels to have 10 ppm or less of elemental sulfur. This has tended to favor hydroprocessing technologies in the refineries. Hydroprocessing is a family of process which includes hydrotreatment of light and middle distillates, vacuum gas oil (VGO) and VGO hydrocracking. A process model is vital requirement for any process optimization process.

The feed (naphtha/ diesel/ VGO) to the hydrotreaters consists of enormous number of molecules in the order of 10^4-10^5 from carbon number ranging from C_5- C_{33}. A laboratory assay doesn't provide information on number and type of compounds. So far, the hydrotreating 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. These lumped models do not reveal the underlying reaction mechanisms and mask the true kinetics since the actual composition of the lumps in terms of molecular components may differ with changes in the kind of feed. Because of the lack of molecular level details as input to these models, the model output cannot be able to predict the composition of the product and its properties. Hence there is a need to develop a more realistic kinetic model based on detailed feed description to predict product composition and properties. This motivated the present approach aimed at the development of feed characterization module that will allow the prediction of molecular composition of petroleum fractions. This molecular composition information is a direct input for molecular reaction models in the reactor simulation

which can subsequently be used to predict the product molecular composition and properties for various operating scenarios.

The main objectives of the present work are as follows:

1. *Develop a feed characterization module:* The first step in the development of the (pure) molecule-based kinetic model is the molecular characterization and representation of the feed stream. The main aim of the present work is to transform the analytical information into a *molecular* representation that represent the feed using an optimization algorithm and use this molecular composition to model the reactions in the industrial hydrotreating reactor.
2. *Kinetic modeling and parameter estimation*: To model the important reaction pathways in the hydrotreating process. The reaction pathways considered in this study are hydro desulfurization (HDS), hydro denitrogenation (HDN), olefin saturation (OSAT) and aromatic saturation (ASAT). To conduct experiments for kinetic studies and to estimate the kinetic parameters from pilot plant studies.
3. *Reactor simulation*: To frame a set of model equations for the simulation of *industrial* reactors and solving these model equations to predict the boiling point distribution, composition, temperature, pressure, etc., at the exit of the reactor.

In the present feed characterization model, the optimal composition of the *pure* components representing the feed is generated from a given true boiling point (TBP) data and *a few* global properties of the feed. An appropriate number of *pure* molecules are selected to represent the feed, such that the experimental properties of the latter, e.g., the true boiling point, specific gravity, refractive index, etc., match those computed from the selected set of pure molecules (using appropriate mixing rules) representing it. From among *all* the available

molecules of various detailed hydrocarbon analysis (DHA), commonly occurring paraffins, naphthenes, aromatics and olefins are taken as representative molecules for the naphtha feed constituting the carbon numbers from C_5 - C_{11}. VGO feed is represented by molecules from carbon number ranging from C_{14} - C_{33}. For naphtha feed, the criterion followed for the selection of components was the difference in boiling points between them should be around $1^{\circ}C$ in any one group. For heavier fractions we have used the criteria that each group (PNA) should be represented by only one carbon number to limit the number of molecules. With this criterion, a data base with important physical properties has been built for naphtha comprising 95 components and VGO comprising 120 components. The composition of the pure compounds in the mixture is found by an optimization routine (real-coded Genetic Algorithm (GA) in Matlab^{TM}). This component data base has been tested for several feeds with different boiling ranges and found to be satisfactorily matching with the TBP curve and other properties.

Hydrotreating modeling at the pathways level has four reaction families: desulfurization, denitrogenation, olefin saturation and aromatic saturation. Development of detailed kinetic model requires modeling of HDS/HDN/OSAT/ASAT chemistry at the reaction pathways level for each molecule in the process. Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism type rate expressions were used for the four reaction families considered in the study. A steady state isothermal kinetic model has been developed to estimate the product composition in the pilot plant reactor. 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. Experiments were conducted at various process parameters namely temperature, pressure, gas to oil ratio and liquid hourly space velocity. The values of the kinetic parameters were calculated as a function of reaction temperature by minimizing an objective function based on sum of square

deviations between the model-predicted and experimental values of the total sulfur, total nitrogen, olefin and aromatic contents. The minimization is done using the Genetic Algorithm (GA) code in Matlab™.

Industrial hydrotreating reactors are adiabatic fixed bed reactors. Modeling of temperature rise in the industrial reactors is carried out by considering an energy balance equation for the reactor. As the present model deals with pure molecules, standard heat of reaction with reaction temperature is calculated from the individual component specific heats and standard heat of formation. In this work industrial naphtha and VGO hydrotreaters were modeled and configured for one of the Indian operating refineries. A detailed molecule-level reactor model (a one dimensional steady state non isothermal pseudo homogenous plug flow model) for naphtha hydrotreating with 95 components, from carbon numbers C_5 to C_{11} and 36 reactions, has been developed. A three phase one dimensional plug flow non isothermal trickle bed reactor model for VGO hydrotreating with 120 components, from carbon numbers C_{14} to C_{33} and 48 reactions has been developed.

The present reactor models with a feed characterization module prove to be a powerful tool for simulating industrial naphtha/VGO hydrotreating reactors. Simulation results showed that the model is capable of generating detailed product composition, boiling point distribution of the reactor effluent and major process trends for a wide range of operating conditions. Moreover, the model can be used to calculate the physical properties of interest (e.g., specific gravity, average molecular weight, etc.). Therefore, this model can be used as a good computational tool for process development, operation and optimization of existing naphtha/VGO hydrotreating units.

सार

रिफाइनरी में आसवन के लिए हाइड्रोप्रोसिंग महत्वपूर्ण शोधन प्रक्रिया के समान है। पिछले कुछ दशकों में पर्यावरण की चिंता ने शोधन उद्योग में हाइड्रोप्रोसेसिंग विकास के लिए रूपरेखा तैयार की है। उच्च हाइड्रोजन, कम एरोमेटिक्स और कम हेट्रो-परमाणुओं (जैसे सल्फर, नाइट्रोजन, आदि) के साथ ईंधन के लिए लक्ष्य, नए घास रूट रिफाइनरियों के विकास के साथ-साथ सुधारों के लिए एक महत्वपूर्ण कारक रहा है। सल्फर को निकालना अब अनिवार्य है गैसोलीन/आसुत ईंधन पर कड़े पर्यावरणीय नियमों को पूरा करना। हाइड्रोप्रोसेसिंग प्रक्रिया का एक परिवार है जिसमें प्रकाश और मध्य डिस्टिलेट्स, वैक्यूम गैस ऑयल (वीजीओ) और अवशेषों, हल्के हाइड्रोकार्बन, वीजीओ हाइड्रोकार्बन, अवशेष हाइड्रोकार्बन और हाइड्रोजनीकरण का हाइड्रोट्रिएंट शामिल है। एक प्रक्रिया मॉडल किसी भी प्रक्रिया अनुकूलन प्रक्रिया के लिए महत्वपूर्ण आवश्यकता है।यह प्रक्रिया मॉडल से है, जिसके कारण और प्रभाव संबंधों के सटीक अनुमान प्राप्त होते हैं जो प्रक्रिया अनुकूलन के लिए आवश्यक है।

इस शोध प्रबंध का उद्देश्य एक फीड कैरेक्टराइजेशन मॉड्यूल (FCM) विकसित करना था, जो फीड को एक आणविक प्रतिनिधित्व में चिह्नित कर सकता है, जिसका उपयोग औद्योगिक रिएक्टर सिमुलेशन के लिए हाइड्रोट्रीटिंग रिएक्शन पाथवे के निर्माण के लिए किया जाएगा। एक च ईद वर्णकरण मॉड्यूल विकसित किया गया है किसी भी विस्तृत प्रयोगात्मक घटक विश्लेषण के बिना फ़ीड गुणवत्ता का प्रतिनिधित्व करने वाले पूर्व-परिभाषित *शुद्ध* अणुओं की संरचना की गणना करने के लिए अभी तक इनपुट के साथ प्रयोगशाला में नियमित रूप से मापा केवल फ़ीड गुणों का उपयोग करें। फ़ीड वर्णकरण मॉड्यूल स्वचालित रूप से फ़ीड के क्वथनांक वितरण के आधार पर डेटाबैंक से घटकों का चयन करता है और शुद्ध अणुओं की संरचना की गणना करेगा एक अनुकूलन एल्गोरिथ्म का उपयोग करना ताकि फ़ीड के साथ मिश्रण के भौतिक-रासायनिक गुणों से मेल खा सके , जैसा कि प्रयोगशाला में मापा गया है। डेटा बैंक में C_5 से C_{33} तक की कार्बन संख्या के 215 घटक शामिल हैं जिन्हें आगे पैराफिन, नैफ्थेन, मोनो / डाय / पॉली-एरोमेटिक्स, सल्फर और नाइट्रोजन घटकों में वर्गीकृत किया गया था।

अध्ययन का 2एनडी उद्देश्य, रिफाइनरी में उनके महत्व के कारण नेफ्था और वीजीओ फीड स्ट्रीम के लिए एक औद्योगिक हाइड्रोट्रीटिंग रिएक्टर मॉडल विकसित करना है। एक विस्तृत अनु स्तर के रिएक्टर मॉडल कार्बन संख्या C_5 से C_{11} तक, 95 घटकों के साथ नेफ्था हाइड्रोट्रीटिंग के लिए और 36 प्रतिक्रियाओं को विकसित किया गया है। वीजीओ के लिए एक तीन चरण ट्रिकल बेड रिएक्टर मॉडल कार्बन संख्या C_{14} से 120 घटकों के साथ हाइड्रोट्रीटिंग C_{33} और 48 प्रतिक्रियाओं को विकसित किया गया है। फ़ीड रिएक्टराइजेशन मॉड्यूल के साथ वर्तमान रिएक्टर मॉडल एस औद्योगिक जल उपचार का अनुकरण करने के लिए एक शक्तिशाली उपकरण साबित होता है रिएक्टरों। चूँकि फ़ीड वर्णकरण योजना गांठ वाले घटकों के बजाय सीधे (शुद्ध) अणुओं के साथ काम करती है, इसलिए मॉडल प्रत्येक फ़ीड घटक की प्रतिक्रिया नेटवर्क को बनाए रखता है और उत्पाद वितरण में व्यक्तिगत घटकों को पकड़ने में सक्षम होता है। सिमुलेशन के परिणामों से पता चला कि मॉडल विस्तृत उत्पाद संरचना बनाने में सक्षम है, रिएक्टर के प्रवाह का क्वथनांक वितरण और परिचालन स्थितियों की एक विस्तृत श्रृंखला के लिए प्रमुख प्रक्रिया रुझान।

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

$A_i - D_i$ – Constants for spline-fitting

A – Aromatic content [wt. %]

A_c – Cross sectional area of the reactor [m^2]

a_s – Specific surface area of the catalyst [m^{-1}]

a_L – Gas- liquid interfacial area [m^2]

C^L_p – Heat capacity of liquid [kJ/kmol-K]

C^G_p – Heat capacity of gas [kJ/kmol-K]

C^q_p – Heat capacity of quench gas [kJ/kmol-K]

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

C_i^L – Concentration of specie *i* in liquid phase [$kmol/m^3$]

C_i^S – Concentration of specie *i* on catalyst (solid) surface [$kmol/m^3$]

C_{H_2} – Concentration of H_2 in liquid phase [$kmol/m^3$]

C_{H_2S} – Concentration of H_2S in liquid phase [kmol/m^3]

C_{Nt}^{S} – Concentration of Nitrogen on catalyst (solid) surface [kmol/m^3]

diA – Di aromatic content [wt. %]

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/hr]

F_{1j} – Molar flow rate of species, *j*, in the outlet stream from bed-1[kmol/hr]

F_j^{out} – Molar flow rate of species, *j*, in the effluent from bed-2 [kmol/hr]

G_{out} – Liquid molar flow rate [kmol/hr]

ΔH_i – Net heat of reaction, *i* [kJ/kmol]

ΔH_{fj} – Heat of formation of component, j [kJ/kmol]

H – Henry coefficient [bar.m^3/kmol]

$k_1 - k_5$ – Rate constants [kmol/kgcat.hr]

K_i – Adsorption constant of component, i [bar^{-1}]

K_m – Adsorption parameter of the ring number based lumps (m^3/kmol)

K_{eq} – Equilibrium constant

$k_{i,o}$ – Frequency factor [kmol/kgcat.hr]

k_i^L – Gas- liquid mass transfer coefficient [m/sec]

k_i^S – Liquid- solid mass transfer coefficient [m/sec]

L_{out} – Liquid molar flow rate [kmol/hr]

MMTPA – Million metric tons per annum

MW – Molecular weight

M – Number of reactions

moA – Mono-aromatic content [wt. %]

moA1– Mono-aromatic product lump content [wt. %]

n – Number of weight increments

N – Naphthenic content [wt. %]

N_c – Number of components

N_t – Nitrogen content [wt. %]

O – Olefin content [wt. %]

P – Paraffin content [wt. %]

p_i – Partial pressure of component, i

p_i^G – Partial pressure of gas 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

$r_{T,\sigma}$, $r_{BT,\sigma}$, $r_{HBT,\sigma}$ – Rate of thiophene, benzothiophene, di-hydrobenzothiophene desulfurization on σ sites [kmol/kgcat.hr]

$r_{BT,\tau}$, $r_{Olefin,\tau}$ – Rate of benzothiophene, olefin saturation on τ sites [kmol/kgcat.hr]

r_s, r_{Nt}, r_{ij} – Rate of hydro desulfurization, hydro denitrogenation, aromatics saturation reactions [kmol/kgcat.hr]

SG – Specific gravity

S – Sulfur content [wt %]

TBP – True boiling point

T_b – Boiling point of any component [^oC]

T – Reaction temperature [^oC]

T_o – Inlet feed temperature [^oC]

TMTPA – Thousand metric tons per annum

u_s – Superficial velocity [m^2]

u_G – Superficial velocity of gas [m^2]

u_L – Superficial velocity of liquid [m^2]

W_o – 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

DBT – di benzothiophene

EB – ethyl benzene

HBT – dihydrobenzothiophene

H_2 – hydrogen

H_2S – hydrogen sulfide

T – thiophenes

NH_3 – ammonia