MODELING OF VACUUM GAS OIL HYDROCRACKING PROCESS USING LUMPING APPROACH

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Dedicated to:

My father and mother
For their love and concerns.

To my supervisor,
Professor Dr. Arshad Ahmad,
Thank you for your kindness and your helpful guidelines.

For all my kind-hearted friends,
Thank you for being so much kind and helpful,
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ABSTRACT

Conversion of heavy feedstock into lighter products in a hydrocracking process has a strong influence on the profitability of petroleum refining. To facilitate initiatives toward improving the process efficiency, a good process model is required. This thesis discusses the development and application of lump modeling strategies in a pilot plant and industrial scale hydrocracking processes. For the pilot plant, two different four-lump models are considered, i.e., combined bed and dual bed models. Unlike the simpler combined bed model, the dual bed model includes hydrogen consumption and hydrotreating reactions, and the reactor is subdivided into two different layers so that the effect of hydrotreating reactions can be integrated. To extend the application to a commercial refinery, a full-lump model is configured to predict the product yields of a commercial hydrocracking unit known as Isomax. Using bed temperatures, flow rate of fresh vacuum gas oil (VGO), recycle rate and catalyst life as process variables, the model is proven capable of predicting the yield of all products. The model also provides improvement to previous works by considering liquefied petroleum gas (LPG), light gases, fresh VGO and recycle feed as separate lumps. This model is then used in optimizing the reactor operation where the bed temperature, flow rate of fresh VGO and combined feed ratio are adjusted to increase the plant profitability whilst maintaining all process limitations and operating constraints. To extend the model for dynamic applications, a modified space-time conservation element and solution element method (CE-SE) is introduced. The results obtained from simulation of the pilot plant based on four-lump model using CE-SE method are comparable to those obtained using finite difference method, thus providing opportunities for further works involving dynamic behavior of the process. Although the study is focussed on hydrocracking, this thesis has proved the practicality of using lumped modeling technique to address model development requirement for complex industrial processes.

ABSTRAK

Penukaran bahan mentah berat kepada produk yang lebih ringan dalam proses pemecahan-hidro mempunyai pengaruh yang kuat ke atas keuntungan proses penapisan petroleum. Untuk memudahkan inisiatif ke arah meningkatkan kecekapan proses, satu model yang baik diperlukan. Tesis ini membincangkan pembangunan dan aplikasi strategi permodelan tergumpal dalam proses pemecahan-hidro berskala loji pandu dan industri. Untuk proses berskala loji pandu, dua model empat-gumpal dipertimbangkan, iaitu model lapisan-tergabung dan model dwi-lapisan. Berbeza dengan model lapisan-tergabung yang lebih mudah, model dwi-lapisan mengambil-kira penggunaan hidrogen dan tindakbalas hidrorawat, dan reaktor dibahagikan kepada dua bahagian yang berbeza supaya kesan daripada tindakbalas hidrorawat boleh disepadukan. Bagi membolehkan penggunaan untuk penapisan komersil, model gumpal-penuh telah dibentuk untuk meramalkan hasil produk unit pemecahan-hidro yang dipanggil Isomax. Dengan menggunakan suhu lapisan, kadar aliran minyak gas vakum (VGO) segar, kadar kitar semula dan hayat pemangkin sebagai input kepada model, peramalan yang baik untuk semua produk telah diperolehi. Model ini juga menyediakan penambahbaikan kepada kerja-kerja sebelumnya dengan mempertimbangkan VGO, LPG, gas ringan, suapan segar dan kitar semula sebagai gumpalan berasingan. Seterusnya, ia digunakan dalam mengoptimumkan operasi reaktor di mana suhu lapisan, kadar alir VGO segar dan nisbah suapan tergabung diselaraskan untuk meningkatkan keuntungan loji dengan mengambilkira semua batasan proses dan kekangan operasi. Untuk menambah penggunaan model gumpalan kepada aplikasi dinamik, teknik permodelan ruang-masa elemen keabadian elemen penyelesaian (CE-SE) diperkenalkan. Keputusan yang diperolehi dari simulasi loji pandu berasaskan empat-gumpal adalah setanding dengan apa yang diperolehi dengan menggunakan kaedah beza terhingga, sekaligus membuka peluang kepada kajian lanjut yang melibatkan tingkah laku dinamik. Walaupun kajian ini memfokus kepada proses pemecahan-hidro, tesis ini telah membuktikan kesesuaian penggunaan teknik permodelan tergumpal bagi memenuhi keperluan permodelan bagi proses-proses yang kompleks di industri.

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LIST OF ABBREVIATIONS

AAD	-	Absolute Average Deviation, %
ABT	-	Average bed temperature
ACM	-	Aspen Custom Modeler
ANOVA	-	Analysis of variance
AGO	-	Atmospheric gas oil
BASF	-	Badische Anilin und Soda Fabrik
CE-SE	-	Conservation element-solution element
CFR	-	Combined feed ratio
Co	-	Courant number
DF	-	Degree of freedom
FBP	-	Final boiling point, °C
FCC	-	Fluid catalytic cracking
FD	-	Flash drum
FDM	-	Finite difference method
FEM	-	Finite element method
FVM	-	Finite volume method
Frac	-	Fractionation tower
GS	-	Stabilizer tower
HCGO	-	Heavy cycle gas oil
HDA	-	Hydrodearomatization
HDC	-	Hydrocracking
HDN	-	Hydrodenitrogenation
HDS	-	Hydrodesulfurization
HDT	-	Hydrotreating

HPS	-	High pressure separator
IBP	-	Initial boiling point, °C
LCO	-	Light cycle oil
LCGO	-	Light cycle gas oil
LHSV	-	Liquid Hourly Space Velocity, h^{-1}
LPG	-	Liquefied petroleum gas
LPS	-	Low pressure separator
ODE	-	Ordinary differential equation
SE	-	Solution element
SPA	-	Sponge absorber
Sp.gr	-	Specific gravity
SQE	-	Sum of squared error
SRD	-	Straight Run Diesel
Stab Gas	-	Stabilizer gas
VGO	-	Vacuum Gas Oil
WABT	-	Weighted average bed temperature

LIST OF SYMBOLS

A	-	Space-time region A in the domain
B	-	Price of the unit of product, feed or electricity
C	-	Mass concentration, kg/m^3
C'	-	Functional mass concentration, kg/m^3
C_p	-	Heat capacity of lumps, kJ/kg.°C
C_{pf}	-	Heat capacity of VGO feed, kJ/kg.°C
C_{ph}	-	Heat capacity of hydrogen, 14.21 kJ/kg.°C
C_1	-	Methane in light gas
C_2	-	Ethane in light gas
C_3	-	Hydrocarbons with 3 carbons in LPG
C_4	-	Hydrocarbons with 4 carbons in LPG
C_5	-	Hydrocarbons with 5 carbons in LPG
C_6	-	Hydrocarbons with 6 carbons in LN
D	-	Distillate or Diesel
E	-	Apparent activation energy, kcal/mol
E_{fht}	-	Fuel consumption of the furnace, m^3/h
E_{fhx}	-	Fuel consumption of the reactor furnace, m^3/h
E_{E-l}	-	Fuel consumption of reboiler, m^3/h
E_{p-l}	-	Electrical consumption of the pump, kW
E_{T-502}	-	Fuel consumption of the turbine 502 in Isomax plant, m^3/h
E_{T-531}	-	Fuel consumption of the turbine 531 in Isomax plant, m^3/h
Eff_{ht}	-	Thermal efficiency of the furnace, 0.735
Eff_{hx}	-	Thermal efficiency of the reactor furnace, 0.685
Expen	-	Energy consumption of Isomax unit

f	-	Concentration-flow function
F	-	Feed lump
F_m	-	Mass flow rate of stream through the reactor, kg/h
G	-	Gas
$\vec{h}$	-	Current density vector in the domain
H_2	-	Hydrogen
H_2S	-	Hydrogen sulfide
H_f	-	Heating value of the fuel gas, 5.327×10^4 kJ/kg
HN	-	Heavy Naphtha
i	-	Cell number
j	-	Discretized volume of the catalyst
k	-	Reaction rate constant, $m^3/(h.m^3$ cat)
k_{E-l}	-	Energy coefficient of reboiler, kJ/m^3
k_h	-	Consumed mass of hydrogen per converted mass of VGO
k_{p-l}	-	Energy coefficient of pump, $kW.h/m^3$
k_{T-502}	-	Fuel coefficient of H_2 turbine 502 in Isomax plant, m^3/h
k_{T-531}	-	Fuel coefficient of feed turbine 531 in Isomax plant, m^3/h
k_0	-	Frequency factor, $m^3/(h.m^3$ cat)
K	-	Kerosene
K_c	-	Proportional gain, °C/%)],
LN	-	Light Naphtha
meas	-	Measured yield
m^0	-	Mass flow rate, kg/h
M	-	Element of catalyst in the commercial reactor
Mw	-	Molecular weight
Mw_s	-	Molecular weight of sulfur (32)
Mw_N	-	Molecular weight of nitrogen (14)
n	-	Time step-size
$\vec{n}$	-	Outward unit normal of a surface element
N	-	Naphtha
NH_3	-	Ammonia
N_v	-	Number of cells (200)
N_t	-	Number of total experiments

Opc	-	Operating charges of Isomax unit
p	-	Number of test runs
P_m^0	-	Mass flow rate of product leaving fractionator, kg/h
Pred	-	Predicted yield
Profit	-	Profit of the Isomax plant
Q	-	Volume flow rate
$Q_{E\text{-}l}$	-	Fluid flow rate of the heavy naphtha reboiler, m^3/h
$Q_{p\text{-}l}$	-	Fluid flow rate of the product in Isomax , m^3/h
r	-	Rate of VGO converted to the hydrocracking products, kg/h
R	-	Ideal gas constant, 1.987 $kcal.kmol^{-1}.K^{-1}$
R_l	-	Reaction rate of lump l, $kg/(h.m^3$ cat)
$R_{1\text{-}3}$	-	Reactors of Isomax plant (three parallel reactors)
S	-	Surface region or Real plant selectivity
S_{sp}	-	Set point selectivity
$\hat{S}$	-	Surface region
t	-	Time domain (h)
t_c	-	Accumulated feed
T	-	Temperature, K or R
T_{eff}	-	Temperature of the effluent exchanger, 363°C
T_H	-	Output stream of the furnace, 120°C
u	-	Feed, distillate, naphtha and gas lumps
UN	-	Unconverted oil
V	-	An arbitrary but constant volume element of the domain
V_b	-	Total Volume of bed, m^3
V_{cat}	-	Volume of catalyst per cell, m^3
W	-	Weight of catalyst
wt%	-	Weight percent
x	-	Catalyst volume domain; Number of Isomax reactor
X	-	Mass fraction of lumps
X_c	-	Weight fraction of catalyst in Isomax bed.
Y	-	Yield of products
α	-	Consumed mass of hydrogen per mass of VGO (chapter 4) or Catalyst deactivation (chapter 5)
$\beta_0,..\beta_{12}$	-	Coefficient values for the hydrogen consumption

σ	-	Area unit normal of a surface element
Δ	-	Difference between actual and optimized values
Δt	-	Time-step
Δv	-	Volume step
ε	-	Dissipation factor
ε'	-	Catalyst void fraction
η	-	Effectiveness factor
ν	-	Catalyst volume element
ρ	-	Density, kg/m^3
φ	-	Time-Space function in the integral (chapter 6) or Decay function (Chapter 5)
τ	-	Stiff function
actual	-	Actual value of Isomax plant
Af	-	Aromatic in feed
Ap	-	Aromatic in product
b	-	Catalytic bed
cat	-	Catalyst
D	-	Diesel
Dj'	-	Distillate to lighter lumps
Dh	-	Diesel in the output stream of hydrotreating bed
e	-	Electricity
fh	-	VGO feed or residue in the output stream of hydrotreating bed
f	-	VGO feed

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

The needs for processing heavy feedstock into high value products are exacerbated by the increasing demand of light oil fractions and decreasing reserves of light crude oils. This steady growth in fuel demands can only be fulfilled by the inclusion of heavier feedstock into refinery operations (Hsu and Robinson, 2006), which can be converted to lighter ones using thermal and/or catalytic processing in the absence or presence of hydrogen pressure (Gary and Handwerk, 2001). This has been responded by the introduction of several process licenses for industrial use. Considering economic aspects, hydrocracking is seen as a suitable option as it improves the quality and quantity of the refined petroleum products simultaneously (Balasubramanian and Pushpavanam, 2008), especially if optimum design and operations are realized. The versatility and flexibility of the process makes it economically attractive to convert different types of feedstocks into various products including gas, LPG, naphtha, kerosene and diesel, leading to its widespread applications.

To enhance the efficiency of the hydrocracking process, the kinetics of the reactions involved must be fully defined so that the process behavior can be predicted. This can only be achieved if both the kinetic model and its corresponding parameters are correctly estimated. Having accurate models, the reactor operations

can be configured so that desirable product yield distribution was obtained in the most economical manner.

Ideally, the kinetic model should take into account all elementary reactions, which include all the different components in the feedstock (Balasubramanian and Pushpavanam, 2008). However, the complexity of hydrocracking feed makes it extremely difficult to characterize and describe its kinetic at a molecular level (Ancheyta *et al.*, 1999). This has given rise to the use of simplified approach by combining several similar components into groups called lumps. Using "black-box" concept, the input-output relationships among the lumps are configured to form a network of reactions that define the process. These models can then be extended for variety of tasks to facilitate the hydrocracking process including (Valavarasu *et al.*, 2005):

1) Design tool
2) Automation and optimizing control
3) Finding the optimum operation
4) Catalyst deactivation

In hydrocracking research, two major lumping methods have been used, i.e., continuous and discrete lumping approaches. In the first method, the reactive mixture is considered to form a continuum mixture with respect to its properties such as boiling point, molecular weight, carbon number or chemical species (Basak et al., 2004; Elizalde *et al.*, 2009; Elizade and Ancheyta, 2011); but, in the discrete lumping approach, the reaction network is reduced to the limited number of reactions among the lumped components. The lumps, based on compound types present in feedstock and products (e.g., lumps of diesel, kerosene, gasoline, etc.), are often defined by boiling point ranges. This approach is attractive for kinetic modeling of complex mixtures because of its simplicity (Ancheyta *et al.*, 2005).

1.2 Problem Statement

Optimal operating conditions are required in an industrial process operation to ensure profitability. This is nevertheless hampered by the fact that the plant is subjected to various uncertainties such as variability in feedstock, changing environmental condition and upsets in the process itself. To effectively handle these difficulties, the process behavior must be understood and predictable using some form of process models. Using these models product yields are estimated and sensitivity analyses can be carried out so that the effect of operating parameters like reactor temperature, pressure and space velocity on product yields can be sensed. The model can also be extended for the use in optimization, control, design of new plants and selection of appropriate hydrocracking catalysts.

A number of works have been presented in the literatures, but a full lump model for an industrial hydrocracking plant that predicts and optimizes the yield of all products has not been reported. Furthermore, if the steady state model can be extended to a dynamic form, it can be used in dynamic optimization and control. Additionally the prediction of the dynamic behavior of the reactor during start up or shut down can be facilitated. It is essential that the chemical engineer have a better understanding from the dynamic relationship among process and operating variables. In this instance, little knowledge is a dangerous matter for the process operation (Wozny and Jeromin, 1994). These serve as motivations for this work.

1.3 Research Objectives

The main objectives of this research are as follows:

i. Developing a kinetic based steady state model for a pilot scale vacuum gas oil (VGO) hydrocracking unit by using the discrete-lumping approach.

ii. Developing a practical steady state model and simulator for a commercial VGO hydrocracking unit.

iii. Applying discrete-lumping approach in the constrained optimization of a commercial VGO hydrocracking plant.

iv. Developing a new dynamic model for a pilot scale VGO hydrocracking reactor by applying the “conservation element-solution element” or “CE-SE” method.

1.4 Scope of Study

The scope of this work consists of the following actions:

I. Gathering the experimental data from a pilot scale VGO hydrocracking plant

II. Developing a steady state lumped kinetic-based model for the pilot scale plant and comparing the effect of hydrogen consumption on the accuracy of the yield prediction.

III. Gathering the industrial data from a commercial VGO hydrocracking plant.

IV. Developing a commercial full lump kinetic-based model including of catalyst deactivation to simulate the yield of all precious products such as diesel and gasoline.

V. Optimizing the operating parameters of an industrial VGO hydrocracking plant to maximize the profit of the process.

VI. Developing a dynamic model for the pilot scale plant using the lumping approach. To simulate and verify the dynamic behavior of the pilot plant.

Figure 1.1 illustrates the flow of this research for covering all the mentioned scopes of study.

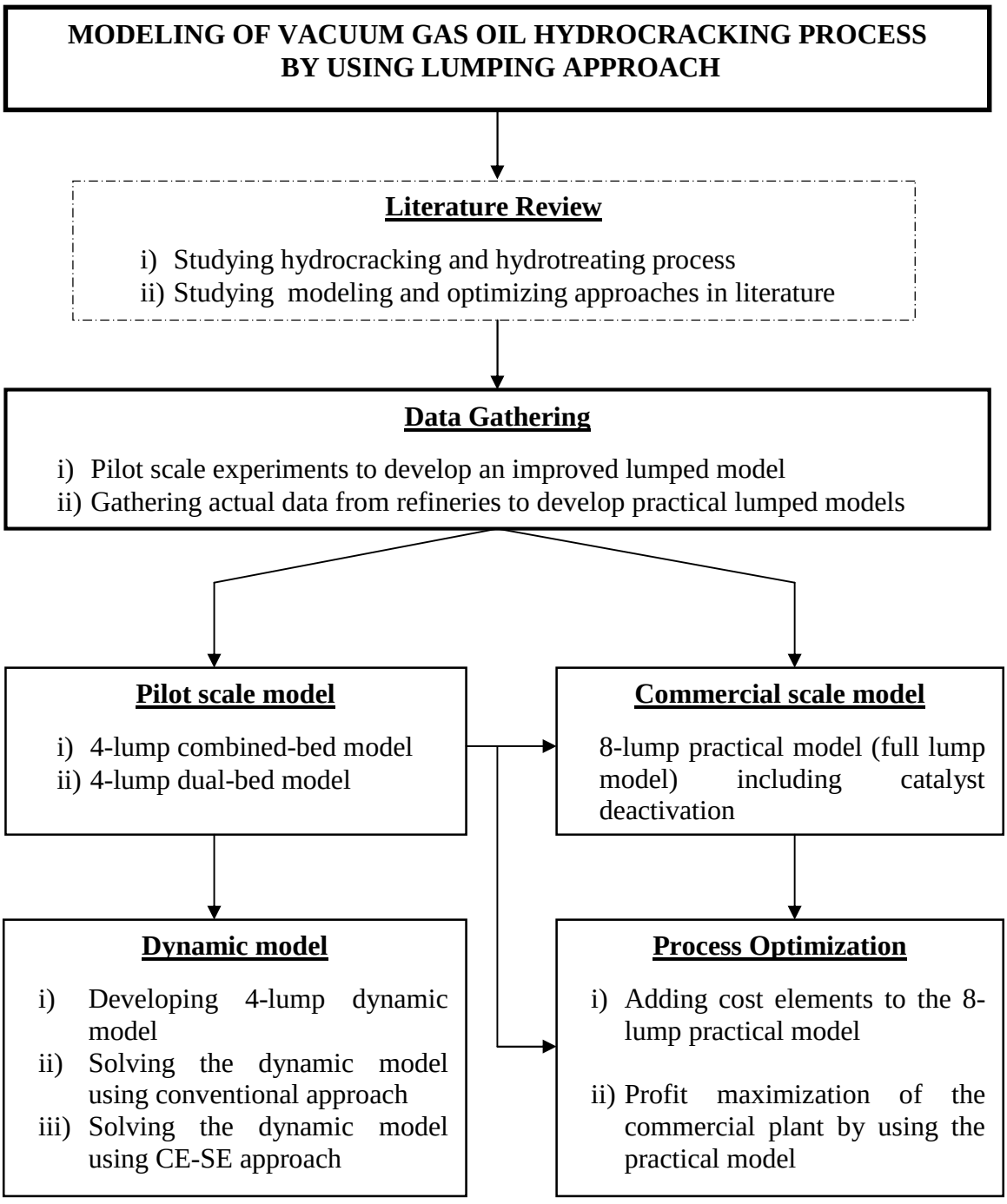

Figure 1.1 Flowchart of the research design

1.5 Significance of the study

The work proved the applicability of lump modeling approach in representing industrial hydrocracking effectively. Two model configurations for the pilot scale plant have been investigated and their applications in process analysis and optimization have been conducted. A simple and practical optimization strategy has been put forward which can serve as a useful guide in plant operation. The model has also been extended to include dynamic capability using a powerful, but less common, CE-SE method. This allows further investigations that require dynamic process information such as process control, dynamic optimization, alarm analysis and other control-safety related studies.

In short, this work has brought forward the following contributions:

i. Introducing discrete lumping models for a pilot scale hydrocracking plant. The main advantage of that over those previously reported in the literatures is consideration of the hydrogen consumption in kinetic equations and overall mass balance. This model can predict the yield of hydrocracking products and hydrogen consumption reasonably well.

ii. Introducing an applicable approach to simulate the product yields of commercial hydrocracking units during their cyclic operation.

iii. Investigating selective modeling of the catalyst life by using the commercial data.

iv. Introducing a simple and applicable approach to access the maximum profit in a commercial hydrocracking unit and/or the similar refinery processes.

v. Incorporating a discrete-lumped kinetic approach to simulate the dynamic behavior of hydrocracking plants with accurate and robust results.

vi. Developing CE-SE solving approach to be used for simulating the dynamic behavior of a VGO hydrocracking reactor. Its accuracy is studied against the conventional solving method.

1.6 Layout of the Thesis

This thesis is divided into 7 chapters. Following this introductory chapter, literature review is presented in chapter 2. Then in chapter 3, the research methodology and the required data to develop pilot and industrial scale lumping models have been presented.

In chapter 4, after discussing on the results of the pilot scale experiments, it is explained how by using lumping approach, 4-lump models are developed for the pilot scale plant. Two different steady state strategies (combined-bed and dual-bed) have been developed and compared together in this chapter.

Chapter 5 is allocated to develop an applicable discrete lumping model for being used to predict the product yields of an industrial plant. At first the gathered data from the understudy commercial plant is presented. Then, a full lump industrial model is developed, and finally it is used to optimize the profit of the commercial hydrocracking plant by manipulating the significant process variables.

Then in chapter 6, due to the importance of the dynamic model to control the performance of hydrocracking process, the steady state results of chapter 4 are applied to develop a dynamic lumped model. It is shown that this model is capable of simulating the response of the pilot scale model to the process disturbances. To solve the developed dynamic model, modern of art conservation element-solution element (CE-SE) method is used and its accuracy is compared against a conventional solving approach.

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