



# PREDICTIVE MODELING AND OPTIMIZATION FOR AN INDUSTRIAL COKER COMPLEX HYDROTREATING UNIT

### By Eslam Samir Elsbaaei Ali

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
in
Chemical Engineering

# PREDICTIVE MODELING AND OPTIMIZATION FOR AN INDUSTRIAL COKER COMPLEX HYDROTREATING UNIT

### By Eslam Samir Elsbaaei Ali

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
in
Chemical Engineering

Under the Supervision of

**Dr. Tamer Samir Mohamed Ahmed** 

Associate Professor of Chemical Engineering Faculty of Engineering, Cairo University

FACULTY OF ENGINEERING, CAIRO UNIVERSITY GIZA, EGYPT 2017

# PREDICTIVE MODELING AND OPTIMIZATION FOR AN INDUSTRIAL COKER COMPLEX HYDROTREATING UNIT

### By Eslam Samir Elsbaaei Ali

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
in
Chemical Engineering

Approved by the
Examining Committee

Assoc. Prof. Dr. Tamer Samir Mohamed Ahmed, Thesis Main Advisor

Prof. Dr. Mai Mohamed Kamal Eldeen Elsayed, Internal Examiner

Eng. Ashraf Hassan Kamal Eldeen, External Examiner

(Department Manger Technical Study at Suez Oil Processing Company)

FACULTY OF ENGINEERING, CAIRO UNIVERSITY GIZA, EGYPT 2017 **Engineer's Name:** Eslam Samir Elsbaaei Ali

**Date of Birth:** 13/ 7/ 1990 **Nationality:** Egyptian

E-mail: eslam.sbaaei@yahoo.com

**Phone:** 01004673871

**Address:** Suez, Faisal, Najd quarter, structure:84

Registration Date: 1/10/2014
Awarding Date: ..../..........

Degree: Master of Science

Department: Chemical Engineering

**Supervisors:** 

Dr. Tamer Samir Mohamed Ahmed

**Examiners:** 

Prof. Mai Mohamed Kamal Eldeen Elsayed (Internal examiner)

Eng. Ashraf Hassan Kamal Eldeen (External examiner)

(Department Manger Technical Study at Suez Oil Processing Company)

Dr. Tamer Samir Mohamed Ahmed (Thesis main advisor)

#### **Title of Thesis:**

Predictive Modeling and Optimization for an Industrial Coker Complex Hydrotreating Unit

#### **Key Words:**

Coker Complex; TBR Model; Hydrotreating Unit; Model Calibration; Process Optimization

#### **Summary:**

A process model for an industrial Coker Complex Hydrotreating process was developed using Aspen HYSYS Petroleum Refining Hydroprocessor Bed module. The model could track the plant performance competently. In addition, the model was utilized for investigating the effect of each process variable on the process performance. Among all process variables, feed boiling range and inlet temperature of the trickle bed reactor (TBR) were the most dominant factors to influence the process performance. Finally, the model was used for optimizing the process at steady state conditions. Results acquired from the model showed that a considerable increase in product yield with improved specifications could be achieved by adjusting the TBR feed boiling range to reach the IBP and FBP which the TBR is designed to treat, while lowering the hydrogen partial pressure inside the TBR to the lowest possible practical value and increasing the TBR inlet temperature to the equilibrium limit. The surplus in make-up gas may be diverted to fuel gas system, resulting in significant fuel savings. Applying the optimization scheme saves the plant consumption of energy as well as enhances the plant productivity of diesel fuel with better specifications. The model may also be integrated into a real time optimization scheme. In this situation, the model should be finely tuned to match the plant performance strictly.

Insert photo here

## Acknowledgments

Thanksgiving and praise to Allàh alone on the bounty and grace He helped me to finish this work.

And I acknowledge with appreciation the support, encouragement, suggestions and advices of Dr. Tamer Samir Ahmed.

## **Dedication**

For my father and my mother

## **Table of Contents**

Acknowledgments	i
Dedication	ii
Table of Contents	iii
List of Tables	
List of Figures	viii
Nomenclature	xi
Abstract	xiii
Chapter 1 : Introduction	1
1.1.World Fuel Demand	1
1.2.Crude Oil Refinery	3
1.3. HYDROTREATING ROLE IN OIL REFINERY	4
1.4.Hydrotreating History	
1.5.Diesel Fuel.	
1.5.1.Diesel Fuel Properties.	
1.5.1.1.Sulfur Content.	
1.5.1.2.Carbon Residue.	
1.5.1.3.Oxidation Stability	
1.5.1.4.Water Content.	8
1.5.1.5.Cetane Number	
1.5.1.6.Viscosity	
1.5.1.7.Pour Point	
1.5.1.8.Cloud Point	
1.5.1.10.Specific Gravity.	
1.5.2.Diesel Fuel Additives	
1.6.SCOPE AND ORGANIZATION OF THE THESIS	
Chapter 2 : Literature Review	11
2.1. HYDROTREATING KINETICS MODELING	11
2.2.Process Description	12
2.2.1.Upstream Units	12
2.2.2.Hydrotreating Unit	
2.2.2.1.Reaction Section.	
A.Feed/effluent Heat Exchangers Train	14
B.Reactor Charge Heater	14
C.Reactor (TBR)	14
D.Reactor Effluent Condenser and Water Wash	14
E.Vapor/ Liquid Separators	15
F.DEA Contactor	
2.2.2.2.Fractionation Section	15

2.3.Catalyst	16
2.3.1.Catalyst Composition.	16
2.3.1.1.Cobalt-Molybdenum Catalyst	
2.3.1.2.Nickel-Molybdenum Catalyst	
2.3.1.3.Other Catalysts.	
2.3.2.Catalyst Distribution	
2.3.3.Catalyst Poisoning and Deactivation	
2.3.4.Catalyst Size and Shape.	
2.4.Process Chemistry (VDG)	
2.4.1.Hydrodesulfurization (HDS)	
2.4.2.Hydrodenitrogenation (HDN)	
2.4.3.Hydrodeoygenation (HDO)	
2.4.4.Hydrodemetallization (HDM).	
2.4.5.Halide Removal	
2.4.6.Olefins Saturation	
2.4.7.Aromatic Saturation.	
2.5.PROCESS THERMODYNAMIC	
2.6.Process Kinetics	
2.6.1.Hydrogenolysis Kinetics	
2.6.2.Hydrogenation Kinetics	36
Chapter 3 : Model Development	37
3.1.REACTOR MODEL	37
3.2.Industrial Data	45
3.3.Data Screening.	48
3.4.CRUDE OIL ASSAY DEFINITION.	49
3.5.REACTOR MODEL PARAMETERS	
Chapter 4 : Model Calibration and Validation	
4.1.REACTOR MODEL CALIBRATION AND PARAMETER ESTIMATION	
4.1.1.Reactor Calibration.	
4.1.2.Average Activity Parameters	
4.1.3.Model Validation.	
4.1.4.Testing Model Prediction Power.	
4.2.FEED PREHEAT.	
4.3.DEA CONTACTOR AND FRACTIONATOR MODEL	
4.3.1.Tray Efficiency Vs Overall Column Efficiency	
4.3.2.DEA Contactor Model	
4.3.3.Fractionator Model	
4.3.3.2.Fractionator Model Validation.	
Chapter 5 : Process Variables	
5.1.Reactor Inlet Temperature	
5.2.HYDROGEN TO HYDROCARBONS RATIO.	
5.3.LIQUID HOURS' SPACE VELOCITY (LHSV)	
7 4 KHACTOR PRESSURE	XII

5.5.Bed Pressure Drop.	82
5.6.HYDROGEN SULFIDE AND AMMONIA IN RECYCLE GASES	84
5.7.FEED COMPOSITION	86
5.7.1.Sulfur Compounds	86
5.7.2.Nitrogen Compounds.	87
Chapter 6 : Process Optimization	91
6.1.Process Optimization	91
6.1.1.Reactor Inlet Temperature Optimization	91
6.1.2.Hydrogen to Hydrocarbon Ratio Optimization	91
6.2.MODEL APPLICATION TO PROCESS OPTIMIZATION	91
6.3. Effect of Optimum Operation Scheme on Columns Performance	96
Chapter 7 : Discussion, Conclusions and Recommendations	111
References	115
Appendix A: Reactor's Model Calibration Results	119
Appendix B: Model Prediction Vs Plant Performance	121
Appendix C: Energy and Material Balance	123
Appendix D: Products' Properties	169
Appendix E: Equipment Specifications	173

## **List of Tables**

Table 1.1: General diesel fuel classification and its specifications	6
Table 1.2: Egyptian standard specifications for diesel fuel	
Table 2.1: Catalysts loading inside industrial hydrotreating reactors	
Table 2.2: Deactivation effect of coke and metals on hydrotreating reactions	
Table 2.3: Amount of heat generated by hydrotreating reactions	
Table 2.4: Heat of reactions, Entropies, and Equilibrium constants for some	
hydrotreating reactions	32
Table 3.1: Kinetic Lumps of Hydropressor Bed Model	39
Table 3.2: Component Slate of Hydropressor Bed Model	
Table 3.3: Difference between current operating conditions and design operating	
conditions of the unit under investigation	43
Table 3.4: Flow rates of TBR feed and inlet gases for each data set	46
Table 3.5: H <sub>2</sub> S and H <sub>2</sub> concentration in recycle gases for each data set	47
Table 3.6: TBR product specifications and Temperature rise through TBR bed for ea	ach
data setdata	
Table 3.7: Characteristics of Belyium land-2013 assay in Aspen HYSYS	
Table 3.8: Difference between Aspen HYSYS model identified feed and TBR under	•
investigation feed	
Table 3.9: Composition of TBR feed in Aspen HYSYS Reactor Model	52
Table 3.10: TBR mechanical properties used in Reactor Model	56
Table 3.11: Deactivation parameters of TBR catalyst under investigation	56
Table 4.1: Adjustment factors used for Reactor Model calibration	58
Table 4.2: Measurements included in Reactor Model calibration	58
Table 4.3: Terms included in objective function for Reactor Model calibration and	
applied weighing factors	59
Table 4.4: Estimated average activity parameters for Reactor Model	60
Table 4.5: Typical overall efficiency values for some refinery fractionators	66
Table 4.6: Properties of Diethanolamine used in DEA contactor	67
Table 4.7: Composition of sweet gases and rich DEA	68
Table 4.8: Fractionator specifications	69
Table 5.1: Average composition of recycle gases and make-up hydrogen during the	
study period	74
Table 6.1: Operating conditions of the unit at the base operating point and at the	
optimum operating point	
Table 6.2: Expected remaining lifetime of investigated catalyst after finishing this st	udy
Table 6.3: Variation in plant performance after process optimization	95
Table 6.4: Variation in diesel fuel specifications after process optimization	95
Table 6.5: Net heating value of make-up gas	
Table 6.6: Tray rating profiles of fractionator at base and optimum operating conditi	ons
(panel A view)	98
Table 6.7: Tray rating profiles of fractionator at base and optimum operating conditi	ons
(panel B view)	100
Table 6.8: Tray rating profiles of DEA contactor at base and optimum operating	
conditions	
Table 6.9: Fractionator stages efficiency	104

Table 6.10: DEA Contactor stages efficiency	105
Table A.1: Model Calibration Results	119
Table B.1: Model Prediction Vs Plant Performance	121
Table C.1: Process Streams Conditions	123
Table D.1: Gasoline Properties	169
Table D.2: Kerosene Properties	169
Table D.3: Gas oil Properties	170
Table D.4: Diesel oil Properties	171

## **List of Figures**

Figure 1.1: World liquid fuels consumption	1
Figure 1.2: World liquid fuels production and consumption balance	2
Figure 1.3: U.S. diesel fuel and crude oil prices	
Figure 1.4: A general overall refinery processes flow diagram	3
Figure 1.5: Applications of hydrotreating and its capacities in petroleum refinery	
Figure 1.6: Comparison between Cetane rating of diesel fuel and Octane rating of	
gasolinegasoline	8
Figure 1.7: Effect of fuel viscosity on its spray pattern	9
Figure 2.1: Block Flow diagram of Coker Complex units	.13
Figure 2.2: Reaction Section of Hydrotreating Unit	
Figure 2.3: Fractionation Section of Hydrotreating Unit	.16
Figure 2.4: Active sites distributed on catalyst surface	.17
Figure 2.5: Phenomena occurring on active sites during hydrotreating reactions	.18
Figure 2.6: Catalysts combination distribution inside industrial hydrotreating reactors	320
Figure 2.7: Schematic of catalyst deactivation by coke and metal deposits	.22
Figure 2.8: Variation in metals content of hydrotreating catalyst as a function of time stream	
Figure 2.9: Variation in coke content of hydrotreating catalyst as a function of time o	
stream	
Figure 2.10: Variation in total occupied volume of hydrotreating catalyst by coke and	
metals as a function of time on stream	
Figure 2.11: Effect of temperature on catalyst coke	
Figure 2.12: Effect of hydrogen partial pressure on catalyst coke	
Figure 2.13: Different shapes of hydrotreating catalysts	
Figure 2.14: Removal of sulfur and nickel on CoMo catalysts	
Figure 2.15: Removal of sulfur and vanadium on CoMo catalysts	
Figure 2.16: Reactivity of different S-containing compounds	.27
Figure 2.17: Two mechanisms of HDS of thiophene	
Figure 2.18: Mechanism of HDN	.29
Figure 2.19: Typical micelles structure	.30
Figure 2.20: HDS equilibrium for thiophene and alkylthiophene	.33
Figure 2.21: HDN equilibrium for pyridine and picoline	.33
Figure 2.22: Hydrogenation equilibrium of naphthalene to tetrahydrogenaphthalene	.34
Figure 3.1: Hydroprocessor Bed Model Reaction Network	.38
Figure 3.2: Overall Modeling Strategy	.44
Figure 3.3: Model Development Scheme	.45
Figure 3.4: Overall and Sulfur mass balances errors	.49
Figure 4.1: Estimated activity parameters for Reactor Model	.60
Figure 4.2: Plant versus Model with calibration data sets	.61
Figure 4.3: Plant versus Model for 3 months after calibration	.62
Figure 4.4: Pre-Heat Train and TBR Charge Furnace Flow Sheet	.64
Figure 4.5: Convergence between molar flow rate profiles of Fractionator Model and	
Plant Fractionator	
Figure 4.6: Convergence between pressure profiles of Fractionator Model and Plant	
Fractionator	.70

Figure 4.7: Convergence between temperature profiles of Fractionator Model and Plant
Fractionator71
Figure 4.8: Coker Complex Hydrotreating Unit model
Figure 5.1: Effect of TBR inlet temperature on: A- temperature rise through TBR bed;
B- hydrogen consumption inside TBR; C- sulfur content difference between TBR inlet
and outlet liquid streams; D- nitrogen content difference between TBR inlet and outlet
liquid streams; E- specific gravity difference between TBR inlet and outlet liquid
streams; F- cetane number difference between TBR inlet and outlet liquid streams. TBR
pressure = 35 bar, H2:HC mass ratio = $0.0326$ , LHSV = $0.8752 \text{ h}^{-1}$ , H <sub>2</sub> S concentration
in recycle gases = 464 ppm, TBR feed IBP:FBP = 268:390 °C
Figure 5.2: Variation of catalyst remaining lifetime with TBR inlet temperature during
the study period
Figure 5.3: Effect of hydrogen to hydrocarbons ratio on: A- temperature rise through
TBR bed; B- hydrogen consumption inside TBR; C- sulfur content difference between
TBR inlet and outlet liquid streams; D- nitrogen content difference between TBR inlet
and outlet liquid streams; E- specific gravity difference between TBR inlet and outlet
liquid streams; F- cetane number difference between TBR inlet and outlet liquid
streams. TBR inlet temperature = 290.4 °C, TBR pressure = 35 bar, LHSV = 0.8752 h <sup>-1</sup> ,
H <sub>2</sub> S concentration in recycle gases = 464 ppm, TBR feed IBP:FBP = 268:390 °C77
Figure 5.4: Variation of catalyst remaining lifetime with hydrogen to hydrocarbons
ratio during the study period
Figure 5.5: Effect of liquid hours' space velocity (LHSV) on: A- temperature rise
through TBR bed; B- hydrogen consumption inside TBR; C- sulfur content difference
between TBR inlet and outlet liquid streams; D- nitrogen content difference between
TBR inlet and outlet liquid streams; E- specific gravity difference between TBR inlet
and outlet liquid streams; F- cetane number difference between TBR inlet and outlet
liquid streams. TBR inlet temperature = 290.4 °C, TBR pressure = 35 bar, H2:HC mass
ratio = 0.0326, H <sub>2</sub> S concentration in recycle gases = 464 ppm, TBR feed IBP:FBP =
268:390 °C
Figure 5.6: Variation of catalyst remaining time with liquid hours' space velocity
(LHSV) during the study period80
Figure 5.7: Effect of TBR pressure on: A- temperature rise through TBR bed; B-
hydrogen consumption inside TBR; C- sulfur content difference between TBR inlet and
outlet liquid streams; D- nitrogen content difference between TBR inlet and outlet
liquid streams; E- specific gravity difference between TBR inlet and outlet liquid
streams; F- cetane number difference between TBR inlet and outlet liquid streams. TBR
inlet temperature = 290.4 °C, H2:HC mass ratio = 0.0326, LHSV = 0.8752 $h^{-1}$ , H <sub>2</sub> S
concentration in recycle gases = 464 ppm, TBR feed IBP:FBP = 268:390 °C81
Figure 5.8: Variation of catalyst remaining time with TBR pressure during the study
period
through TBR bed; B- hydrogen consumption inside TBR; C- sulfur content difference
between TBR inlet and outlet liquid streams; D- nitrogen content difference between
TBR inlet and outlet liquid streams; E- specific gravity difference between TBR inlet
and outlet liquid streams; F- cetane number difference between TBR inlet and outlet
liquid streams. TBR inlet temperature = 290.4 °C, TBR pressure = 35 bar, H2:HC mass
ratio = $0.0326$ , LHSV = $0.8752  h^{-1}$ , H <sub>2</sub> S concentration in recycle gases = $464  \text{ppm}$ ,
TBR feed IBP: FBP = 268:390 °C83
Figure 5.10: Effect of H <sub>2</sub> S and NH <sub>3</sub> in recycle gases on: A- temperature rise through
TBR bed; B- hydrogen consumption inside TBR; C- sulfur content difference between

TBR inlet and outlet liquid streams; D- nitrogen content difference between TBR and outlet liquid streams; E- specific gravity difference between TBR inlet and outlet liquid streams; F- cetane number difference between TBR inlet and outlet liquid streams. TBR inlet temperature = 290.4 °C, TBR pressure = 35 bar, H2:HC mas = 0.0326, LHSV = 0.8752 h <sup>-1</sup> , TBR feed IBP:FBP = 268:390 °C.	outlet I ss ratio85
Figure 5.11: Variation of catalyst remaining time with H <sub>2</sub> S and NH <sub>3</sub> in recycle g during the study period	_
Figure 5.12: Effect of sulfur compounds in liquid feed on: A- temperature rise the	
TBR bed; B- hydrogen consumption inside TBR. TBR inlet temperature = 290.4	
TBR pressure = 35 bar, H2:HC mass ratio = $0.0326$ , LHSV = $0.8752 \text{ h}^{-1}$ , H <sub>2</sub> S	07
concentration in recycle gases = 464 ppm.	
Figure 5.13: Variation of catalyst remaining lifetime with sulfur compounds in I feed during the study period	_
Figure 5.14: Effect of nitrogen compounds in liquid feed on: A- temperature rise	
through TBR bed; B- hydrogen consumption inside TBR. TBR inlet temperature	
290.4 °C, TBR pressure = 35 bar, H2:HC mass ratio = 0.0326, LHSV = 0.8752	
concentration in recycle gases = 464 ppm	
Figure 5.15: Variation of catalyst remaining lifetime with nitrogen compounds i feed during the study period	n nquia 89
Figure 6.1: Variation of TBR feed specific gravity with IBP and FBP	
Figure 6.2: Variation of temperature rise through TBR bed with IBP and FBP at	
operating conditions	
Figure 6.3: Variation of hydrogen consumption inside TBR with IBP and FBP a	
operating conditions	94
Figure 6.4: Variation of TBR catalyst remaining lifetime with IBP and FBP at b	ase
operating conditions during the study period	94
Figure 6.5: Thermal and Hydraulic performance of fractionator at base condition	
Figure 6.6: Thermal and Hydraulic performance of fractionator at optimum cond	
Figure 6.7: Thermal and Hydraulic performance of DEA contactor at base condi-	
	108
Figure 6.8: Thermal and Hydraulic performance of DEA contactor at optimum	100
conditions	109

#### **Nomenclature**

Θ Number of active sites on catalyst surface

b<sub>i</sub> Adsorption coefficient of compound i

U<sub>o</sub> Overall heat transfer coefficient

 $\Delta t_{LMTD}$  Log mean temperature difference (LMTD)

F<sub>t</sub> LMTD correction factor

y<sub>n</sub> Average composition of vapor leaving plate n

y<sub>n-1</sub> Average composition of vapor arriving from plate n

\* Theoretical composition of vapor that would be in

y n

\* Swith five with liquid leaving plate n

equilibrium with liquid leaving plate n

ψ<sub>i</sub> Property of a petroleum fraction

θ<sub>i</sub> Known property of a petroleum fraction
 w<sub>i</sub> Weighting factor of process variable i

X<sub>i</sub> Process variable i

Viscosity of feed at average tower temperature in

μ<sub>L</sub> Centipoises

Relative volatility of key components at average tower  $\alpha$ 

temperature

 $H^{o}_{700}$  Standard heat of reaction at 700 K in cal/mol  $S^{o}_{700}$  Standard entropy at 700 K in cal/mol.grd

#### **Abbreviations**

A Surface area available for heat transfer

CCR Conradson carbon residue

DEA Diethanolamine
DMDS Dimethyl disulfide

E Efficiency
EOR End of Run

FBP Final boiling point

HA Heavy aromatic compounds
HDA Hydrodeasphaltenization
HDM Hydrodeasphaltization

HDM HydrodemetallizationHDN HydrodenitrogenationHDO HydrodeoxygenationHDS Hydrodesulfurization

HN Heavy naphthenic compounds

HNA Heavy naphthenic aromatic compounds

HNi Heavy nitrogen compounds
HP Heavy paraffinic compounds