A COMPREHENSIVE STUDY ON INDUSTRIAL DIESEL HYDROTREATING UNIT: NEW INSIGHTS ON DESIGN AND OPTIMIZATION

RAJARSHI BANDYOPADHYAY

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

RAJARSHI BANDYOPADHYAY

Department of Chemical Engineering

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Dedicated to

All with whom I have shared a good laugh

CERTIFICATE

This is to certify that the thesis entitled "**A COMPREHENSIVE STUDY ON INDUSTRIAL DIESEL HYDROTREATING UNIT: NEW INSIGHTS ON DESIGN AND OPTIMIZATION**" being submitted by **Mr. Rajarshi Bandyopadhyay** to Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy,** is a record of the original bona fide research work carried out by him**. Mr. Rajarshi Bandyopadhyay** has worked under my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi and fulfilled the requirements for submission of this thesis, which has attained the standard required for a Ph.D. degree of the Institute. The results contained in this thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

Prof. Sreedevi Upadhyayula

Professor
Department of Chemical Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi-110016

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Once one of my seniors from the university where I did my under-graduation told me, “Be absolutely clear to yourself before entering a Ph.D. program. Ph.D. is not just a degree; it is a way of life.” As I write this section, I can only say that I have realized how true his words were. An attempt to do a Ph.D. while maintaining a full-time job is really ambitious—and it gives me great pleasure to have come so far. This long and tortuous journey would not have been possible without the support of many, and I take this opportunity to thank them from the bottom of my heart.

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(RAJARSHI BANDYOPADHYAY)

ABSTRACT

A diesel hydrotreating (DHT) unit holds a considerable significance in a petroleum refinery, owing to the ever increasing focus on processing heavier crudes on the one hand, and stringent environmental regulations on the other hand. The present work is aimed at developing a deeper understanding of the plant layouts of modern DHT units, and suggesting suitable improvements to get the maximum benefit out of them.

Thermodynamic analysis of the main DHT reactions—Hydrodesulfurization (HDS), Hydrodenitrogenation (HDN) and Hydrodearomatization (HDA)—have been carried out over a wide range of temperatures and pressures to ascertain the most favourable operating condition for a DHT reactor from a thermodynamic perspective.

Two popular configurations of a DHT unit—'hot separator layout' and 'cold separator layout'—have been studied in detail from different perspectives. Both the layouts have been studied from a perspective of energy efficiency as well as economic feasibility. Design prototypes of the layouts have been developed in a commercial simulator and energy efficiency studies have been carried out by application of pinch and exergy analyses. Detailed profitability analysis of both the layouts has been carried out by a net present value (NPV) approach. The dependence of profitability on the price variation of product and utility prices has been studied in detail using response surface methodology (RSM). These studies have helped in ascertaining the optimum DHT layout at different feed, product, and utility prices as well as at different operating conditions.

Furthermore, data reconciliation and multi-variable optimization (MVO) of an operating DHT unit have been carried out using state-of-the-art process optimization software. The scope of improvement of profitability of a running unit by proper adjustment of operating parameters has been analyzed and highlighted. The optimization has helped in an annual saving of ~ 2.7 million €/yr.

Overall, a detailed study of an industrial DHT unit has been carried out and novel approaches for improvement of its design approach and operating parameters have been developed. This work will help researchers and industry technologists to develop methodologies for selection of optimum process layout – not only for DHT units, but also for any industrial chemical process in general.

सार

एक डीजल रिफाइनरी (डीएचटी) इकाई एक पेट्रोलियम रिफाइनरी में काफी महत्त्व रखती है, जिसके कारण एक तरफ भारी क्रूड के प्रसंस्करण पर ध्यान केंद्रित किया जा रहा है, और दूसरी ओर कड़े पर्यावरणीय नियम। वर्तमान काम का उद्देश्य आधुनिक DHT इकाइयों के संयंत्र लेआउट की गहरी समझ विकसित करना है, और उनमें से अधिकतम लाभ प्राप्त करने के लिए उपयुक्त सुधारों का सुझाव देना है।

मुख्य DHT अभिक्रियाओं का ऊष्मागतिकीय विश्लेषण- हाइड्रोडेसल्फ्यूराइज़ेशन (HDS), हाइड्रोडाइनाइट्रोजिनेशन (HDN) और हाइड्रोडाइरोमैटिज़ेशन (HDA) -एक थर्मोडायनामिक परिप्रेक्ष्य से DHT रिएक्टर के लिए सबसे अनुकूल परिचालन स्थिति का पता लगाने के लिए तापमान और दबावों की एक विस्तृत श्रृंखला पर किया गया।

एक DHT इकाई के दो लोकप्रिय विन्यास- गरम सेपरेटर लेआउट ’और कोल्ड सेपरेटर लेआउट- का अलग-अलग दृष्टिकोणों से विस्तार से अध्ययन किया गया है। दोनों लेआउटों का अध्ययन ऊर्जा दक्षता के साथ-साथ आर्थिक व्यवहार्यता के दृष्टिकोण से किया गया है। लेआउट के डिजाइन प्रोटोटाइप एक वाणिज्यिक सिम्युलेटर में विकसित किए गए हैं और ऊर्जा दक्षता अध्ययन चुटकी और बाहरी विश्लेषण के आवेदन द्वारा किए गए हैं। शुद्ध वर्तमान मूल्य (NPV) दृष्टिकोण द्वारा दोनों लेआउटों का विस्तृत लाभप्रदता विश्लेषण किया गया है। प्रतिक्रिया सतह कार्यप्रणाली (आरएसएम) का उपयोग करके उत्पाद की उपयोगिता भिन्नता और उपयोगिता की कीमतों पर लाभप्रदता की निर्भरता का विस्तार से अध्ययन किया गया है। इन अध्ययनों ने विभिन्न फीड, उत्पाद और उपयोगिता की कीमतों के साथ-साथ विभिन्न ऑपरेटिंग परिस्थितियों में इष्टतम DHT लेआउट का पता लगाने में मदद की है।

इसके अलावा, एक ऑपरेटिंग DHT इकाई के डेटा सामंजस्य और बहु-चर अनुकूलन (MVO) को अत्याधुनिक प्रक्रिया अनुकूलन सॉफ्टवेयर का उपयोग करके किया गया है। ऑपरेटिंग मापदंडों के उचित समायोजन द्वारा किसी रनिंग यूनिट की लाभप्रदता के दायरे का विश्लेषण और हाइलाइट किया गया है। अनुकूलन ने ~ 2.7 मिलियन €/yr की वार्षिक बचत में मदद की है।

कुल मिलाकर, एक औद्योगिक DHT इकाई का एक विस्तृत अध्ययन किया गया है और इसके डिजाइन दृष्टिकोण और ऑपरेटिंग मापदंडों के सुधार के लिए उपन्यास दृष्टिकोण विकसित किए गए हैं। यह काम शोधकर्ताओं और उद्योग प्रौद्योगिकीविदों को इष्टतम प्रक्रिया

लेआउट के चयन के लिए कार्यप्रणाली विकसित करने में मदद करेगा – न केवल डीएचटी इकाइयों के लिए, बल्कि सामान्य रूप से किसी भी औद्योगिक रासायनिक प्रक्रिया के लिए भी।

PERMISSIONS

Permissions have been taken from the respective journals for the publications related to work presented in this thesis.

List of publications related to work presented in this thesis as on date of submission of thesis

PEER-REVIEWED JOURNAL PUBLICATIONS

R. Bandyopadhyay, S. Upadhyayula, Thermodynamic analysis of diesel hydrotreating reactions, Fuel 214 (2018) 314–21.

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NOMENCLATURE

Symbols

€	Euro
A	Heat transfer area (m^2)
a_o, a_i, a_{ii}, a_{ij}	Regression coefficients
e	Measurement error
F	Molar flow rate (kmol/hr)
Ex, B (for Pro/II only)	Exergy
f_{eco}	Economic objective
H	Enthalpy (J/kg)
j, k	Element of time step
K_{eq}	Equilibrium constant
m	Input horizon
p	Partial pressure (bar(a))
Q	Amount of heat transferred (J)
r	desired value
S	Entropy (J/K)
T	Temperature (K)
U	Overall heat transfer coefficient (kcal/(m^2hr^oC))
u	Control input
v	Output horizon

W	Amount of work done (J)
W_1,W_2,W_3	positive weights
x	Mole fraction in liquid phase
X	Fractional conversion of a component in a reaction
x_l	Mole fraction in liquid phase
x_v	Mole fraction in vapor phase
y	Mole fraction in vapor phase
ÿ	Measurement value
Y	Predicted response
Z	Measured data
z	Solution of data reconciliation

Greek letters

ε	Standard chemical exergy (MW)
ξ	True value

Sub- and superscript

0	Environment/reference state
l	Liquid phase
in	Properties associated with inlet material stream
out	Properties associated with outlet material stream
v	Vapor phase

Abbreviation

ATF	Aviation Turbine Fuel

bbl	Barrel
BP	Biphenyl
BPSD	Barrel Per Stream Day (1 US barrel (oil) = 0.159 m^3)
CAPEX	Capital Expense
CDU	Crude Distillation Unit
CFD	Computational Fluid Dynamics
CGO	Coker Gas Oil
CHB	Cyclohexylbenzene
CVD	Chemical vapor deposition
DBT	Dibenzothiophene
DCFR	Discounted Cash Flow Rate
DCU	Delayed Coker Unit
DDS	Direct Desulfurization
DFT	Density functional theory
DHT	Diesel Hydrotreating
EDTA	Ethylene diamine tetraacetic acid
EMTD	Estimated Mean Temperature Difference
FBP	Final Boiling Point
FCC	Fluidized Catalytic Cracking
GRM	Gross refining margin

HADF-STEM	High-angle annular dark-field scanning transmission electron microscopy
HC	Hydrocarbon
HDA	Hydrodearomatization
HDM	Hydrodemetallization
HDN	Hydrodenitrogentation
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HER	Heat Exchanger Network
HYD	Hydrogenation/ Olefin Hydrogenation
HYK	Hydrocracking
IBP	Initial Boiling Point
LHSV	Liquid Hourly Space Velocity
LP	Linear Programming
LPG	Liquefied Petroleum Gas
MER	Minimum Energy Requirement
MPC	Model Predictive Controller
MT	Metric Ton
MVO	Multi-variable Optimization
MWh	Mega Watt-hour

NPV	Net Present Value
NTA	Nitriloacetic acid
OPEX	Operating Expense
ORC	Organic Rankine Cycle
PAH	Polynuclear Aromatic Hydrocarbons
PM	Particulate Matter
SRGO	Straight run gas oil
STM	Scanning tunnelling microscopy
TAC	Total Annual Cost
TBP	True Boiling Point
ULSD	Ultra Low Sulfur Diesel
v/v	Volume by volume basis
VOC	Volatile Organic Compound
WABT	Weighted Average Bed Temperature

Abbreviations used for blocks in flow diagrams

C	Column
CP	Compressor
E	Process heat exchangers, air cooler, water cooler
F	Heater
P	Pump
R	Reactor

V	Vessel
VLV	Throttling valve